Pyrolysis of waste plastics into chemicals as an alternative to landfilling or incineration

by

Evans Mwila Chomba

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Supervisor

Prof. Johann. F. Görgens

Co-Supervisor

Dr. François-Xavier Collard

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Abstract

World population growth has brought about high production and consumption trends on the petroleum resources. One aspect contributing to this trend is plastic manufacture accounting for considerable petroleum resource consumption. Plastic production is increasing because of its versatile usage in many industries culminating into significant waste plastics generation. Plastic waste management is a large financial burden to local authorities aside from littering communities, blocking sewerage systems and drainages among other negative impacts on the environment and public health.

Plastic waste recycling into chemicals through pyrolysis technology is a promising alternative to incineration or landfilling in providing an environmentally sustainable route to plastic waste management. This method can supplement the already established mechanical recycling of plastics in South Africa in diverting significant plastic wastes from landfill and achieve an industrial initiative of zero waste to landfill by 2030.

The aim of this study was to determine the major plastic components in South Africa's plastic stream and to establish if valuable chemicals can be recovered from polystyrene as well as polyethylene terephthalate through pyrolysis. Literature survey of the South African plastic stream revealed that there are six main plastics contained in the stream namely: high density polyethylene (HDPE), low density polyethylene (LDPE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC) and polyethylene terephthalate (PET).

Before pyrolysis could be performed, physical and thermal characterisation was done to determine the suitability of the plastics to thermal conversion. It was established that the waste samples isolated from a commingled sample were pure enough and possessed significant volatile matter required for conversion to chemicals. In the order of increasing thermal stability PS, PET, PP, LDPE and HDPE plastics were all found to degrade in a single step over about 130 °C temperature change, before completion around 500 °C for heating rates between 10 – 20 °C/min. PVC plastic could not be considered for the study because of its corrosiveness and low content in the landfill stream at Kraaifontein waste management facility.

Optimisation of slow and vacuum pyrolysis work conducted on PS and PET revealed that valuable styrene and terephthalic as well as benzoic acids could be recovered from the

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plastics respectively and quantified. It was concluded that slow pyrolysis was a better technology of converting PS to styrene as it gave about 41 wt% styrene yield at slightly over 58 wt% concentration against 36 wt% produced in vacuum pyrolysis at 56 wt% concentration. Both slow and vacuum pyrolysis of PET gave similar TPA and BA yield range of 4 – 5 wt% and 5 – 8 wt% respectively. The concentration of TPA was better in vacuum process, while BA concentration was significantly improved in slow pyrolysis.

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Opsomming

Wêreld-populasie-groei het hoë tendense verroorsaak in die produksie en verbruiking van petroleum-hulpbronne. Een van die aspekte wat bydra tot die tendens is plastiekvervaardiging wat verantwoordelik is vir aanmerklike verbruiking van petroleum. Plastiek is ‘n veelsydige materiaal wat in verskeie nywerhede gebruik word en daarom is die produksie daarvan aan die toeneem wat gevolglik lei tot aanmerklike voortbrenging van plastiekafval. Die bestuur van plastiekafval is ‘n groot finansiële las op plaaslike owerhede en het negatiewe impakte op die omgewing en publieke gesondheid, onder andere rommelstrooing in gemeensakappe en die verstopping en dreinering van rioolsisteme.

Die herwinning van plastiekafval om chemikalieë te maak deur pirolisetegnologie bied ‘n omgewingsvolhoubare roete vir die bestuur van plastiekafval en is daarom ‘n belowende alternatief tot verbranding of terreinstorting. Die metode kan die bestaande meganiese herwinning van plastiek in Suid-Afrika aanvul deur die afleiding van ‘n aanmerklike hoeveelheid plastiekafval vanaf stortingsterrein om sodoende ‘n nywerheidsinisiatief van geen afval na stortingsterrein teen 2030 te behaal.

Die doelwit van die studie was om te bepaal wat die hoof plastiek komponente in Suid-Afrika se plastiekstroom is en om vas te stel of waardevolle chemikalieë kan herwin word vanuit die pirolise van polistireen en poli-etileen-tereftelaat. Literatuurstudie van Suid-Afrika se plastiekstroom onthul dat daar ses hoof plastieksoorte in die stroom is, naamlik: hoë-digtheid-poli-etileen (HDPE), lae-digtheid-poli-etileen (LDPE), polipropileen (PP), polistireen (PS), polivinielchloried (PVC) en poli-etileen-tereftelaat (PET).

Voor pirolise kon uitgevoer word, was fisiese en termiese karakterisering van die plastieke gedoen om te bepaal of die plastiek geskik is vir termiese-omskakeling. Dit was vasgestel dat die afval-monsters verkry vanaf ‘n gemengde monster suiwer genoeg en aanmerklike vlugtige materie besit het wat nodig is vir die omskakeling na chemikalieë. In die orde van toenemende termiese stabiliteit is dit PS, PET, PP, LDPE, en HDPE. Dit was bevind dat die plastieke in ‘n enkele stap afbreek oor ‘n temperatuurverandering van ongeveer 130℃, voor voltooing by ongeveer 500℃ vir verhittingstempo’s tussen 10 en 20 ℃/min. PVC-plastiek kon nie oorweeg word vir die studie nie as gevolg van die plastiek se bytende aard en die lae

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inhoud van die plastiek in die stortingsterreinstroom by die afval-bestuur-fasiliteit in Kraaifontein.

Optimiseringstudie van stadige-en vakuum-pirolise van PS en PET het onthul dat waardevolle stireen en tereftelaat asook bensoë-sure herwin kon word van die onderskeie plastieke. Die gevolgtrekking was gemaak dat stadige-pirolise ‘n beter tegnologie is om PS na stireen om te skakel omdat dit 41 wt% stireen opbrengs by bietjie hoër as 58 wt% konsentrasie gegee het. Dis in teenstelling met vakuum-pirolise wat 36 wt% geproduseer het met 56 wt% konsentrasie. Albei stadige- en vakuum-pirolise het soortgelyke TPA en BA gegee met opbrengs in die omgewing van 4 - 5wt% en 5 - 8 wt% onderskeidelik. Die konsentrasie van TPA was meer in vakuum-pirolise, terwyl BA konsentrasie aanmerklik verbeter was in stadige-pirolise.

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Dedication

I dedicate this work to my family members. Thanks very much father and mother for the sacrifice you made for me. My only sister, thanks for everything. Last but not least my wife whose support and understanding has brought me this far. I love you all; you are so dear to me.

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Abbreviations and nomenclature

ABS	Acrylonitrile butadiene styrene
amu	Atomic mass unit
ASTM	American standard testing method
BA	Benzoic acid
BFBR	Bubbling fluidised bed reactor
BTX	Benzene, toluene and xylene
Conc	Concentration
D_{max}	Maximum polymer degradation rate
DOE	Design of experiments
DTG	Derivative thermogravimetry
EGA	Evolved gas analysis
EI	Electron impact
FC	Fixed carbon
FID	Flame ionization detector
FP	Fast pyrolysis
FTIR	Fourier transform infra-red spectroscopy
GC-MS	Gas chromatography-mass spectroscopy
GHG	Greenhouse gas
gpl	Grams per litre
HDPE	High density polyethylene
HPLC	High performance liquid chromatography
HR	Heating rate
ID	Internal diameter
KWMF	Kraaifontein waste management facility
LDPE	Low density polyethylene
MC	Moisture content
MPSW	Municipal plastic solid waste
NIST	National Institute of Standards and Technology
PA	Polyamide

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PC	Polycarbonate
PCDD	Polychlorinated dibenzo dioxins
PCDF	Polychlorinated dibenzo furans
PE	Polyethylene
PET	Polyethylene terephthalate
PetCo	Polyethylene terephthalate recycling company
Plastics SA	Plastics South Africa
PMMA	Poly(methyl methacrylate)
PP	Polypropylene
POLYCO	Polyolefin recycling company
PU	Polyurethane
PS	Polystyrene
PV	Polyvinyl chloride
PSW	Plastic solid waste
RSD	Relative standard deviation
SD	Standard deviation
SAPRO	South African plastics recycling organisation
SEM	Secondary electron multiplier
SP	Slow pyrolysis
SR	Solid residue
T_1	Polymer degradation onset temperature
T_2	Polymer degradation offset temperature
T_{max}	Polymer degradation peak temperature
TCD	Thermal conductivity detector
TGA	Thermal gravimetric analyser
THF	Tetrahydrofuran
TIC	Total ion chromatogram
TPA	Terephthalic acid
VM	Volatile matter
VP	Vacuum pyrolysis

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1 Introduction

1.1 Background to the study

World population growth has resulted in increasing production and consumption trends for petroleum resources. One aspect responsible for this trend is plastic manufacture, which accounts for about 4 – 8 % of petroleum resource consumption (Sasse and Emig, 1998, Ali and Siddiqui, 2006). Plastic production is increasing because of its versatile usage in packaging, automobile, construction, agriculture and many other industries. This has culminated into significant increases in waste plastics generation (Kayacan and Doğan, 2008), because of short life cycles of many plastic products (Adrados et al., 2012). Unsurprisingly, waste plastics have become a major constituent of up to 11% (Green and Sadrameli, 2004,Faravelli et al., 1999) in municipal solid waste. This plastic waste increase threatens the financial resources of local authorities tasked with solid waste management and sanitation. Plastics litter communities and block sewerage systems, among other negative impacts on the environment and public health.

Plastic waste recycling into chemicals (Faravelli et al., 1999, Kiran et al., 2000, Pinto et al., 1999) as an alternative to incineration or landfilling can provide an environmentally sustainable route to plastic waste management. This measure can conserve resources and mitigate greenhouse gases (GHG) emissions (Salhofer et al., 2007) as many countries are faced with increased pressure on dwindling natural resources due to their economic growth (Singh et al., 2012).

The current economic growth of South Africa is unsustainable if fossil sources like natural gas and coal are not conserved. Thus, it is necessary to turn to alternative energy such as biomass and waste recycling to reduce the consumption of non-renewable resources. Plastic solid waste (PSW) in South Africa is mainly landfilled, indiscriminately dumped and/or incinerated (combusted). According to PlasticsSA, about 26 % of PSW is recovered. The organisation has thus set a target of zero waste to landfill by 2030, to encourage research on alternative methods of plastic waste management. The plastic wastes usually contain six common polymers namely: high density polyethylene (HDPE), low density polyethylene (LDPE), polypropylene (PP), polystyrene (PS), polyvinylchloride (PVC) and polyethylene terephthalate (PET) mixed in varying proportions based on economic, cultural and living

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standards of the people in a region or nation. This study was aimed at determining the suitability of pyrolysis technology to recover valuable chemicals from polystyrene and polyethylene terephthalate plastics.

1.2 Problem statement

Pyrolysis of waste plastics from landfill stream that cannot be mechanically recycled was studied, to determine the suitability for valuable products recovery. Pyrolysis appears as an interesting option to convert PE and PP in liquid fuel, especially when the level of contamination is limited (Xingzhong, 2006 and Miller et al., 2006). In the case of PS and PET, the pyrolysis product contains too high concentration of aromatics to be considered for diesel or gasoline substitution (SANS 342, 2006 and SANS 1598, 2006). On the other hand, there is limited literature focused on the recovery of monomers/valuable chemicals from waste plastics pyrolysis. This study has been conducted as such to determine pyrolysis conditions enabling valuable chemicals recovery from waste polyethylene terephthalate (PET) and polystyrene (PS) plastics.

1.3 Research questions

1. What is the composition of South Africa’s plastic stream?
2. What is the composition of the landfill plastics stream from the Kraaifontein waste management facility?
3. Can high value aromatic chemicals be recovered from PET and PS waste plastics?
4. What are the pyrolysis conditions for the recovery of these chemicals?
5. What are the yields and concentrations of these chemicals, and are these suitable to consider these processes for further development into industrial solutions?

1.4 Research objectives

In order to make a significant contribution towards the understanding of plastic pyrolysis in South Africa, the following objectives were proposed:

1. To identify common plastic polymers in South Africa’s plastic stream and study the composition of the stream.
2. To estimate the composition of the plastics landfill waste stream at Kraaifontein waste management facility (KWMF)

3. To compare the thermal behaviours of the individual plastics isolated from KWMF with those of pure plastics reported in literature.
4. To get some insight on the pyrolysis mechanism of PS and PET at particle scale through an analysis technique coupling thermal gravimetric and on-line mass spectrometry (TG/MS).
5. To study the influence of temperature and heating rate on PS and PET pyrolysis conversion at bench-scale. Slow and vacuum pyrolysis technologies were considered for the maximising of high value chemicals or monomer production.
6. To identify and quantify the valuable chemicals produced from PS and PET pyrolysis process.

1.5 Significance of the study

There are few reports on the recycling of plastic wastes by pyrolysis in South African context, especially in the area of high value chemical recovery. This probably is due to the fact landfilling and mechanical recycling are currently the most common methods of plastic waste management in the country. However, owing to industry and government policy shift, other options such as chemical recovery need to be considered for plastics that cannot be recycled by physical means. While pyrolysis products obtained from the conversion of some plastics such as PE and PP can be used for diesel fuel substitution, other applications need to be found for PET and PS. The number of scientific research articles related to the conversion of PET and PS into valuable chemicals is limited. It is, therefore, hoped that this study will contribute significantly to filling the knowledge gap in this area.

1.6 Scope and limitations of the research

1. Special attention was given to two plastics, PS and PET, because of their limited potential for fuel application and their potential for yielding interesting valuable chemicals. On the other hand HDPE, LDPE and PP randomly degrade giving rise to waxy hydrocarbons that are suitable for fuel applications. The choice of the plastics for the study was also based on the amount of common plastics found in South Africa’s municipal waste stream. PVC was excluded because it is normally used in long term applications making a low contribution in the waste stream, and its conversion through pyrolysis produces high yield of very corrosive hydrogen chloride.

2. The work was focused on the study and optimisation of pyrolysis conversion but no assessment in terms of economic viability and comparison with other options was done. However, as the materials considered for this are currently landfilled, it is anticipated that there would be a lot of economic and environmental benefits.
3. The use of the gas and char products would be critical to the viability of the pyrolysis process as both products could be utilised for fuel application. The analysis of the properties of these products is out of the scope due to time constraints. However it is anticipated that combustion of part of gas and char products could provide the heat required for pyrolysis conversion, making the process self-energy sufficient.
4. The chemicals of interest were recovered in a mixture composed of several compounds. While the isolation of the chemicals of interest from the mixture was not studied, particular attention was given to the product selectivity in order to limit the cost related to its downstream isolation and purification.

1.7 Assumptions

1. Quantitative data on the plastic wastes that are incinerated is not readily available in South Africa, thus it has been assumed that polymers that are not recycled end up in landfills.
2. Conversion of PP and PE into fuel products is more economically viable than into chemicals.
3. The sample collected for the study was representative of what is landfilled at Kraaifontein waste management facility (KWMF).

1.8 Thesis structure

The thesis is set out as follows: chapter one introduces the study by giving a synopsis of how plastic waste has increased and became an environmental problem. The chapter additionally outlines the need to address the plastic waste problem and presents an opportunity that exists to mitigate the problem. Research questions, objectives, study significance and scope are given in this chapter. Chapter two forms the first part of literature review of the report, the definition of a plastic is given and elaborated upon. The types of plastics in existence as well as the sources of waste plastics are discussed here. There are different waste management techniques being practiced worldwide and a brief account of this aspect is given in chapter two.

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The potential of pyrolysis has been tackled in chapter three as part of continued literature review. The types of pyrolysis processes, factors affecting the process including the advantages of the technology are discussed. Further in this chapter the degradation mechanisms during thermal conversion of the six common plastics are explained with a particular attention to PS and PET.

The research methodology is expounded on in chapter four where materials and analytical equipments that were used in the study, have been explained. The safe work methods that were followed to operate experimental equipment and obtain results are given and discussed in this part of the report.

Chapter five includes the results section of the thesis and firstly details the waste characterisation of the waste plastics done in the context of South Africa as well as Kraaifontein Waste Management Facility (KWMF) landfill stream. Then thermal characterisation of common plastic, in addition to the investigation of PS and PET pyrolysis mechanisms using thermal gravimetric – mass spectrometric (TG – MS) results are presented and discussed. Lastly, bench-scale slow and vacuum pyrolysis results of PET and PS are outlined and discussed in line with literature.

Chapter six marks the end of the report where conclusions drawn from the study are highlighted. The recommendations are also given in this chapter.

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2 Plastic waste management

2.1 What is a Plastic?

A plastic is a polymer formed from a repeating unit called monomer, for example as styrene monomers used to create the polystyrene polymer (ASTM D 883, 2004). The polymers can contain thousands to millions of atoms and are manufactured by polymerisation. Polymerization is the process by which individual monomers of similar or different molecules chemically combine to form macromolecules with long chain structures, having different properties from those of starting molecules.

Plastic spans a wide range of synthetic polymerization products which can be moulded into any desired shape when subjected to heat and pressure. Plastics usually contain other ingredients which impart certain properties such as lubricant, filler, plasticizer, stabilizer and colouring material (Chanda and Roy, 2012, Sen, 2005). The densities of common single plastics are given in Table 2.1 below according to the following sources: (Panda et al., 2010, ASTM D 883, 2004 and ASTM D 792, 2004)

Table 2.1 Densities of common plastics

Plastic	Density (gpl)
PET	1290-1400
HDPE	952-965
PVC	1300-1580
LDPE	917-932
PP	900-910
PS	1040-1050

2.1.1 Types of plastics

There are mainly two types of plastics namely thermoplastics and thermosetting plastics. Thermoplastics such as high and low density polyethylene (HDPE and LDPE), polyvinylchloride (PVC), polypropylene (PP) and polystyrene (PS) can be melted and reformed repeatedly without loss of mechanical or physical properties (Sen, 2005). On the other hand thermosetting plastics cannot be remoulded or reformed through heating and cooling (Klar et al., 2014). The plastic sets to a permanent form on cooling and is likely to decompose on reheating (Sen, 2005).

2.2 Plastic waste sources

Plastic wastes can be classified into two categories on the basis of their origins (Chanda and Roy, 2012, Demirbas, 2004, Buekens and Huang, 1998).

2.2.1 Pre-consumer sources

Pre-consumer plastic wastes, which are also known as primary (industrial) waste, emanate from manufacturing, processing and packaging industries (Patni et al., 2013). They are a result of process purging and as scrap during virgin plastic manufacture (Chanda and Roy, 2012).

2.2.2 Post-consumer sources

Post-consumer plastic wastes are basically a fraction of municipal solid waste (MSW) whose life cycle range from medium to short term (Chanda and Roy, 2012). They are used in the food, detergent, pharmaceutical, shopping, packaging and many other industries. There are six common plastics that contribute to the plastic fraction in MSW namely HDPE, LDPE, PP, PS, PET and PVC (Williams and Williams, 1999, Williams and Williams, 1997). The composition of municipal plastic waste (MPW) can vary depending on the lifestyle and economy of the people as well as the season of the year. MPW include items such as disposable plastic plates, food containers, packaging foam, disposable cups, compact disks, cutlery, cushioning foams, carbonated drink bottles and plastic pipes.

2.3 Plastic waste management strategies

There are several options available for managing waste plastics as detailed in Figure 2.1. Primary recycling is practiced within the plastic production line when plastic scrap and off cuts are reused in the manufacturing process, while secondary recycling involves reuse of end of life plastic articles (Patni et al., 2013). On the other hand, quaternary recycling, typically combustion or incineration, is done with the main aim of heat recovery, while tertiary recycling is focused on recovery of valuable chemicals and/or fuels. Some of these options are briefly described further in this section.

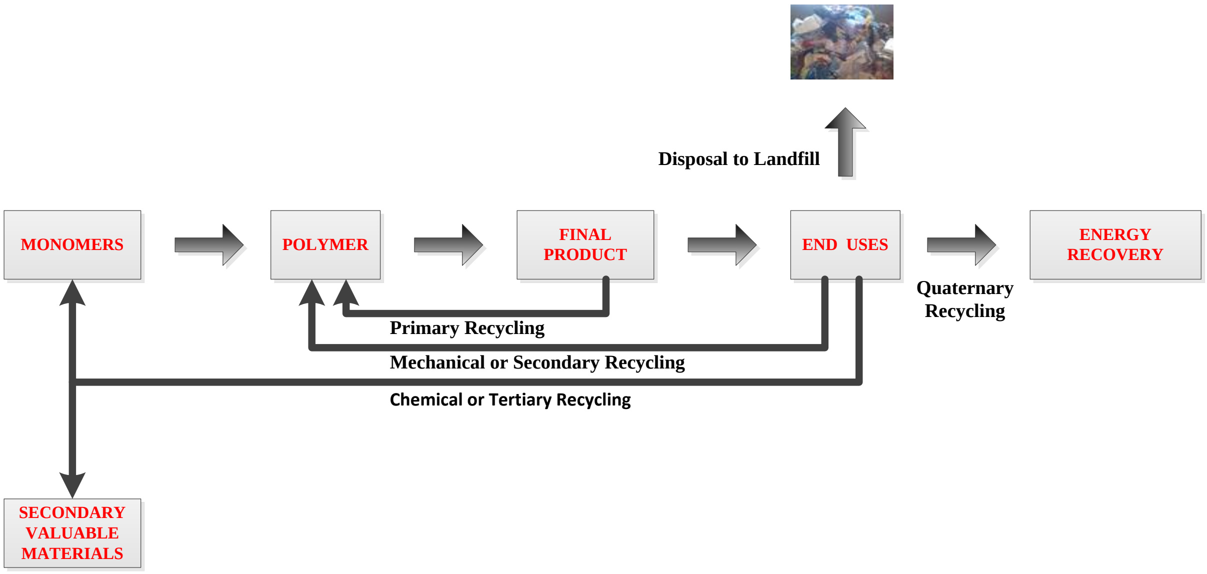

Figure 2.1 Plastic waste management strategies

2.3.1 Land filling

Land filling is an engineered method of solid waste disposal on land. This is done by spreading and compacting the waste into cells and covering it each day with earth to avoid posing threats to public health and environment. This is the most common method of waste plastic management in the world (Harris and Gaspar, 1988, Mo et al., 2014). It has been established in this study that more than 70% of plastic wastes end up in landfills in the Republic of South Africa.

This method of plastic waste management does not allow resource recovery from plastics and is being strongly discouraged nowadays. Landfill space has become both scarce and expensive because plastics take up large land volumes as a result of the large volume to weight ratio. Monitoring of gaseous emissions from landfills has revealed significant quantities of toxic gases such as vinyl chloride, toluene and methane (Morris et al., 1988). Additionally, ground water systems near landfills usually get polluted with landfill leachates (Macdonald et al., 1972). The above reasons together with restrictive policy and industrial initiative changes on landfilling have led to the quest for better management options of plastic wastes (Achilias et al., 2007).

2.3.2 Combustion

Generating energy from plastic waste incineration (combustion) is an alternative treatment route but is now being discouraged to reduce GHG emission load on the planet and high flue gas pollution abatement costs (Bockhorn et al., 1999). The polymer wastes typically replace conventional fuels in this process and proponents argue this reduces the CO_2 load on the environment as additional fresh fossil fuels are not exploited. The calorific values of plastics are shown in Table 2.2 and some of them (PE, PP) compare well with that of fossil fuels and can thus be used as fuel. However, highly toxic pollutants like dioxins (Patni et al., 2013), polychlorinated dibenzo dioxins (PCDD) as well as polychlorinated dibenzo furans (PCDF) are produced at accelerated rates due to the presence of PVC in waste streams (Conesa et al., 2009, Safadi and Zeaiter, 2014).

Table 2.2 Plastics and fossil fuels calorific values (Williams and Williams, 1997)

Fuel	Calorific value (MJ/kg)
Gasoline	44
Diesel	43
Heavy Fuel Oil	41
Coal	24
Polyethylene (PE)	46
Polyvinylchloride (PVC)	18
Polystyrene (PS)	41
Polypropylene (PP)	46
Polyethylene Terephthalate (PET)	22

2.3.3 Mechanical recycling

This is probably the best option of waste plastics management as the polymers are sorted into specific components, crushed, milled and re-extruded into other plastic items avoiding fresh fossil fuel extraction. This industry is very active in South Africa and, according to PlasticsSA, is responsible for about 26% of plastic recovery. However, sometimes it is not possible to recover plastics due to the following problems:

- Degradation during processing and lifetime (thermal mechanical degradation and photo oxidation).

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- Incompatibility between different polymers.

The latter point refers to mixed plastics (multilayer), films and those which are not labelled, cannot easily be identified, sorted and recycled in this method. Moreover, mixed plastics have different melting points rendering the processing of mixed, heterogeneous plastics even more difficult. There is the need therefore to find alternative ways of managing plastic wastes that cannot be treated by mechanical recycling. In this instance other options such as chemical recycling need to be considered to increase recovery rates of waste plastics.

2.3.4 Chemical recycling

Feedstock recycling, called chemical recycling, is used to convert waste plastics to new compound units or high value chemicals (ISO 15270, 2006). These products are usable as feedstock to different industrial processes or upgraded to transportation fuels and in some cases as monomers (Patni et al., 2013, Liu et al., 2000, Sasse and Emig, 1998). There are three common types of chemical recycling: depolymerisation, gasification and cracking (thermal, catalytic as well as hydrocracking). In this study the focus is on thermal cracking (pyrolysis) as a promising treatment technology (Westerhout et al., 1997) and an attempt to describe the other methods is not made here.

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3 Pyrolysis of waste plastics

Generally pyrolysis is defined as controlled thermal degradation of materials in an oxygen-free (inert) environment (Jamradloedluk and Lertsatitthanakorn, 2014, Demirbas, 2004 Adrados et al., 2012, Patni et al., 2013). During this process the feed material is decomposed into char and volatiles. At the exit of the reactor a fraction of the volatiles is condensed to oil and the non-condensable fraction can be collected as a permanent gas. In plastics pyrolysis, polymer macromolecular structures are cleaved into smaller molecules, oligomers or sometimes monomeric units (Green and Sadrameli 2004). Subsequent decomposition of these to low molar mass molecules is dependent on several process conditions and the chemistry of depolymerisation. These include but are not limited to temperature, heating rate, residence time of the sample and released volatiles in the reactor, particle size, inherent or added catalysts, reactor type and feed composition (Jung and Fontana, 2006). Generally, the reactivity of plastic polymer is influenced by the size of the substituent in the side chain. The order of increasing side chain size of the polymers under this study is polyethylene, polypropylene, polyethylene terephthalate and polystyrene. The pyrolysis technology appears to be a favourable plastic waste treatment method (Mastral et al., 2007, Green and Sadrameli 2004) as it is able to reduce plastic landfilling volumes by more than 80% with more environmentally friendly gaseous emissions than incineration (Ceamanos et al. 2002, Artetxe et al., 2015, Mo et al., 2014). In addition, valuable hydrocarbons for utilization as fuels or feedstock could economically be obtained through pyrolysis of plastic wastes (Kim and Kim, 2004, Faravelli et al., 2001). The majority of plastic wastes occur as polyolefins, i.e. LDPE, HDPE and PP (Williams and Williams, 1999, Jamradloedluk and Lertsatitthanakorn 2014, Arabiourrutia et al., 2012, Kayacan and Doğan 2008) and unsurprisingly extensive research has been done on these polymers (Ceamanos et al., 2002), but research work on PET and PS with a special focus on valuable chemicals recovery is limited.

3.1 Advantages of pyrolysis

There are many advantages of pyrolysis as an emerging technology that can help cushion the impact of fossil fuel resource depletion, by recycling plastics for fuel and valuable chemicals recovery. It is a suitable method of recycling waste mixed plastics that cannot effectively be recycled by other means such as mechanical recycling, in addition to permitting recycling of

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plastics with little pre-treatment. Pyrolysis is further more able to treat plastic laminates and multi-layered packaging films that are not recycled using the traditional reprocessing technologies. Pyrolysis processes significantly reduce the mass of waste by 50 – 90 wt% (Jung and Fontana, 2006, Patni et al., 2013) in addition to pollutant emission minimisation, owing to the fact that the process is carried out in an air-devoid environment (Patni et al., 2013). The process is cheaper in terms of off gas handling equipment capital and operating costs in comparison to incineration counterparts. This aspect comes from the fact that pyrolysis technology comparatively produces a much smaller off gas load which needs simpler and smaller pollution abatement off gas handling equipment.

3.2 Types of pyrolysis

There are mainly three types of pyrolysis: Slow, vacuum and fast. The classification is based on how fast the feed material is heated and how fast the volatile products are withdrawn from the reactor hot zone.

3.2.1 Slow pyrolysis

Slow pyrolysis (SP) is conducted between 400-600 °C with slow heating rates of 1-100 °C/min and long vapour residence times (1-60 min) (Ali and Siddiqui, 2006). In slow pyrolysis bigger feed particle sizes can be used without significant thermal lag within the particles, because of low heating rates.

3.2.2 Fast pyrolysis

Fast pyrolysis (FP) reaction proceeds rapidly in a few seconds. This process is therefore controlled by the chemical reaction, heat and mass transfer as well as phase transition. This is accomplished by operating at high temperatures (>500°C) with short vapour residence times (< 3 s). High heating rates as high as 1000 °C/s (Ojha and Vinu, 2015) are employed for rapid bond breaking. Secondary reactions of primary products are avoided by rapid cooling of vapours (Ali and Siddiqui, 2006). Feed particle sizes used in this process is generally small to minimize heat and mass transfer limitations.

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3.2.3 Vacuum pyrolysis

Vacuum pyrolysis (VP), a more recent technology, is similar to slow pyrolysis but is conducted under vacuum, as opposed to an inert gas used in SP to purge pyrolytic vapours. The vacuum quickly sucks volatiles from the reaction zone limiting secondary reactions. This results in lower gas and char yields but higher oil yields. VP is usually conducted between 10-20 kPa vacuum, whereas slow pyrolysis is conducted at atmospheric conditions. The temperature range remains the same as conventional pyrolysis.

3.3 Factors affecting pyrolysis

There are many factors influencing pyrolysis product composition such as feed composition, presence of catalysts and operating conditions. These factors are explained in the following sections.

3.3.1 Feed composition

The primary products of pyrolysis are strong functions of the chemical structure as well as the composition of polymers (Pinto et al., 1999, Walendziewski, 2006, Scheirs, 2006). The decomposition mechanisms of polymers, which differ from polymer to polymer, determine the distribution of products between the three phases (Scheirs and Kaminsky, 2006). In Figure 3.1 below, the elemental compositions of the pure polymers are given. It can be observed from the figure that HDPE, LDPE and PP have similar carbon and hydrogen proportions; this fact explains the similarity of the nature of products obtained from pyrolysis of these polymers. On the other hand PS and PET have higher and lower carbon: hydrogen ratios respectively and therefore are expected to thermally behave differently. PET possesses even a third atom in the name of oxygen, which is expected to impart peculiar thermal characteristics to the polymer molecule, due to difference in thermal stability of the C-O bond when compared to the C-H and C-C bonds. The presence of highly stable aromatic rings in PET and PS is likely to give a condensable fraction (pyrolysis oil) composed of a large amount of aromatic compounds through pyrolysis.

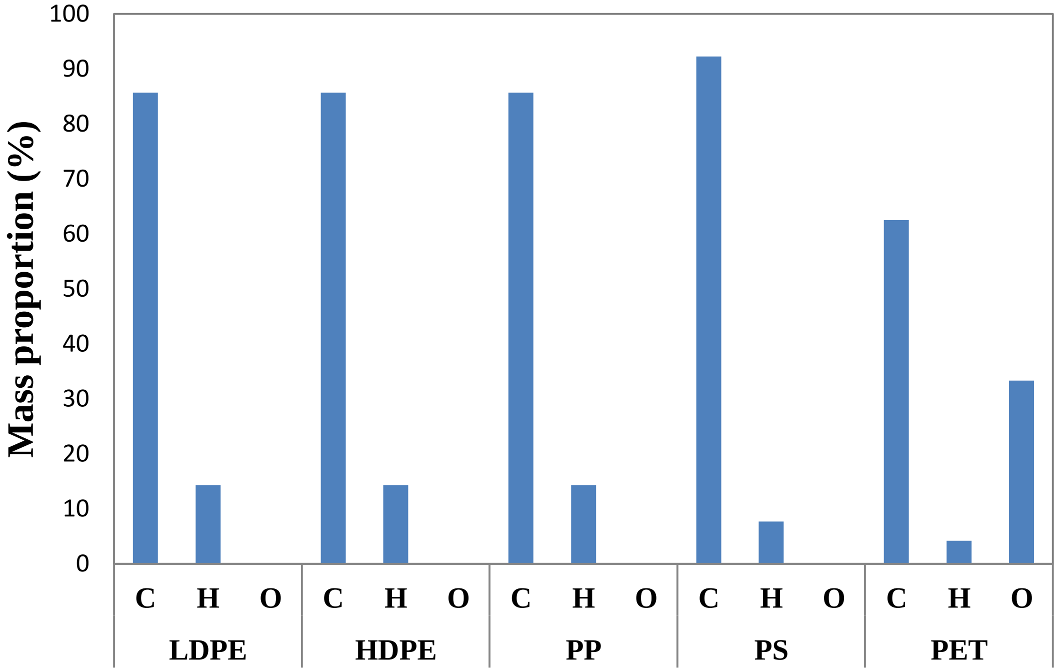

Figure 3.1 Theoretical elemental compositions of polymers studied (based on pure polymers without any additive)

3.3.2 Catalysts

The use of catalysts influences the kinetics and mechanisms of thermal degradation and hence, the pyrolysis product distribution (Patni et al., 2013). Catalysts lower the temperature of operation and some of them can give a more specific spectrum of products than without catalyst (Lin and Yen, 2005). The lower temperature of operation in this instance reduces the energy penalty to the operator (Xingzhong, 2006), but that happens at an added catalyst cost and eventual issues related to catalyst recovery or treatment. Therefore a balance is to be sought such that the catalyst cost is offset by the additional revenue gained from the increased productivity and product purity (Miller et al., 2006). Due to the exploratory character of this study, pyrolysis optimization without catalyst was considered as a first approach.

3.3.3 Temperature

High operating pyrolysis temperatures and heating rates as a rule of thumb enhance bond cleavage of polymers, which favours the formation of volatile compounds (Scheirs, 2006). The distribution of compounds depends on the temperature. The higher the temperature, the more secondary reactions happen and the higher the gas yield.

3.3.4 Volatile residence time

Long residence times of the volatile products inside the reactor favour secondary conversion of primary products (López et al., 2011). This yields more gas, coke and thermally stable products such as aromatics (Ali and Siddiqui, 2006, Arena and Mastellone, 2006), thus obscuring the effect of the original polymer structure on pyrolysis product distribution.

3.3.5 Particle size

The particle size of the polymer influences pyrolysis product distribution through their resistance to heat transfer as the size varies (Luo et al., 2005). Fine particles are reported to offer high mass transfer rates to escaping condensable gases before they undergo secondary cracking, leading to higher liquid yields (Hatakeyama and Quinn, 1999). Larger particles, on the contrary, limit heat transfer and facilitate secondary cracking. This is partly because of high resistance they pose to the escaping primary pyrolysis products.

3.3.6 Reactor type

The type of reactor is critical in determining the quality of mixing, heat transfer and volatiles residence times. The reactor geometry will determine the escape dynamics of primary decomposition products and thus different reactors give variable product quality and quantity. Typical reactors that have been used in the pyrolysis of waste plastics research include:

1. Batch reactors

In these reactors, feedstocks are fed in batches into the reactor at the start of the pyrolysis process. When the process is complete, the reactor is emptied of products as well as residues and prepared for another batch. These reactors have been utilised by several researchers such as Pinto et al (1999) and Paradela et al (2009).

2. Semi-batch reactors

In semi-batch reactors, the volatile pyrolysis products are continuously removed from the reaction zone with the help of an inert purge gas flow or the reactor is initially pressurised with an inert gas while the product is continuously withdrawn. The feed polymers are initially loaded into the reactor before the pyrolysis process is started. Williams and Williams, (1997), Miranda et al. (2001), Kim and Kim, (2004) and Mo et al. (2014) have used this reactor setup to conduct plastic pyrolysis research.

3. Continuous reactors

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These are reactors normally used to study fast pyrolysis of plastics. The following two reactors are typical examples of continuous reactors.

- Fluidised bed reactor

This is a reactor that can be run both continuous and batch modes with solid bed of material that is evenly distributed around the cylindrical section of the reactor to enhance heat and mass transfer. This reactor type has been used by several researchers to study pyrolysis of various feedstocks (Westerhof et al., 2011, Scott et al., 1990, Lin and Yen, 2005)

- Conical spouted bed reactor

This is a continuously operated reactor whose solid fluidised bed exhibits vertical cyclic movement as the fluidising gas is fed through the conical section of the reactor. This reactor was used by Arabiourrutia et al. (2012), Artetxe et al. (2015) and Elordi et al. (2007) when conducting research on plastic feedstocks.

3.4 Thermal degradation mechanisms

The reaction mechanisms of polymer cracking are closely related to the type of polymer being treated. There are three main categories of thermoplastic decomposition mechanisms (Van Krevelen and Te Nijenhuis, 2009, Patni et al., 2013) These mechanisms are briefly described below and will further be explored in section 3.5, where the pyrolysis of individual plastic polymers is discussed.

3.4.1 Side chain elimination

This thermal decomposition mechanism is also known as chain stripping and usually occurs in two steps. In the first step, side groups attached to the polymer parent chain are eliminated. This process eventually leaves an unstable polyene macromolecule. The polyene molecule undergoes further random scission reactions to form smaller fragments, aromatic compounds and char.

PVC is a typical polymer that decomposes according to this mechanism. The initial step of PVC thermal degradation is chlorine side group elimination to produce hydrogen chloride (Buekens, 2006a), Scheirs, 2006). The remaining polyene macromolecule undergoes scission and cyclisation reactions to form smaller compounds and aromatic molecules, usually toluene, benzene, and naphthalene (Jung and Fontana, 2006).

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3.4.2 Depolymerisation

Depolymerisation (unzipping) or end chain scission is classified a free-radical mechanism but this time the polymer is chiefly decomposed into the monomer that constitutes the polymer. The free radicals formed from the polymer chain causes the polymer to go through scission reactions, which produce unsaturated low molecular weight molecules. This mechanism is considered the reverse of polymerisation, because monomer units are cleaved from the end of polymer chains. Polystyrene is a typical polymer that can be depolymerised to a large extent according to this mechanism, depending on system conditions of temperature, heating rate, holding time and reactor configuration (Scheirs, 2006). Condensation polymers such as PET can also thermally depolymerise according to this mechanism, under carefully controlled temperature conditions (Scheirs, 2006, Arena and Mastellone, 2006). The polymer is well known for its chemical depolymerisation behaviour as opposed to thermal one.

3.4.3 Random scission

Random scission occurs by free radical formation at the weakest point along the polymer chain (Patni et al., 2013). This process produces a series of smaller, repeating oligomers with differing carbon chain lengths. When these random scission reactions occur repeatedly, the molecular weight of the polymer and its initial degradation products keep on decreasing until small enough to escape the reaction front into the gas phase and eventually removed as volatiles from the pyrolysis reactor. The degraded products have a wide distribution of carbon numbers because of the random nature of the reaction.

Polyolefins (PE and PP) which are addition polymers, randomly produce fragments upon application of heat. These fragments have larger molecular weights than those of monomers (Walendziewski, 2006). The degree of depolymerisation is limited in this case, as a result the yield of monomers from polyolefins is low.

3.5 Thermal conversion of individual plastics

This section discusses various aspects of thermal conversion of the individual most common plastics in the waste streams. These plastics are polyethylene, polypropylene, polystyrene, polyethylene terephthalate and polyvinyl chloride. Studies on polyvinyl chloride pyrolysis are rare because of the production of hydrochloric acid, which is very corrosive to equipment. More information can be found on the conversion of polyethylene and polypropylene due to the fuel potential of the pyrolysis products. Particular attention has been given to the pyrolysis of polystyrene and polyethylene terephthalate due to their high proportion in the waste stream collected during this study, as can be observed in section 5.1.2. The discussion is also focused on type of products obtainable from individual plastics. Since polymer thermal degradation process is endothermic in nature, the C-C bond dissociation energy is required to decompose the polymer. This factor is critical in polymer stability determination. There is a direct relationship between degradation temperature and dissociation energy (Aguado and Serrano, 1999) for various polymers as shown in. Figure 3.2.

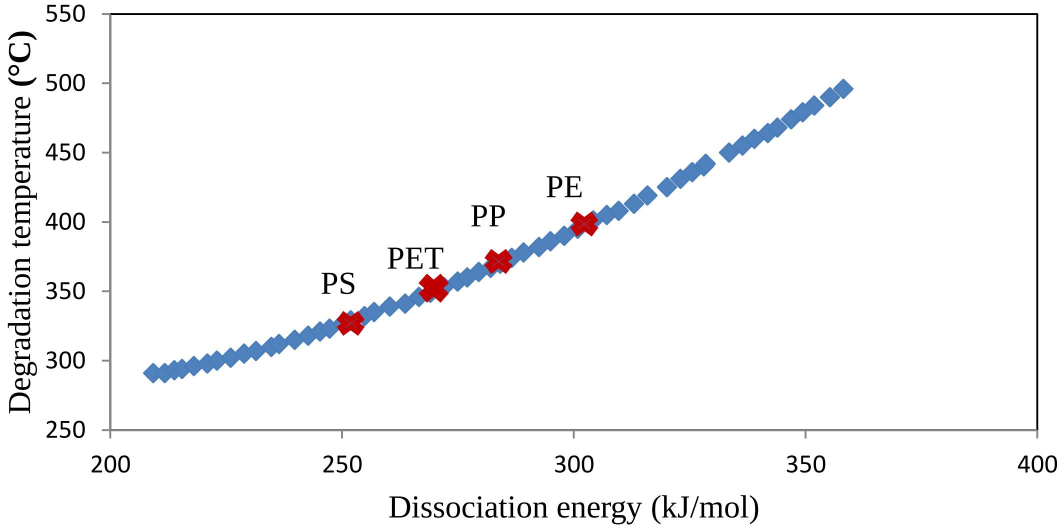

Figure 3.2 Degradation temperatures versus dissociation energies for various polymers (Redrawn from Aguado and Serrano, 1999).

3.5.1 Polyethylene

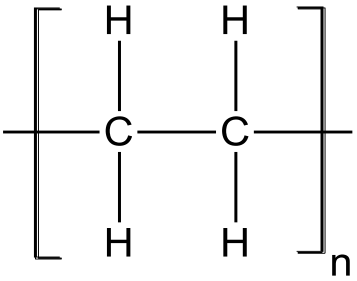

Figure 3.3 Polyethylene polymer structure

Polyethylene, represented in Figure 3.3 above, is a major contributing polymer to plastic wastes due to its wide use in plastic bags and packaging containers. This plastic has two classes, HDPE and LDPE, which are both present in waste plastics. In South Africa’s waste stream HDPE contributes 19 wt % while LDPE contributes 31 wt % (PlasticsSA, 2012).

Low density polyethylene and high density polyethylene are aliphatic hydrocarbons. The low density of LDPE comes from a large degree of chain branching. Polyethylene (PE) in its pure form contains 85.7 wt% carbon and 14.3 wt% hydrogen. These figures can differ slightly from ones reported for waste PE polymers (Kumar and Singh, 2013), because of additives used during plastic article production.

3.5.1.1 Thermal behaviour of polyethylene

In Table 3.1 the degradation range and peak temperatures of HDPE and LDPE are shown. Peak temperature is determined by thermogravimetric analysis. It corresponds to the maximum degradation rate of the sample (peak on the dTG curve, which is the derivative of the curve corresponding to the evolution of the mass sample). It can be observed from Table 3.1 that the polymer degradation temperature range and peak temperatures are dependent on the heating rates. The low thermal conductivity of plastics causes significant thermal lags (Jenekhe et al., 1983, (Buekens, 2006a) when analyses are undertaken at higher heating rates and the polymers tend to degrade at slightly higher temperatures.

Table 3.1 Thermal decomposition temperatures of PE in TGA experiments

Heating rate (°C/min)	Polyethylene	Temperature range (°C)	Peak temperature (°C)	References
5	PE	370 – 520	470	(Senneca et al., 2002)
10	HDPE	405 – 510	480	(Sorum et al., 2001)
10	LDPE	395 – 504	472	(Aboulkas et al., 2008)
20	HDPE	410 – 515	493	(Senneca et al., 2002)
20	PE	400 – 520	480	(Heikkinen et al., 2004)
20	LDPE	405 – 515	491	(Heikkinen et al., 2004)
20	LDPE	434 – 523	485	(Aboulkas et al., 2008)
50	LDPE	447 – 567	503	(Aboulkas et al., 2008)
100	PE	460 – 560	520	(Senneca et al., 2002)
900	PE	500 – 660	600	(Senneca et al., 2002)

PE – Not specified as LDPE or HDPE

From the thermogravimetric analysis (TGA) of the pure plastics at a heating rate of 5 °C/min, it can be observed from Figure 3.4 that LDPE decomposition commences at a slightly lower temperature than that of HDPE. HDPE is a less linear and more crystalline plastic than LDPE and these aspects make LDPE more thermally unstable than HDPE. The high degree of branching in LDPE provides it with more reactive tertiary carbons leading to less thermal stability in comparison with HDPE (Ballice et al., 1998, Aguado and Serrano, 1999).

The HDPE and LDPE polymers are completely volatilised in a fast single step below 500 °C. The polyolefins undergo extensive mass loss between 350 – 500 °C with maximum degradation temperature (also named peak temperature) around 480 °C (for heating rates in the range of 5 – 20 °C/min) as indicated in the above table. These degradation characteristics would be used to check the purity of LDPE and HDPE isolated from KWMF.

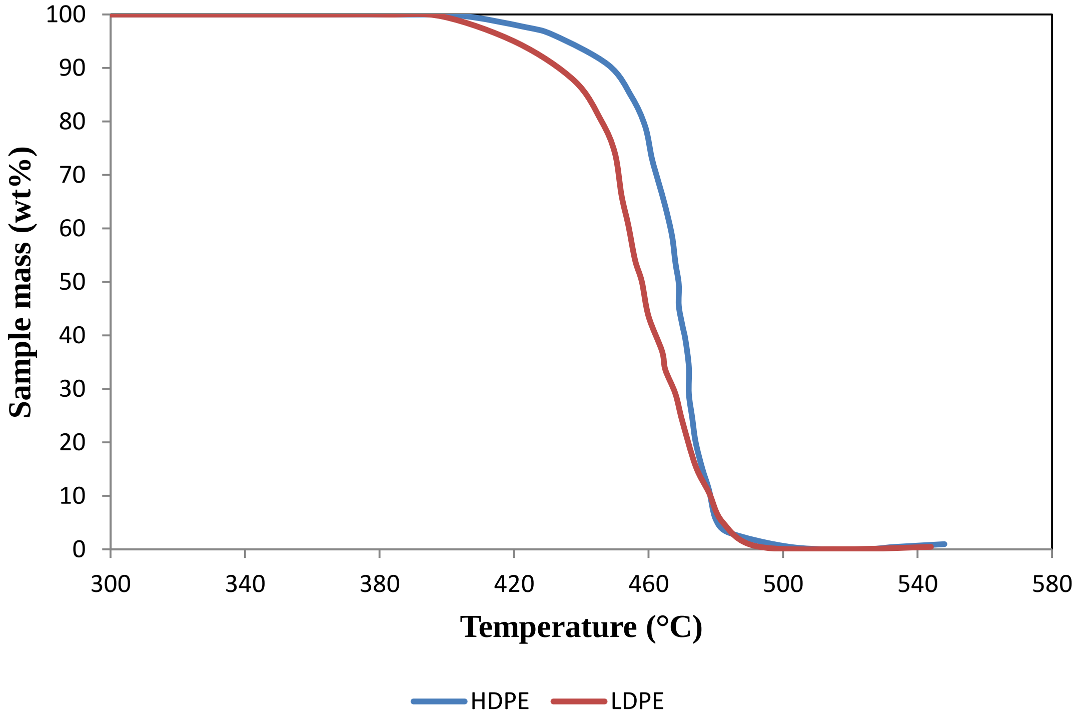

Figure 3.4 Comparison of the thermogravimetric analysis curves of LDPE and HDPE performed at 5 °C/min heating rate (Redrawn from Ballice et al., 1998)

3.5.1.2 Thermal decomposition mechanism of polyethylene

Polyethylene is widely reported to be decomposed via random chain scission mechanism (Faravelli et al., 1999, Ceamanos et al., 2002, Jamradloedluk and Lertsatitthanakorn, 2014). Since scission of PE chains occurs randomly, a broad hydrocarbon product spectrum is therefore inevitable. The scheme shown in Figure 3.5 illustrates the degradation mechanism of PE that has been proposed by many researchers (Bockhorn et al., 1999, Patni et al., 2013, Walendziewski, 2006). The following have been suggested as the main stages taking place during the decomposition process:

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- Initiation; this involves the breaking of the first polymer chain bonds, resulting into two radicals and may occur at random or end-chain positions.
- Propagation, involves the evolution of low molecular weight alkenes from primary alkane radicals.
- Hydrogen transfer reactions, intermolecular or intramolecular hydrogen abstraction may occur. In this process in which radicals abstract hydrogen, alkene species and polymeric fragments are formed. In addition, intermolecular hydrogen abstraction reaction between primary radicals and polymeric fragments lead to formation of secondary radicals.
- Secondary radicals get cleaved to produce a primary radical and an end-chain alkene group.
- Side chains formation, result from two secondary radical or secondary and primary radical interactions.
- Termination; this occurs when two primary radicals (bimolecular mode) or primary macro-radicals (disproportionation or recombination) combine to yield stable molecular species to end these chain reactions.

The scheme is a radical-mechanism initiated by heat effects of the weak C-C homolytic bond cleavage into primary radicals R_p (1). These weak points can be regions of structural faults or distorted electron cloud (Miskolczi, 2006). The scission of the primary radicals in the beta position leads to ethene evolution (2). The production of ethene gas is more pronounced at higher temperatures when the unzipping reaction (decomposition into monomers) is more evident. On the other hand, high stability secondary radicals R_s are produced at low temperatures following β-scission and intramolecular hydrogen transfer (3). The repetitive β-scissions of the secondary radicals propagate the radical mechanism (4) to give off olefins and primary radicals as well as polyene backbone. Intermolecular hydrogen transfer (5) at high temperatures promotes short chain primary radicals leading to enhanced alkane formation. Termination process (6) takes place with the combination of two primary radicals.

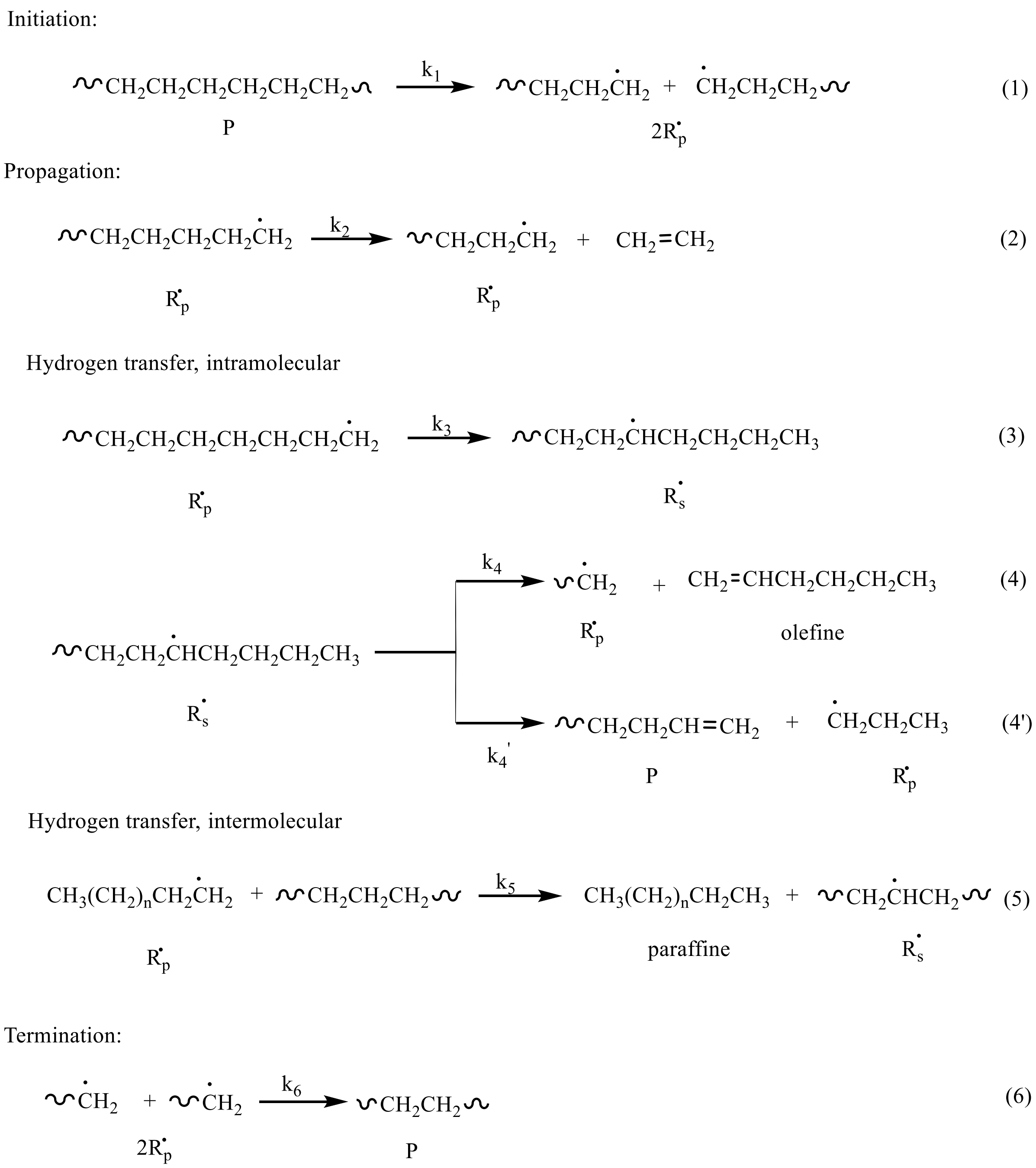

Figure 3.5 Random scission degradation mechanism of PE (Redrawn from Bockhorn et al., 1999)

3.5.1.3 Products from pyrolysis of polyethylene

Research shows that decomposition of polyethylene results in a broad range of hydrocarbons, from methane to aromatics, varying with the temperature at which degradation occurs (Bockhorn 1985, Sodero et al. 1996, Kaminsky et al. 1996, Kaminsky et al. 1995, Ikura et al. 1999, Aguado et al. 2014, Mastral et al. 2003, Williams & Williams 1999, Walendziewski

2005). This has been attributed to the random nature of the polyolefin decomposition process. Williams and Williams, (1997) conducted slow pyrolysis in a fixed bed reactor at 700 °C and reported oil/waxy yield for HDPE and LDPE of about 80 and 84 wt %, respectively, while the corresponding gas yields were 17 and 15 wt %, respectively. Experiments conducted by Walendziewski in 2005 on polyethylene showed that between 420–440 ºC, the yield was 84.5 wt % liquid, 10.2 % gas, while that of solid residue was 5.1 wt%. The researchers observed that the gaseous products increased as the liquid fraction decreased, when the temperature tended towards 500 ºC. The liquid composition was largely mixtures of olefinic C_5-C_{25} and paraffinic hydrocarbons, while the gases were composed mainly of C_1–C_5 hydrocarbons.

The proportions of condensable and permanent gases depend on the temperature and volatile residence time. The higher the temperature and residence time, the higher the gas yield and aromatic content (Kaminsky and Kim, 1999, Williams and Williams, 1999, Aguado et al. 2014, Kaminsky et al. 1995).

3.5.2 Polypropylene

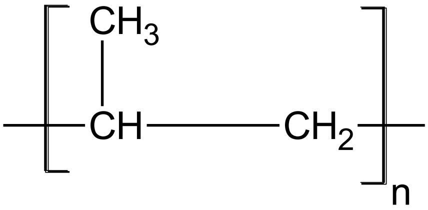

Figure 3.6 Polypropylene polymer structure

Polypropylene represented in Figure 3.6 above is a polyolefin thermoplastic made from propylene monomer by polymerisation. This is another plastic found in high proportions in the municipal waste streams owing to its wide usage in packaging applications. In South Africa’s context in particular its proportion can be as high as 26 wt % (PlasticsSA, 2012). It is a hydrocarbon whose composition is 86 wt% carbon and 14 wt% hydrogen on a pure basis but these values slightly differ from those obtained for the waste polymer. Waste PP carbon content has been reported between 83 – 86 wt% carbon and 14 – 16 wt% hydrogen (Wang, 2001, Grammelis et al., 2009, Kim and Kim, 2004).

3.5.2.1 Thermal behaviour of polypropylene

In Table 3.2 the degradation temperature range and peak temperature of polypropylene are shown. The thermogravimetric analysis **(**TGA**)** of the plastic carried out by several researchers in inert atmospheres from 25 – 600 °C between temperature ramp rates of 5 - 25 °C/min revealed a decomposition temperature range of 320 - 513 °C as can be noted from the table below.

Table 3.2 Thermal decomposition temperatures of PP in TGA experiments

Heating rate (°C/min)	Temperature range **(**°C)	Peak temperature **(**°C)	References
5	403–448	431	(Jing et al., 2014)
5	324–501	433	(Saha et al., 2008)
10	397–477	450	(Saha et al., 2008)
10	413–462	442	(Jing et al., 2014)
15	412–505	458	(Saha et al., 2008)
15	418–471	448	(Jing et al., 2014)
20	412–497	464	(Saha et al., 2008)
20	422–479	453	(Jing et al., 2014)
20	420–500	472	(Heikkinen et al., 2004)
25	423–513	470	(Saha et al., 2008)

Polypropylene contains methyl side groups at every second carbon in the polymer chain. This means that 50% of the carbons in the PP backbone are tertiary carbons and consequently, the PP is less thermally stable than PE (Çit et al., 2010). Indeed, PP decomposes at a slightly lower temperature than polyethylene as can be observed from the peak decomposition temperatures in the range 430-470 °C from Table 3.2 above. The thermal degradation is a single step process as shown in Figure 3.7 with maximum mass loss rate occurring around 430 °C with low range heating rates of 5 – 10°C/min. This information is important as it forms the standard of comparison with thermal degradation behaviour of PP samples obtained from KWMF.

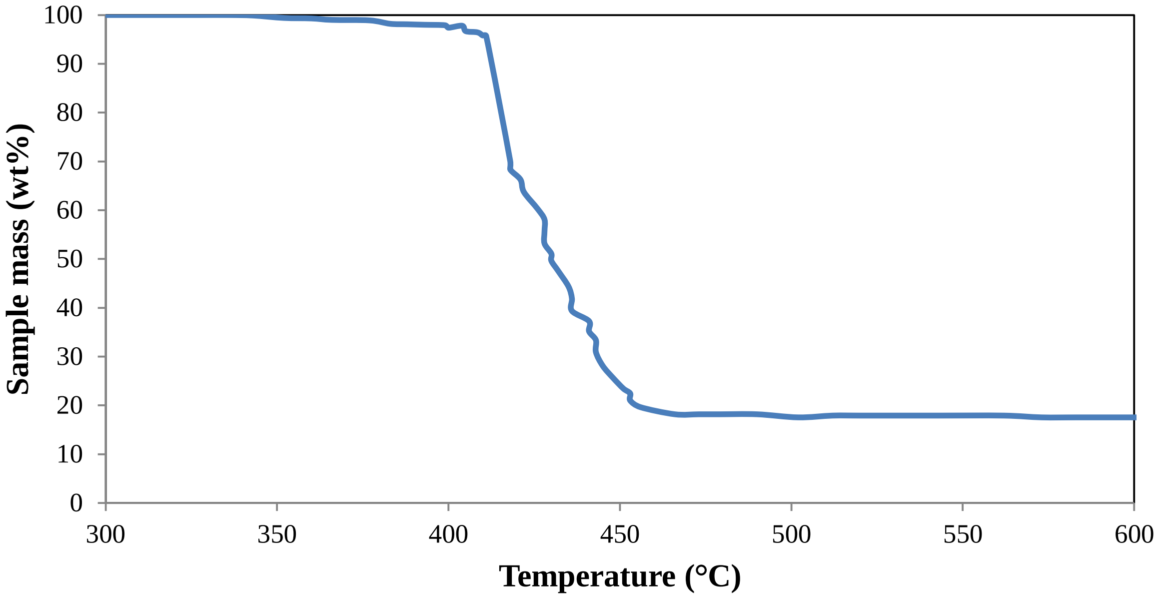

Figure 3.7 Thermal gravimetric analysis of PP in an inert atmosphere with a heating rate of 10 °C/min (Redrawn from Çit et al., 2010)

3.5.2.2 Thermal decomposition mechanism of polypropylene

As polypropylene is a polyolefin just like polypropylene, it decomposes by a similar random chain scission reactions (Aguado and Serrano, 1999, Westerhout et al., 1998, Westerhout et al., 1997). The detailed random chain scission mechanism has been described in section 3.5.1.2. However, tertiary carbon sites in polypropylene allow cleaved fragments to rearrange to produce predominantly olefins. In PP pyrolysis process, intramolecular radical transfer predominates the intermolecular counterpart leading to low molecular weight oligomer formation (Aguado and Serrano, 1999). Thus, the carbon number distribution in the liquid product stream is biased towards the lower side with resultant more volatile PP pyrolysis oil than that of PE (Westerhout et al., 1997, Williams and Williams, 1999).

3.5.2.3 Products from pyrolysis of polypropylene

Polypropylene pyrolysis liquid products predominantly contain olefins with a structure similar to the branched molecular PP backbone. A peculiar aspect of the PP pyrolysis products is the dominant composition of C_9 olefin. The compound identity has been tied to 2,4-dimethylhept-1-ene and its composition has been reported to be as high as 25 wt% (PlasticsSA, 2012). The low temperature slow pyrolysis of PP between 400 – 500 °C has been reported to produce about 80 wt% waxy/oil product (Williams and Williams, 1999, Williams and Williams, 1997) that contains linear paraffins and olefins between $C_6 - C_{53}$ (Achilias et al., 2007). Major branched olefins such as 2-methyl-1-pentene and 2,4,6-trimethyl-1-nonene have also been identified in PP pyrolysis product stream (Kim and Kim, 2004). The non-condensable gas stream has been reported to contain high proportions of propylene, isobutylene and n-pentane. The pyrolysis temperature range of 400 – 500 °C favoured high propene yields (Miranda et al., 2001), but ethene becomes the main component in the gas stream as the temperature was increased (Jung and Fontana, 2006). Several researchers reported that pyrolysis of PP between 400 –720 °C leads to propene and ethene yields in the range of 20 – 60 wt%, of which about 15 wt% is in the gaseous fraction (Westerhout et al., 1998, Williams and Williams, 1997, Williams and Williams, 1999, Miranda et al., 2001), but as the temperature increased towards 800 °C the proportion of thermodynamically stable products such as methane, propane and aromatics increased. The production of propene monomer has generally been observed to be high at lower temperatures and short residence times (Westerhout et al., 1998).

3.5.3 Polystyrene

Polystyrenic plastics form a significant fraction of municipal and industrial wastes, as they are widely used in the food packaging and article cushioning applications. Polystyrene is represented as shown in Figure 3.8.

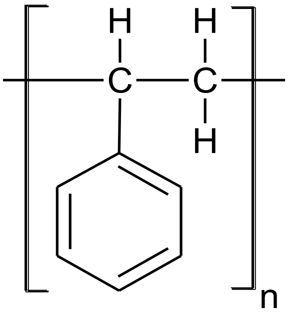

Figure 3.8 Polystyrene polymer structure

In its pure form, carbon is responsible for 92.3 wt% of the chemical composition while the balance is hydrogen. This composition can slightly be different from waste polystyrene due to fillers, colourants and plasticizers that are used during packaging manufacturing. Mo et al. (2013) reported 92.28 wt% carbon, 7.80 wt% hydrogen; 89.28 wt% carbon, 8.87 wt% hydrogen and 91.97 wt % carbon, 8.02 wt% hydrogen for virgin, expanded and container polystyrenes respectively. Similar values of 89.56 wt% carbon and 7.83 wt% hydrogen for expanded polystyrene have been reported by Kim et al. (2003). The ones for the container polystyrene results were close to those reported by Kim and Kim, (2004).

3.5.3.1 Thermal behaviour of polystyrene

The decomposition temperature range and temperatures at which maximum polystyrene polymer degradation occurred as reported in literature are shown in Table 3.3. As usually observed with TGA, the peak temperature shifts at higher temperatures as the heating rates were increased.

Table 3.3 Thermal decomposition temperatures of PS in TGA experiments

Heating rate (°C/min)	Temperature range (°C)	maximum temperature (°C)	References
0.5	360–460	376	(Kim and Kim, 2004)
1	370–460	391	(Kim and Kim, 2004)
2	384–460	400	(Kim and Kim, 2004)
10	350–480	440	(Lee and Shin, 2007)
15	370–475	425	(Brems et al., 2011)
20	369–486	445	(Aboulkas et al., 2009)
50	378–487	448	(Brems et al., 2011)

Similar to polypropylene, half of the carbons in the polystyrene chain are tertiary, because of the phenyl group presence. Thermal degradation of polystyrene is initiated at relatively low temperatures, consistent with the large size of the phenyl substituent. From thermogravimetric analysis in inert conditions as illustrated in Figure 3.9 at 10 °C/min heating rate, PS decomposes between 350 °C and 480 °C (Lee et al., 2007). PS generally is thermally degraded in a single step within the temperature range of 350 – 500 °C and maximum degradation of the polymer occurs in the interval of 376 – 440 °C (Park et al., 2003, Kiran et al., 2000) as can also be noted from the above table. These thermal degradation parameters form an important range that the PS samples need to conform to assess purity and an operating temperature envelope for experimental work.

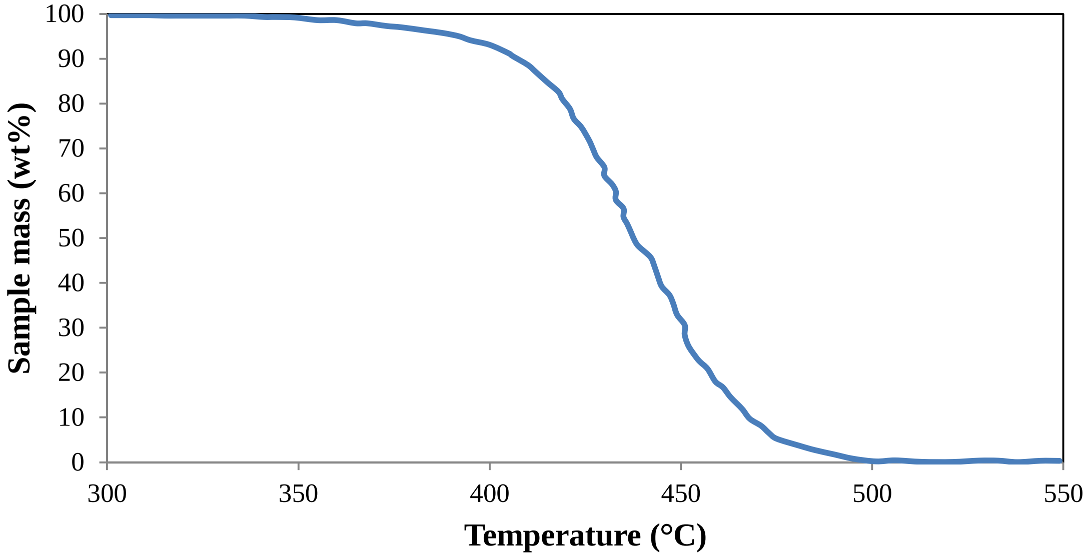

Figure 3.9 Thermogravimetric analysis of PS in an inert atmosphere at 10 °C/min heating rate (Redrawn from Lee et al., 2007)

3.5.3.2 Thermal decomposition mechanism of polystyrene

The thermal degradation of PS is characterised by a random chain scission free-radical mechanism (Jang and Wilkie, 2005, Faravelli et al., 2001). Primary, secondary and tertiary radicals are involved in a series of transformations, mainly hydrogen transfer reactions and β-scissions, to yield the final degradation products (Ohtan et al., 1990, Ojha and Vinu, 2015). Polystyryl radical (R_1) and methylene end group radical (R_2) are usually formed, leading to either recombination or intramolecular hydrogen abstraction (disproportionation). This initial process gives rise to an unsaturated thermally unstable double bond chain end and a saturated benzylic chain end as illustrated in Figure 3.10 below.

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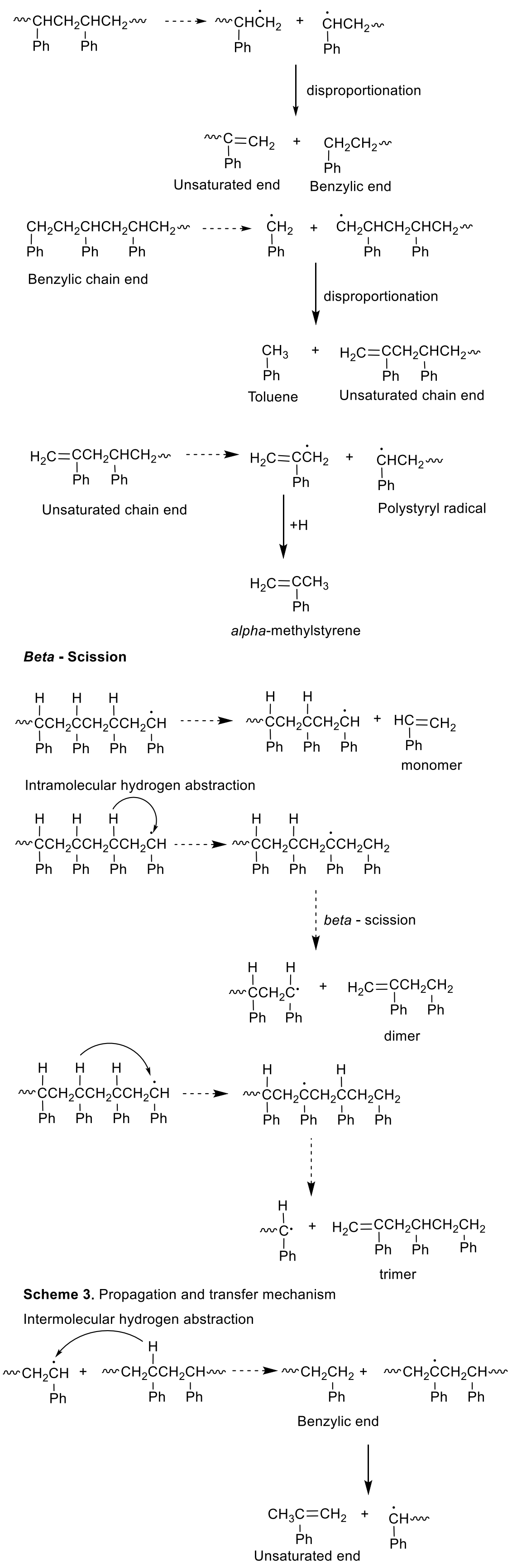

Figure 3.10 PS thermal degradation mechanisms (adapted from Ohtan et al., 1990)

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The unsaturated chain ends are very reactive above 300 °C and precursors for further thermal degradation. The volatile products consist chiefly of styrene monomer (Costa et al., 1982), dimer (diphenylbutene) trimer (triphenylhexene), smaller amounts of benzene, ethylbenzene, toluene and α-methylstyrene.

When the temperature of the polymer reaches 330 – 350 °C radicals are primarily generated from the end chain sites. This leads to the production of a toluyl radical at a benzyl group chain end, which yields toluene with hydrogen transfer. The unsaturated chain end cleaves further to α-methyl styryl and polystyryl radicals, responsible for α-methyl styrene and styrene production upon stabilisation with hydrogen transfer.

The formation of polystyryl radicals (R_1) above 350 °C increases the degradation process with production of volatiles that can escape the reaction front. Three reactions namely; Β-scission, intramolecular and intermolecular hydrogen transfers, which are propagation and transfer reactions, account for the majority of volatile products released (Dean et al., 1989, Costa et al., 1982, Mo et al., 2014).

The most frequent reaction is β-scission involving polystyryl radical (R_1) resulting in the formation of styrene (Ojha and Vinu, 2015, Artetxe et al., 2015) and one unit shorter polystyryl radical (unzipping) (Costa et al., 1982, Jang and Wilkie, 2005). The main polymer chain is more amenable to hydrogen abstraction reactions. In this case tertiary hydrogen intramolecular abstraction takes place one unit from the chain end and is followed by β carbon to carbon bond scission to produce styrene oligomers (Levine and Broadbelt, 2008, Artetxe et al., 2015, Mo et al., 2014) and polystyryl radical. Styrene trimer is produced when hydrogen abstraction takes place two units from the chain end and β-scission occurs farther away. These series of hydrogen abstraction reactions are called back-biting reactions. Unsaturated chain end, polystyryl and benzylic radicals on the other hand result from intermolecular hydrogen abstraction.

Dean et al. (1989) proposed another mechanism involved in oligomer formation. The researchers obtained results which suggested the likelihood of dimer and trimer formation by monomer recombination taking place in the molten and vapour phases of polystyrene decomposition system.

Termination reactions have been evaluated as first order reactions, suggesting that intramolecular transfer takes place, followed by scission to produce small enough oligomers which readily escape the reaction system (Lehrle et al., 1982, Cameron et al., 1978).

3.5.3.3 Products from pyrolysis of polystyrene

Polystyrene plastic depolymerises during pyrolysis process to predominantly yield the styrene monomer. The polymer has been reported to crack to styrene, toluene, ethylbenzene, trimethyl benzene and benzene as major products composed of a single aromatic ring. Low yields of benzene (1–3 wt %) are produced, despite that the majority of the carbon atoms of PS are assembled into phenyl side groups in this polymer. This has been ascribed to the stronger aryl – alkyl bond (linking the phenyl group to the PS polymer chain), when compared to the alkyl - alkyl carbon bonds along the chain.

Pyrolysis of polystyrene has been studied by many researchers for a variety of reasons. Some researchers have focused on kinetic studies, while others have extensively studied the mechanisms responsible for polystyrene pyrolysis product distribution in different reactors. In this section a discussion of literature results from PS pyrolysis is presented. The results are from various reactor types and a wide spectrum of operating conditions.

Pyrolysis GC-MS of polystyrene plastic has been used to study the influence of temperature on the evolution of products. In this kind of studies fast pyrolysis conditions have been employed with typical temperatures ranging between 400 – 800 °C, while vapour residence times of less than 10 s are characteristic (Audisio and Bertini, 1992, Dean et al., 1989). The main product evolved has been reported to be styrene (Ahmad et al., 2010) with 80 wt% at around 400 °C but the yield decreased with temperature increase (Ojha and Vinu, 2015, Audisio and Bertini, 1992). Other important products that have been identified during PS pyrolysis are toluene, benzene, methylstyrene, and ethylbenzene, but the yields were low as compared to styrene. The evolution of styrene dimer and trimer has also been studied. and were found to decrease with temperature (Ahmad et al., 2010, Ojha and Vinu, 2015) as higher temperature than 400 °C promoted further decomposition. In these studies the authors envisaged that the high styrene monomer yields were as a result of short volatiles residence times in the reactors. This aspect prevented styrene forming primary pyrolysates from further decomposition to yield secondary products.

Artetxe et al. (2015) conducted a fast pyrolysis study on polystyrene using a conical spouted bed reactor (CSBR) to establish the influence of temperature on the distribution of products. The authors found that the major polystyrene degradation product was styrene monomer and the optimum yield occurred between 450 – 600 °C. It was also reported that the yield of styrene began dropping as the temperature approached 600 °C as observed in other studies

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(Chauhan et al., 2008). The other important parameter that greatly influenced the product yields was the residence time of volatiles in the reactor hot zone. The researchers reported that the yield of styrene increased with an increase in the fluidising nitrogen gas flow rate to a certain level; thereafter the yield began dropping. This observation is in agreement with Mo et al., 2014, whom established a quadratic functional relationship between residence time and styrene yield. The optimum temperature at which the researchers found the maximum styrene yield was 500 °C. This optimum temperature well lies in the temperature envelope of 450 – 600 °C within which other researchers have found maximum styrene yields (Mo et al., 2013, Ojha and Vinu, 2015, Audisio and Bertini, 1992).

In another fast pyrolysis study of polystyrene decomposition products between 450 – 700 °C, Liu et al. (2000) reported that other chemical products such toluene, methylstyrene, ethylbenzene and styrene oligomers were produced as well. The same chemicals have been reported by many other researchers (Mo et al., 2013, Ojha and Vinu, 2015, Audisio and Bertini, 1992 and Artetxe et al., 2015). The researchers concluded from the studies that high liquid yields of over 80 wt % (Lee et al., 2003, Bartoli et al., 2015, Kim et al., 2003, Mo et al., 2014, Jung et al., 2013) were obtainable, as long as the condensation train efficiency remained high and the major polystyrene degradation product was styrene, with a maximum yield of over 70 wt % at 600 °C. This result is good agreement with those reported by Artetxe et al. (2015) and Ojha and Vinu, (2015) at the same temperature. The difference in the results could be attributed to the different reactor configurations and the residence times employed, in addition to the efficiency of the condensation train. The authors attributed the high yield of the monomer to the high thermal energy transfer between the feed and the reactor set up as such thermal lags as well as cold spots did not exist in the reactor environment.

Slow pyrolysis studies on polystyrene polymer performed in semi-batch reactors by several researchers between 350 – 600 °C have revealed that similar styrene yields to those obtained in fast pyrolysis setups are achievable. In the earlier research work conducted in the temperature range given above, it has been reported that styrene is the major PS degradation product with yields over 70 wt% (Zhang et al., 1995, Park et al., 2003). The major product spectrum was the liquid phase of over 80 wt% (Mccaffrey et al., 1996, Bartoli et al., 2015, Mo et al., 2014), while the gas fraction, mainly composed of methane, ethane, ethene and propane, constituted less than 15 wt%. The styrene yield was observed to decrease with an increase in temperature as noticed in fast pyrolysis studies. Volatile residence time in the

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reactor has been reported to be a major parameter influencing the products spectrum from PS pyrolysis. In light of the foregoing, Williams et al. (1993) observed a slightly different product distribution when primary polystyrene pyrolysates were subjected to secondary cracking between 500 – 600 °C. The major reported compound evolved was still styrene but with reduced yield of slightly over 50 wt% as in the study by Mccaffrey et al. (1996). Other chemicals produced were benzene, xylene and toluene at increased yields. The authors attributed the increase in yields to the long vapour residence time which probably encouraged cyclic Diels-Alder reactions producing xylene.

In a more recent study performed to enhance styrene monomer yield from pyrolysis of polystyrene, Mo et al., (2014) concluded that temperature and residence time factors had a maxima quadratic influence on styrene yield, while material heating rate had an increasing linear relationship. This trend of temperature on styrene yield has been supported by other studies (Artetxe et al., 2015, Chumbhale et al., 2004), while linear heating rate influence on polystyrene pyrolytic oil composition has been also found by Ahmad et al. (2010) and Aboulkas et al. (2009). On the other hand, longer reaction times on PS pyrolysis lead to product distribution with low styrene yields (Park et al., 2003, Bartoli et al., 2015). The optimised styrene yield was slightly over 64 wt% at a concentration of over 70 wt% in the liquid fraction and between temperatures of 470 – 505 °C at a heating rate of 40 °C/min and a nitrogen carrier gas flow rate of between 0.12 – 0.14 L/min.

Bartoli et al. (2015) conducted pyrolysis studies on polystyrene to establish the influence of low pressure on product distribution. A semi-quantitative method of pyrolysis product analysis was done as yields of the compounds were reported as percent of the areas under total ion chromatograms (TIC), with compound identification performed using NIST mass spectral library. The researchers reported an enhanced liquid yield of over 90 wt % with styrene as the major pyrolysis product at a yield of around 49 % (based on surface area) when the vacuum pressure was about 21 kPa and reactor temperature of 514 °C. It was observed that the yield of styrene increased to about 50 % when the vacuum pressure was reduced to around 7 kPa. This observation led to the conclusion that low pressures resulted into short volatile residence times in the reactor. This aspect has been widely accepted to limit the extent of secondary cracking reactions responsible for altering initial pyrolysis product distribution.

There have been many research studies spanning from 1992 to 2015 on pyrolysis of polystyrene using various operating conditions and reactors. In all the studies, the conclusion has been that styrene is the major compound produced with yields between 49 – 85 wt% in the temperature range 350 – 600 wt% and is produced by a dominant depolymerising reaction during PS thermal decomposition. Contradictory results can be found for heating rate factor while residence time should be set such that secondary reactions are limited.

3.5.4 Polyethylene terephthalate

Polyethylene terephthalate is a condensation polyester polymer. The thermoplastic is produced from ethylene glycol and terephthalic acid (Chiu and Cheng, 1999) and melts in the temperature range of about 120 – 130 ºC. The fraction PET in waste plastics stream has been increasing due to its wide applications packaging such as carbonated beverage bottles and electronics. The polymer is represented as shown in Figure 3.11 below. Additive free PET contains 62.5 wt% carbon, 33.3 wt% oxygen and 4.2 wt% hydrogen. Senneca et al. (2002) and Heikkinen et al. (2004) reported approximately the same composition of waste PET as follows: carbon 63 wt %, oxygen 33 wt % and hydrogen 4 wt %. Martın-Gullon et al. (2001) reported 62.2 wt % for carbon, 4.2 wt % for hydrogen and 33.6 wt % oxygen.

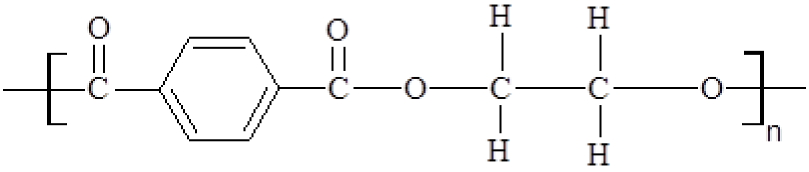

Figure 3.11 Polyethylene terephthalate polymer

3.5.4.1 Thermal behaviour of polyethylene terephthalate

Polyethylene terephthalate starts decomposing around 370°C in a single step as can be seen from Figure 3.12 below obtained at a heating rate of 5 °C/min. Decomposition is virtually complete in the region of 520 °C at low heating rates but can be as high as 650 °C with heating rates above 100 °C/min. The decomposition characteristics of PET from various researchers are given in Table 3.4. It is clear that the decomposition temperatures are highly influenced by the heating rate applied to the polymer. The presence of oxygen atom in PET has been thought of as a precursor to complex reactions occurring during thermal degradation, some of them leading to the formation of char product. PET has therefore comparatively high yield of solid residue after thermal conversion, as was observed in TGA. This thermal behaviour of PET from literature was used to bench mark the characteristic decomposition parameters of PET isolated from KWMF landfill stream and assess its purity.

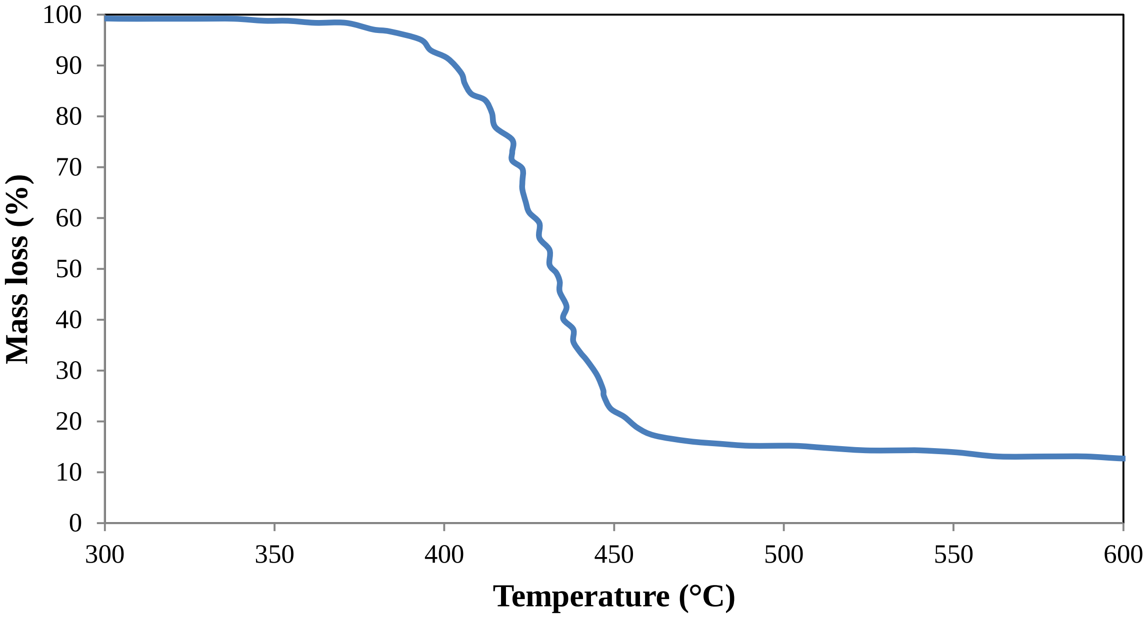

Figure 3.12 Degradation behaviour of PET in TGA at 5 °C/min heating rate (Redrawn from Dimitrov et al., 2013)

Table 3.4 Thermal decomposition of PET in TGA experiments.

Heating rate (°C/min)	Temperature range (°C)	Maximum temperature (°C)	References
5	370–500	414	(Senneca et al., 2002)
10	383–513	440	(Saha and Ghoshal, 2005a)
20	366–511	*	(Senneca et al., 2002)
20	*	444	(Heikkinen et al., 2004)
100	400–520	467	(Senneca et al., 2002)
900	500–630	560	(Senneca et al., 2002)

*, Not reported

3.5.4.2 Thermal decomposition mechanism of polyethylene terephthalate

The thermal decomposition mechanism of polyethylene terephthalate has been a subject of ongoing disagreements. This section will review the different views that have been put forth.

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An earlier account of PET thermal mechanistic degradation was given by Buxbaum, 1968. It was envisaged that the ester linkage primary scission is most likely not homolytic as thermal decomposition of PET was independent of free radical agents' influence. The researchers studied the decomposition mechanism of model esters to draw conclusions on the degradation mechanism of polyethylene terephthalate. It was concluded that a cyclic transition state resulted from esters containing a β-hydrogen atom decomposing into an olefin and acid (Dimitrov et al., 2013). It has been clearly established that heterolytic C-O bond cleavage occurs and the rate of an ester decomposition at a given temperature is more dependent on the stability of alkoxy C-O bond than the C-H bond cleavage or formation of a carbon to carbon double bond (C=C). The authors have argued also that the point of weakness in PET chain is the β-methylene functional group. This is the point where transeterification reactions take place with degradation occurring as hydroxyl end-groups get consumed.

Levchik and Weil, (2004) agreed with Buxbaum, (1968) that primary scission is believed to occur when a β-hydrogen atom containing ester linkage decomposes to yield carboxyl and vinyl ester end groups (Martın-Gullon et al., 2001). It is, however, still unclear if heterolytic and homolytic scissions occur exclusively or mutually in PET degradation or perhaps in different bias, depending on experimental conditions. The authors have postulated that there are in general three major PET degradation products namely monovinyl terephthalate, acetaldehyde and terephthalic acid. Products such as carbon dioxide, carbon monoxide, benzoic acid and benzene are secondary products emanating from the decomposition of the above primary products. The yield of the secondary products are influenced by prolonged reaction times and high temperatures (500 °C for benzoic acid), leading to promotion of further chain scission with resultant smaller molecule formation. Edge et al. (1996) proposed that, since PET end-groups are mostly hydroxyesters, then vinyl esters produced during degradation could transesterify to vinyl alcohol which further could transform into acetaldehyde (Khemani, 2000). It was further postulated that acetaldehyde could be produced from carboxylic end groups as well. Other researchers have explained the possible reaction of vinyl carboxylate and carboxylic acid units through intramolecular or intermolecular hydrogen shifts to form vinyl alcohol which upon isomerisation yields acetaldehyde (Vijayakumar et al., 1982).

Contrary to the Buxbaum, (1968) postulation, Bounekhel and McNeill, (1995) reported from the vacuum PET degradation studies that homolysis would initially occur in two ways. The first would be the scission of alkyl oxygen bond, while the second would be cleavage of acyl oxygen bond. The authors supported this argument with an observation that only homolytic bond scission would explain the evolution of carbon monoxide and carbon dioxide products for example over the entire PET degradation temperature range. This was so because a heterolytic scission route would only form such products at the high side of degradation temperature of up to 500 °C.

Considering all the above arguments on the right polyethylene terephthalate polymer decomposition mechanism, PET decomposition mechanism can be summarised as shown in Figure 3.13 below based on the severity of pyrolysis conditions. Low temperatures and short volatile residence time on one hand favouring terephthalic acid, ethylene and unstable acetaldehyde production. On the other hand high severity pyrolysis conditions (high temperature and long residence time) favouring the decomposition of primary products to produce benzoic acid, carbon dioxide and benzene.

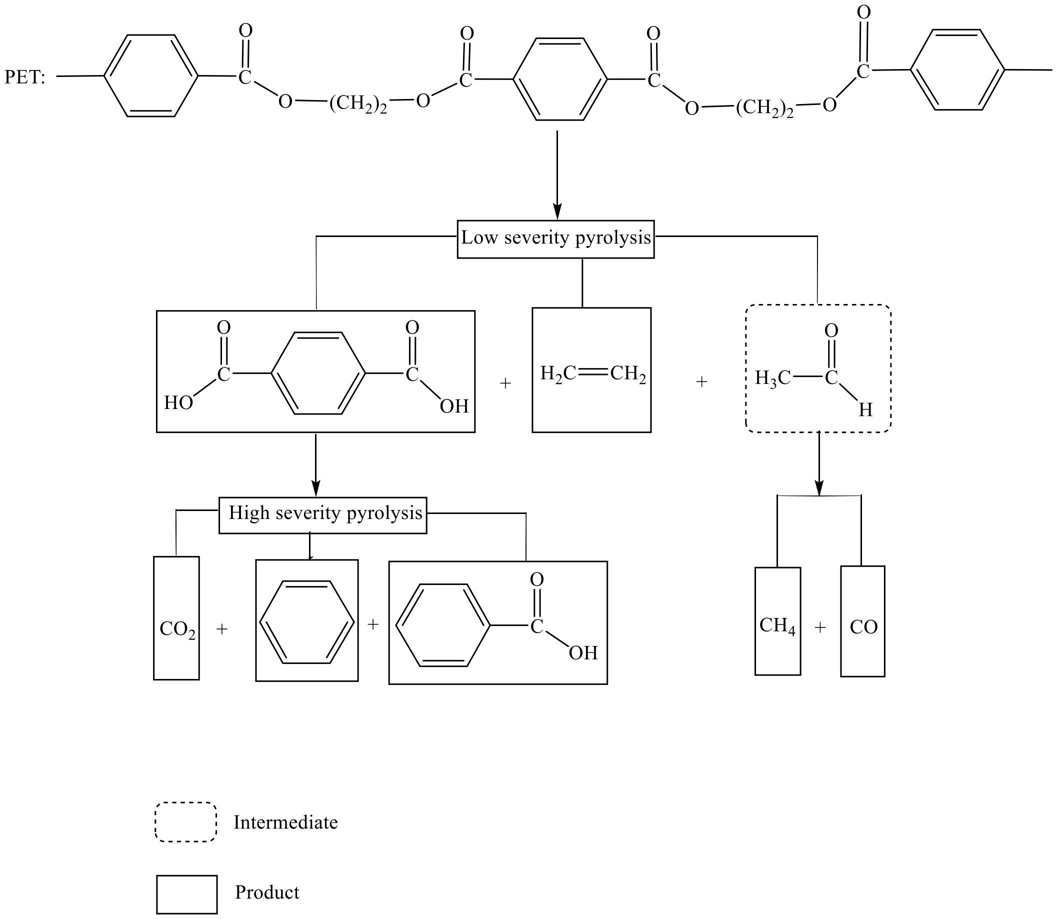

Figure 3.13 PET thermal decomposition mechanism

3.5.4.3 Products from pyrolysis of polyethylene terephthalate

Pyrolysis of PET has been studied by many researchers for many reasons among them to understand product phase distribution, mechanism of decomposition and chemical yield. In the pyrolysis study conducted by Artetxe et al., 2010 in a spouted bed reactor between 500 – 600 °C, four product phases were reported. These were gas (43 – 49 wt%), wax (35 – 41 wt%), liquid (6 – 14 wt%) and residue/char (4 – 8 wt%). The main product in the wax phase was benzoic acid ranging between 15 – 27 wt% yield.

Investigation of PET pyrolysis using TGA – EGA (evolved gas analysis) has shown a wide spectrum of organic compounds. A temperature range of 500 – 600 °C has yielded chemicals such acetaldehyde, benzoic acid, vinyl benzoate, ethyl benzoate, carbon dioxide, benzene, terephthalic acid, divinyl terephthalate and ethan-1, 2-diyldibenzoate (Oudhuis et al., 1991, Dimitrov et al., 2013). The number of chemicals produced and their yields of course depend on the pyrolysis heating rate and volatile residence time employed. Semi-quantitative benzoic acid concentration determination revealed about 10 wt%, in the research work done by Dimitrov et al., 2013 in a micro furnace pyrolyser at a heating rate of 5 °C/min to final temperature of 600 °C.

Literature report that mild pyrolysis conditions of PET favour formation of terephthalic acid (TPA) and lower acid yield is observed under more severe conditions (Yoshioka and Grause, 2006). This has been attributed to further breakdown of TPA into benzene, benzoic acid and carbon oxide compounds, with carbon dioxide content as high as 37 wt % (Yoshioka et al., 2005, Artetxe et al., 2010). In a study by Sakata, et al. (1996), the pyrolysis of PET at 430 °C in a semi-batch reactor did not yield any liquid fraction. The condensable product was composed of a yellowish wax (yield of 67 wt %) in addition to 33 wt % of gas stream (Williams and Williams, 1997).

Yoshioka et al., 2004 studied PET pyrolysis in a fluidized bed reactor and observed solid product yields of benzoic acid, carbon oxides and monomethyl terephthalate. The content of the acidic products decreased with temperature increase from about 45 wt% to 13 wt % after a temperature increase of 120 °C from about 510 °C. This meant that organic acids decomposed to more stable oxides of carbon as the temperature was increased. The yield of the wax fraction (condensable product) however increased with temperature to the level of 40 wt% at about 730 °C.

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The proportion of carbon oxides was observed to be fairly constant at over the study temperature range, validating the Bounekhel and McNeill, (1982) proposition that PET degradation is initiated by homolytic bond scission of alkoxy or acyl-oxygen groups. The yield of pyrolysis residue has been reported between 15 and 20 wt % (Chiu and Cheng, 1999, Saha and Ghoshal, 2005, Williams and Williams, 1997) in the PET degradation studies between 400 – 700 °C.

In a study of polyethylene terephthalate pyrolysis in the conical spouted bed reactor between 500 – 600 °C by Artetxe et al. (2010), similar yields of gas and wax solids (condensable product) to that reported by Yoshioka et al. (2004) were observed. This might mean that PET pyrolysis always produces solid products despite the change in residence time, reactor configuration and heating rate. The researchers did not report production of terephthalic acid at the pyrolysis conditions employed probably because of thermal decomposition of the acid above 400 °C to benzoic and benzoylformic acids. The production of benzoic acid was reducing with temperature due to further break down to benzene and oxides of carbon compounds.

It must be pointed out that several works done on the pyrolysis of PET have not focused on the optimisation of terephthalic and benzoic acids yield. But rather, the focus has been on avoiding the acid production due to their high sublimation points leading to piping blockages upon cooling. On the other hand a good deal of literature has dealt with explanation of PET thermal degradation mechanisms and kinetic evaluations.

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4 Research methodology

4.1 Materials

4.1.1 Plastic samples

The plastics that were used for the pyrolysis study were HDPE, LDPE, PP, PS, PET and a waste mixture. The samples were collected from Waste plan in Kraaifontein, Western Cape (more details section 4.3). The company is one of the many firms involved in material recovery from municipal solid waste.

4.1.2 Solvent

Acetone solvent (purity 95%) was used to clean many equipment accessories. The solvent was used to clean TGA crucibles and slow pyrolysis reactor set up parts. Analytical acetone of 99.9 % purity was used to prepare standard solutions and dilute polystyrene pyrolysis oil samples prior to GM-MS analysis.

Methanol solvent was used to prepare standard solutions and dilute polyethylene terephthalate pyrolysis condensable products. The solvent was particularly chosen because terephthalic acid was found to be more soluble in it than in acetone and dichloromethane which are also often used as analytical solvents. The grade of the solvent was 99.9 % pure to safeguard the integrity of high performance liquid chromatography (HPLC) machine.

4.1.3 Standards

Four standards namely styrene, toluene, ethylbenzene and methylstyrene were used to make calibration curves in order to quantify the condensable products obtained from the pyrolysis of polystyrene. Terephthalic and benzoic acids were used in a similar manner for quantification work on HPLC. The standards were purchased from Sigma Aldrich and the purity was 99.9 %.

4.2 Analytical equipment

In this section all the pieces of equipment that were used in carrying out the research are briefly described and the parameters used are given as well.

4.2.1 Thermogravimetric analyser (TGA)

TGA is an analytical tool used to determine the stability and kinetic properties of materials when subjected to controlled heat treatment. It has an analytical balance connected to the sample located in a furnace which records the mass loss of the material as a function of time and temperature. TGA records the heat flow into and out of the material as well; this gives information on the endothermic and exothermic nature of the material. A Mettler Toledo TGA/DSC 1 was used in this study. Nitrogen and argon (both 99.999% Afrox Baseline 5.0) were used in the study. Argon was used in TGA – MS runs instead of nitrogen to avoid confusing it with released volatiles having the same mass number (for instance carbon monoxide produced during pyrolysis). TGA was used for proximate analysis of feed stock as well as pyrolysis studies.

4.2.2 Mass Spectrometer (MS)

A mass spectrometer works on the principle of ion fragment identification. The fragments are produced from volatiles when they are bombarded with high energy electrons which cause material ionisation. A quadrupole mass filter Pfeiffer vacuum thermostar GSD320 MS was coupled to a Mettler Toledo TGA/DSC 1 for online plastic pyrolysis volatile analysis. The transfer line was kept at 200 °C.

The MS was operated in electron impact mode (EI) with ionisation energy of 70 eV (6754 kJ/mol). The detector used was secondary electron multiplier (SEM) with a scan speed of (2 – 60) ms/amu and mass scan range of (1 – 300) amu.

4.2.3 Gas chromatography-mass spectroscopy (GC-MS)

The gas chromatography unit was used to separate the compounds in the liquid products based on their interaction on the solid phase of the column before they were analysed on a mass spectrometer for quality and quantity determination. An Agilent 7890A/5975C GC-MS was used in the study for quantification of monomers from bench-scale plastic pyrolysis liquid products.

4.2.4 High performance liquid chromatography (HPLC)

The Dionex Ultimate 3000 high pressure liquid chromatography was used to separate the components in polyethylene terephthalate pyrolysis condensable products based on their interaction with the liquid phase and the solid phase of the column. The eluted and separated components were then analysed on an ultra violet light detector.

4.2.5 Muffled furnace

The Nabertherm muffled furnace was used to clean TGA crucibles as well as sample boats from slow pyrolysis fixed bed reactor. The furnace has a temperature operating range of 30 - 1 000 °C. TGA crucibles temperature cleaning program was a ramp rate of 45 °C/min to 900 °C which was kept constant for 30 minutes. The bench-scale sample boat was cleaned using the same method but the isotherm temperature was reduced to 750 °C.

4.2.6 Slow/vacuum pyrolysis reactor

A slow pyrolysis unit was used to study conversion at bench-scale stage. The same set up was used for vacuum pyrolysis but the nitrogen flow from the cylinder was replaced with a vacuum pump. The slow pyrolysis unit at Stellenbosch University is as shown in Figure 4.1 below while Figure 4.2 depicts a pictorial version of the flow sheet. It is a fixed bed reactor which has 530 mm diameter by 1000 mm length quartz glass tube and can be fed with plastics material. The tube is surrounded by an electric furnace for heat energy supply to the pyrolysis reactions and is controlled at a set temperature. In the case of vacuum pyrolysis, a vacuum pressure of less than 15 kPa absolute pressure required was generated by a vacuum pump.

The pyrolysis vapours were condensed to oil/solid in the cascading condensation train. The first condenser was maintained at ambient temperature while the other ones were at low temperatures by means of ice and wet carbon dioxide.

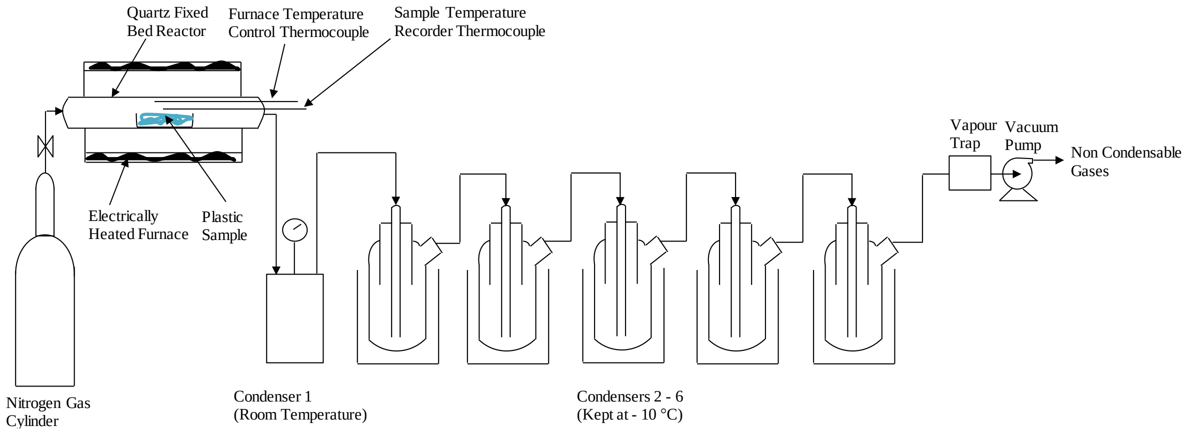

Figure 4.1 Stellenbosch University fixed bed reactor flow sheet (nitrogen is used to purge the reactor for slow pyrolysis, while the vacuum pump is connected for vacuum pyrolysis)

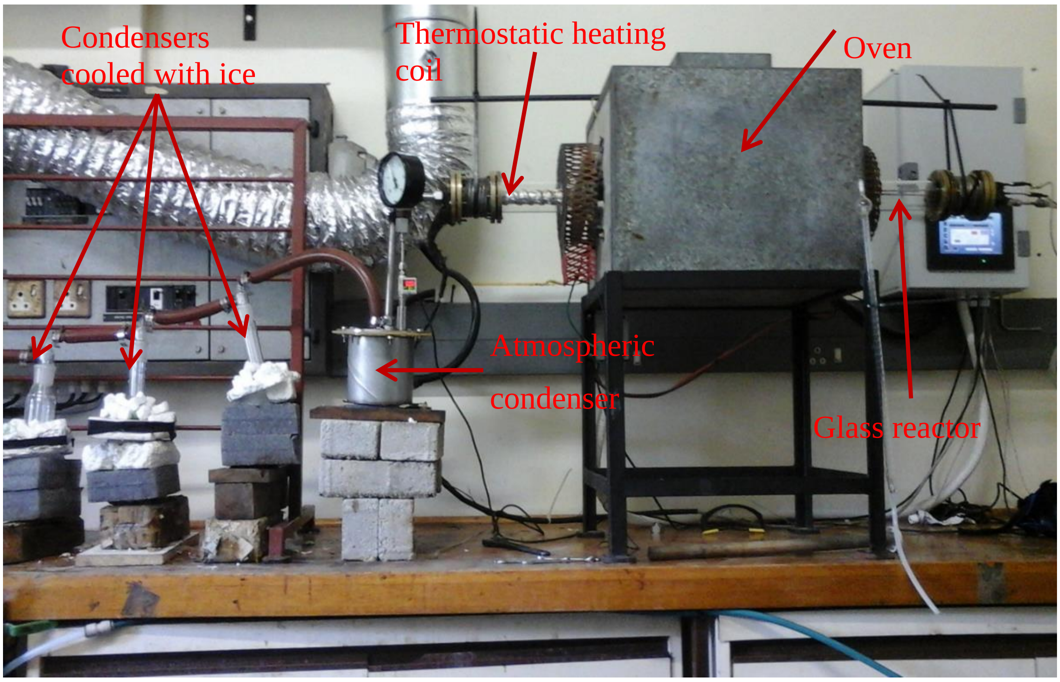

Figure 4.2 Pictorial experimental setup used for slow/vacuum pyrolysis

4.3 Methods

4.3.1 Composition of waste plastics in South Africa

The scheme depicted in Figure 4.3 below was considered in balancing the individual plastic polymers flowing through South Africa's environment mainly generated from manufacturing and imports.

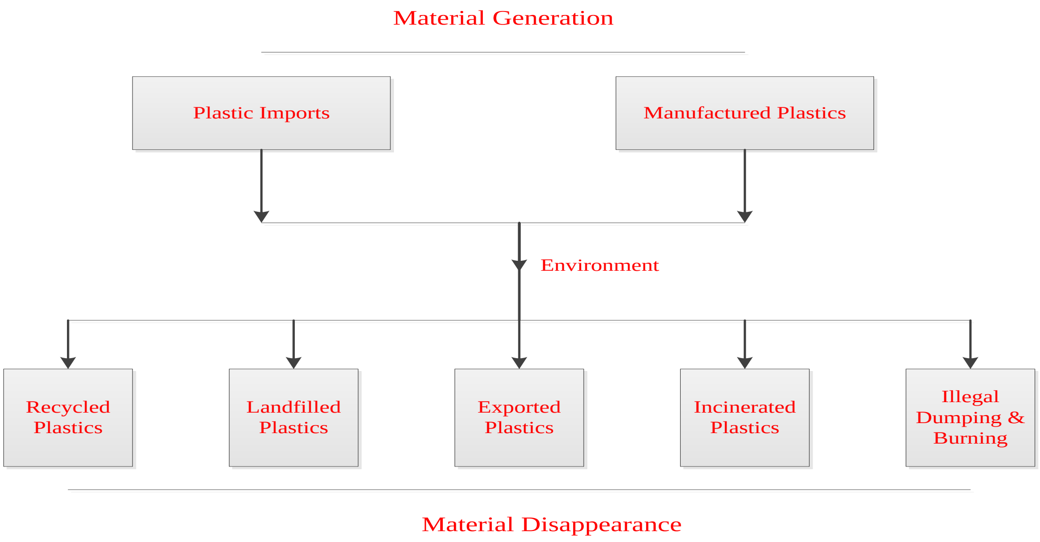

Figure 4.3 Schematic of plastic material balance in South Africa

The composition of MPW stream in South Africa was determined from the individual plastic flows in the country as a percentage of the total manufactured plastics flow. This approach therefore assumed that the plastics produced in a particular year are disposed of the same year. The data was acquired from Plastics Federation, PlasticsSA, PetCo, POLYCO and SAPRO through personal email communication and plastic recycling reports by the same stake holders. The data consisted of plastic tonnages manufactured and recycled in particular years. The tonnages of plastics exported and imported have not been taken into consideration because it has not been easy to track these figures by plastic business stake holders. As a result, the exported plastic tonnages were assumed equal to imports. The difference between plastics manufactured and recycled was assumed to largely end up in landfills while a minor fraction is either incinerated or indiscriminately dumped/burned. There is little report on plastic incineration in South Africa as such the plastic mass balance on the disappearance end is not very accurate. The composition of the waste plastics was given in terms of the six main plastics found on the environment.

4.3.2 Waste plan landfill stream composition determination

Municipal solid waste collected from different municipalities around Cape Town is introduced on a running conveyor belt at Wasteplan as depicted in Figure 4.4 below. The workers along the belt then manually sort the plastics fraction according to the codes given in Table 4.1

The material that is rejected as landfill material at Waste plan contains about 14 wt% recyclable plastics according to the company's personnel. The material was sampled three times a day for a week so that a representative sample could be collected. The material was sampled from the drop off point (after removal of recyclable plastic) by coning and quartering method to ensure sample homogeneity. The material accumulated by the seventh day was sorted manually by visual identification using plastic codes into plastic fractions of HDPE, LDPE, PET, PS, PVC and PP which were weighed separately. The composition of each plastic in the landfill stream was then calculated as the mass fraction of the total sample mass. This approach was used by (Adrados et al., 2012) when the authors were estimating the composition of a real plastic mixture. Individual plastics were collected for pyrolysis study and the plastics of major interest would be decided from the composition of the tailing.

Figure 4.4 Waste plan municipal solid waste sorting chain in Kraaifontein Western Cape

The tailing stream is picked up with front end loaders and loaded in trucks for disposal at a landfill site within Cape Town at a fee. Figure 4.5 below is a picture of part of the commingled landfill sample which was separated into individual plastics for composition analysis.

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Table 4.1 Types of plastics and their recyclates (adapted from Panda et al., 2010)

Code	Recyclate	Plastic	Full name & Common uses
♳	Yes	PET	Polyethylene Terephthalate Beverage & water bottles, transparent food containers.
♴	Yes	HDPE	High-Density Polyethylene Milk, toys, detergent, lotion & oil bottles, containers, parts and Plastic bags.
♵	Yes, But not common	PVC	Polyvinyl Chloride. Food wrap, vegetable oil bottles, blister packages and automotive parts.
♶	Yes	LDPE	Low Density Polyethylene, Many plastic bags, garment bags, shrink-wraps & refuse bags.
♷	Yes	PP	Poly Propylene. Refrigerated containers, some carpets and bags, most bottle tops and some food wrappers as well as compact disks.
♸	Yes	PS	Polystyrenes. Throw away utensils, meat packing, and protective packing.
♹	Some	------------	Other. Usually multi layered or mixed plastics.

Figure 4.5 Commingled landfill sample collected from Waste plan in Kraaifontein

4.3.3 Feedstock preparation

The samples were cut by hand into approximately 50 X 50 mm pieces, which were then washed with soap and sun dried for 4 days. The material was then milled with a Retsch SM 100 machine shown in Figure 4.6 to the particle sizes suitable for the study at particle (TGA) and bench-scales. The material was then screened to less than 2 mm particle size for thermogravimetric analysis studies and about 4 mm for bench-scale experiments. In Figure 4.7 below milled polypropylene plastic material is shown.

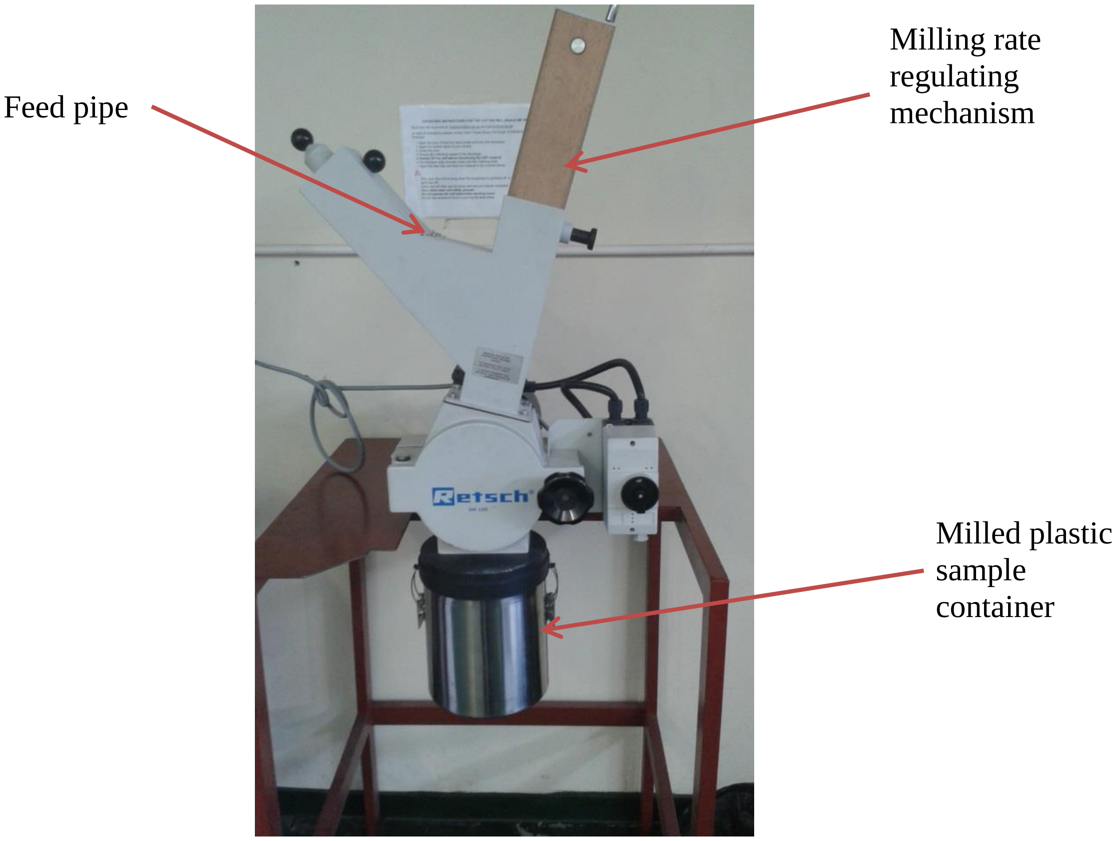

Figure 4.6 Retsch milling machine used to mill plastic samples

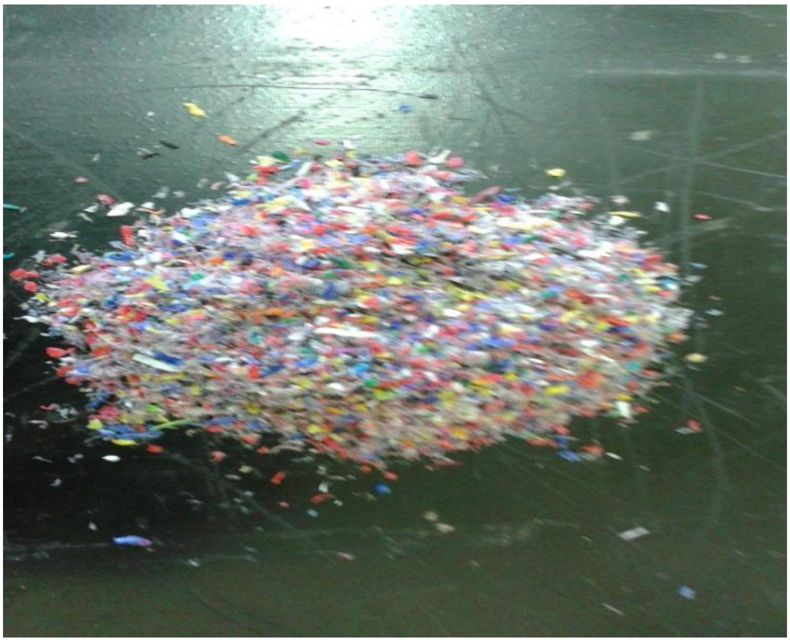

Figure 4.7 Milled and sieved polypropylene waste plastic

4.3.4 Density determination

The bulk density of plastics is important in determining storage and conveying characteristics as well as storage hopper designs. The density of materials is important as well in separation operations based on density differences. Additionally, the densities of the waste polymers can be used to assess the purity and identity by comparison with densities of the pure counterparts. It is defined as the mass of plastic material per unit volume occupied.

$$\textbf{Bulky density} = \frac{\textbf{Mass of plastic sample (g)}}{\textbf{Volume of plastic (l)}} \qquad \textbf{Equation 4.1}$$

The density was measured for plastics of less than 2 mm particle size. A 500 ml graduated cylinder container was filled with the plastic sample. The mass of the cylinder was measured before and after filling with the sample. Equation 4.1 was used to calculate the density of the plastics. This method of bulk density determination was done according to (ASTM D 1895, 2004) standard.

4.3.5 Proximate analysis

Proximate analysis of the feed is important to perform in order to determine its potential fraction convertible to products i.e. volatile matter. The moisture content (MC), volatile matter (VM), fixed carbon (FC) and ash content for plastics was determined in triplicate according to the American Standard Testing Method (ASTM) E 1131. This was performed in a Mettler Toledo STARe Thermogravimetric Analyser (TGA). Plastic sample size of between 20 – 60 mg was placed into a 600 μL alumina crucible and heated in an inert atmosphere of nitrogen and then in an oxygen oxidising environment. The sample was heated at a ramp rate of 50 °C/min from 30 °C to 110 °C where it was isothermally maintained for 5 minutes under 80 mL/min flow rate of nitrogen (99.999% Afrox Baseline 5.0). The temperature was thereafter increased to 900 °C at a rate of 100 °C/min under the same atmosphere and maintained for 5 minutes. The final stage was oxidation of the plastic sample at 900 °C for another 5 minutes with the same flow rate as nitrogen of oxygen (99.998% Afrox Baseline 4.8).

The process involves drying, decomposition in inert atmosphere and finally combustion in an oxygen rich environment. The first stage in proximate analysis of up to 110 °C involves moisture removal. The inert stage between 110 - 900 °C is where decomposition takes place to give volatile matter while the last combustion stage lead to determination of fixed carbon and ash (solid residue).

The TGA curve is generated from the procedure described above from which volatile matter, ash, water content as well as fixed carbon values were read off.

The temperature program of the proximate analysis performed on waste plastics is summarised in Figure 4.8 below. The heating rate for stage 1 was 50 °C/min, stage 2 had a hold time of 5 minutes, 100 °C/min heating rate was applied to stage 3 while stages 4 and 5 both had 5 minutes hold time. The last segment was a combustive stage using oxygen to perform the oxidation process.

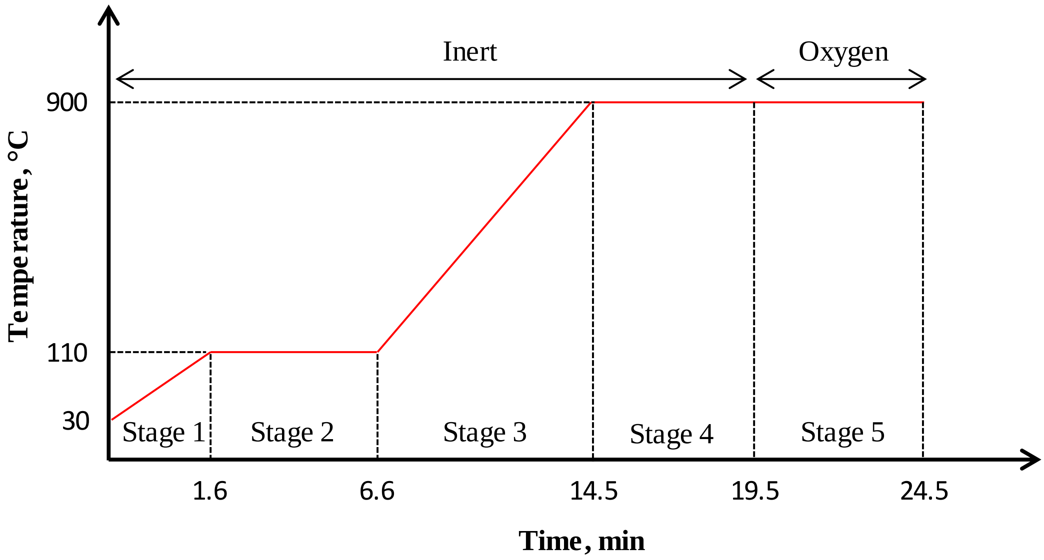

Figure 4.8 Temperature program used for proximate analysis

4.3.6 Thermal characterisation of the plastics

Thermal characterisation of the plastics was performed on Mettler Toledo thermal gravimetric analyser at atmospheric pressure to investigate the kinetic degradation behaviour of the individual plastic components isolated from the commingled waste stream. TGA is a useful tool to study weight loss behaviour of materials under thermal stress and has been used by many researchers for this purpose (Kiran et al., 2000, Jung et al., 2013, Mo et al., 2013). The data acquisition rate of the TGA instrument was every 0.4 s. The dynamic method was used in which the temperature was ramped from 25 °C to 650 °C at a heating rate of 10 °C/min with argon purge gas flow rate of 80 ml/min. The other heating rates of 5, 20 and 40 °C/min were also investigated to study the effect of heat transfer limitations on the 2 mm plastic samples. This characterisation technique enabled determination of the onset, maximum and offset degradation temperatures of the plastics at various heating rates. Figure 4.9 below illustrates how these characteristic temperatures were determined from a differential thermal gravimetric curve.

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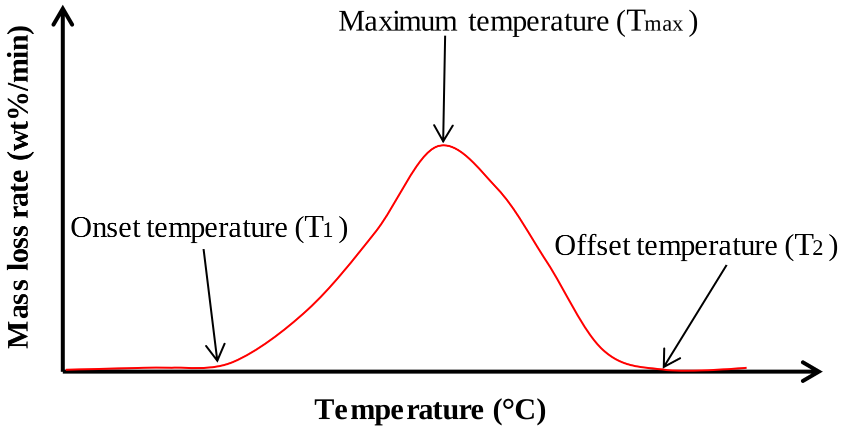

Figure 4.9 Differential thermal gravimetric (dTG) curve

4.3.7 Thermogravimetric mass spectrometric (TGA – MS) experiments

These experiments were done to screen favourable conditions for the production of high value chemicals from plastics especially monomers. This approach has also been used by (Artetxe et al., 2015) as a preliminary study to apply the information in bench-scale pyrolysis experiments and was utilised by Singh et al., 2012 to study the product distributions from pyrolysis of various waste materials. The settings that were used on the mass spectrometer have been given in section 4.2.2 while conditions on the TGA were varied in order to determine significant experimental factors affecting yield of chemical monomers.

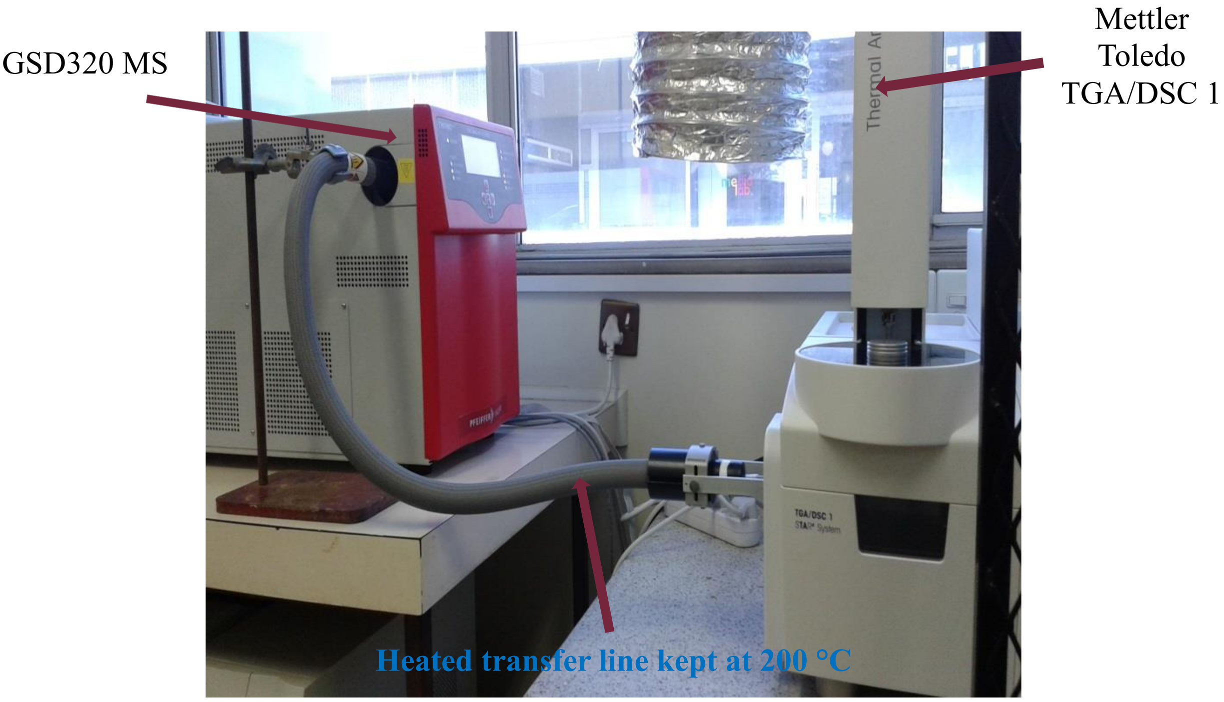

Figure 4.10 Photo of coupled TGA-MS (Source: Author)

In Table 4.2 below the pyrolysis conditions that were investigated are tabulated. A dynamic program was utilised where the final temperature was maintained, but the heating rates where varied. This enabled investigation of the thermal behaviour of plastics over a wide range of temperature as a function of heating rate. The helium purge gas flow rate was kept constant throughout the study so that the results obtained at various heating rates could be compared. The sample mass used in the study was between 20 – 40 mg.

Table 4.2 TGA conditions for thermal characterisation of polymers

Heating rate (°C/min)	Initial temperature (°C)	Final temperature (°C)	Purge gas flow rate (l/min)
5 10 20 40	30	650	80

The ion fragments used to monitor the evolution of PS pyrolysis products are tabulated in Table 4.3 below. The ions were selected from NIST library based on the abundances.

Table 4.3 Selected ion fragments for GC - MS

Name of Compound	Probable Fragments	Fragment Intensities	Selected Fragment
Styrene	104 103 78 51	999 485 687 569	104
Toluene	91 92	999 776	91
Methylstyrene	118 117	999 318	118
Ethylbenzene	91 106	999 282	106

- 104 ions were the most abundant ion fragments from styrene monomer.

- 91 ions were assigned to the production of toluene and ethylbenzene.
- 106 ions were assigned to the production ethylbenzene.
- 118 ions were assigned to the production α-methylstyrene.

4.3.8 Bench-scale slow and vacuum pyrolysis experiments

Slow and vacuum pyrolysis experiments were carried out in the set up described in section 4.2.6. The glass reactor was pre-weighed and centrally placed in the electrically heated furnace. The sample boat was then weighed and a 10 – 20 g sample of plastics was placed on the boat which was centrally placed in the reactor thereafter.

Thermocouples for temperature measurement were used to record and monitor the sample and reactor temperatures. The thermocouple close to the reactor wall (reactor temperature) was used for temperature control. The relevant temperature (close to the sample) was used and reported thereafter when discussing the influence of temperature. Similarly the condensation train pieces were weighed before the experiment and tied up together. Five condensers were kept at a temperature below -10 °C using a mixture of ice and wet carbon dioxide and the first one was kept at ambient temperature.

The whole set up was finally checked for air leaks using a vacuum pump. The procedure for running the setup can be found in Appendix A. The system was depressurised to about 2 kPa, then the vacuum pump was switched off and if the pressure stabilised at that level then the set up was substantially considered air tight and a run could then be performed. The set up pieces were all weighed after the experiment was over to determine the mass balance of the products of pyrolysis. The yield of condensable products (oil or wax/solid) was determined by the difference between the masses of the set up pieces before and after the experiment using Equation 4.2 below. In some cases the condensable products were found at the cold end of the reactor, which is the reason the reactor mass was considered for the mass balance.

$$\mathbf{Y_{Condensable}} = \frac{(\mathbf{R_1}+\mathbf{C_1} + \mathbf{RC_1}) - (\mathbf{R_0}+\mathbf{C_0}+ \mathbf{RC_0})}{\mathbf{M_S}} \mathbf{\ x\ 100} \qquad \textbf{Equation 4.2}$$

Where

$Y_{Condensable}$ = Yield of condensable volatiles (wt %).

R_0 = Mass of reactor before the experiment (g).

C_0 = Total mass of condensers before the experiment (g).

RC_0 = Total mass of rubber connectors before the experiment (g).

R_1 = Mass of reactor after the experiment (g).

C_1 = Total mass of condensers after the experiment (g).

RC_1 = Total mass of rubber connectors after the experiment (g).

M_S = Mass of the feed sample (g).

The yield of char was calculated as the fraction of the difference in mass between the sample boat content before and after the experiment as shown in Equation 4.3 below.

$$\mathbf{Y_{Char}} = \frac{(\mathbf{B_1 - B_0})}{\mathbf{M_S}} \mathbf{\ x\ 100} \qquad \textbf{Equation 4.3}$$

Where

Y_{Char} = Yield of char (wt %)

B_0 = Mass of sample boat and sample before the experiment (g).

B_1 = Mass of sample boat and char after the experiment (g).

The gas yield (Y_{Gas}) was calculated by the difference from 100 wt % of the condensable volatiles and char yield sum as illustrated in the equation below.

$$\mathbf{Y_{Gas} = 100 - (Y_{Condensable} + Y_{Char})} \qquad \textbf{Equation 4.4}$$

The overall conversion is the fraction of the feed that ends up as products in the pyrolysis process and was determined according to Equation 4.5 shown below.

$$\textbf{Conversion } (\alpha) = \frac{(\mathbf{M_S - M_C})}{\mathbf{M_S}} \mathbf{\ x\ 100} \qquad \textbf{Equation 4.5}$$

Where

M_C = Mass of char (g).

The parameters chosen for the study at this scale are listed in Table 4.4 below.

Table 4.4 Pyrolysis process parameters for slow/vacuum experiments

Parameter	Unit	Range
Temperature	°C	410 - 550
Heating Rate	°C/min	5 & 25
Plastic Particle Size	mm	4
N_2 Flow Rate (Slow pyrolysis)	L/min	0.5
Pressure (Vacuum pyrolysis)	kPa	2 - 12
Plastic Sample Weight	g	5 - 20
Hold Time	min	30

The temperature and heating rate variables were chosen after screening tests on TGA scale experiments as the potential range for valuable chemicals production and have been recommended in literature (Kaminsky et al., 2004). The vacuum pressure range utilised in the experiments was similar to other studies on one hand (Bartoli et al., 2015). On the other hand nitrogen flow rate in slow pyrolysis experiments was arrived at after a series of screening tests with varying flow rates. Thereafter a flow rate of 0.5 l/min was selected as it seemed to offer enough residence time for condensation of the volatiles across the condensation train. Due to early condensation, the sample mass of about 15 g for PET was selected to prevent clogging of the tubes as pyrolysis of sample masses greater than that lead to serious tube blockages.

The holding time of the sample in the reactor was arrived at after conversion results of PET tests conducted at 0, 30 and 60 minutes were compared. The conversion of PET without holding time was lower than the ones from 30 and 60 minutes which were similar. This led to the choice of 30 minutes for the process.

The design of experiments for both slow and vacuum pyrolysis experiments is given in Table 4.5 below. The design which included three temperatures and two heating rates was used for both PET and PS with tests done in duplicate. The table shows twelve experiments that were completed for each plastic and technology (slow & vacuum) in a randomised manner to filter noise and reduce the chance of random errors. Three temperatures (410, 480 and 550 °C) and two heating rates (5 and 25 °C/min) were considered for the experimental work.

Table 4.5 DOE for slow and vacuum experiments

Standard Run Order	Temperature (°C)	Heating rate (°C/min)
1	410	5
8	410	25
6	550	5
10	480	25
7	410	25
3	480	5
2	410	5
11	550	25
12	550	25
4	480	5
5	550	5
9	480	25

4.3.9 Gas chromatography-mass spectroscopy (GC-MS)

Pyrolysis liquid fraction (condensable product) of PS was qualitatively and quantitatively analysed by utilising Hewlett Packard 5890 Series II model gas chromatography (GC) coupled with Hewlett Packard 5973 (Agilent Technologies, Palo Alto, CA, United States) mass spectrometer (MS). Four calibration curves for styrene, toluene, ethylbenzene and methylstyrene were prepared to quantitatively analyse PS oil on GC/MS. An internal standard addition method with 2 - octanol was utilised. The GC oven temperature program was as set out below:

1. Started at 45 °C and hold time of 10 min,
2. The temperature was then increased to 100 °C at a heating rate of 2 °C/min,
3. Thereafter the temperature was ramped at 7 °C/min to 260 °C, and
4. Finally held at 260 °C for 24 min.

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Sample injections at split ratio 1: 30 were performed at a temperature of 280 °C on a 60 m x 0.25 mm ID x 0.25 µm film thickness, Zebron ZB-1701 capillary column. Helium (99.999% purity) was used as a carrier gas at a constant linear velocity of 1.3 ml/min.

MS operating conditions were: ionisation energy 70 eV with ion source temperature of 230 °C and 150 °C for quadrupole. The scan was performed between 20 and 500 amu.

40 µl PS derived oil was weighed, then 1 ml of 2 – octanol internal standard solution and the mixture were finally diluted with 2 ml of acetone. The internal standard (IS) was previously prepared in acetone at a concentration of 2.93 g/l. The concentration of the IS in all the samples was maintained at 0.962 g/l.

The standards were prepared at four different concentrations for the preparation of calibration curves. These standard samples were analysed on the GC/MS machine to obtain the response of surface area for the four chemicals, which was compared to the surface area of the internal standard to make quantification possible by internal calibration. In Table 4.6 the concentrations of the chemicals in the standard solutions are tabulated.

Table 4.6 Concentrations of standard solutions

Chemical	Concentration (mg/ L)			
	Standard 1	Standard 2	Standard 3	Standard 4
Styrene	27749	5254	1050	210
Methylstyrene	6391	1518	303	61
Toluene	5854	1269	253	51
Ethylbenzene	5553	549	110	22
2 – Octanol	926	849	1099	949

A plot of the response against concentration for each chemical gave a linear curve through the origin and the linearity coefficient (R^2) was greater than 0.99 in each case.

4.3.10 High performance liquid chromatography (HPLC)

Dionex Ultimate 3000 System with quaternary pump HPLC was used to analyse PET degradation products in the samples. It was equipped with a diode array detector set a wavelength of 240 nm. The column was a Water Xselect HSS T3 column (250 mm, 3 µm particle diameter and 4.6 mm internal diameter).The oven regulated the column temperature at 37 ^{o}C. The mobile phases utilised to create gradient for elution were deionised water and HPLC grade methanol. The gradient conditions used in the study are shown in Table 1. The flow rate was 0.7 ml/min with an injected sample volume of 30 µl.

Table 4.7 Gradient and elution conditions for HPLC analysis

Time (min)	Water (v/v %)	Methanol (v/v %)
0	40	60
5	40	60
20	0	100
25	0	100
30	40	60
45	40	60

The yields of terephthalic and benzoic acids from PET pyrolysis were calculated based on external calibration using standards of the two acids prepared in methanol. The calibration concentration range of terephthalic acid was 0.4 – 24.0 mg/l while that of benzoic acid was 0.7 – 38.0 mg/l. The PET pyrolysis product sample was first weighed and then dissolved in 5 ml of methanol using a magnetic stirrer for two minutes. The solution was finally filtered and diluted 200 times by pipetting 0.25 ml of the solution into a volumetric flask which was made up to the 50 ml mark with methanol.

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5 Results and discussions

5.1 Plastic stream characterisation

As estimate of the average composition of the total stream of waste plastics going to landfill in South Africa was made, as a reference point for consideration of the impact of waste plastics composition on pyrolysis processing.

5.1.1 South African context

According to PlasticsSA, 1.37 million tonnes of plastic were manufactured and recycled in 2012 and were composed of the six common polymers given as in Table 5.1 below. The total mass flows of plastics in the country is however likely to be slightly either under or above the manufactured plastics. This is because of plastic importation and exportation and estimating the mass flows of these two aspects has proved to be a challenge. The recycling rate of plastics in the country was 19.90 wt% with the balance of over 80 wt% reporting mainly to landfill and a minor portion being indiscriminately burnt or dumped (Matete and Trois, 2008). The stream named other in Table 5.1 is mainly composed of Acrylonitrile butadiene styrene (ABS), polyamide (PA), polycarbonate (PC), poly (methyl methacrylate) (PMMA) and polyurethanes (PU). The highest recycling rate was recorded for PET exclusively coming from beverage bottles, as food packaging PET trays are not recycled. However some of the beverage bottles cannot be recycled because of the presence of pigments in their composition. A fraction of the packaging trays is reported to be baled for export by other recyclers. The recycled PET is mainly used for making bottles, tapes and fibres for home as well industrial apparel markets. Polyolefins (PP, HDPE and LDPE) were the majority plastics at a composition of 58.76 wt% and were being recycled at a combined rate of 23.85 wt%. These were the plastics that were being sorted from waste collected around Cape Town and sold by Kraaifontein Waste Management Facility. When the plastics cannot be recycled, then pyrolysis conversion into fuel product for diesel substitution is a promising alternative.

The content of polyolefins in the manufactured plastic stream was similar to other international plastic stream polyolefin proportion of between 60 – 70 wt% (Sarker et al., 2012, Lin and Yen, 2005). PS was found to be the plastic with the lowest recycling rate (5.39 wt%). Given the general low recycling rates of plastics and an assumption of equal mass flows of imported and exported plastics, it can be inferred that the composition of waste plastic stream in South Africa is close to that of manufactured plastics.

Table 5.1 Manufactured and recycled plastics in South Africa (PlasticsSA, 2013)

Plastics	Manufactured (tons)	Composition (wt%)	Recycled (tons)	Recycling rate (wt%)
LDPE	345 000	25.18	98 971	28.69
PP	260 000	18.98	47 080	18.11
HDPE	200 000	14.60	45 950	22.98
PET	160 000	11.68	54 424	34.02
PVC	159 000	11.61	16 812	10.57
PS	63 000	4.60	3 394	5.39
Others	183 000	13.36	6 060	3.31
Total	1 370 000	100	272 691	19.90

5.1.2 Kraaifontein waste management facility landfill stream

A total of 47.9 kg sample was collected and sorted according to the method outlined in section 4.3.2 of the research methodology (Chapter 4). The composition of Wasteplan tailings (plastic rejects going to landfill) is shown in Figure 5.1 below. PVC polymer is mainly utilised in long-term applications and insignificant quantity was found in the tailing stream. Therefore the smaller PVC fraction observed in the tailing was mostly found in the form of lotion containers. The reduced content of polyolefins in this stream, compared to the national average mass flows of plastics (Table 5.1), was expected due to large interest and potential for recycling of these, which were therefore sorted out of the waste. These plastics are sold to companies that remould the plastics into other plastic articles like park chairs. Though PET is largely recycled in the form of beverage bottles, the increase in the proportion of the plastic however was attributed to the other form of PET (transparent food trays), which was not collected.

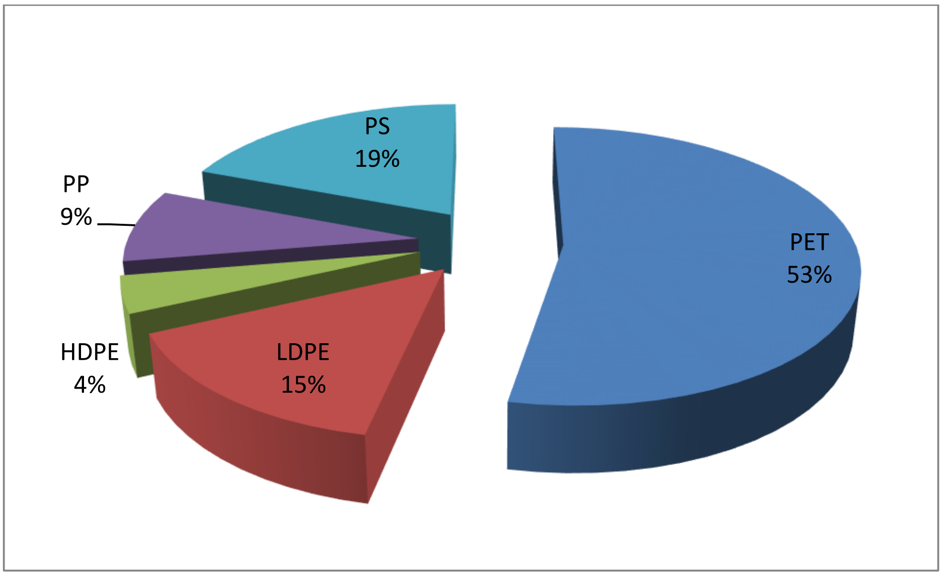

Figure 5.1 Composition of identified plastics in Wasteplan tailing stream (wt%)

The tailing stream contained 19 wt% PS and 53 wt% PET, while polyolefins contributed a total of 28 wt%. The results from this landfill stream characterisation indicate that PET and PS pyrolysis conversion deserve a particular interest, as 72 wt% of the stream of identified plastic was constituted by the two plastics. PVC was not considered in the study because of the negligible contribution the plastic made to the waste stream. Additionally, one of its thermal degradation products, HCl is highly corrosive to pyrolysis process equipment. Characterisation study was done for five plastics (PS, HPDE, LDPE, PP and PET), while optimisation of pyrolysis conversion (TG – MS and bench-scale) were done for PS and PET because of their significant contribution to the tailing stream (Figure 5.1). In addition, polyolefin pyrolysis conversion normally leads to production of randomly distributed hydrocarbons more suitable for fuel applications, than for the production of specific chemicals, where PS and PET show better potential, due to the presence of relatively stable aromatic ring.

5.2 Waste polymer densities

The results of the bulk density determinations for individual waste plastics are given in Table 5.2 below. The tests were done in duplicate. The average result was then compared with the range of pure polymer densities given in section 2.1 to have an assessment of the purity of the components after the physical separation of the mixed plastics. All the results were in the range corresponding to pure plastics.

Table 5.2 Waste polymer density determination results (SD: standard deviation)

Polymer		PP	HDPE	LDPE	PS	PET
Density (gpl)	Pure	900 - 910	940 - 960	917 - 932	1040 -1050	1290 -1400
	Average	908	950	925	1043	1368
	SD	2	4	5	1	8

5.3 Proximate analysis

Proximate analysis was performed according to the TGA method outlined in section 4.3.5. Proximate analysis of the plastics was conducted to determine the volatiles content, which is an important estimate of the potential yield of chemicals from pyrolysis. The moisture content of all the polymers was below 1 wt%. The average results on a wet basis obtained from a duplicate of proximate analysis runs for the five plastics under study are presented in Table 5.3 and discussed below.

Table 5.3 Polymer proximate analysis results (wt %)

Polymer	MC	VM	FC	ASH
LDPE	0.07	92.52	0.16	7.56
HDPE	0.09	98.29	0.09	1.71
PP	0.06	98.67	0.05	1.79
PS	0.39	96.86	0.84	1.29
PET	0.30	88.38	11.02	0.55

Note: MC – Moisture content, VM – Volatile matter and FC – Fixed carbon

Ash content was less than 2 wt% for all plastics except LDPE, which might be due to presence of higher inorganic additives content. With regards to organic content on ash free basis, all are essentially composed of VM greater than 97 wt% except for PET. Similar results can be found in literature for hydrocarbon plastics (Aboulkas et al., 2008, Kumar and Singh, 2013, Grammelis et al., 2009, Mastellone et al., 2002, Grammelis et al., 2009, Jung et al., 2010, Jung et al., 2013). In case of PET, the significant amount of fixed carbon was also reported in literature (Chattopadhyay et al., 2016). This high fixed carbon content has been linked to complex rearrangement reactions occurring because of the presence of oxygen during thermal decomposition.

5.4 Thermal characterisation of the plastics

This section of the study focused on the determination of the thermal degradation kinetics of the plastic components under inert (pyrolysis-like) conditions. Thermal characteristics such as decomposition temperatures, decomposition steps and heating rate effects were noted during the experiments. Thermal degradation characteristic parameters of initial degradation temperature (**T_1**), final degradation temperature (**T_2**) and peak degradation temperature (**T_{max}**) were noted during the study. These parameters have been defined as follows: **T_1** and **T_2** are temperatures at which deviation from linearity is observed from the sample baseline at the start and end of degradation process (Hatakeyama and Quinn, 1999). **T_{max}** on the other hand is the temperature at which maximum degradation rate occurs (Jung and Fontana, 2006). The results were consequently used to confirm the plastic wastes had similar behaviour to what is reported in literature and to validate the sampling and cleaning method. The influence of heating rate on polymer decomposition rates is discussed as industrial reactions are run to optimise reaction rates and minimise reaction cycle time in order to improve production rates. The thermal behaviours of the plastics are described from TGA and DTG curves generated at 10 and 20 °C/min heating rates. It was observed that at higher heating rates the decomposition temperature increased, this has been attributed to heat transfer limitations on the polymers due to poor plastic thermal conductivity (Mo et al., 2013, Artetxe et al., 2015) but the decomposition rate increased resulting in shorter reaction times. The thermal degradation behaviour shown in figures 5.2 through to 5.6 in the following sections displayed by the plastics confirmed their purity and identity.

5.4.1 High density polyethylene (HDPE)

The polymer degradation occurred between 410 – 510 °C at a heating rate of 10 °C/min in a single step, as shown by the presence of one DTG peak in Figure 5.2. The temperature at which peak polymer degradation took place was 489 °C at 10 °C/min heating rate. The increase in heating rate increased the degradation temperature range as well as the peak temperature and was consistent with literature as discussed in section 3.5.1.1. In this case doubling the heating rate increased the onset decomposition temperature of HDPE to 430 °C, while the peak reaction rate increased as well and occurred at 503 °C; the offset temperature was around 528 °C. These findings were comparable to literature, studies conducted by

Senneca et al (2002) and Sorum et al (2001) on the plastic at the same heating rates, which revealed maximum degradation temperatures between 480 – 495 °C.

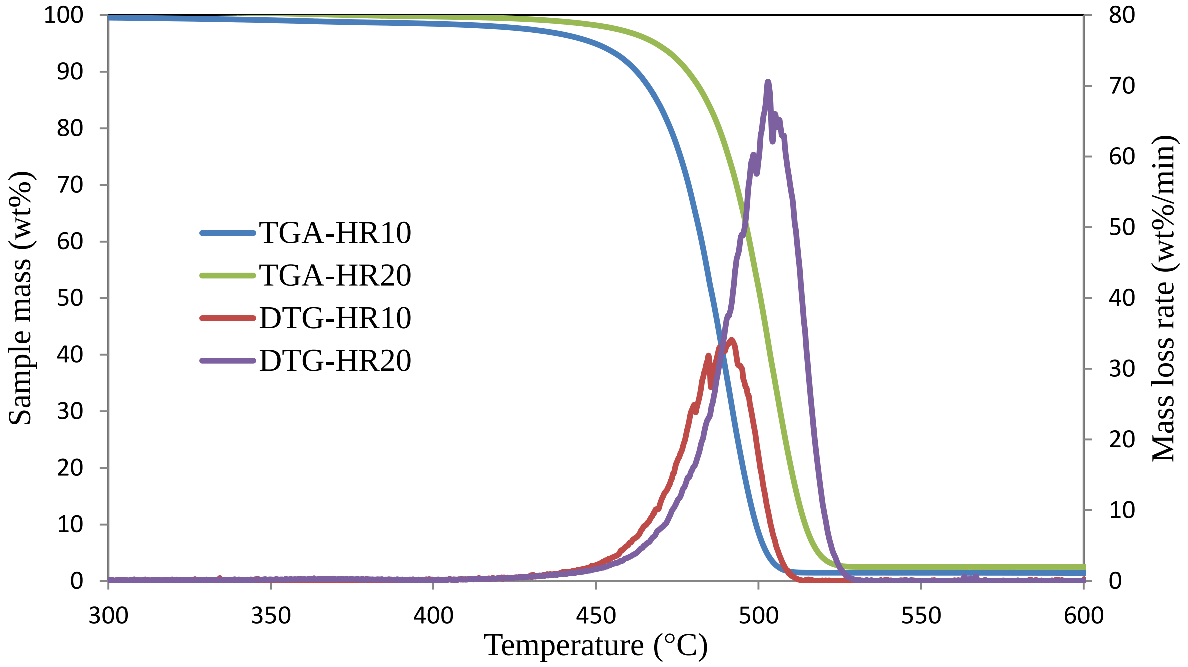

Figure 5.2 HDPE decomposition behaviour at different heating rates

5.4.2 Low density polyethylene (LDPE)

The thermal gravimetric and derivative curves for the thermal behaviour of LDPE are shown in Figure 5.3. As can be seen from the curves at the two heating rates, the degradation of the plastic occurred in a single step and the degradation temperatures varied directly with heating rates. At a heating rate of 10 °C/min, the degradation temperature range of LDPE was 400 – 503 °C with maximum degradation rate occurring at 480 °C. As expected, the higher heating of 20 °C/min raised the onset degradation temperature of the plastic to 426 °C, which was reported within the range of 400 – 435 °C by Heikkinen et al. (2004) and Aboulkas et al. (2008), before reaction completion at 526 °C. It is worth noting that the decomposition temperature of LDPE was lower than that of HDPE because of the fact that LDPE is more linear than crystalline HDPE. This aspect means that the former polymer has more tertiary carbons making it more reactive than the later polymer (Aguado and Serrano, 1999).

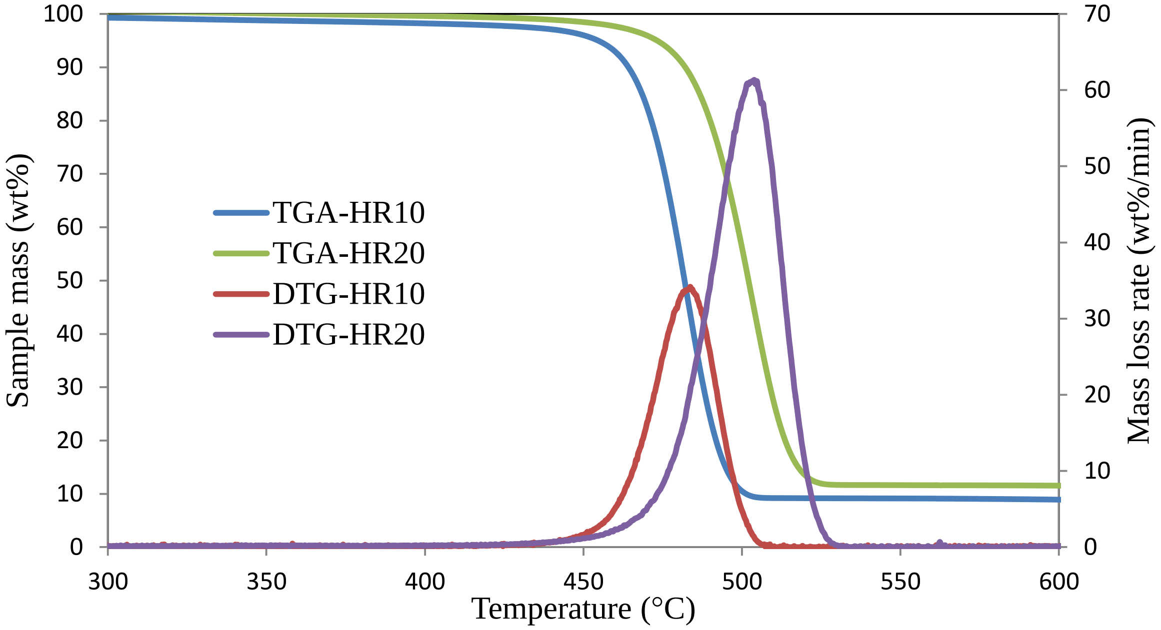

Figure 5.3 LDPE decomposition behaviour at different heating rates

5.4.3 Polypropylene (PP)

Polypropylene polymer, just like HDPE and LDPE, degraded in a single step within the temperature range of 387 – 497 °C at a heat ramping rate of 10 °C/min as shown in Figure 5.4 below. The maximum degradation rate happened at 468 °C, which shifted to 494 °C when the heating rate was increased to 20 °C/min. The latter heating rate increased the onset temperature to 401 °C and the degradation was completed at 523 °C. Literature survey indicated onset temperature range of 390 – 410 °C at the two heating rates with maximum degradation temperatures in the range of 470 – 500 °C (Saha et al., 2008, Jing et al., 2014, Heikkinen et al., 2004). The onset temperatures for thermal degradation of HDPE and LDPE were higher than that of PP. This was attributed to the higher proportion of tertiary carbons in PP, compared to HDPE and LDPE (Aguado and Serrano, 1999). This aspect increased the reactivity of the carbon chain in PP and the polymer therefore decomposed at a lower temperature than that of both HDPE and LDPE (Williams and Williams, 1999). Similar to observations made in the decomposition behaviour of HDPE and LDPE, increasing heating rate of the PP degradation process increased the plastic degradation rate.

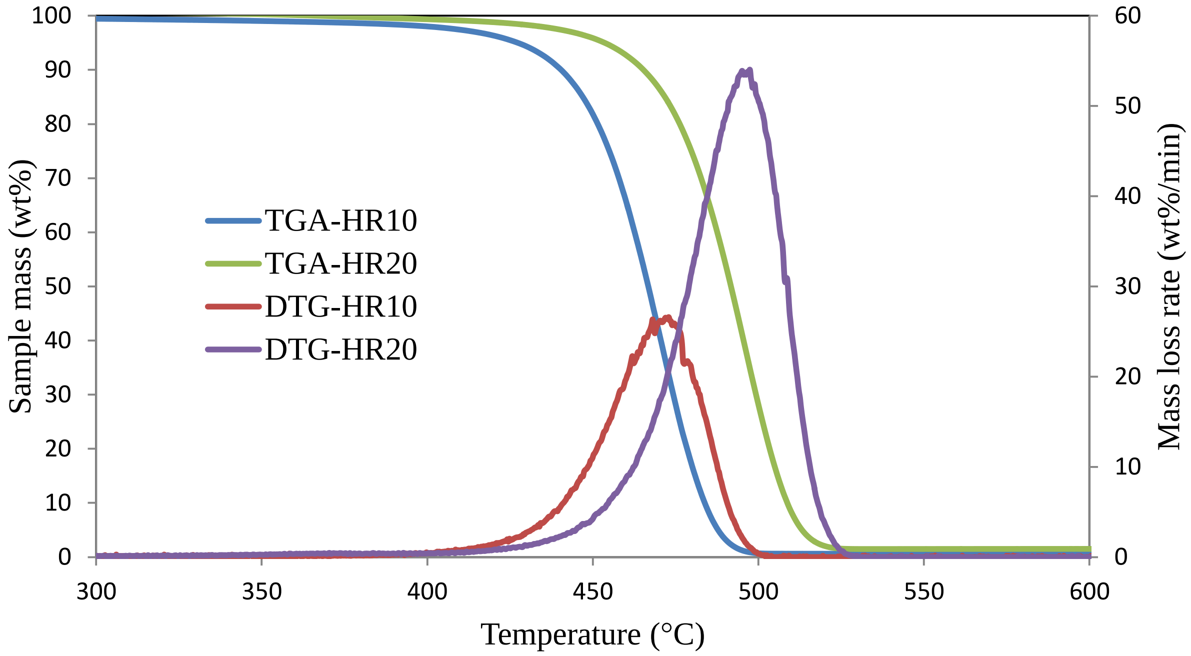

Figure 5.4 PP decomposition behaviour at different heating rates

5.4.4 Polystyrene (PS)

Among the polymers studied, PS has the largest amounts of substituents on the polymer backbone, and therefore has the weakest thermal stability (Aguado and Serrano, 1999). A consequence from this was that the polymer comparatively decomposed at the lowest temperature, but still in a single step as shown in Figure 5.5 below. Polystyrene was decomposed between 329 – 460 °C at a heating rate of 10 °C/min with maximum degradation rate occurring at 417 °C. The degradation interval was shifted to between 366 – 496 °C when the heating rate was increased to 20 °C/min, with the maximum polymer degradation rate occurring at 442 °C. These characteristic temperatures were in agreement with those reported by Liu et al. (2000), Lee and Shin, (2007), Aboulkas et al. (2009) and Onwudili et al. (2009), whom found an onset temperature degradation range of 350 – 369 °C and maximum degradation temperature of 440 – 450 °C at these heating rates.

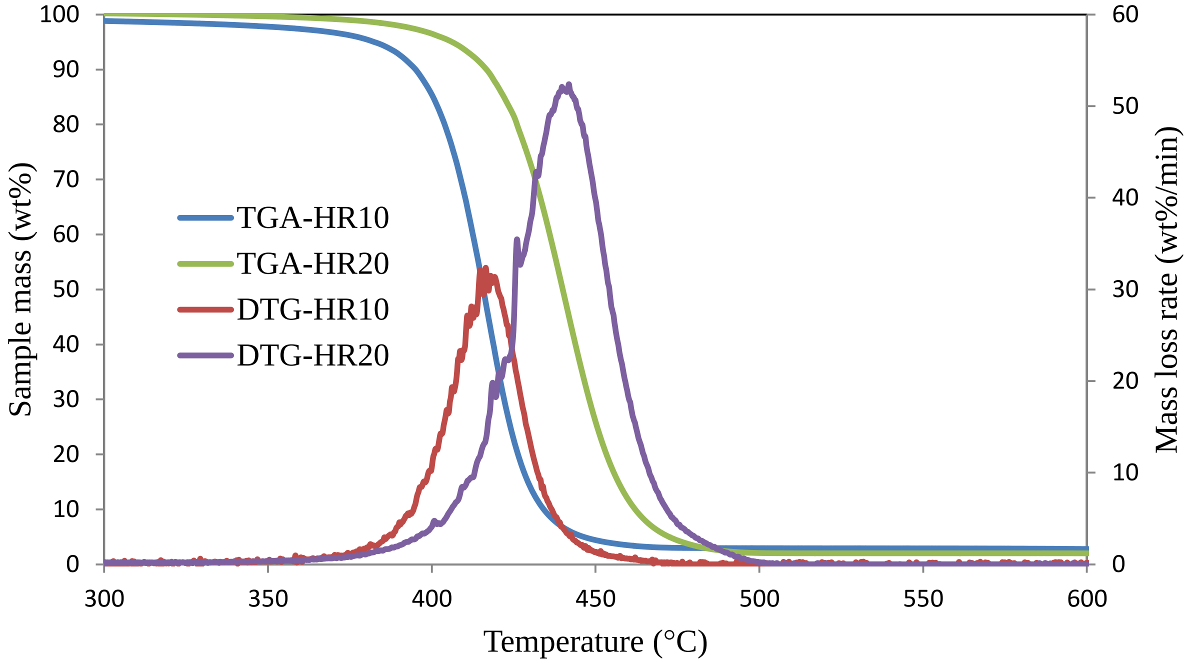

Figure 5.5 PS decomposition behaviour at different heating rates

5.4.5 Polyethylene terephthalate (PET)

Polyethylene terephthalate has tertiary carbons because of its substituents on the carbon chain backbone. These carbons, together with the presence of C-O bonds, are sources of weakness where bond fission is initiated and eventually propagated to other more stable ones (Levchik and Weil, 2004, Martın-Gullon et al., 2001). PET was found to be the second most thermally unstable polymer after polystyrene at it decomposed at lower temperatures than the polyolefins (PP, HDPE and LDPE). The thermal degradation behaviour of polyethylene terephthalate is shown in Figure 5.6 below. The degradation temperature regime at a heating rate of 10 °C/min was between 380 – 489 °C and at 20 °C/min increased to between 399 – 521 °C. The temperatures at which maximum degradation occurred for the two heating rates were 439 °C and 457 °C, respectively. At these heating rates, degradation range of 380 – 515 °C and maximum temperatures of between 440 – 450 °C were found in literature (Saha and Ghoshal, 2005, Senneca et al., 2002, Heikkinen et al., 2004).

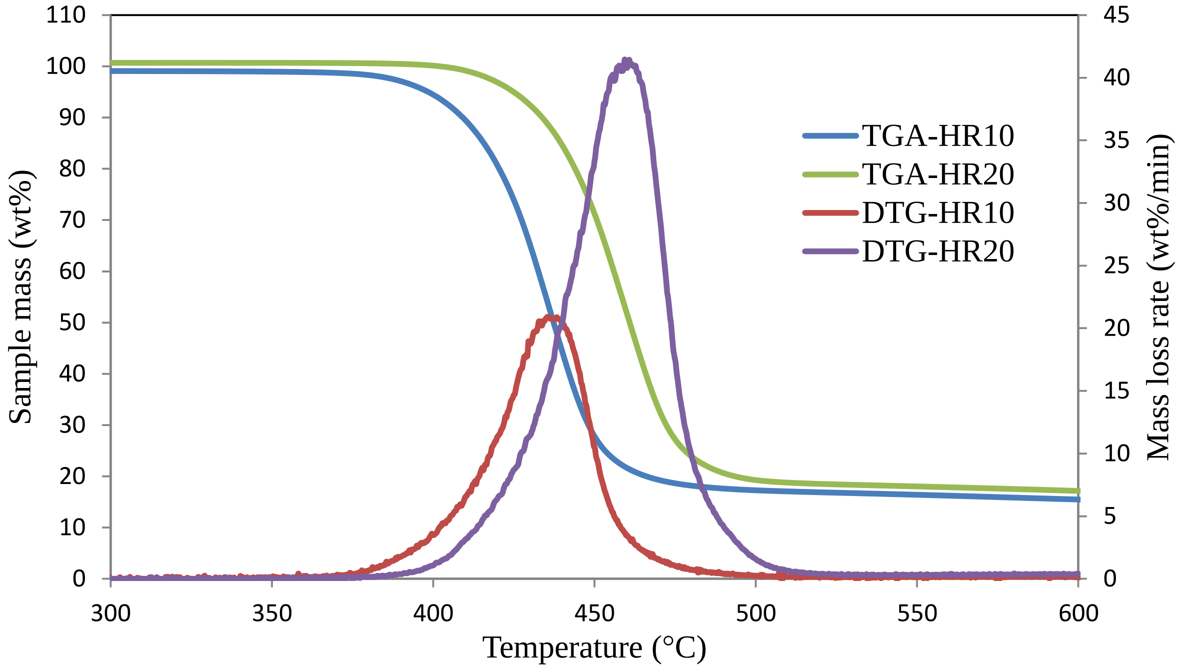

Figure 5.6 PET decomposition behaviour at different heating rates

The thermal characteristic parameters of the polymers obtained during this study are shown in Table 5.4. These parameters were found to be in line with literature thereby confirming that the plastic samples were pure. Additionally, temperatures for application at bench-scale pyrolysis conversion could be identified from the degradation range found.

Table 5.4 Thermal characteristic parameters of polymers

Polymer	**Heating rate (°C/min)**	**T_1 (°C)**	**T_2 (°C)**	**T_{max} (°C)**	**D_{max} (wt %/min) at T_{max}**
PS	10	344	460	417	32
PP		388	497	468	26
LDPE		400	503	480	32
HDPE		420	506	489	34
PET		385	480	439	20
PS	20	354	500	442	52
PP		392	521	499	51
LDPE		410	527	504	59
HDPE		430	524	503	70
PET		404	507	462	41

D_{max} – Maximum degradation rate of the polymer.

5.5 Thermogravimetric mass spectrometric (TGA–MS) experiments

In order to better understand the pyrolysis conversion mechanisms of the plastics, a mass spectrometer was directly coupled to a thermogravimetric analyser (TGA). The coupling cable contained a capillary that was heated to 200 °C, in order to limit the condensation of high boiling point volatiles from condensing before reaching the mass spectrometer detector. The polymer degradation compounds of interest were identified from literature, and then searched in NIST library to predict the characteristic fragmentation ions. The currents of these characteristic ions were monitored as a function of time. Since the time of flight of the volatiles is a few seconds to reach the MS detector, the ion currents could be plotted against the temperature of the thermogravimetric analyser. These experiments served as a screening phase to predict suitable heating rate and temperature ranges before bench-scale study could be undertaken, with the aim of maximising the yields of the chemical products of interest under pyrolysis conditions. This route has also been used by Artetxe et al., 2015, before the authors carried out a bench-scale study of polystyrene pyrolysis in a conical spouted bed reactor. The investigated heating rates were 5, 10, 20 and 40 °C/min, while maintaining the final pyrolysis temperature at 650 °C, which is much higher than the offset temperature for both PS and PET. The product evolution of PS pyrolysis is discussed in text with Figure 5.7and Figure 5.8 at heating rates of 5 and 20 °C/min respectively. The other evolution profiles at 10 and 40 C/min heating rates are presented in Appendix B.

5.5.1 Polystyrene (PS)

Literature review of polystyrene pyrolysis products revealed that the most common thermal degradation products are: styrene, styrene dimer, styrene trimer, toluene, ethylbenzene and α-α-methylstyrene (Zhang et al., 1995, Liu et al., 2000, Artetxe et al., 2015, Audisio and Bertini, 1992, Ahmad et al., 2010, Ojha and Vinu, 2015). In this study the major focus was to understand the products evolved from PS polymer. The selection of ions from NIST library to monitor using MS was then based on the most abundant ion fragment produced by PS pyrolysis products (styrene for instance) when subjected to ionisation energy of 70 eV. In Figure 5.7 below, the evolution profiles of some characteristic fragmentation ions from PS pyrolysis products are shown as well as the accompanying degradation behaviour of the polymer at a heating rate of 5 °C/min. The monitored ion fragments were therefore assigned to the compound that produces it in much more abundance than the other expected products.

The ion fragments 91, 104, 106 and 118 represented toluene, styrene, ethylbenzene and α-methylstyrene respectively.

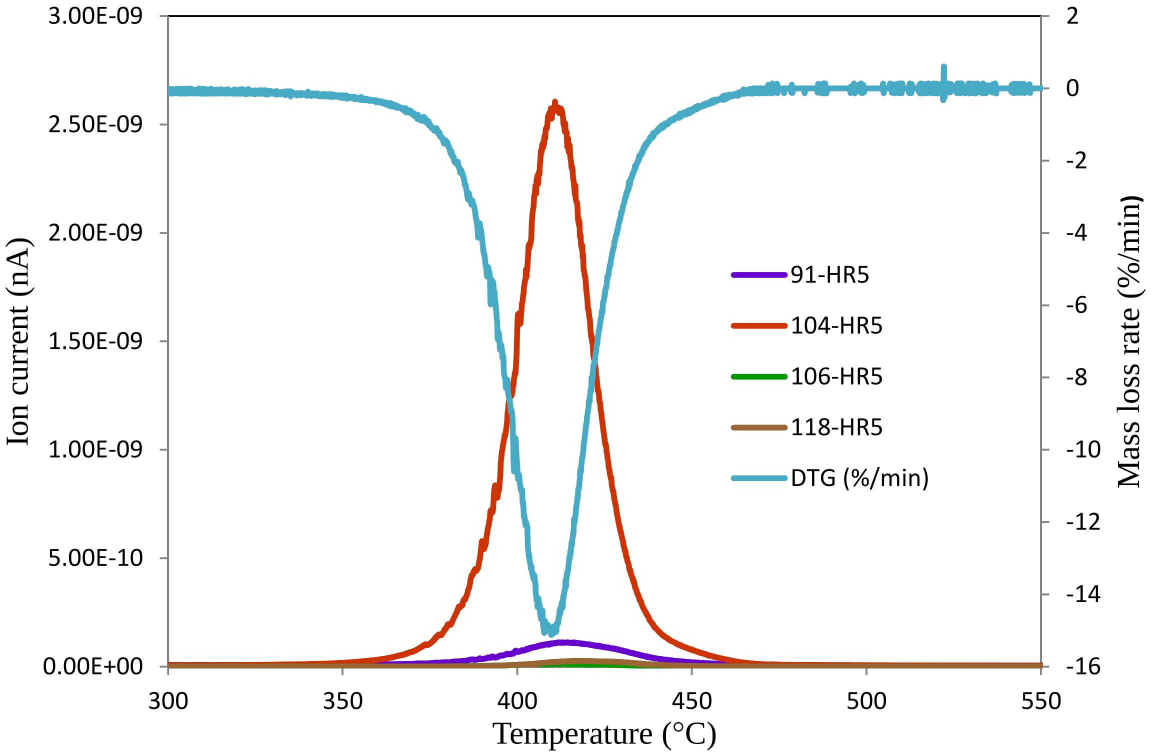

Figure 5.7 Selected ion current evolution profiles during PS pyrolysis at 5 °C /min heating rate

It was observed that the product evolution from polystyrene pyrolysis process in thermogravimetric analyser (TGA) occurred between 350 – 465 °C and that peak chemical production was concurrent with maximum polymer weight loss rate of 14.95%/min at 5 °C/min temperature ramping rate. The ion fragments in this study were assigned according to Table 4.3 in section 4.3.7.

The major ion fragment was 104 which is characteristic of styrene but could be produced by styrene dimer and trimer as well. It could therefore be inferred that styrene was the major polystyrene pyrolysis product and was mostly evolved around 410 °C. Styrene detection began as early as 365 °C, while fragment 91 was detected a bit later at temperatures of around 390 °C, which probably was a result of secondary reactions.

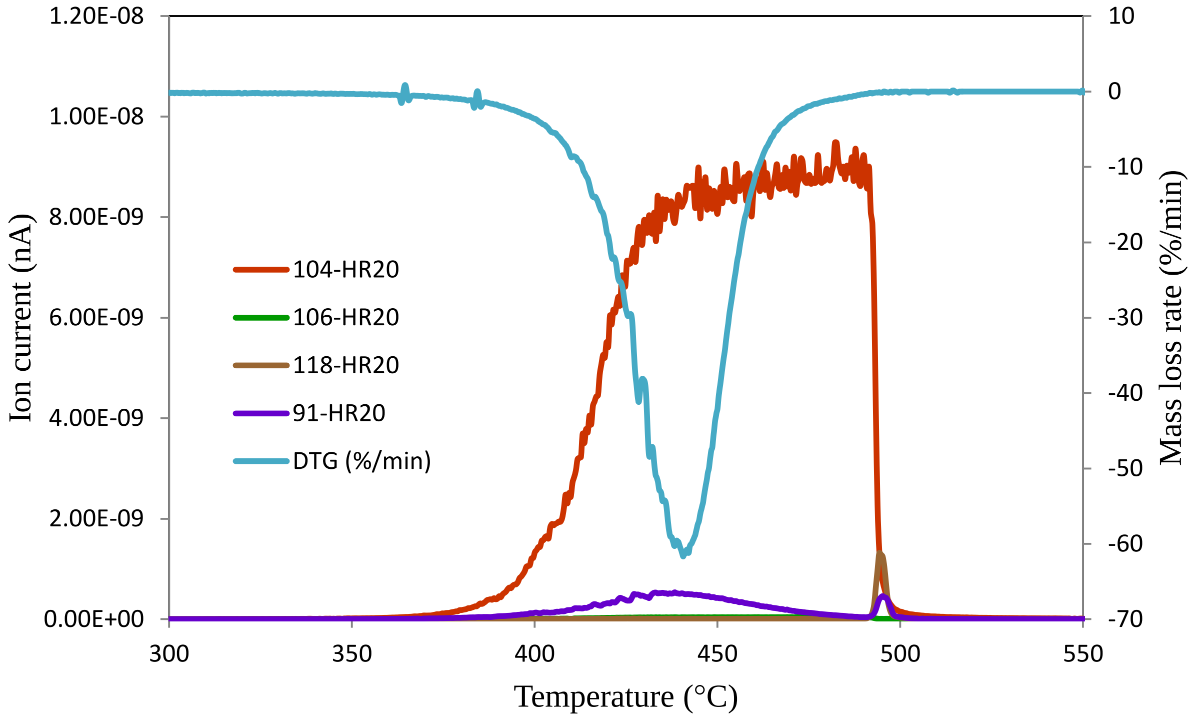

Figure 5.8 Selected ion current evolution profiles during PS pyrolysis at 20 °C /min heating rate

The qualitative investigation of polystyrene polymer pyrolysis was done at the other heating rates of 10, 20 and 40 °C/min for a comparative study. The pyrolysis and MS curves emanating from the study at 20 °C/min heating rate are shown in Figure 5.8. It is observable from the graphs that the increased heating rate caused a temperature lag between the sample temperature and the reference one, due to low thermal conductivity of the PS plastic. This meant that the rate of heat addition (heating rate) to plastic was higher than the rate at which the plastic absorbed (conducted) the thermal energy leading to a temperature lag (Jenekhe et al., 1983, Buekens, 2006). These aspects therefore led to the styrene evolution taking place at a higher temperature range of 368 – 500 °C. Styrene peak production was almost reached before fragment 91 got evolved which might be produced from toluene and ethylbenzene. This meant that these products were mostly likely evolved from secondary reactions.

In order to assess the influence of heating rate on the evolution of the chemicals in these studies, the normalised surface areas based on sample size under the curves of ion current versus time were evaluated and compared at various heating rates. The surface areas under the curves of the MS curves are related to yields, based on this surface area result could be used as response variable to study influence of heating rate (Bartoli et al., 2015). It was however observed that the standard deviation of the results was high on the experiments done. One aspect that could have contributed to this was the fact that it was not possible to place MS capillary inside the TGA furnace at exactly the same position from one experiment to the other. The other challenge could have been partial capillary blockage resulting from partial compound condensation. These challenges therefore affected MS signal intensity resulting into appreciable differences in response surfaces areas.

In Figure 5.9 below it can be observed that the major ion fragment was 104 which most likely was produced by styrene (Liu et al., 2000). Ion fragment 91 (Toluene or/and ethylbenzene) was the major competitor to styrene evolution. All the ions except 104 were insignificantly influenced by heating rate as can be observed from the figure below.

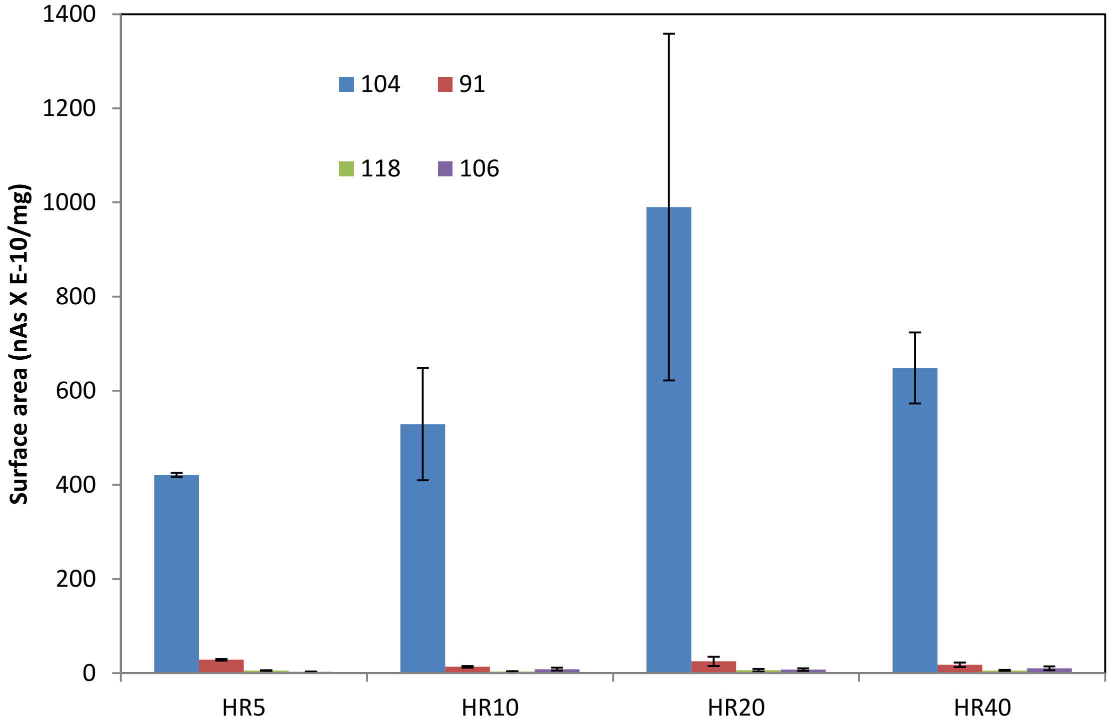

Figure 5.9 Surface areas of polystyrene pyrolysis ions at various heating rates

The ratios of 104 fragment surface area to the surfaces areas of other fragments monitored in polystyrene pyrolysis process, were computed and compared as can be seen in Figure 5.10. This was done on the premise that there would be no discrimination between compounds, providing indications of the relative yields of other chemicals to styrene. The other corrective measure that was taken was running a TGA cleaning program after every run with the capillary in place so that any volatiles that might have condensed in the line from the previous experiment could be dislodged. In Figure 5.10 below the chemicals that were

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detected in TGA – MS experiments are given and the productivity of ions is given as ratios between 104 and the other ions.

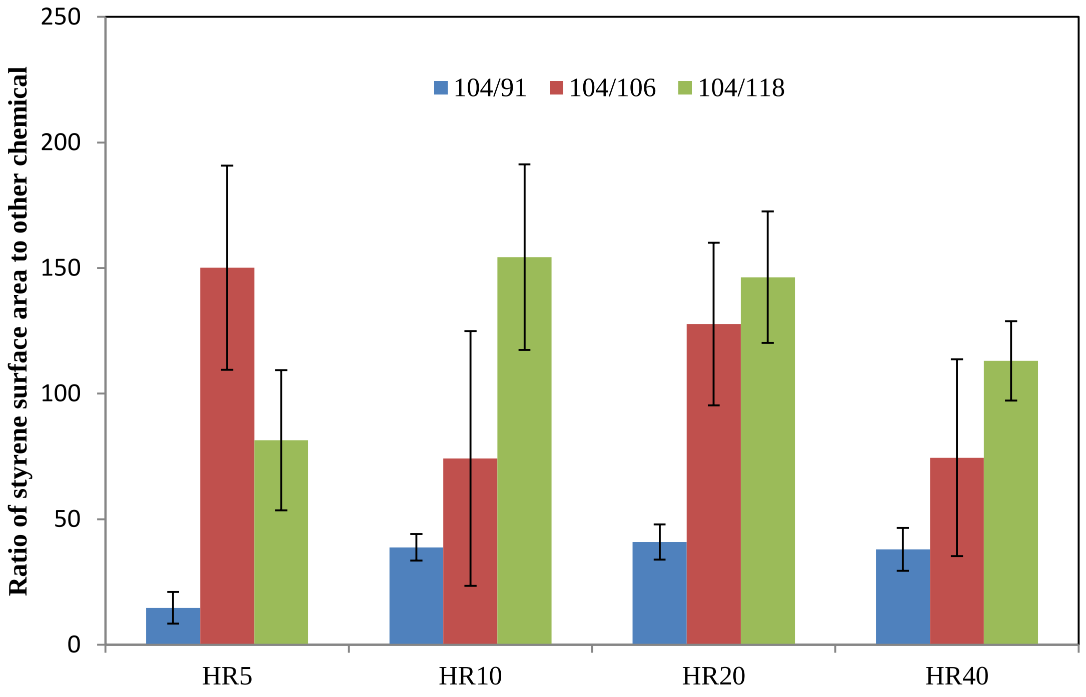

Figure 5.10 Ratios of polystyrene pyrolysis ions at heating rates (HR) from 5 to 40 ˚C/min

These results should be analysed carefully because standard deviations were still relatively high and some were not statistically different, however, it was observed that 91 and 118 ions were promoted at lower heating rates while 106 ion evolution was enhanced as the heating rate was increased (Figure 5.10). Additional tables and figures of results for the TG – MS experiments done at various heating rates are given in Appendix B: TG – MS results.

The main conclusion from this experimental stage was that 104 ion fragment was the major ion evolved from PS pyrolysis and was characteristic of styrene monomer though it could also be produced from styrene dimer and trimmer. The influence of heating rate on the evolution of the ions was also observed. Further styrene production (104) was seemed to get significant competition from 91 ions which could have been evolved by mainly toluene and to some extent by ethylbenzene.

5.5.2 Polyethylene terephthalate (PET)

Figure 5.11 below illustrates typical product signals that were obtained from TG-MS pyrolysis experiments on polyethylene terephthalate polymer. The signals were generated from a TGA experiment with a dynamic temperature program of 20 °C/min heating rate to 650 °C final temperature. The following fragment ions were selected from NIST library to monitor the evolution of the two important acids typically obtained from PET pyrolysis: 122 ion fragment was used to monitor benzoic acid evolution, while 166 was utilised for monitoring terephthalic acid evolution. The ion currents for the two important chemicals were weak and full of noise as can be seen from Figure 5.11. The poor signal strength was interpreted as a result of volatiles condensation before reaching the detector, as TPA has a sublimation temperature of about 400 °C, while BA has a sublimation temperature around 249 °C (Yoshioka and Grause, 2006). This approach as a result could not be used to study the mechanism of PET pyrolysis.

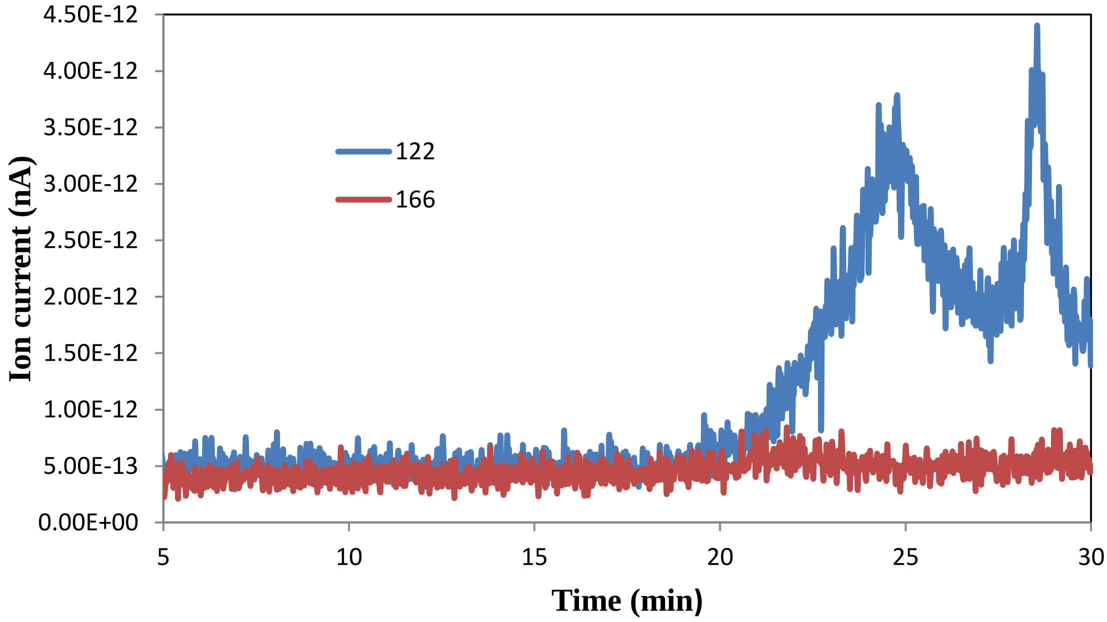

Figure 5.11 Evolution of characteristic fragment ions from benzoic acid (BA) and terephthalic acid (TPA) from PET pyrolysis

5.6 Bench-scale pyrolysis experiments

A set of bench-scale experimental work was done to study the yield and better understand the influence of heating rate on monomer production during pyrolysis conversion of waste plastics. During TGA-MS experiments, the heating rate applied to PS polymer was shown to have an influence on the selectivity of chemicals produced, there was therefore need to study this observation on bench-scale level. On the other hand, TG-MS screening tests on PET were not successful and the only way to study the possibility of valuable chemical yield from PET pyrolysis was through bench-scale experiments. These experiments were done on individual plastics at conditions detailed in section 4.3.8 of the methodology chapter, including both slow and vacuum pyrolysis conditions.

5.6.1 Polystyrene (PS) bench-scale pyrolysis

5.6.1.1 Slow pyrolysis experiments

Slow pyrolysis experiments were done as fully described in section 4.3.8 above, in which the inert conditions were made possible by continuously feeding the reactor with nitrogen at flow rate of 500 ml/min. The temperature selection was based on TGA results with the goal of detecting the influence of conditions on yield taking place at different temperatures. A lower limit temperature of 410 C° was chosen because it was before the peak temperature and appreciable degradation was initiated at this temperature. The maximum temperature studied was 550 ºC at which degradation was complete as a higher temperature would not give a higher yield or different mechanism. On the other hand, a temperature of 480 ºC around the maximum degradation point was studied to try to find the optimum PS conversion.

Mass balance of product streams

In all the experiments, accurate mass measurements of feed and products (solid residue and liquid) were captured in the various parts of the experimental set up. The mass of the gas product was calculated by the difference between the feed mass and that of the products collected as shown in Equation 4.4. This procedure has been used by (Kim et al., 2003, Mo et al., 2014, Undri et al., 2014) to conduct mass balance in the study of PS pyrolysis and was found suitable as the main product of interest (styrene) is condensable and should be collected in the liquid fraction.. The mass balances of all the experiments performed at various conditions are given in Table C.0.3 of Appendix C, while averaged results are detailed below in order to discuss the points of interest.

Effect of temperature on yields

The conversion of polystyrene during slow pyrolysis was more than 90 wt% at all the temperatures studied. This result is justified as volatile matter was more than 96 wt% for the plastic as shown in Table 5.3 given in section 5.3. In addition, pyrolysis of the plastic during TGA screening experiments showed a conversion of over 95 wt% as can be seen from Figure 5.5 in section 5.4.4. The conversion of polystyrene has been found to be similarly high in many other studies (Audisio and Bertini, 1992, Chauhan et al., 2008, Artetxe et al., 2015 and Mo et al., 2013).

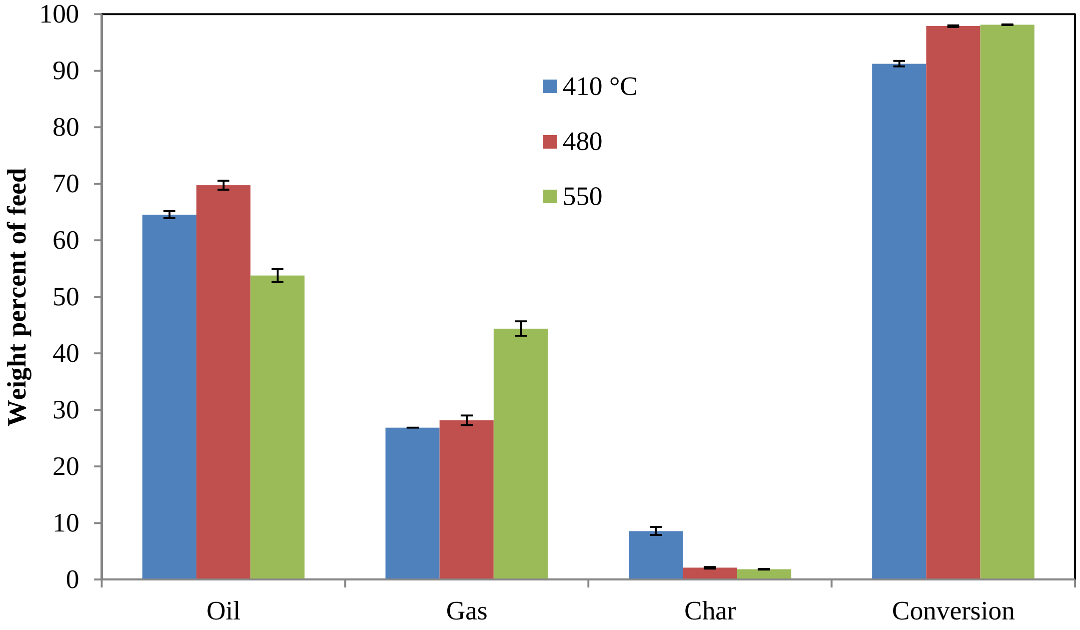

Figure 5.12. Measured (oil, char) and calculated (gas) yields from slow PS pyrolysis at 5 °C/min heating rate.

Char yield of 8.6 wt% was higher at 410 °C signifying full conversion was not achieved, while for higher temperatures char yield was around 2 wt%, consistent with PS volatile matter of 97 wt%. Looking at oil yield, the yield of 69.75 wt% at 480 °C was higher than 64.55 wt% at 410 °C by 5.2 wt% which was close to the char yield at 410 °C. The lower oil yield at 410 °C could then be explained by the incomplete conversion. The yield of oil at 480 °C was greater than 53.80 wt% at 550 °C, as can be seen from Figure 5.12 . This result could be the result of further decomposition of oil into gas as was observed by Artetxe et al. (2015)

as higher temperatures favours rapid bond breaking to smaller molecules, this assumption is consistent with higher gas yield observed at 550 °C. Similar behaviour of the mass yields with temperature was observed at a heating rate of 25 °C/min as shown in Figure 5.13 below.

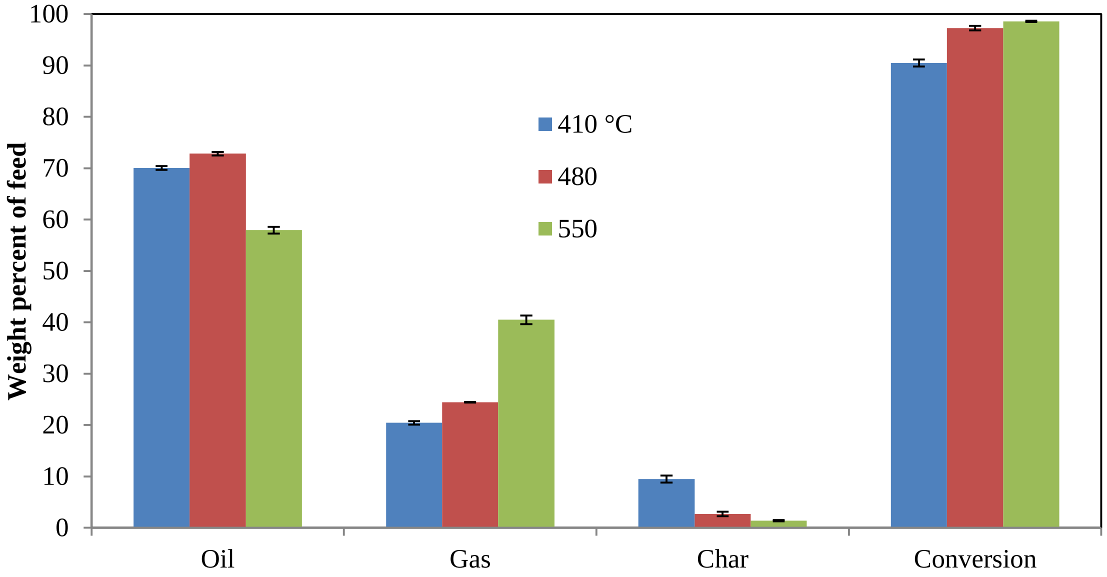

Figure 5.13. Measured (oil, char) and calculated (gas) yields from slow PS pyrolysis at 25 °C/min heating rate.

Pyrolysis of polystyrene is known to lead to the evolution of styrene in significant yield as per discussions in section 3.5.3.2 of chapter 3. The results in Figure 5.14 below confirmed that styrene monomer was the main product of PS pyrolysis. The resultant main chemicals produced from PS in this study have also been reported by other researchers (Mo et al., 2014, Ojha and Vinu, 2015, Artetxe et al., 2015) and that, amongst monomer derived compounds, toluene as well as α-methylstyrene is the main competitor to styrene yield as shown in Figure 5.13.

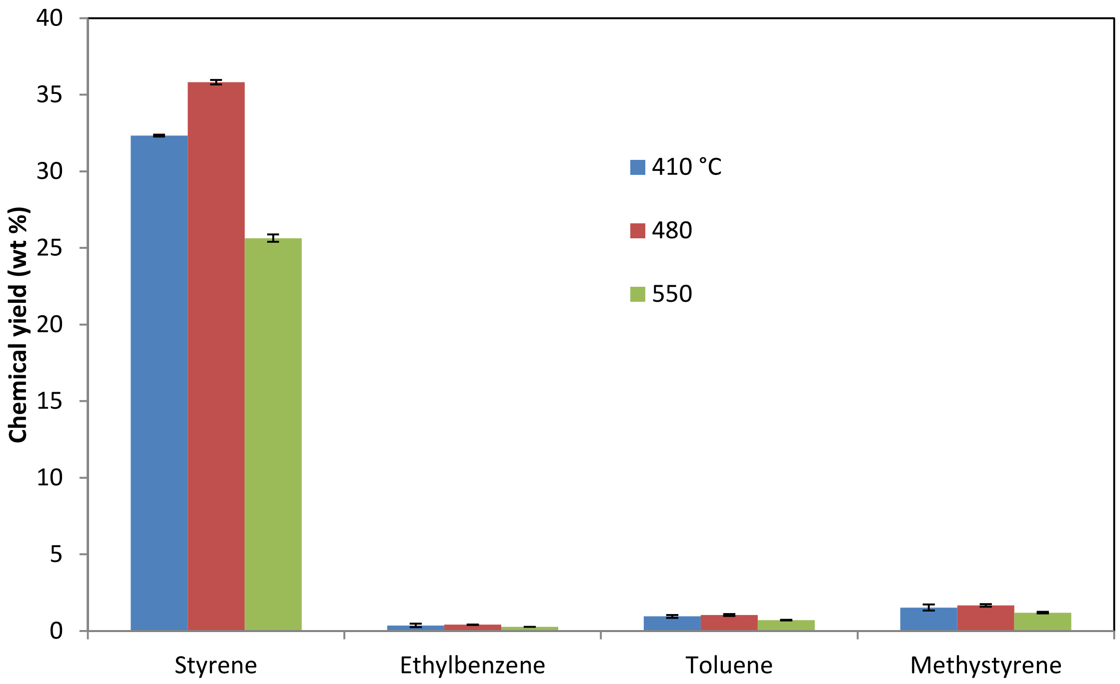

Figure 5.14 Chemical yields from slow PS pyrolysis at 5 °C/min heating rate.

Temperature had an influence on the yield of the chemicals as can be observed from Figure 5.13 and this is consistent with findings of (Mo et al., 2014 and Chumbhale et al., 2004), whom reported temperature to have a strong influence on styrene yield. Zang et al., 1995 and Park et al., 2003 also reported that temperature had a strong influence on the yield of styrene and the yield of the chemical reduced with temperature beyond the optimum point. The yield of styrene increased from 32.33 wt% at 410 °C to 35.82 wt% at 480 °C, but sharply decreased to 25.64 wt% at 550 °C. This could be explained by the lower oil as the temperature was increased to 550 °C.

The influence of temperature on the yield of the chemicals at a higher heating rate (25 °C/min) is shown in Figure 5.15 below. As can be seen from the figure, similar yields of styrene were obtained from conversion at 410 and 480 °C. However, the yield of styrene at 550 °C was again clearly lower than those obtained at the previous temperatures. The yields of ethylbenzene, toluene and α-methylstyrene were also influenced by temperature over the investigated range as also reported by other researchers (Audisio and Bertini, 1992, Ojha and Vinu, 2015). At 25 °C/min heating rate, the yield of styrene was highest at 410 °C with 40.88 wt% as opposed to the trend at 5 °C/min heating rate. This could be explained by the faster kinetics of depolymerisation at the higher heating rate (Artetxe et. al., 2015).

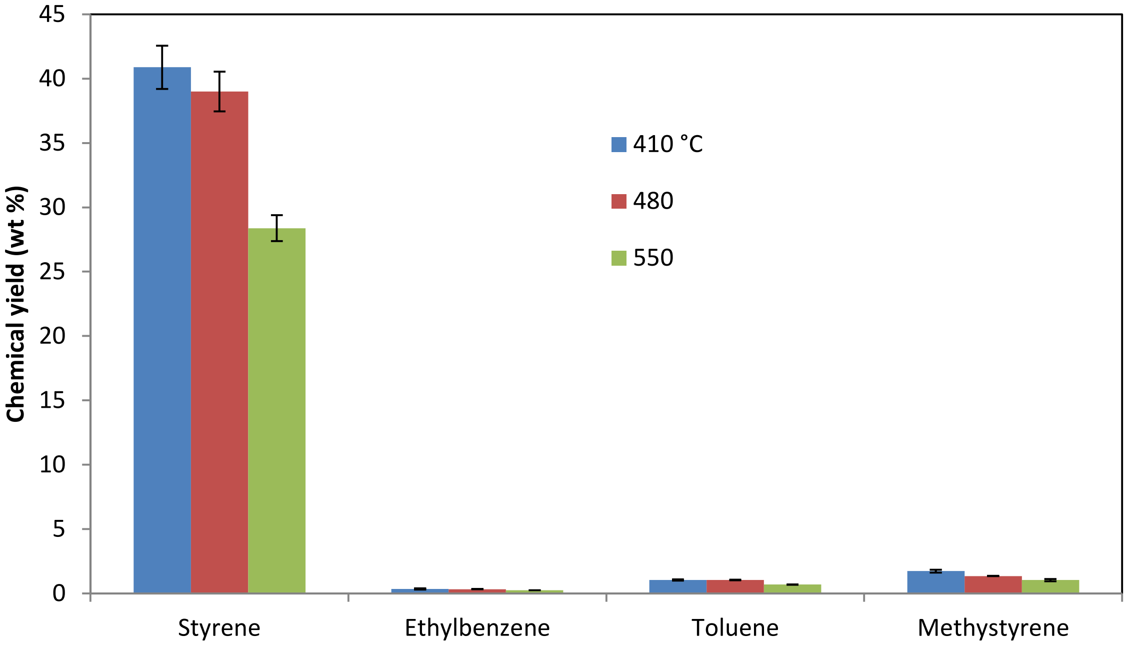

Figure 5.15 Chemical yields from slow PS pyrolysis at 25 °C/min heating rate.

The concentration of styrene in the liquid phase is important when considering a separation unit to further purify the chemical. The chemical concentrations obtained in the slow PS pyrolysis experiments are shown in Figure 5.16 below. It can be observed that temperature to a large extent affected the concentration of styrene in the temperature range considered. The concentrations of styrene at 410 °C and 480 °C were the same but a marked difference with those at 550 °C. The concentrations of the other chemicals remained steady over the temperature range.

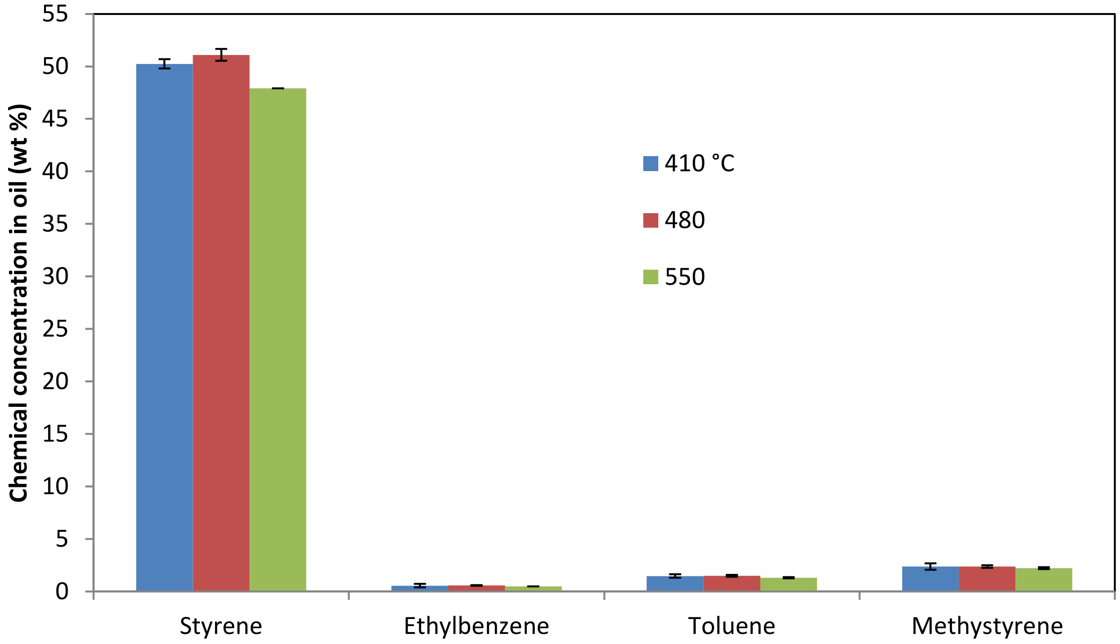

Figure 5.16 Chemical concentration from slow PS pyrolysis at 5 °C/min heating rate

The effect of temperature on the concentration of styrene in the oil at a heating rate of 25 °C/min is shown in Figure 5.17 below. It is apparent from the figure that styrene chemical concentration at 410 °C was highest at 58.42 wt%.

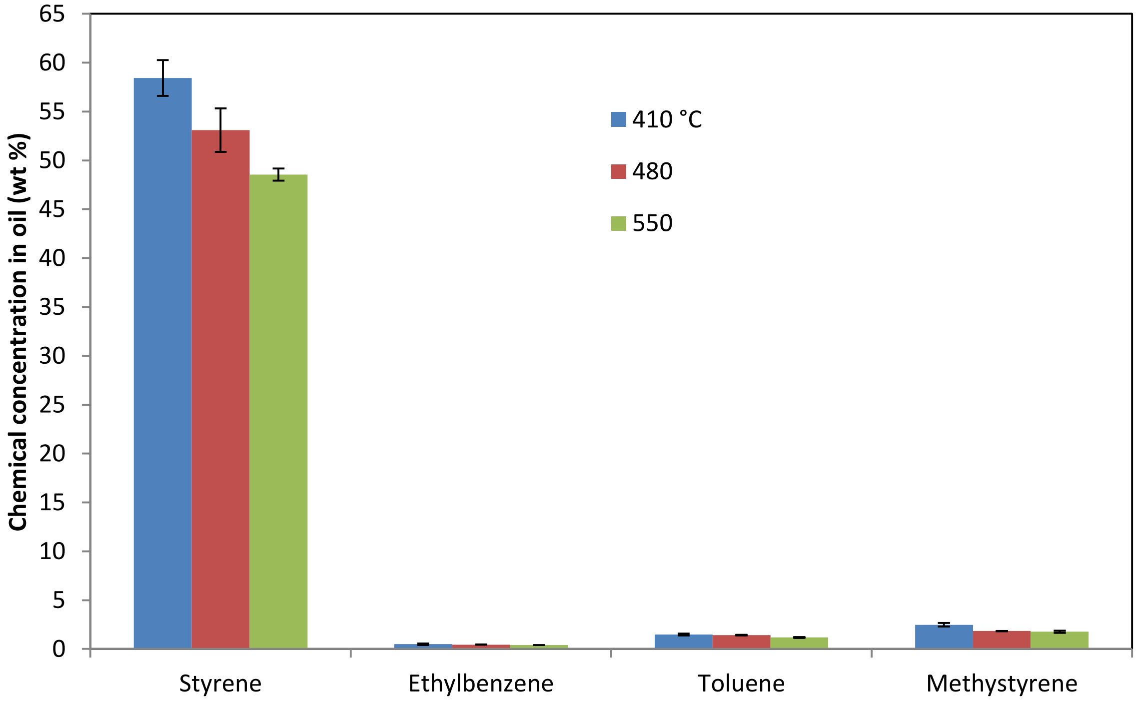

Figure 5.17 Chemical concentration from slow PS pyrolysis at 25 °C/min heating rate

However, the concentration of styrene at 410 °C and that at 550 ºC was marked by a noticeable drop of approximately 10 wt % because of the styrene yield decrease at 550 °C. The concentration of ethylbenzene almost remained constant at around 5 wt%, while toluene and α-methylstyrene decreased at 550 ºC from 410 ºC.

Effect of heating rate on yields

The mass yields of the oil increased with increase in heating rate at the three temperatures studied as can be observed from Figure 5.18 below.

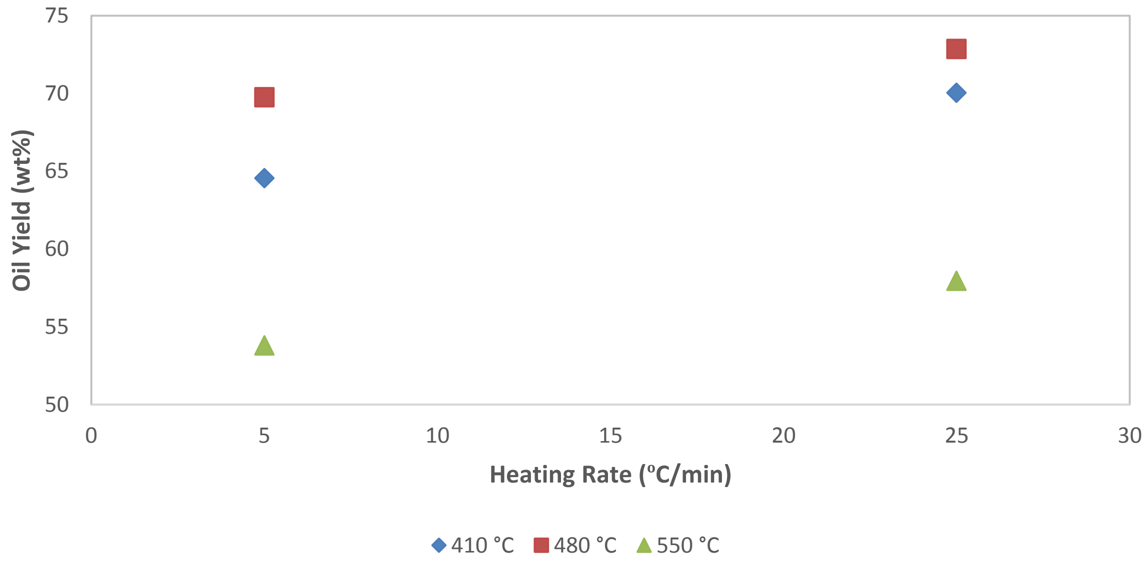

Figure 5.18 Effect of heating rate on oil yield

The yields of the liquid fraction increased by over 3 wt % at all the temperatures, when the heating rate was increased from 5 °C/min to 25 °C/min. This phenomenon could be explained by the fact that at a higher heating rate, the potency of bond breaking in the polymer increased and the broken down molecules had higher kinetic energy to escape the reaction front (Kim and Kim, 2004). This then increased the volatile fraction from PS degradation process which upon condensation increased the oil yield. This aspect has also been investigated on by Mo et al., 2014 and the authors reported that heating rate linearly increased oil and styrene yields within the studied range of 10 – 40 °C/min. Ahmad, et al., 2010 and Aboulkas et al., 2009 have made similar observations on the effect of heating rate on volatile yield in the range of 2.5 – 50 °C /min.

The average yield of styrene at the two heating rates and various temperatures are given in Table 5.5 below. The yield of styrene was increasing with the increase in heating rate. The largest increase of about 8 wt % in styrene yield was obtained at 410 °C while about 3 wt% was recorded at both 480 °C and 550 °C.

Table 5.5 Yield of styrene at different heating rates in slow pyrolysis

Heating rate (°C/min)	Styrene yield at various temperatures (wt %)					
	410 °C	SD	480 °C	SD	550 °C	SD
5	33.33	0.06	35.82	0.15	25.64	0.24
25	40.88	1.68	38.99	1.54	28.37	1.01

The concentration of styrene in the oil increased as the heating rate was increased as can be seen from Table 5.6 below, except at 480 °C. The increase in styrene concentration was over 8 wt % at 410 °C and less than 1 wt % at 550 °C. These results are in line with literature as regards the effect of heating rate on polystyrene pyrolysis product concentrations and yields. It was therefore observed that heating rate strongly influenced the yield of styrene and its concentration in the oil similar to observations made by Mo et al. (2014). The authors obtained the highest styrene yield and concentration of 65.41 wt% and 75.25 wt% respectively. In this study the best styrene yield was 40.88 wt% while the concentration was 58.42 and the variance with literature can be explained by the reactor set up and pyrolysis conditions differences.

Table 5.6 Concentration of styrene at different heating rates in slow pyrolysis

Heating rate (°C/min)	Styrene yield at various temperatures (wt %)					
	410 °C	SD	480 °C	SD	550 °C	SD
5	50.23	0.44	51.10	0.56	47.92	0.00
25	58.42	1.83	53.10	2.22	48.55	0.61

5.6.1.2 Vacuum pyrolysis experiments

These experiments were done with a view that vacuum conditions could lead to shorter vapour residence times. This could limit secondary reactions and give higher styrene yield.

Effect of temperature on yields

The conversion of the PS polymer at the three investigated temperatures is compared and shown in Figure 5.19 below. The polymer conversion was more than 95 wt% at all the temperatures and both heating rates and consistent with TGA volatile matter content obtained in the study (section 5.3).

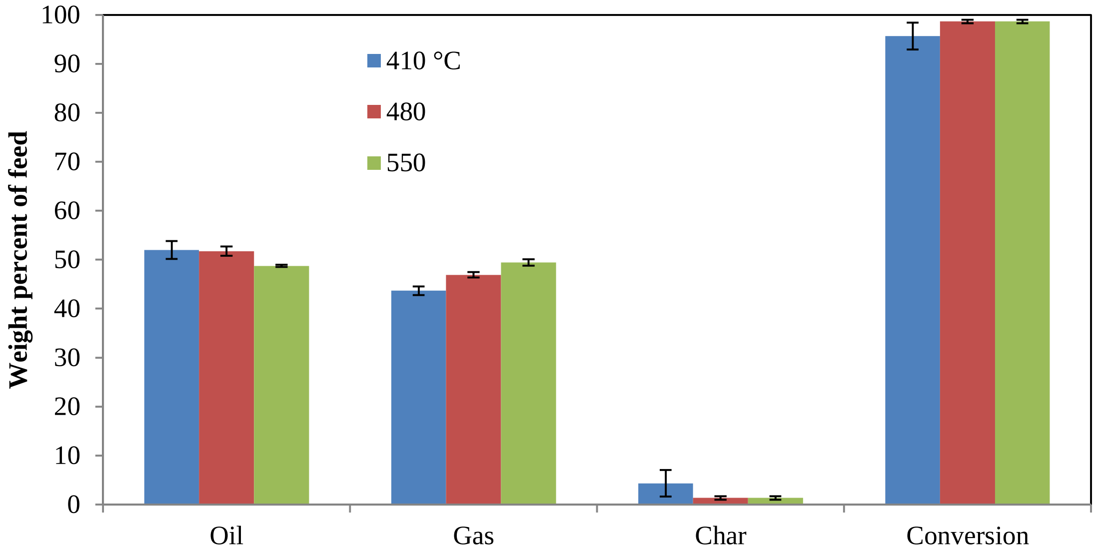

Figure 5.19 Measured (oil, char) and calculated (gas) yields from vacuum PS pyrolysis at 5 °C/min heating rate.

The yield of char was around 3 wt% at all the temperatures. Oil yield at 410 and 480 °C was the same but reduced when the temperature was increased to 550 °C. The decrease could be explained by the increase in gas yield due to further oil break down.

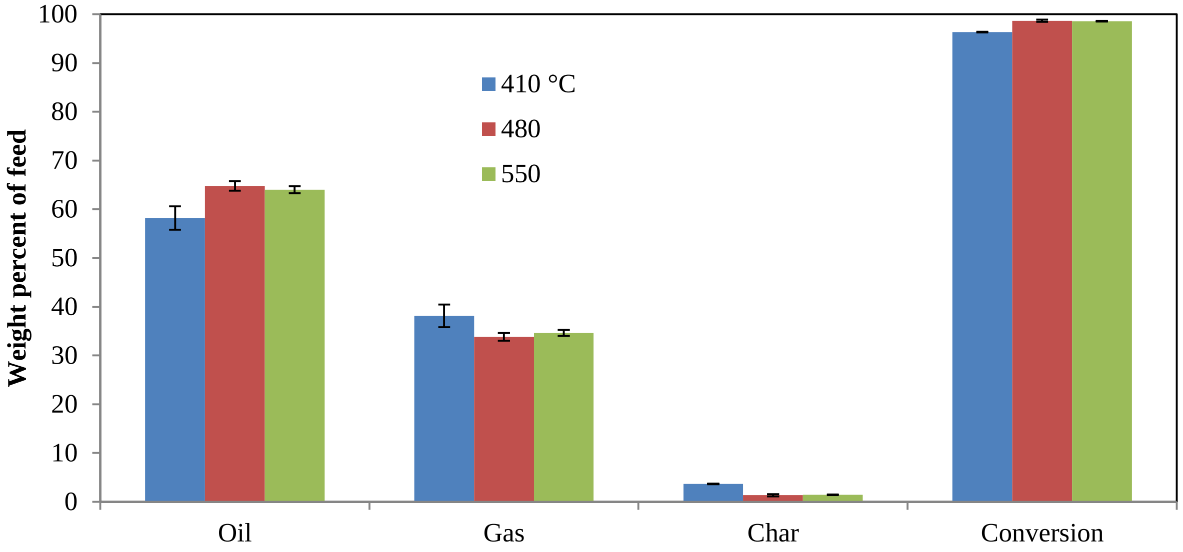

Figure 5.20 Measured (oil, char) and calculated (gas) yields from vacuum PS pyrolysis at 25 °C/min heating rate.

Similarly, conversion of over 96 wt% was observed at 25 °C/min condition as observed in Figure 5.20 above. In the case of char yield, it was about 4 wt% at 410 °C and remained at slightly over 1 wt% at higher temperatures of 480 and 550 °C. Oil yield increased from 410°C to 550 °C although it relatively remained constant at 480 °C. This was consistent with the drop in calculated gas yield as the temperature was increased.

The tests done under vacuum were more challenging to reproduce as the pressure was constant. This resulted into higher variability in the yield of the chemicals. The yields of chemicals from vacuum pyrolysis of polystyrene at 5 °C/min are shown in Figure 5.21 below. Styrene yield at 480 °C was significantly lower than at 410°C. The trend could not be confirmed at 550 °C due to the large standard deviation on the average yield but based on the decrease in oil yield (Figure 5.19), it likely that styrene yield also decreased. The yield of toluene was negligible while that of both ɑ-methylstyrene and ethylbenzene was below 1 wt% regardless of temperature. This could mean there was a change in the mechanism of conversion of PS to styrene.

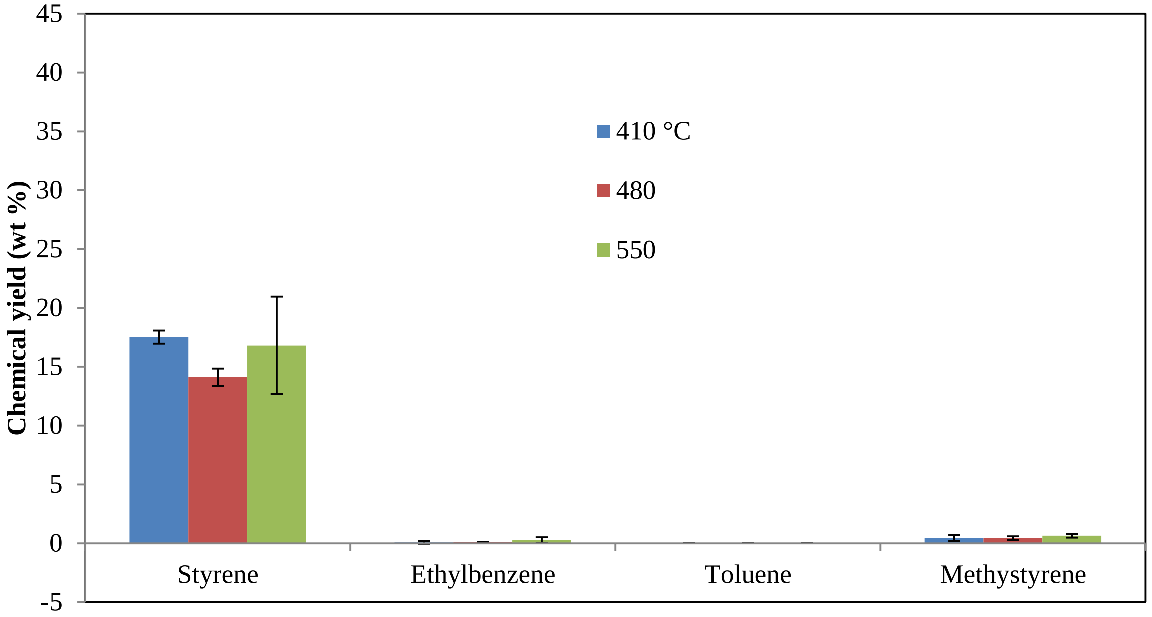

Figure 5.21 Chemical yields from vacuum PS pyrolysis at 5 °C/min heating rate

The yield of styrene at 25 °C/min is shown in Figure 5.22 below with marked effluence of temperature. The styrene yield increased from 12.45 wt% at 410 °C to 36.07 wt% at 550 °C. Once again the yield of α-methylstyrene and ethylbenzene was not influenced by temperature as at 5 °C/min while toluene yield was insignificant.

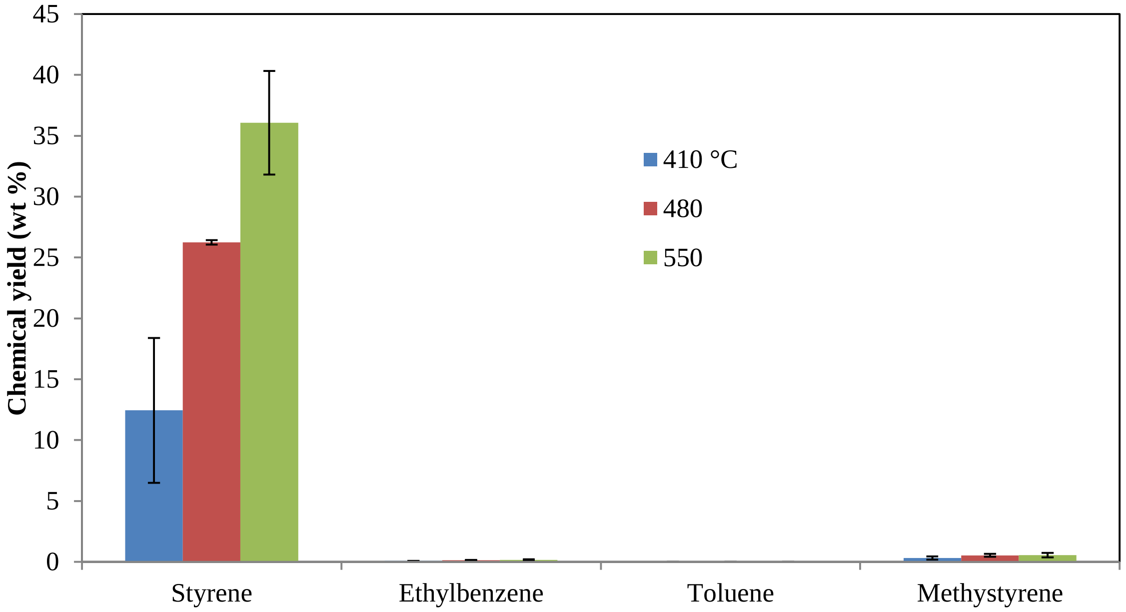

Figure 5.22 Chemical yields from vacuum PS pyrolysis at 25 °C/min heating rate

Similar to the case of chemical yields in Figure 5.21 above, it could be concluded that styrene concentration decreased with temperature while the other chemicals remained insignificant. It was however apparent that styrene was the major chemical in the pyrolysis oil.

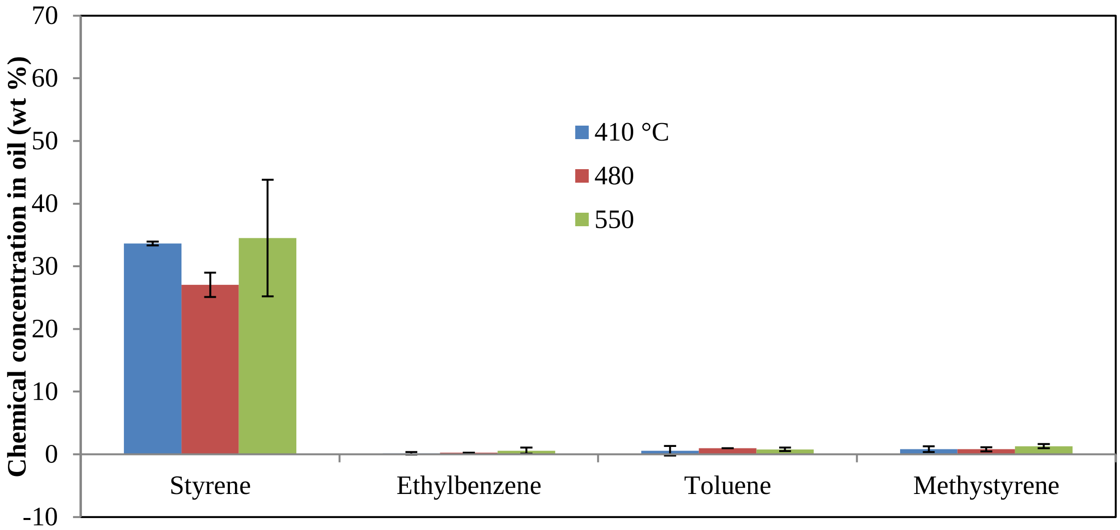

Figure 5.23 Chemical concentrations from vacuum PS pyrolysis at 5 °C/min heating rate

The influence of temperature on the concentration of chemicals at 25 °C/min is shown below in Figure 5.24. The concentration of styrene increased with increase in temperature from 21.55 wt% at 410 °C to the highest of 56.28 wt% at 550 °C while α-methylstyrene, toluene and ethylbenzene response were the same.

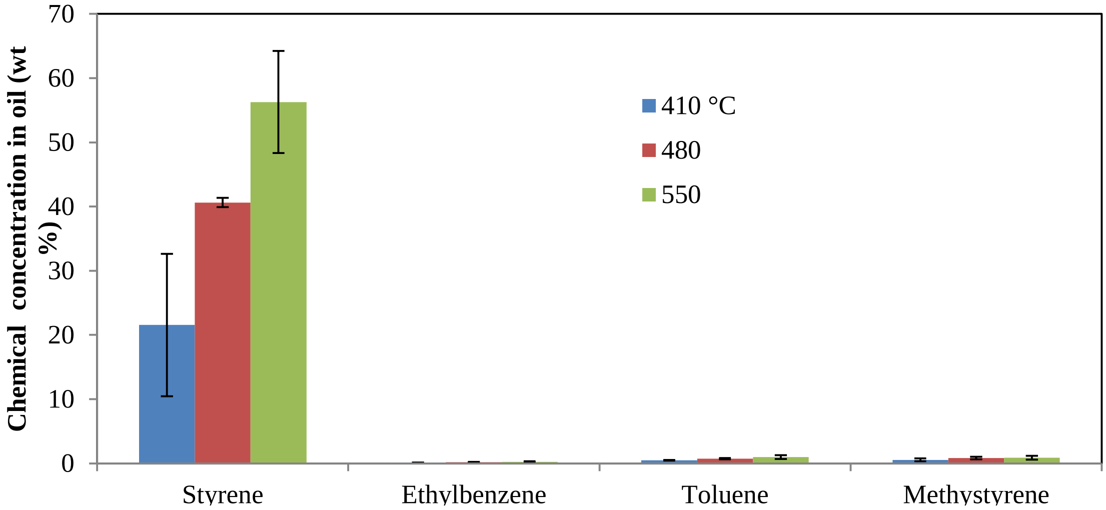

Figure 5.24 Chemical concentrations from vacuum PS pyrolysis at 25 °C/min heating rate

Effect of heating rate on yields

The effect of temperature on mass yields of the oil as heating rate was varied is illustrated in Figure 5.25 below. As can be noticed from the graphs, the oil yield increased as the heating rate was ramped up.

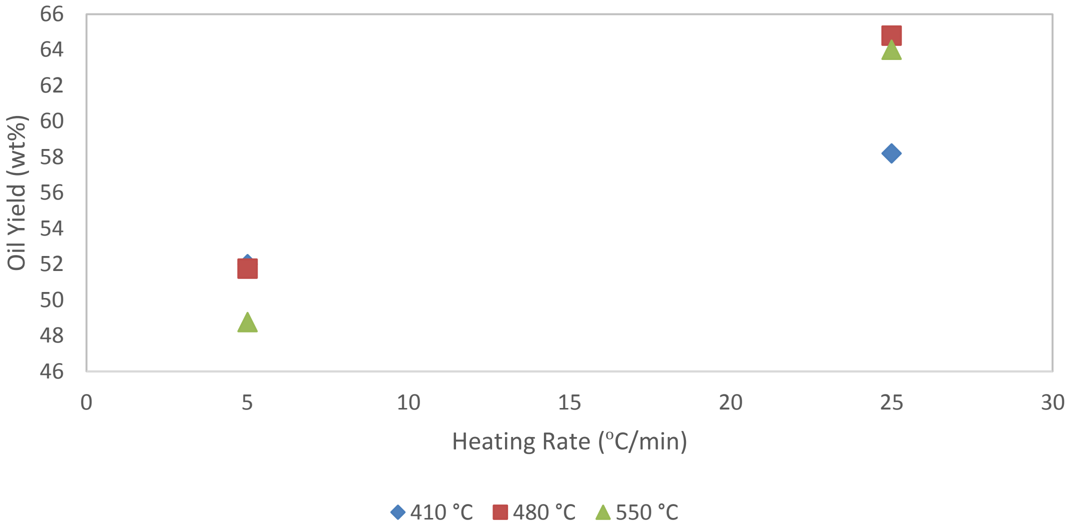

Figure 5.25 Effect of heating rate on oil yield in vacuum pyrolysis

The yield of oil at 410 °C increased by over 6 wt% while that at both 480 and 550 °C increased by more than 10 wt% as the heating rate was changed from 5 °C/min to 25 °C/min. This behaviour was observed also in the slow pyrolysis oil yields as the heating rate was changed and could therefore be explained in a similar manner as outlined in section 5.6.1.1 above under the effect of heating rate.

The average yields and concentrations of styrene and the corresponding standard deviations at the two heating rates and various temperatures are given in Table 5.7 and Table 5.8 below. The yield and concentration of styrene were increasing with the increase in heating rate at both 480 and 550 °C. However, a conclusion could not be made at 410 °C due to large deviations in the results. This trend was in line with the increase in oil yields observed from Figure 5.25 above as the heating rate was increased.

Table 5.7 Yield of styrene at different heating rates in vacuum pyrolysis

Heating rate (°C/min)	Styrene yield at various temperatures (wt %)					
	410 °C	SD	480 °C	SD	550 °C	SD
5	17.51	0.55	14.09	0.74	16.81	4.14
25	12.45	5.95	26.02	0.19	36.07	4.26

Table 5.8 Concentration of styrene at different heating rates in vacuum pyrolysis

Heating rate (°C/min)	Styrene yield at various temperatures (wt %)					
	410 °C	SD	480 °C	SD	550 °C	SD
5	33.65	19.79	27.05	1.96	34.52	9.30
25	21.55	11.08	40.63	0.73	56.28	7.96

5.6.1.3 Comparison of slow and vacuum pyrolysis results

Effect of temperature on yields

The polymer conversion was more than 90 wt% at all the temperatures and both heating rates in slow pyrolysis but was more than 96 wt% in the vacuum pyrolysis process. These conversions were similar to the ones obtained in TGA screening experiments of over 98 wt%. This could be attributed to the promoted devolatilisation introduced by low pressure in the later set up. Low pressure is said to increase the fugacity (escape tendency) of the volatiles from the degrading particles thereby limiting recombination reactions into char and oligomers (Bartoli et al., 2015).

While the effect of temperature was apparent in slow pyrolysis experiments as shown in Figure 5.26, the influence of temperature on oil yield in vacuum pyrolysis was not observed at both heating rates because the results were similar. Generally, the yield of oil in vacuum pyrolysis process was less than that in slow pyrolysis by 5 – 18 wt% at both heating rates considered.

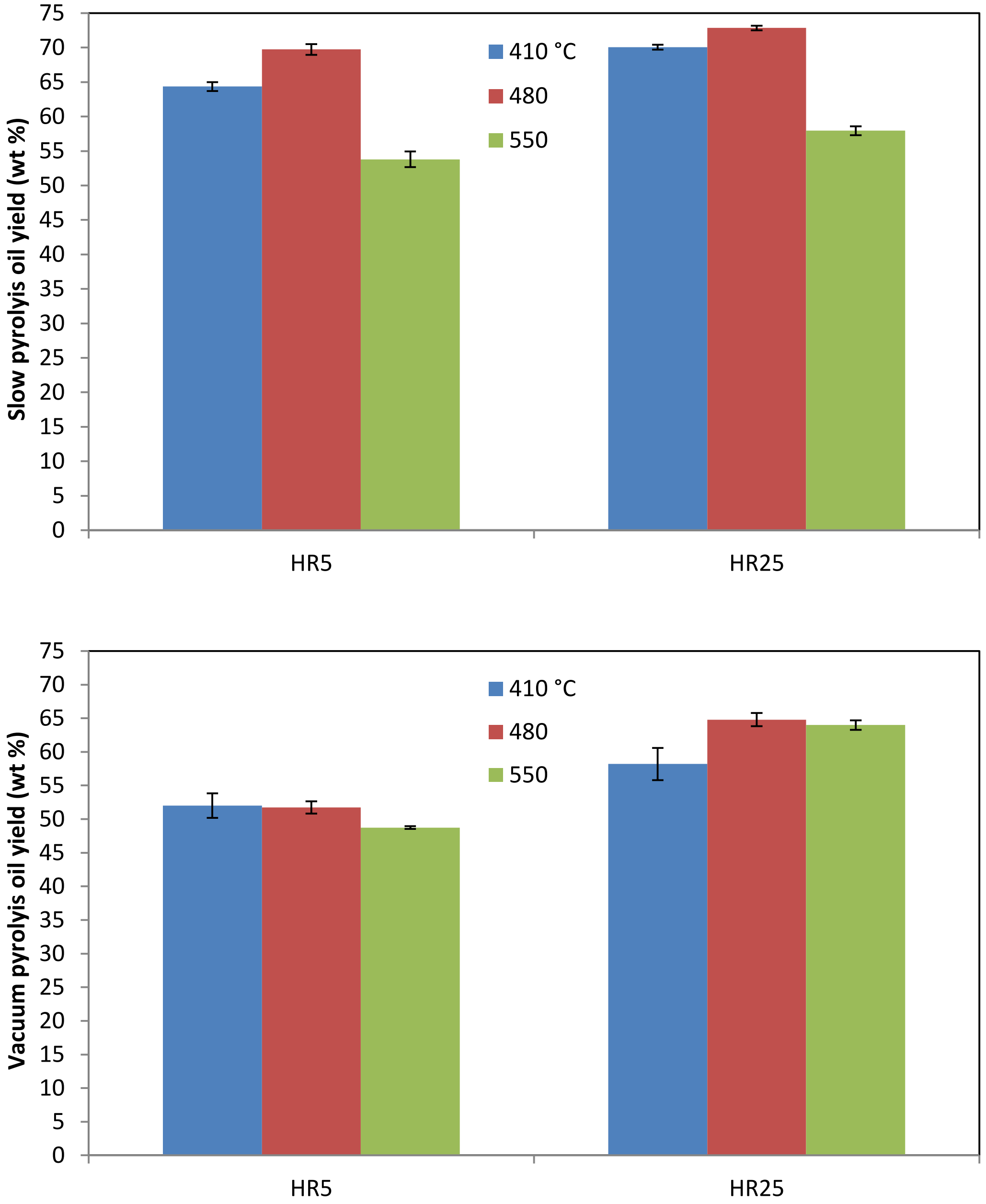

Figure 5.26 Comparison of oil yields in slow and vacuum pyrolysis experiments

The styrene yields for the two processes at both heating rates are shown Figure 5.27 below. The highest yield of styrene was 40.88 wt% in slow pyrolysis and occurred at 410 °C and a heating rate of 25 °C/min, while vacuum pyrolysis yielded maximum styrene of 36.07 wt % at 550 °C and a heating rate of 25 °C/min. Higher styrene yields were obtained in slow pyrolysis at the conditions except at 550 °C and heating rate of 25 °C/min in vacuum pyrolysis.

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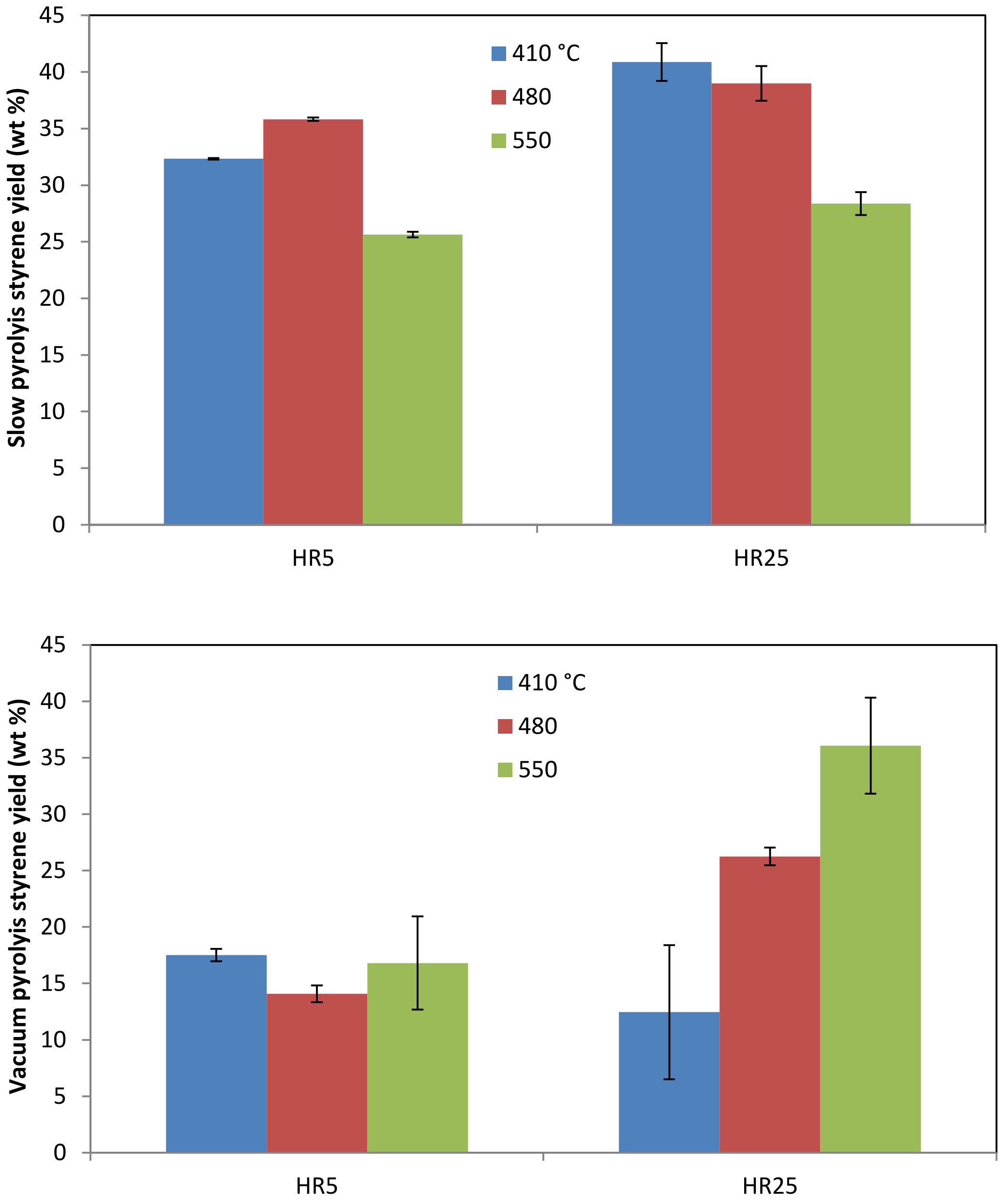

Figure 5.27 Comparison of styrene yields in slow and vacuum pyrolysis experiments

The concentration of styrene in the oil showed a similar behaviour to that of the chemical yield at both heating rates as shown in Figure 5.28 below.

Higher concentrations of styrene in the oil were achieved in slow pyrolysis at all the conditions except at 550 °C and a heating rate of 25 °C/min. The concentration of styrene increased with temperature in vacuum pyrolysis at a heating rate of 25 °C/min while the opposite seemed to be true at 5 °C/min heating rate. In slow pyrolysis the concentration of styrene in the oil was decreasing with temperature at both heating rates. The highest styrene concentration of 58.42 wt% was achieved at 410 °C while 56.28 wt% was obtained in vacuum pyrolysis at 550 °C. The maximum styrene concentrations in the two processes both occurred at a heating rate of 25 °C/min.

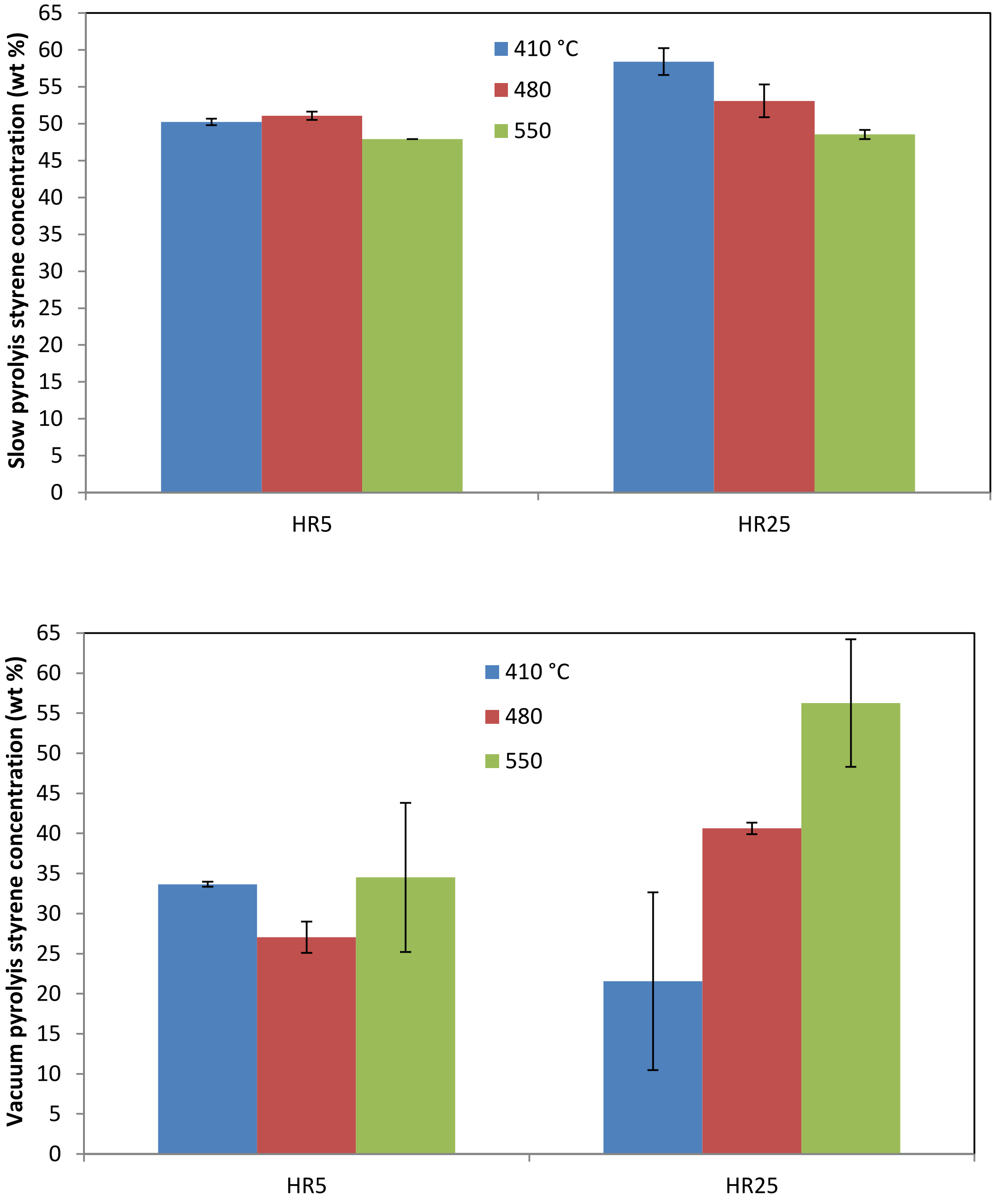

Figure 5.28 Comparison of styrene concentration in slow and vacuum pyrolysis experiments

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Effect of heating rate on yields

The average conversion of the polymer in slow pyrolysis was 96 wt% at both heating rates, while for vacuum pyrolysis it was 98 wt%. Heating rate in vacuum pyrolysis had an influence on the yield of oil as can be seen from Figure 5.26 above. The increase in heating rate from 5 to 25 °C/min increased the yield of oil at all the temperatures with over 6 wt%. The effect of heating rate on the yield of oil was more pronounced in vacuum pyrolysis as slow pyrolysis produced less than 6 wt% increase in oil yield at the considered temperatures. This could be explained by the fact that the reduced pressure assisted with volatile removal once produced from the PS particles undergoing rapid bond breaking process as the heating rate was increased (Bartoli et al., 2015).

The yield of styrene was also influenced by the change in heating rate as can be seen by making reference to Figure 5.27. The yield of styrene increased by over 12 wt% in vacuum pyrolysis when heating rate was ramped to 25 °C/min except at 410 °C. Once again, heating rate was more influential in vacuum pyrolysis than slow pyrolysis as the later process just increased the yield by 4 wt%. Similar arguments could be advanced to the response of styrene concentration as the heating rate was changed in vacuum pyrolysis as shown in Figure 5.28, over 13 wt% increase in styrene concentration occurred as the heating rate was step increased to 25 °C/min. On the contrary, heating rate increase in slow pyrolysis resulted in less than 5 wt% increase in styrene concentration.

5.6.2 Summary of PS bench scale results

The surface plot showing the combined effect of heating rate and temperature on the yield of oil in slow pyrolysis is shown in Figure 5.30 below. It was observed that the yield of oil increased as both temperature and heating rate were increased but later started decreasing with temperature. The highest oil yield was 72.85 wt% at 480 °C and 25 °C/min heating rate.

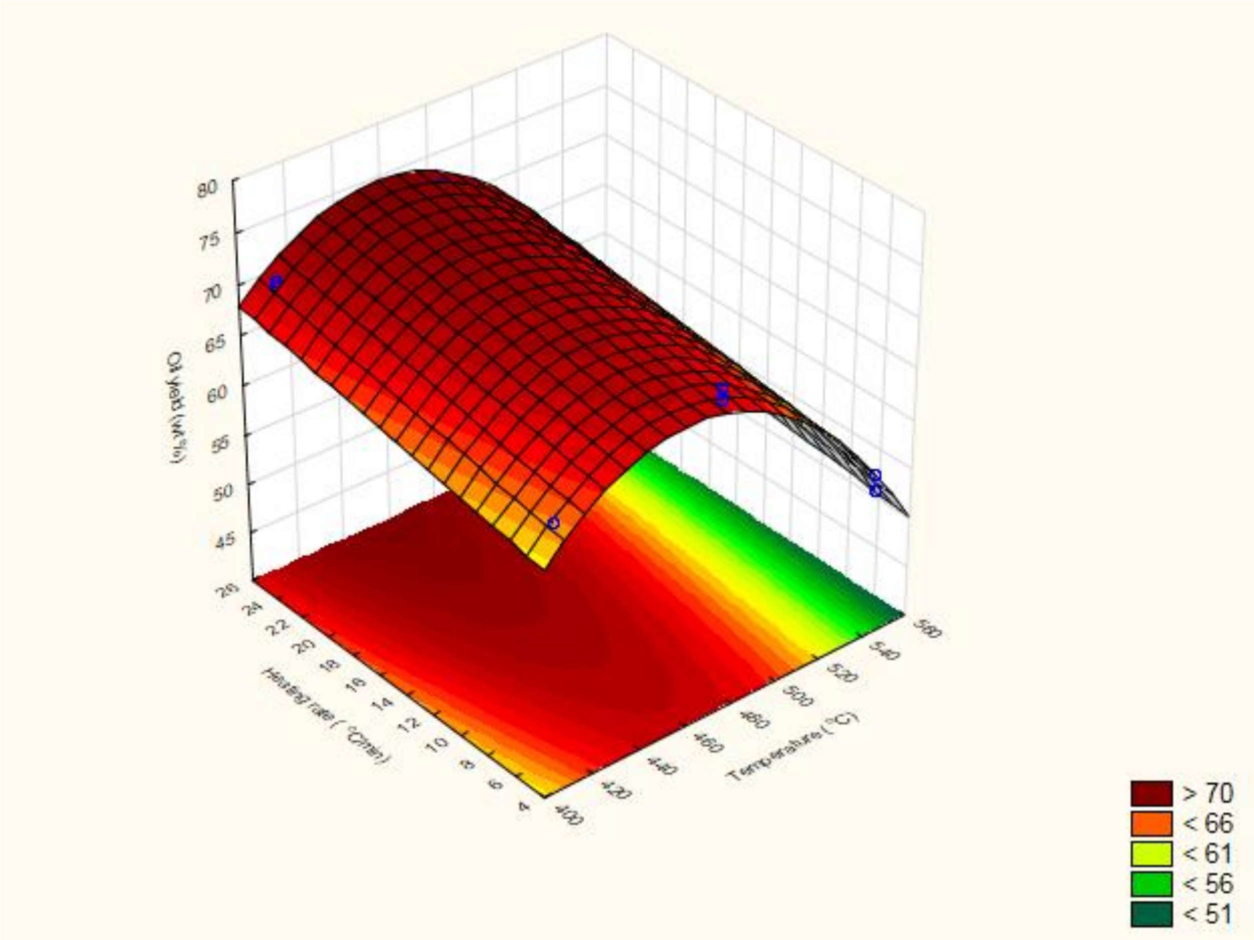

Figure 5.29 Surface plot of oil yield in PS slow pyrolysis

The surface plot of the styrene yield is shown in Figure 5.30 below. The influence of temperature on the yield was quadratic while that of heating rate was linear. The highest styrene yield of 40.88 wt% at 410 °C and 25 °C/min heating rate was obtained. As can be observed from the two surface plots, there was an importunity to improve the yields by increasing heating but could not be performed due to reactor limitation.

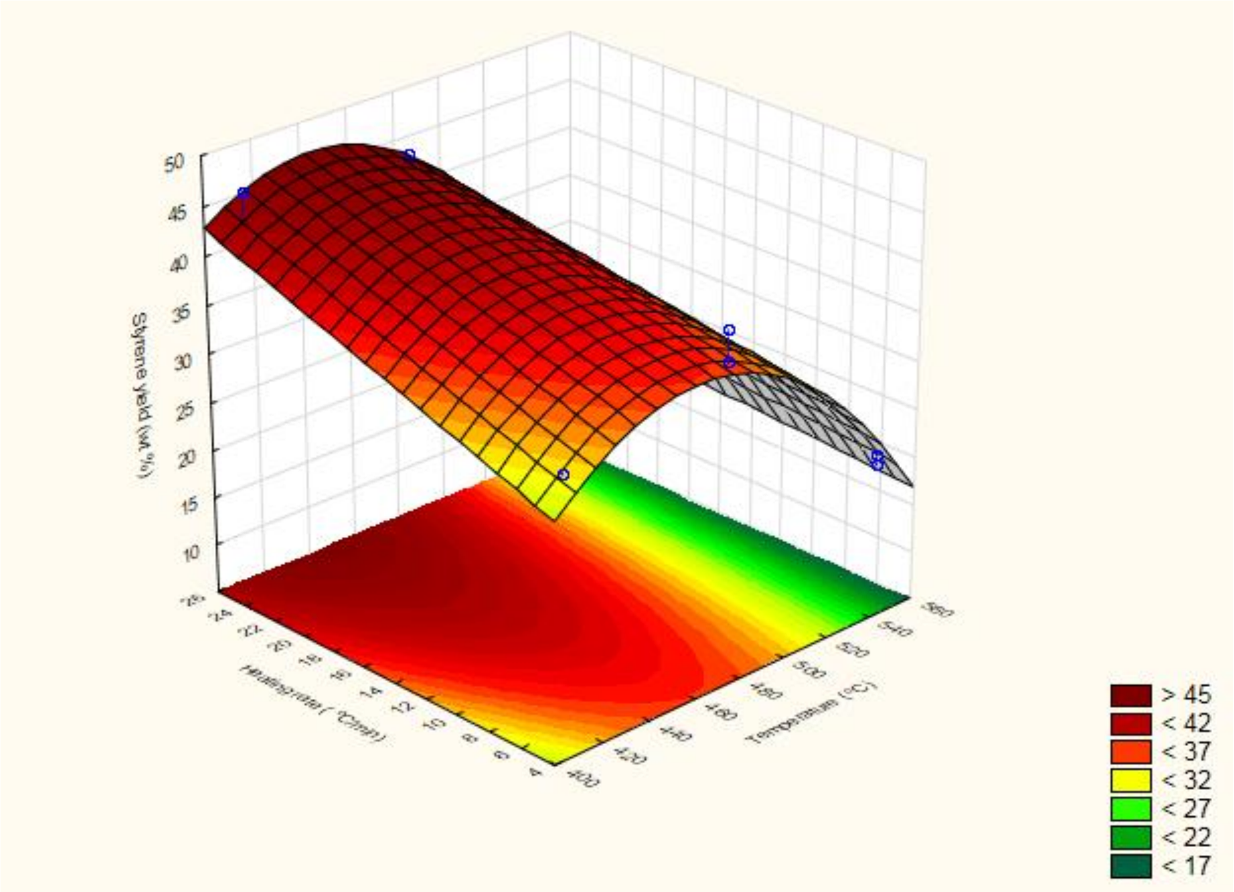

Figure 5.30 Surface plot of styrene yield in slow pyrolysis

The surface plot of oil yield from PS pyrolysis shown in Figure 5.31 below clearly illustrate that temperature and heating linearly increased the yield of oil in the process. The highest oil yield obtained in the vacuum pyrolysis process was 64.80 wt% at 480 °C and 25 °C/min heating rate.

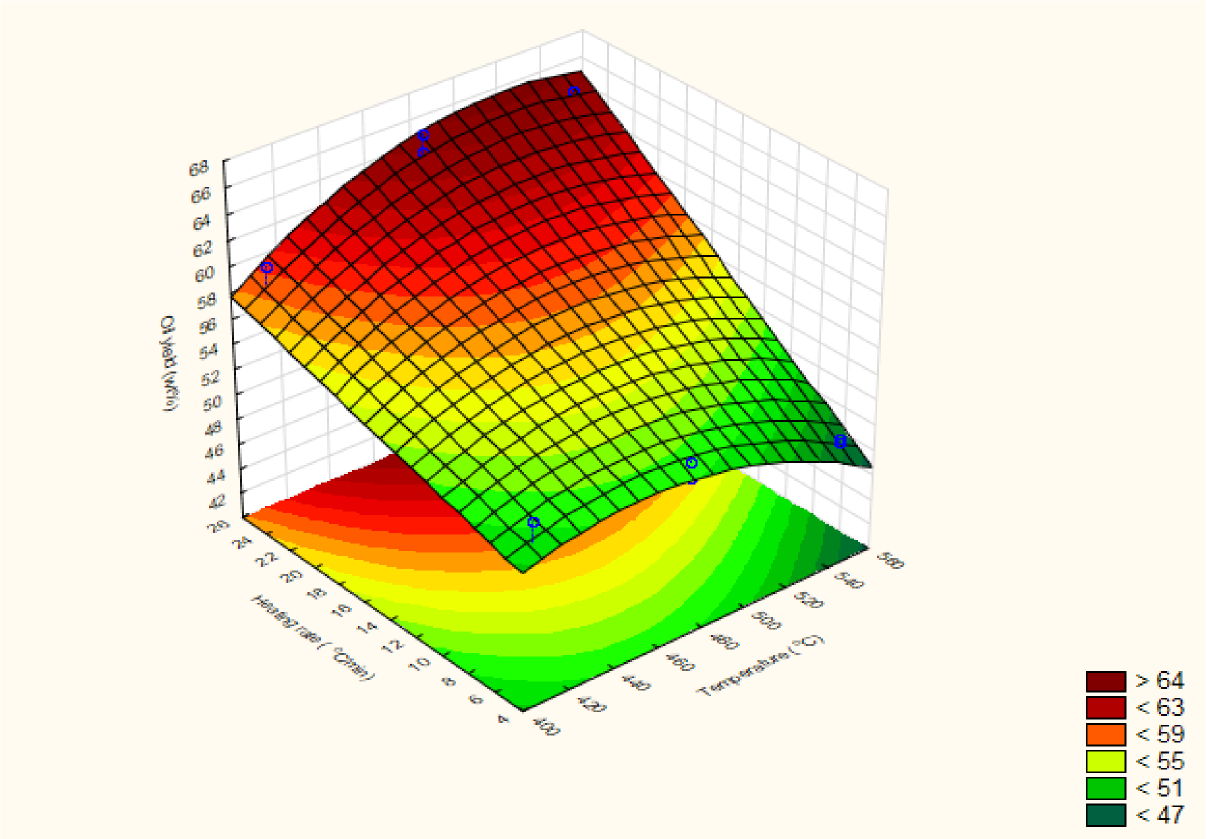

Figure 5.31 Surface plot of oil yield in PS vacuum pyrolysis

In the vacuum process as shown Figure 5.32 below, the yield of styrene seemed to linearly increase with both temperature and heating rate just as in the case of oil yield. The highest styrene yield in the study was 36.07 wt% at 550 °C and 25 °C/min heating rate conditions.

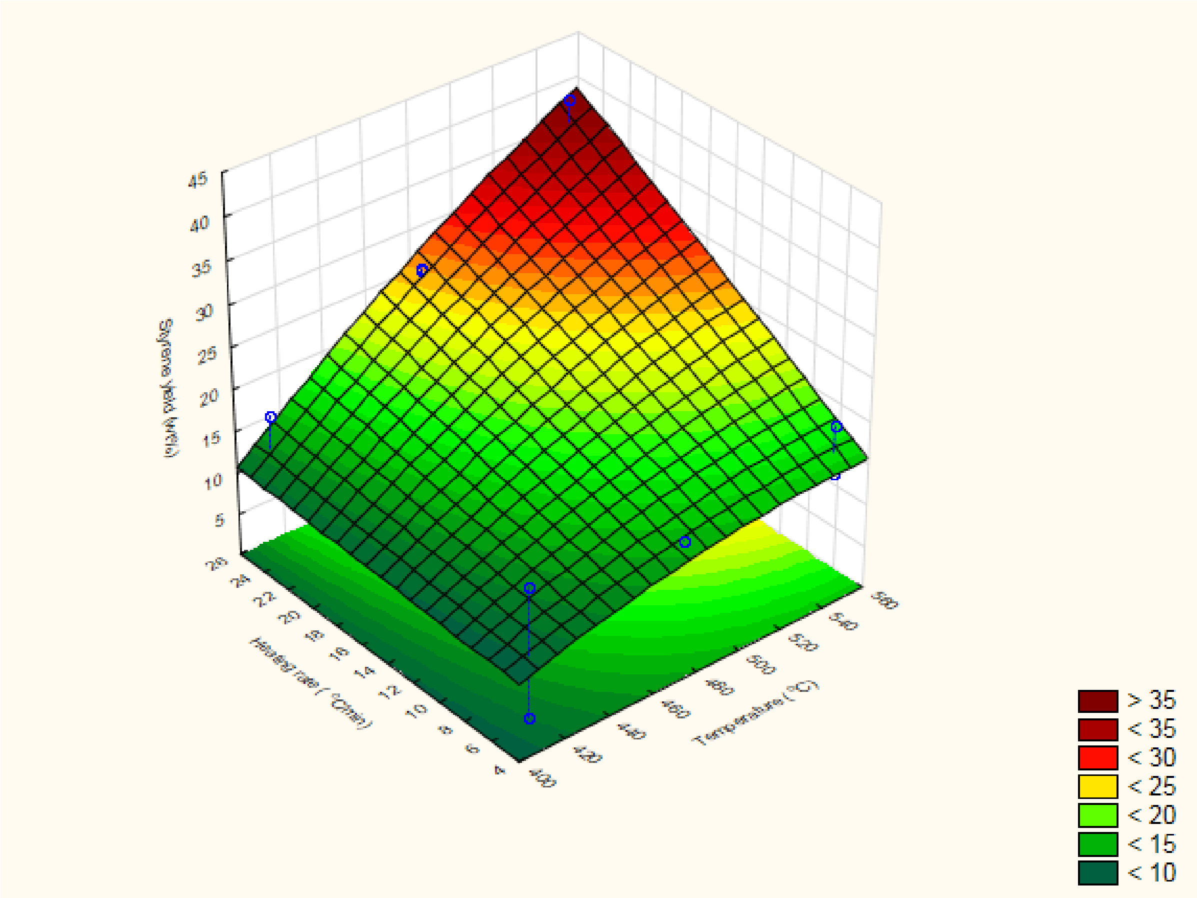

Figure 5.32 Surface plot of styrene yield in vacuum pyrolysis

The highest oil yield of 72.85 wt% was achieved at 480 °C and a heating rate of 25 °C/min in slow pyrolysis while the one in vacuum pyrolysis was 64.80 wt% at the same conditions as in slow pyrolysis. These levels of oil yields produced in the study are in line with literature oil yields ranging between 65 – 90 wt% (Ahmad et al., 2010, Mo et al., 2014, Zhang et al., 1995, Park et al., 2003). The variations in the yields could be attributed to different reactor set ups and pyrolysis conditions.

On the other hand the highest yield of styrene in slow pyrolysis was 40.88 wt% at 410 °C and 25 °C/min heating rate while that in the vacuum process was 36.07 wt% at 550 °C and 25 °C/min heating rate. These yields were on slightly on the lower side of literature yields of between 49 – 85 wt% (Ahmad et al., 2010, Mo et al., 2014, Zhang et al., 1995, Park et al., 2003, Audisio and Bertini, 1992, Mccffrey et al., 1996, Liu et al., 2000, Kim et al., 2003, Chumbhale et al., 2004, Jung et al., 2013, Artetxe et al., 2015, Bartoli et al., 2015, Ojha and Vinu, 2015). However, the yield of styrene in slow pyrolysis could be improved by testing a higher heating rate. In vacuum pyrolysis the yield could be improved by testing at higher

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temperature and heating rate. All these conditions could not be performed because of reactor limitation. Further the condensation train design could be improved by replacing the longer one with a lot of connections with a robust simplified model.

The concentration of styrene in the oil in slow pyrolysis was highest (58.42 wt%) at 410 °C and 25 °C/min heating rate while that in vacuum pyrolysis was 56.28 wt% at 550 °C and a heating rate of 25 °C/min. Styrene concentrations in the oil between 64 – 75 wt% have been reported in literature (Mo et al., 2014, Bartoli et al., 2015).

This study has laid the foundation on styrene production from PS upon which future research can be based in terms of improving styrene yield. The information gained from this study can also be used to model styrene separation systems in the process economic viability studies before a production plant can be designed.

5.6.3 Polyethylene terephthalate (PET) bench-scale pyrolysis

The pyrolysis process of PET yielded wax products, char and gas only without oil when using the bench-scale set up explained in section 4.3.8 of the methodology part of the report. The solid products started condensing at the end of the reactor because the temperature was lower than in the middle and this brought about challenges of material recovery for yield estimation and sampling. One cause for this challenge was the colder parts of the reactor where wax products collected, while the heated exit tube temperature was limited to 200 °C as compared to about 400 °C wax products volatilisation temperature. Despite this challenge a mechanism was devised to determine the mass balance as accurately as possible. The physical nature of the solid products obtained from PET pyrolysis is shown in Figure 5.33 below.

Figure 5.33 Photo showing the nature of PET solid products obtained

5.6.3.1 Slow pyrolysis experiments

Effect of temperature on yields

The mass balance of PET pyrolysis is shown in Figure 5.34 below at 5 °C/min heating rate and a set of PET slow pyrolysis mass balance at 25 5 °C/min is given in Figure 5.35. It can be observed from the figures that the yields of wax, gas and char had between 20 – 50 wt% yield distributions. The conversion of PET at 410 °C was lower than that at the two other temperatures (480 and 550 °C) by around 17 wt% due to incomplete degradation. The conversion of between 78.17 – 83.70 wt% obtained at these temperatures agree with results obtained by Çit et al., 2010 between 480 – 700 °C. This observation could be explained by the increased chance of breaking more bonds in the polymer at higher temperatures to yield volatiles.

Though different degrees of conversion were observed at the different temperatures, the yield of the yellowish wax collected from the reactor, exit tube and condensers did not produce a statistically significant variation with temperature as shown in Figure 5.34 and Figure 5.35. The yield of wax was ranged between 32.30 – 35.12 wt% at 5 °C/min heating rate and this was in agreement with literature with reported yields of between 20 – 60 wt% (Çit et al., 2010, Artetxe et al., 2010, Yoshioka et al., 2005). The calculated gas yield on the other hand has been found to range between 15 – 50 wt% (Williams and Williams, 1999, Saha and Ghoshal, 2005, Chiu and Cheng, 1999). The gas yield in this study increased with temperature at 5 °C/min heating rate from 29.28 wt% at 410 °C to about 47.85 wt% at 550 °C as a higher PET proportion got decomposed.

At the higher heating rate of 25 °C/min, polymer conversion increased with temperature from 63.17 wt% at 410 °C to 80.20 wt% at 550 °C as shown in Figure 5.35. It can be observed from the figure that wax yield increased from 30.50 wt% at 410 °C to 39.70 wt% at 550 wt%, while the gas yield at the higher heating rate was 30.85 wt% at 410 °C and increased to 44.00 wt% at both temperatures (480 and 550 °C).

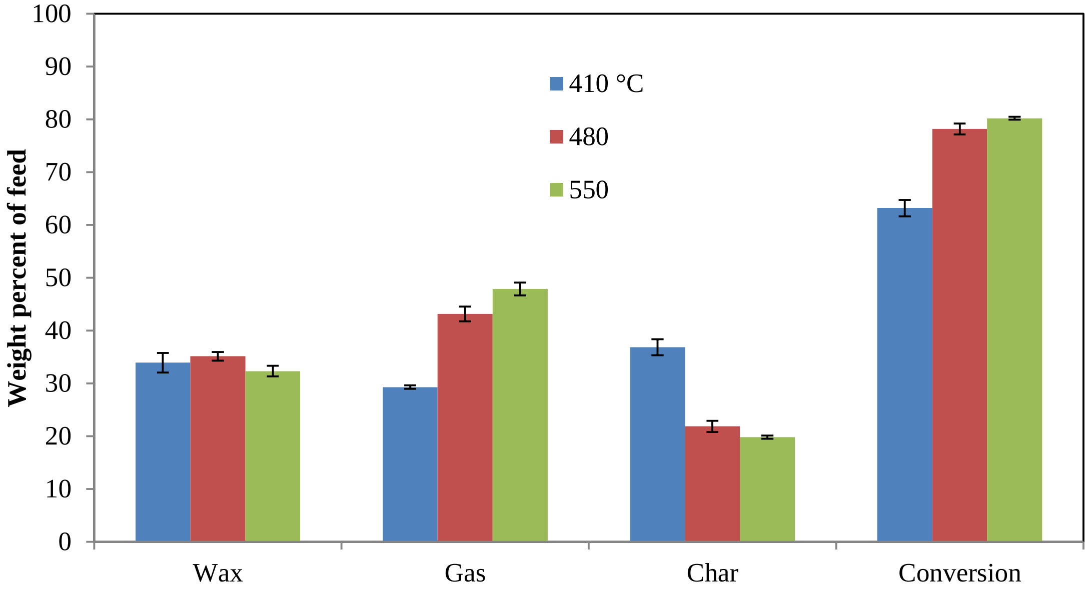

Figure 5.34 Measured (wax, char) and calculated (gas) yields from slow PET pyrolysis at 5 °C/min heating rate.

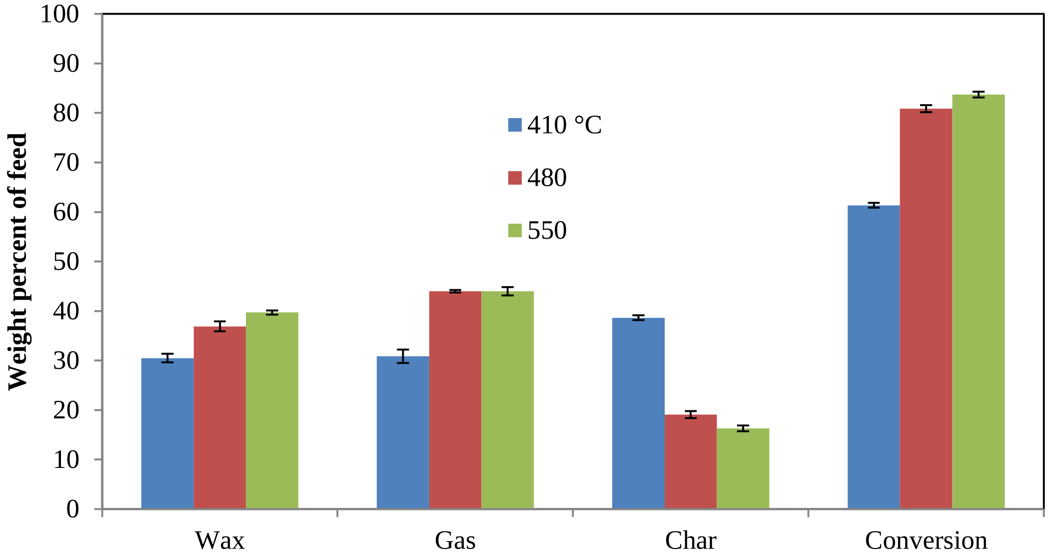

Figure 5.35 Measured (wax, char) and calculated (gas) yields from slow PET pyrolysis at 25 °C/min heating rate.

Wax produced in the study was subjected to TPA and BA compositional analysis using a high-performance liquid chromatography (HPLC) according to the method outlined in section 4.3.10. The yields and concentrations of the acids obtained from all the experimental runs are presented in Table D.0.5 of Appendix D. The results from the tests at a heating rate of 5 °C/min are presented in Figure 5.36 below. The yield of terephthalic acid (TPA) of 5.43 wt%, obtained at 410 °C was highest, and reduced to 4.42 and 4.28 wt% at higher temperatures of 480 and 550 °C respectively. In the case of BA there was a large standard deviation at 410 °C but yield decreased between 480 and 550 °C from 8.10 wt% to 6.71 wt%. The yield of benzoic acid decreases with temperature due to decomposition of the acid to carbon dioxide, carbon monoxide and benzene as reported by Yoshioka et al. (2004), Artetxe et al. (2010) and Samperi et al. (2004) in studies conducted in the similar temperature range.

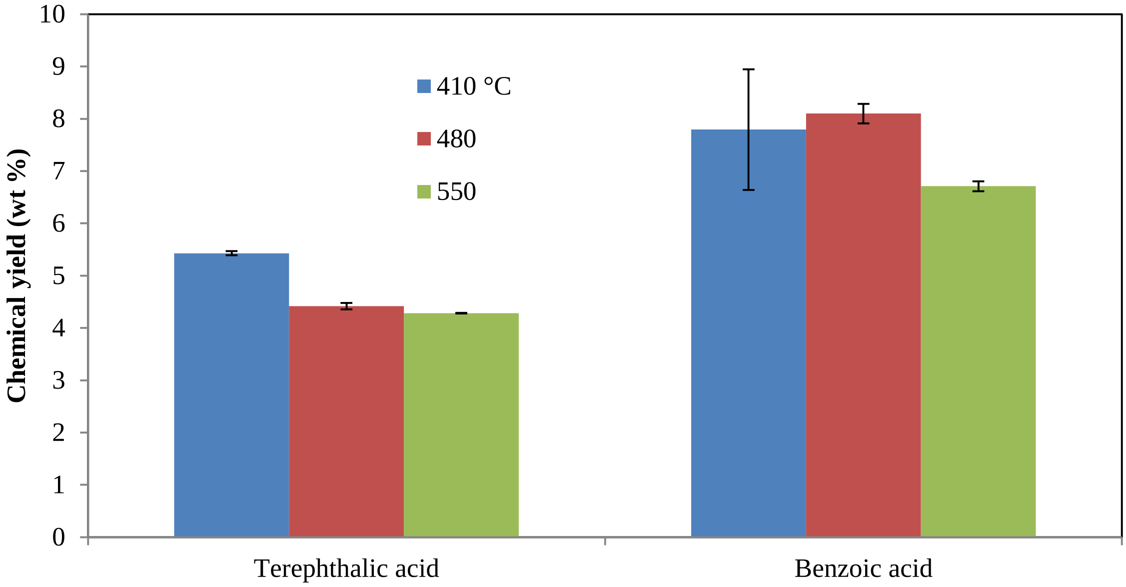

Figure 5.36 Yields of TPA and BA from slow pyrolysis at 5 °C/min heating rate

The yields of the acids at 25 °C/min heating rate are given in Figure 5.37 below, it was seen that TPA yield decreased with temperature (410 to 480 °C) from 5.03 wt% to 2.61 wt% with a large standard deviation at 550 °C. BA yield of 5.88 wt% at 410 °C increased directly with temperature to 8.77 wt% and 9.03 wt% at 480 ºC and 550 ºC respectively. The decrease in TPA yield could be due to further decomposition of the chemical to benzoic acid as expounded in section 3.5.4.2 of the report.

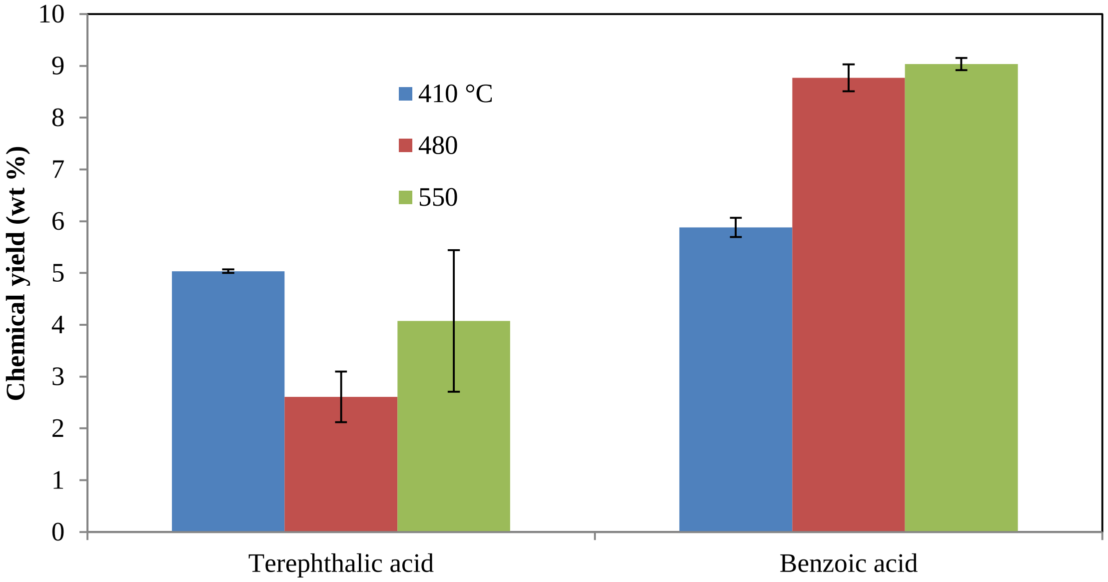

Figure 5.37 Yields of TPA and BA from slow pyrolysis at 25 °C/min heating rate

The concentrations of TPA and BA in the wax product are presented in Figure 5.38 at 5 °C/min heating rate. The concentration of TPA was maximum at 410 °C then decreased due to decomposition. On the other hand the concentration of BA was in the range of 20.39 – 22.90 wt% with a decreasing trend probably due to further conversion to oxides of carbon (Yoshioka et al., 2004, Artetxe et al., 2010).

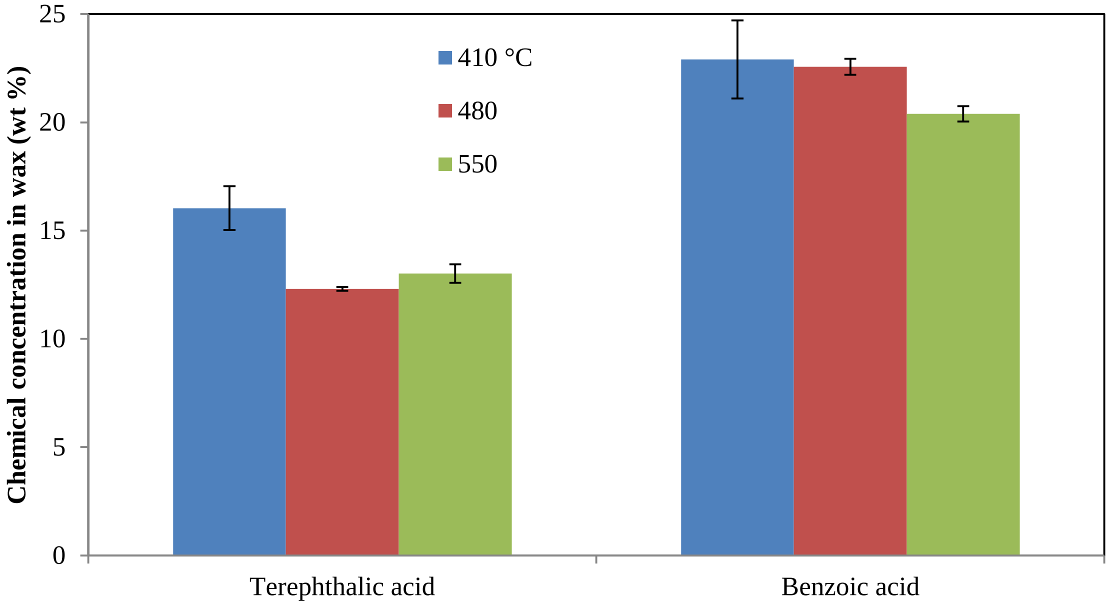

Figure 5.38 Concentration of TPA and BA in the wax product obtained from slow pyrolysis at 5 °C/min heating rate

The graph of TPA and BA concentrations in the wax product at a heating rate of 25 °C/min is given in Figure 5.39 below. Regarding TPA, the results showed a similar trend to that observed at a heating rate of 5 °C/min. Terephthalic acid concentration was reducing with temperature from 16.73 wt% at 410 °C to 10.40 wt% at 550 °C but the opposite was observed for benzoic acid where the increase was from 19.54 wt% at 410 °C to 23.43 wt% at 480 °C with a slight drop at 550 °C but still above that at 410 °C.

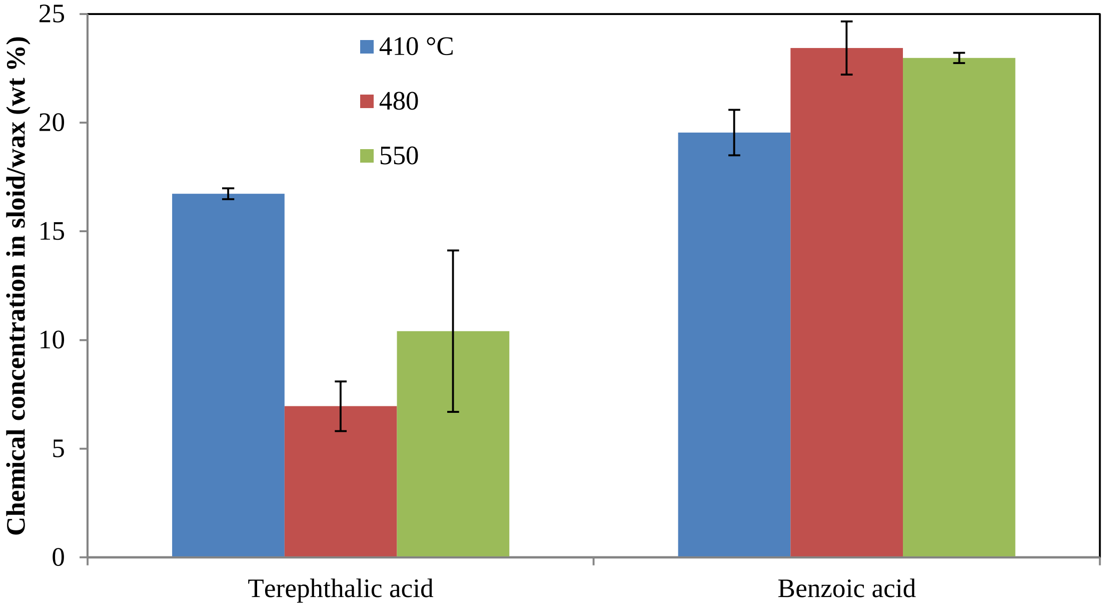

Figure 5.39 Concentration of TPA and BA from slow pyrolysis at 25 °C/min heating rate

Effect of heating rate on yields

The mass balance of PET pyrolysis products at the two studied heating rates are given in Figure 5.34 and Figure 5.35. The conversion of the polymer increased by about 4 wt% except at 410 ºC while wax yield increased by between 2 – 8 wt% when heating rate was increased from 5 to 25 °C/min. It can be said that high heating rates increased bond breaking severity in PET resulting in high release of oligomers responsible for wax production (Yoshioka et al., 2004). Table 5.9 below details the yields of acids produced at the two heating rates. It can be observed that heating rate increase reduced TPA yield at both 410 and 480 ºC while a large standard deviation occurred at 550 °C. In the case of BA the yield increased with heating rate at both 480 and 550 ºC while a drop was observed at 410 ºC.

Table 5.9 Yield of acids at different heating rates in slow pyrolysis

Heating rate (°C/min)	Yield of acids (wt%)											
	410 °C				480 °C				550 °C			
	TPA	SD	BA	SD	TPA	SD	BA	SD	TPA	SD	BA	SD
5	5.43	0.04	7.79	1.15	4.42	0.06	8.10	0.19	4.28	0.01	6.71	0.09
25	5.03	0.03	5.88	0.19	2.61	0.49	8.77	0.26	4.07	1.37	9.03	0.12

Similarly, Table 5.10 below was used to present the concentrations of the two acids in the wax produced from PET pyrolysis. The results at 480 and 550 °C showed that the concentration of TPA decreased with heating rate but the opposite was true at 410 °C. The increase of heating rate at the studied temperatures resulted into higher concentrations of BA at 480 and 550 °C while a decrease was noted at 410 °C.

Table 5.10 Concentration of acids in the wax produced at different heating rates in slow pyrolysis

Heating rate (°C/min)	Concentration of acids (wt%)											
	410 °C				480 °C				550 °C			
	TPA	SD	BA	SD	TPA	SD	BA	SD	TPA	SD	BA	SD
5	16.04	1.01	22.90	1.80	12.31	0.09	22.57	0.37	13.02	0.43	20.39	0.35
25	16.73	0.25	19.54	1.04	6.95	1.15	23.43	1.22	10.40	3.71	22.97	0.23

5.6.3.2 Vacuum pyrolysis experiments

Effect of temperature on yields

The mass balance of products from PET pyrolysis at a heating rate of 5 °C/min is shown in Figure 5.40 below. The polymer conversion was influenced by temperature as a step change existed between 410 °C and the other two upper temperatures at both heating rates. The yield of the wax increased by over 8 wt% when comparing 410 with 480 and 550 °C at 5 °C/min heating rate. Gaseous stream mass yield increased from 27.05 wt% to 41.45 wt% as the temperature was changed from 410 °C to 550 °C.

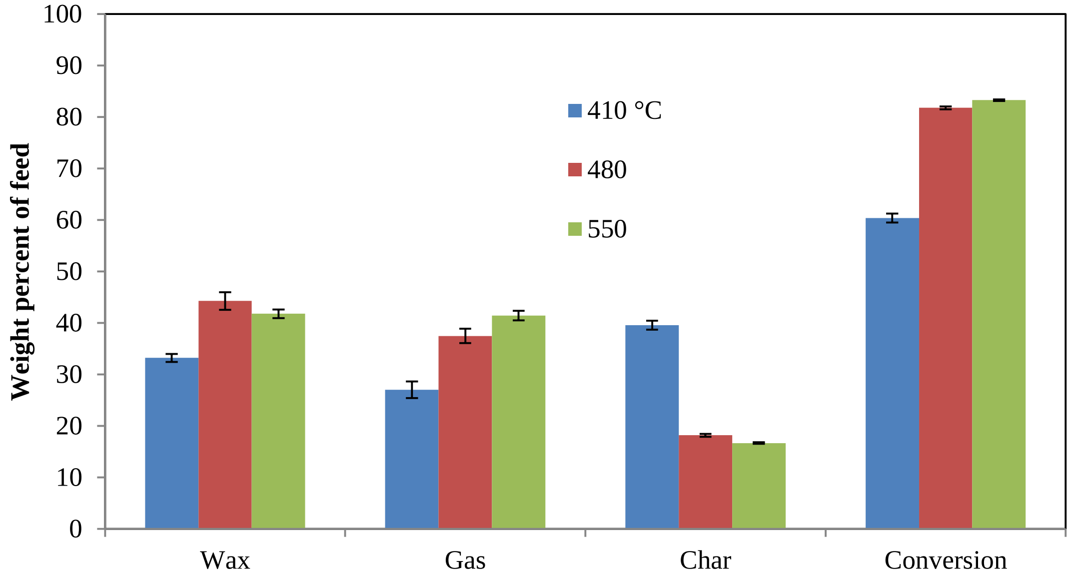

Figure 5.40 Measured (wax, char) and calculated (gas) yields from vacuum PET pyrolysis at 5 °C/min heating rate.

Similar behaviour as regards temperature influence was observed at 25 °C/min as can be observed from Figure 5.41 below. Conversion of the polymer increased to 87.75 wt% from 56.65 wt% when the temperature was ramped up from 410 °C to 550 °C. The yield of wax was also influenced by temperature as it increased from 34.00 wt% at 410 °C to 47.15 wt% at 480 °C which was close to the yield at 550 °C. Similarly, the gas yield increase from 22.65 wt% at 410 °C to 38.80 wt% at 550 °C was observed.

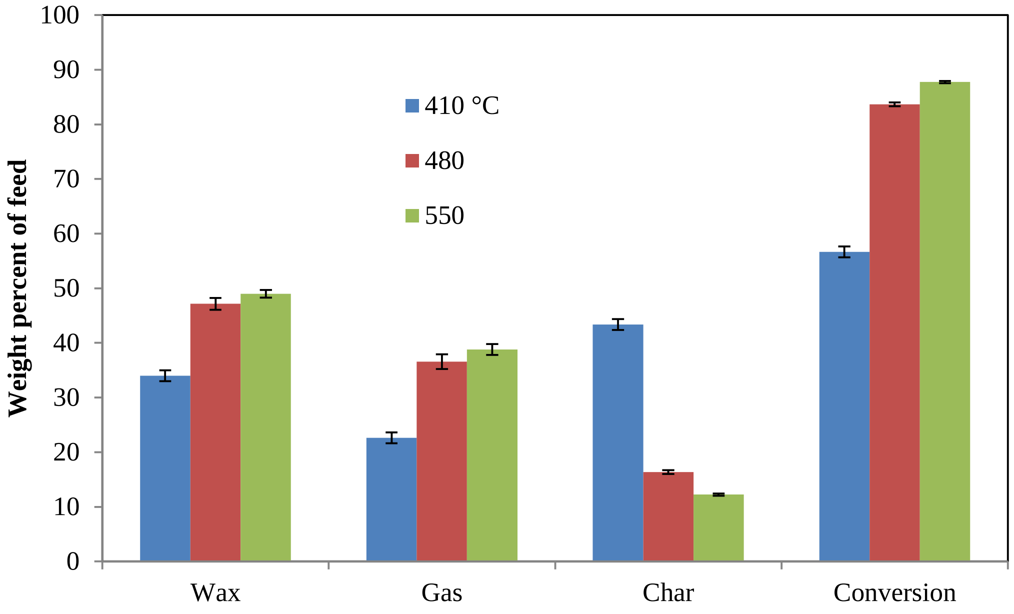

Figure 5.41 Measured (wax, char) and calculated (gas) yields from vacuum PET pyrolysis at 25 °C/min heating rate.

Influence of temperature on the yields of the acids is shown in Figure 5.42 below. At a heating rate of 5 °C/min. The yield of TPA was same whereas that of BA increased from 5.79 wt% at 480 °C to 7.28 wt% at 550 °C. The yield of BA at 410 °C had a large standard deviation but it highly likely that its yield was lower than that at 480 °C looking the wax yield at that temperature.

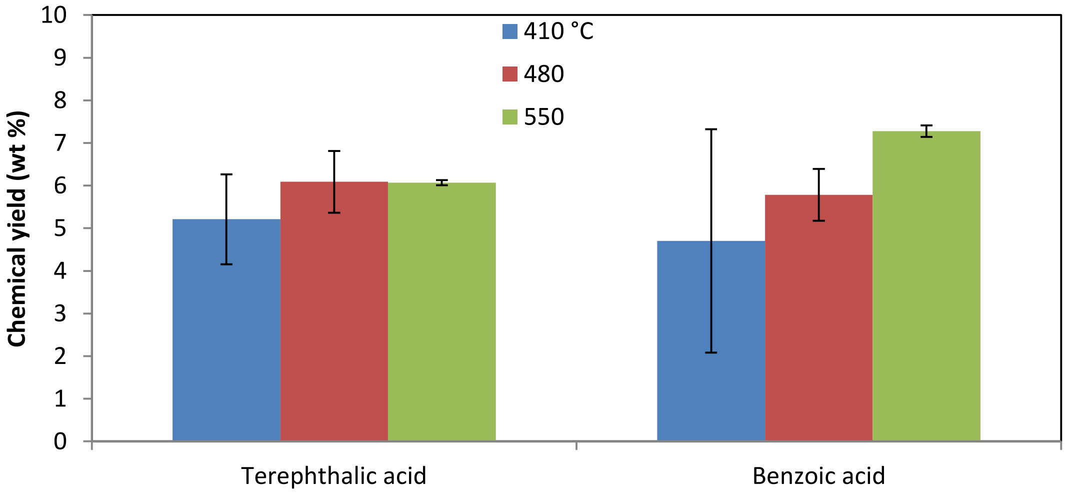

Figure 5.42 Yields of TPA and BA from vacuum PET pyrolysis at 5 °C/min heating rate

In Figure 5.43 below the high standard deviations experienced in the results presented a major obstacle to the analysis of the influence of temperature on the terephthalic acid yields at 25 °C/min heating rate. It was believed that the huge deviation could have emanated from the variation in the vacuum pressure during experimental runs. However, the yields of benzoic acids were not affected the same way. They were observed to be increasing with temperature from 6.32 wt% at 410 ºC to 7.52 wt% at 480 °C and 7.08 wt% at 550 °C.

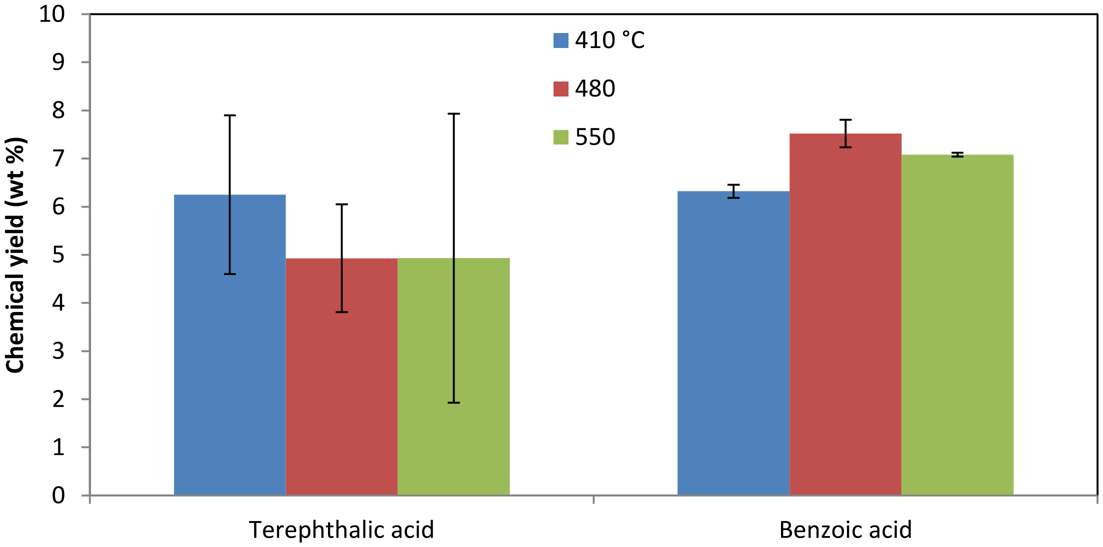

Figure 5.43 Yields of TPA and BA from vacuum PET pyrolysis at 25 °C/min heating rate

Figure 5.44 below illustrates the variation of terephthalic and benzoic acids concentrations in the wax phase of the products. As can be observed from the figure, the results were not statistically different and the concentration of TPA around 14.67 wt% was obtained. The concentration of BA increased at 550 °C (17.46 wt%) from 12.90 wt% at 480 °C with a likely lower concentration at 410 °C since the wax yield was low at this temperature.

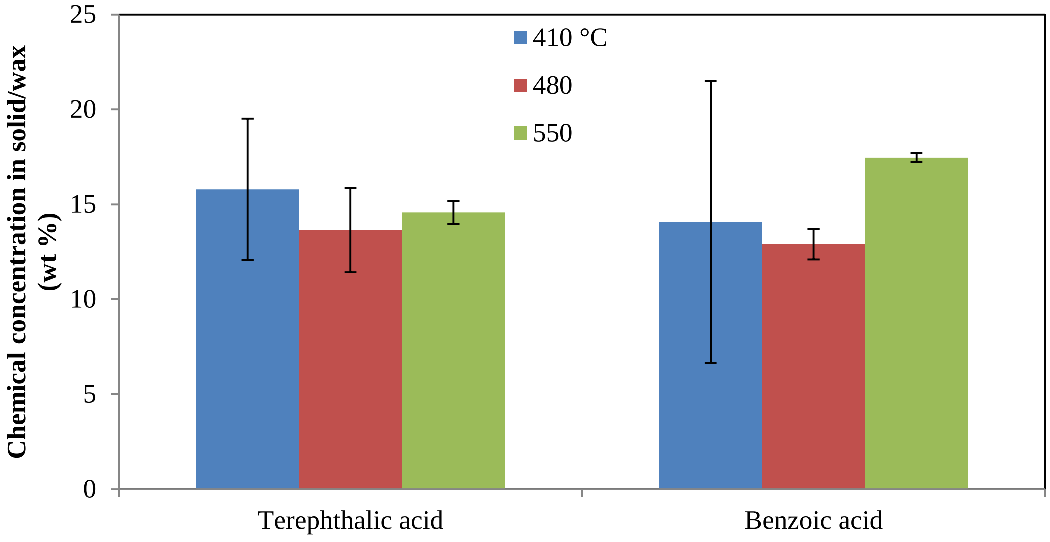

Figure 5.44 Concentration of TPA and BA from vacuum PET pyrolysis at 5 °C/min heating rate

The concentration of the same chemicals in the wax product obtained at a heating rate of 25 °C/min is given in Figure 5.45 below. It can be observed that the concentration variation of TPA with temperature was similar to that of yield at 5 ºC/min heating rate. The results was statistically similar with the concentration around 12.78 wt% On the other hand, the concentration of BA decreased from 18.04 wt% to 14.44 wt% when the temperature was changed from the low 410 ºC to 550 °C.

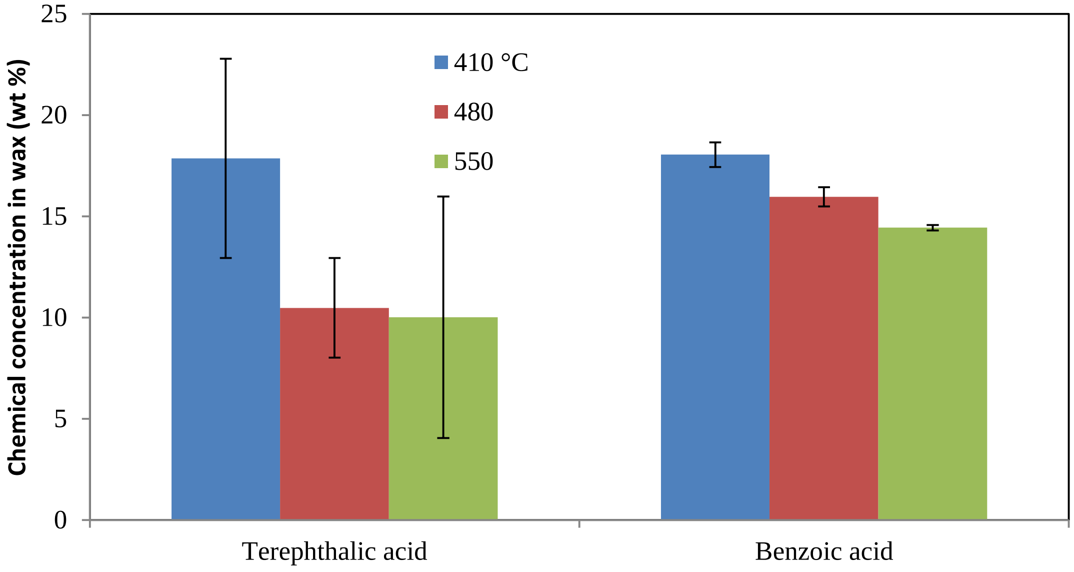

Figure 5.45 Concentration of TPA and BA from vacuum PET pyrolysis at 25 °C/min heating rate

Effect of heating rate on yields

The conversion of the PET polymer in vacuum pyrolysis increased by 2 – 4 wt% with heating rate at all the temperatures except at 410 °C as can be observed from Figure 5.40 and Figure 5.41 above.

Table 5.11 Yield of acids at different heating rates in vacuum pyrolysis

Heating rate (°C/min)	Yield of acids (wt%)											
	410 °C				480 °C				550 °C			
	TPA	SD	BA	SD	TPA	SD	BA	SD	TPA	SD	BA	SD
5	5.21	1.06	4.70	2.62	6.09	0.72	5.79	0.61	6.07	0.06	7.28	0.13
25	6.25	1.65	6.32	0.13	4.93	1.12	7.52	0.29	4.93	3.00	7.08	0.04

With reference to Table 5.11 above, the yield of TPA increased with heating rate at 410 ºC from 5.21 wt% to 6.25 wt% and the results at the other temperatures were the same. The yield of BA increased with heating rate at 480 ºC from 5.79 wt% to 7.52 wt% but dropped slightly at 550 ºC from 7.28 wt% to 7.08 wt%. There was no change in the result of BA yield at 410 ºC.

Table 5.12 Concentration of acids at different heating rates in slow pyrolysis

Heating rate (°C/min)	Concentration of acids (wt%)											
	410 °C				480 °C				550 °C			
	TPA	SD	BA	SD	TPA	SD	BA	SD	TPA	SD	BA	SD
5	15.80	3.73	14.07	7.43	13.64	2.21	12.90	0.79	14.57	0.60	17.46	0.23
25	17.86	4.92	18.04	0.61	10.47	2.46	15.96	0.47	10.01	5.97	14.44	0.13

As can be observed from Table 5.12 above, TPA concentration increased with heating rate at 410 ºC from 15.80 wt% to 17.86 wt% but decreased at 480 ºC from 13.64 wt% to 10.47 wt% The result at 550 ºC was statistically unchanged around 12.29 wt%. On the other hand, the result was the same around 16.06 wt% for BA at 410 ºC followed by an increase at 480 ºC from 12.90 wt% to 15.96 wt% thereafter, the concentration dropped by about 3 wt% at 550 ºC from 17.46 wt% to 14.44 wt%.

5.6.3.3 Comparison of slow and vacuum pyrolysis results

Effect of temperature on yields

The influence of temperature on the pyrolysis of PET was generally more pronounced in vacuum than slow pyrolysis as can be observed from the higher wax yields at both heating rates in Table 5.13 below. There was about 9 wt% increase in wax yield at both 480 and 550 °C in vacuum as compared to slow pyrolysis at 5 °C/min heating rate. On the other hand at 25 °C/min heating rate, there was a wax increase of around 4 wt% at 410 °C. Increases of about 10 and 9 wt% respectively were recorded at 480 and 550 °C temperatures as the process was switched from slow to vacuum. This aspect highlighted the change on PET thermal decomposition mechanism as higher yields were favoured.

Table 5.13 Comparison of oil yields in slow and vacuum pyrolysis experiments

Heating rate (°C/min)	SP wax yields (wt%)						VP wax yields (wt%)					
	410 °C	SD	480 °C	SD	550 °C	SD	410 °C	SD	480 °C	SD	550 °C	SD
5	33.89	1.83	35.12	0.83	32.30	0.99	33.25	0.78	44.30	1.70	41.80	0.85
25	30.50	0.85	36.90	0.99	39.70	0.42	34.00	0.42	47.15	1.06	49.00	0.71

In vacuum as compared to slow pyrolysis, temperature did not have a statistical influence on the yield of the acids at both heating rates except for BA at 25 °C/min heating rate. However, there was an increase in the yield of TPA in vacuum pyrolysis at a heating rate of 5 °C/min of between 1 – 2 wt% when the temperature was increased to 480 and 550 °C. At a heating rate of 25 °C/min, BA yield was higher in slow pyrolysis by between 1 – 2 wt% over the higher two temperatures. Similar observations can be made on the concentration of the chemicals in the wax fraction of the products as can be noticed from Figure 5.38, Figure 5.39, Figure 5.44 and Figure 5.45 above.

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Effect of heating rate on yields

Heating rate in vacuum pyrolysis had an influence on the yield of wax as can be seen from Table 5.13 above. The increase in heating rate from 5 to 25 °C/min increased the yield of wax at all the temperatures with over 2 wt%.

While heating rate in slow pyrolysis seemed to increase the yield of BA by between 1 – 2 wt% at the higher temperature, it appeared not to have a statistically significant influence on the chemical yields in the vacuum process. The chemical concentrations produced similar trends to that of the yields and the same yield interpretation can be advanced to this output parameter.

5.6.4 Summary of PET bench scale results

The surface plot of wax yield in PET slow pyrolysis is shown below in Figure 5.46. It can be observed from the figure that both heating rate and temperature influenced the yield of wax. The highest wax yield of 39.70 wt% was obtained at 550 °C and a heating rate of 25 °C/min. The figure shows that an opportunity to increase the wax yield (which would in turn improve the chemical yields) by increasing both temperature and heating rate existed but could not be explored due to reactor limitation.

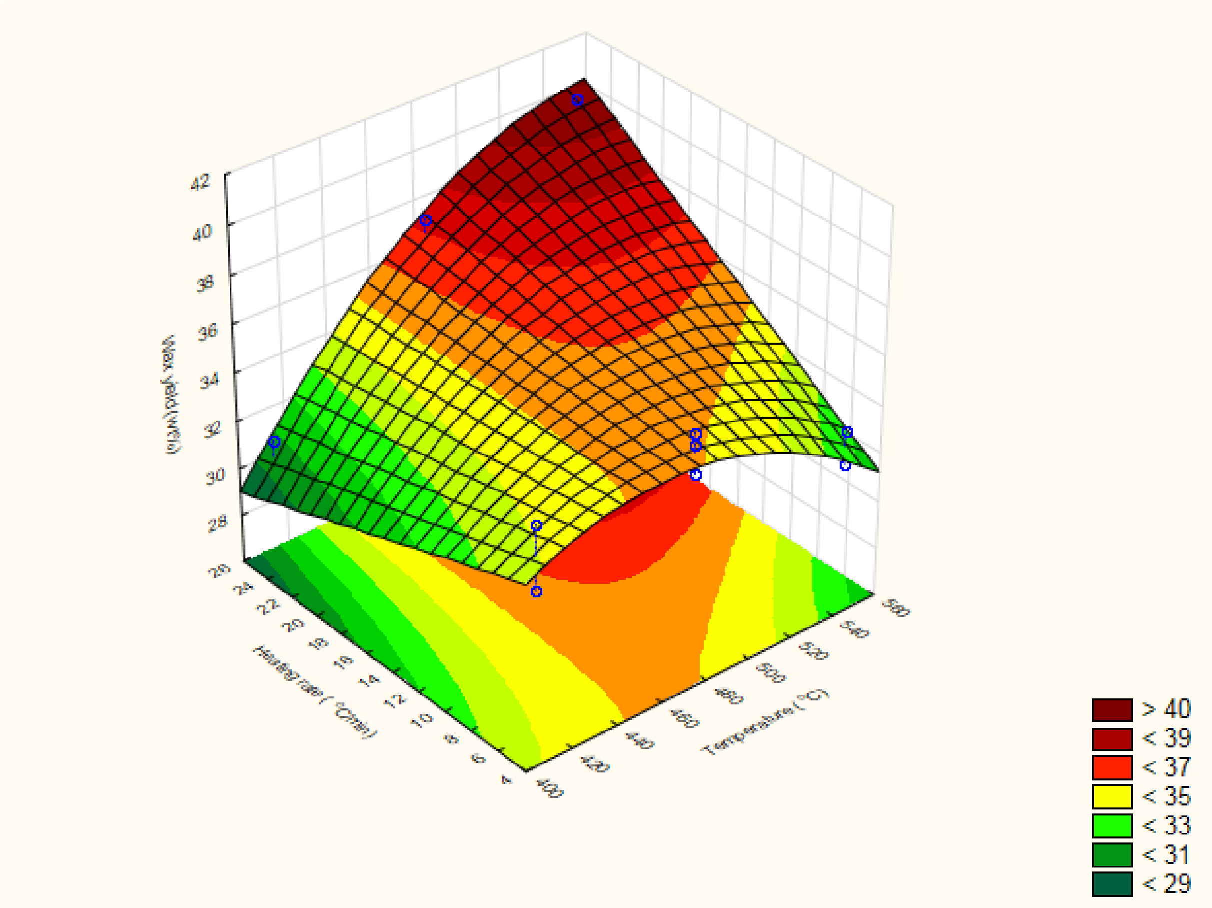

Figure 5.46 Surface plot of wax yield in PET slow pyrolysis

The yields of the chemicals TPA and BA in slow pyrolysis were differently influenced by temperature and heating rate. TPA yield generally reduced with increase in both temperature and heating rate. In the case of BA, heating rate seemed to increase the yield at 480 and 550 °C. The highest yield of terephthalic acid (TPA) was 5.43 wt% at 410 °C and 5 °C/min heating rate. On the other hand, the highest benzoic acid (BA) yield was 9.03 wt% at 550 °C and 25 °C/min heating rate while a 7.79 wt% yield was obtained at 410 °C with a 5 °C/min heating rate.

The plot of wax yield against the variables in vacuum process is shown in Figure 5.47 below. The graph showed a strong influence of temperature on the yield, heating rate was also observed to have a linear relationship with wax yield. The highest yield of wax in this case was 49.00 wt% at 550 °C and 25 °C/min heating rate. Higher temperatures and heating rates could not be tested as the reactor was limited.

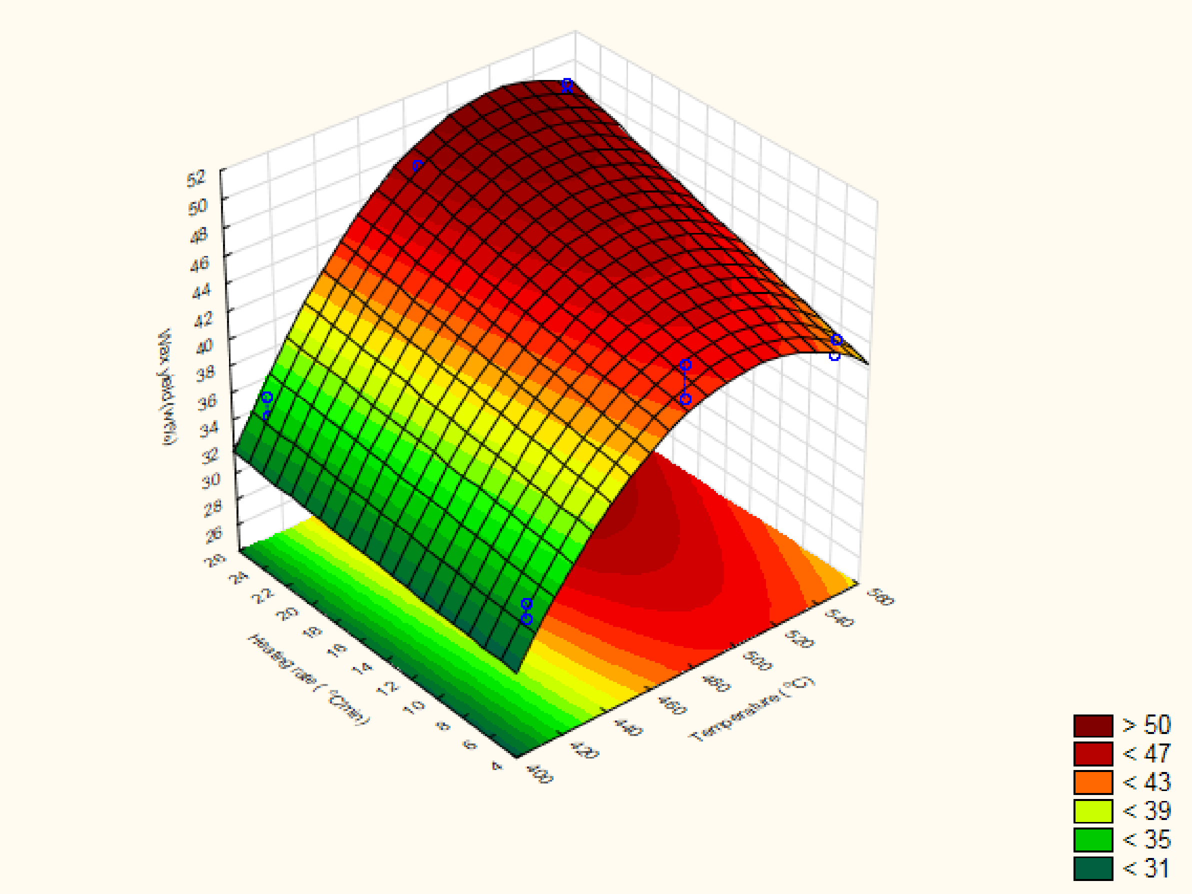

Figure 5.47 Surface plot of wax yield in PET vacuum pyrolysis

The variation of TPA yield with temperature was not statistically significant but was influenced by heating rate. The yield of BA increased with temperature and got an influence from heating rate as well. The highest TPA yield was 6.25 wt% at 410 °C and 25 °C/min heating rate. The highest BA yield was 7.52 wt% at 480 °C and 25 °C/min heating rate while 6.32 wt% was obtained at 410 °C and 25 °C/min heating rate.

The highest yield of wax in vacuum pyrolysis was 49.00 wt% while that slow pyrolysis was 39.70 wt% both obtained at 550 °C and a heating rate of 25 °C/min. These wax yields obtained in the study compared well with those reported by Artetxe et al. (2010) between 35 – 41 wt%. The wax yield of 67 wt% was obtained during PET pyrolysis work by Sakata et al. (1996). The differences in the levels of the yields could be attributed to reactor configuration, condensation modes and pyrolysis conditions employed in these studies.

The yield of benzoic acid in this study was found to be lower than that obtained by Artetxe et al. (2010) of between 15 – 27 wt% while the concentration compared well with 10 wt% reported by Dimitrov et al. (2013). The results for PET pyrolysis could be improved by

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eliminating cold spots in the reactor (new reactor design) and testing higher temperatures and heating rates.

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6 Conclusions and recommendations

6.1 Conclusions

6.1.1 Material physical characterisation

The study of South Africa's plastic stream revealed the six most common plastics observed worldwide, namely high density polyethylene (HDPE), low density polyethylene (LDPE), polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET) and polyvinyl chloride (PVC). The expected composition of the plastic waste stream, as per manufactured plastic mass flows, was LDPE – 25 wt%, PP – 19 wt%, HDPE – 15 wt%, PET – 12 wt%, PVC – 12 wt% and Others – 13 wt%. The recycling of plastics in South Africa is largely centred on polyolefins and PET constituting about 90 wt% of the total plastics recycled.

Characterisation of the landfill stream of plastics rejects from the Kraaifontein waste management facility, to determine the composition of the plastic fraction, revealed that the major components were PET and PS. The combined content of these plastics was 72 wt%, while the rest was polyolefins. This stream therefore formed an interesting feed for conversion of the plastics to chemicals. The stream was subsequently subjected to density analysis to assess the purity of isolated plastics and the result was comparable to pure plastic densities.

6.1.2 Material thermal characterisation

Apart from determining the density of the plastics to assess the purity, thermal characterisation was undertaken in TGA to further scrutinise the purity of the plastics before conversion to chemicals could be performed. The plastics thermal decomposition in a single step with high conversion levels and literature conforming thermal characteristic decomposition temperatures confirmed the purity of the polymers.

6.1.3 Polystyrene pyrolysis

6.1.3.1 TGA – MS

The study of PS thermal at particle scale revealed the styrene was the major high value chemical produced during thermal decomposition. Other chemicals offered negligible competition to styrene evolution leading to the hypothesis that β-scission reaction involving polystyryl radical is the major PS decomposition mechanism. The influence of heating rate on styrene evolution (based on surface area) was studied but results were statistically not different. This was most likely due to high standard deviations probably emanating from unlikelihood of maintaining the MS capillary in the same position from experiment to experiment.

6.1.3.2 Bench-scale

After having identified the main chemicals produced from PS pyrolysis at particle scale, bench-scale experiments were performed to quantify and optimise the valuable chemical yield. The influence of temperature and heating rate changes on the pyrolysis process was studied to better understand the valuable chemical production response.

Slow Pyrolysis

The conversion of the polymer was more than 90 wt% and increased with both temperature and heating rate. The valuable chemical produced in significant amount and quantified was styrene monomer. The major competitors to styrene production were ᶏ-methylstyrene, toluene and ethylbenzene. The yield and concentration of styrene varied with both temperature and heating rate. A lower temperature of 410 °C and heating rate of 25 C/min maximised styrene yield of about 41 wt%. These values are known to promote β-scission reaction responsible for styrene production. The yield of styrene could be improved by testing higher heating rates which could not be done due to reactor limitation.

Vacuum pyrolysis

In this technology the conversion of the polymer was increased by both temperature and heating rate. The main chemicals that competed with styrene production were ᶏ-methylstyrene and ethylbenzene indicating the slight change in the mechanism of PS decomposition. In this technology, styrene yield of around 36 wt% was maximised by using a temperature of 550 °C and 25 °C/min heating rate. In this process the yields could be improved by increasing both temperature and heating rate which were not possible with the reactor set up.

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Technology comparison

Despite the higher polymer conversion of about 5 wt% in vacuum pyrolysis, better yield and purity of styrene was produced in slow pyrolysis. It could be said that the level of styrene yield in these processes have a potential for industrial application given favourable economies of scale and the styrene separation costs. It was also clear from both technologies that high value styrene ($ 1.78/kg) could be recovered from PS pyrolysis.

6.1.4 Polyethylene terephthalate pyrolysis

6.1.4.1 TGA – MS

This scale of experimentation was not successful for PET as the MS signal quality was weak and full of noise. It was concluded that PET thermal decomposition yielded high molecular weight wax products, which condensed before reaching the MS detector consequently leading to weak signal. These condensed wax products were visibly observed in the TGA furnace at the end of the experimental run.

6.1.4.2 Bench-scale

The tests at bench-scale were the only way to study the pyrolysis of PET. The tests were performed despite some challenges particular to the material and set up. PET thermal decomposition lead to production of only solid phase products which caused set up pipe blockages. The problem was significantly averted by working with a feed size of 15 g of polyethylene terephthalate.

Slow pyrolysis

The conversion of the polymer as well wax yield increased with both temperature and heating rate. A temperature of 410 °C and heating rate of 5 °C/min should be considered for maximising TPA and BA yields. These parameters are known to limit the decomposition of the acids to other chemicals. As the wax yield could be improved by careful selection of increased temperature and heating rate, the chemical yields could probably be improved.

Vacuum pyrolysis

The wax yield and conversion of the polymer were influenced by temperature and heating rate. In process, maximum TPA and BA yields could be realised by working with a temperature of 410 °C and 5 °C/min heating rate. Higher heating rate could increase both wax and chemical yields.

Technology comparison

Vacuum pyrolysis produced higher wax yields than slow pyrolysis. However, vacuum pyrolysis technology TPA and BA yield results compared closely with those of slow pyrolysis. In terms of industrial application of these results, the low TPA and BA yields could not viably be applied given the additional costs of separation. On the overall basis the two technologies produced the valuable TPA ($ 1.14/kg) and BA ($ 1.83/kg) chemicals by considerably same magnitude.

6.2 Recommendations

6.2.1 TGA – MS

TGA – MS coupling method can be used to gain insight into polymer product evolution and decomposition pathways but lack resolution power of molecular fragments, it is therefore recommended to consider TG – GC/MS method to improve fragment separation by the GC component.

6.2.2 Bench-scale

- Conversion of the Kraainfontein landfill mixed plastic stream should be considered to assess the yield of valuable chemicals obtainable.
- The dimers and trimers of PS pyrolysis should be quantified in future studies to accurately understand how their production affects styrene yield and concentration.
- The pyrolysis reactor set up should be modified to eliminate cold spots which caused part of the products condensing making closing mass balance challenging. In the same vein, the condensation train need to be modified to improve the condensation efficiency which was seemingly compromised especially at high vacuum and purging gas flow rate.
- Improve vacuum set up sealing to improve vacuum pressure change during the runs by designing a short but effective condensing system with fewer connection points.
- Separation of chemicals from their mixtures should be considered in future studies and evaluate the economic viability of the process.
- Redesign the reactor so that it could run at higher temperatures and heating rates.

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Appendices

Appendix A: Bench-scale experiment running procedure

1- Weigh all the different parts of the system: five condenser, feedstock and pipes.
2- Place and center the quartz tube in the middle of the oven
3- Verify that the two ends of the tube sticking out on either side of the oven are the same lengths.
4- Put the metal flinches, teflon band and the flinch on the Teflon band and between the two flinches
5- Tight the screws to seal the tube, but not too tightly to avoid to crack the tube
6- Dispose the room temperature condenser with a flat rubber sealant between the lid and the container
7- Tight the lid with screws (in star)
8- Dispose all the others condensers with jelly and Teflon band
9- Place water ice around the two first condensers
10- Place dry ice around the two last condensers
11- Set the heating program, Nitrogen flow rate, the temperature of the exit pipe.
12- Switch on the pump (if Vacuum conditions)
13- After the pyrolysis reaction, set a cooling period (2 hours)
14- Stop the control system
15- Weigh the condensers and pipes once cooled.
16- Clean all condensers, pipes and quartz tube with acetone.

OVEN RECOMMENDATIONS:

- Calibration done: 5-25 ºC min^{-1}, single heating rate recommended
- NOT to try and heat up to intermediate temperatures according to a staged temperature profile.
- **VERY important to NEVER leave the furnace alone when switched on, even if the controller is switched off.**

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Appendix B: TG – MS results

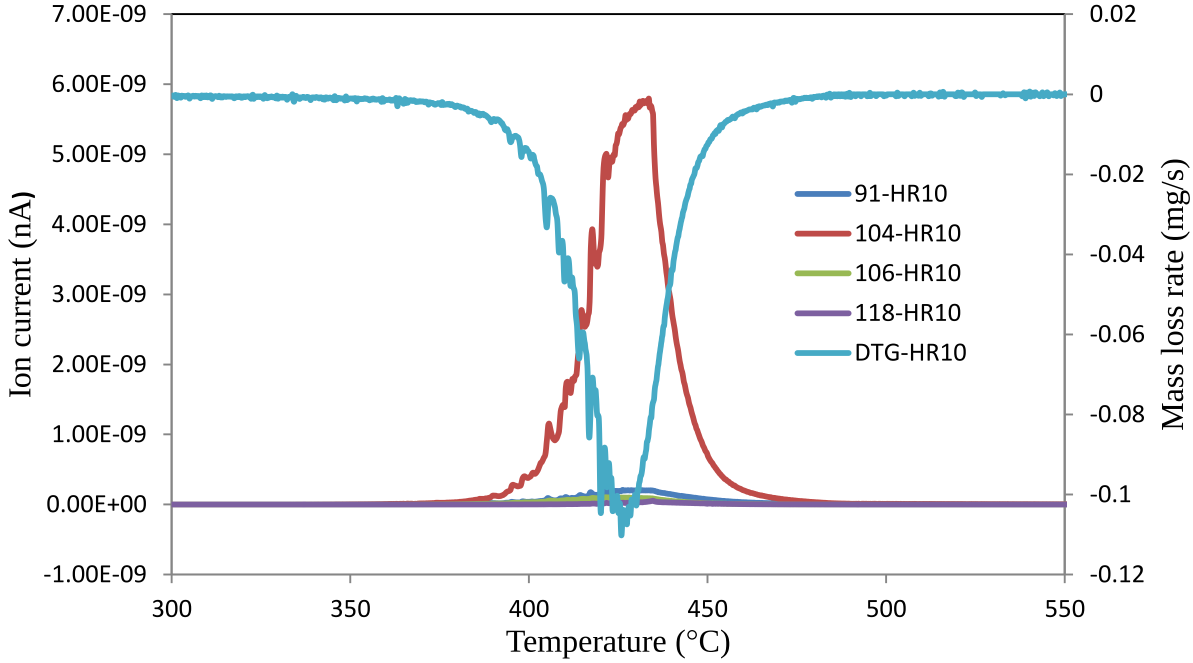

Figure B.0.1 PS pyrolysis products selected ion current evolution profiles at 10 °C /min heating rate

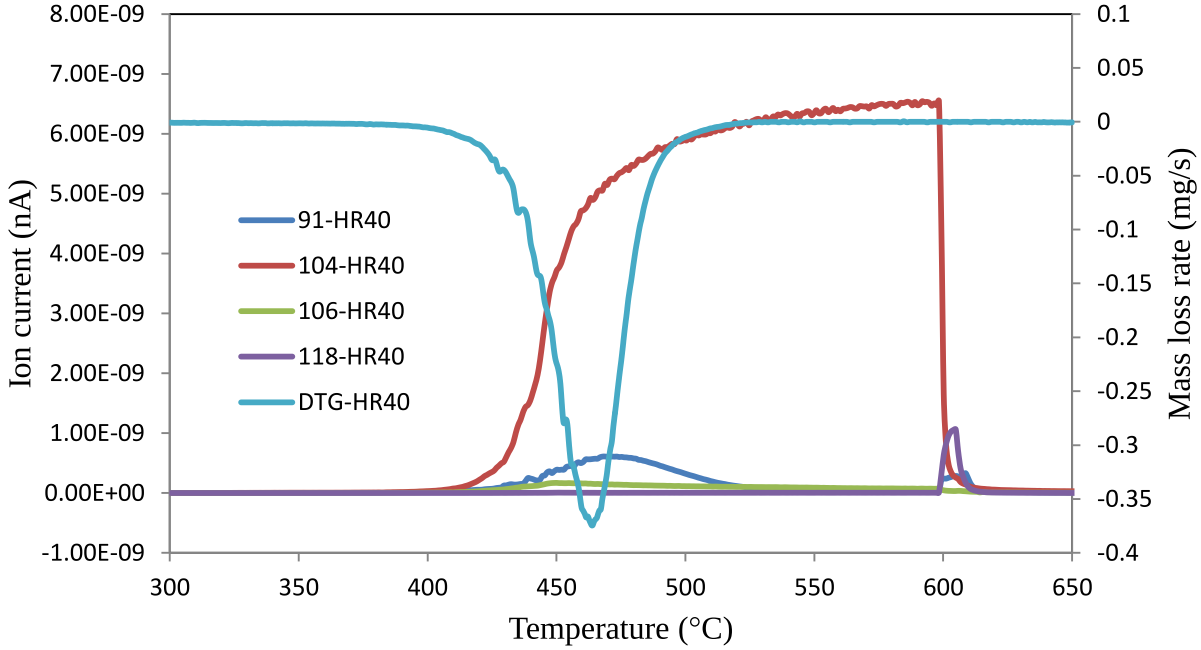

Figure B.0.2 PS pyrolysis products selected ion current evolution profiles at 40 °C /min heating rate

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Table B.0.1 Yield (surface area) of chemicals from TG – MS pyrolysis of PS at various heating rates

	Surface area per milligram of sample (E-10)															
Condition	**Toluene**	**Average**	**SD**	**RSD (%)**	**Styrene**	**Average**	**SD**	**RSD (%)**	**Ethylbenzene**	**Average**	**SD**	**RSD (%)**	**Methystyrene**	**Average**	**SD**	**RSD (%)**
HR5	28.40	28.4333	1.67	5.87	417.29	421.02	4.25	1.01	2.78	2.83	0.37	13.16	5.13	5.70	0.52	9.12
	26.78				420.13				3.23				6.15			
	30.12				425.65				2.49				5.81			
HR10	15.10	13.53	1.60	11.83	665.00	529.00	119.25	22.54	5.02	8.54	3.28	38.36	3.83	3.43	0.57	16.61
	11.90				461.00				11.50				2.78			
	13.60				456.00				9.11				3.69			
HR20	10.50	25.01	9.90	39.58	386.00	990.44	368.12	37.17	3.09	7.50	2.67	35.61	2.24	6.75	2.50	37.07
	29.40				1010.00				5.30				8.38			
	21.30				1020.00				4.89				5.70			
	39.30				1570.00				8.64				9.76			
	33.70				1380.00				10.40				9.71			
	34.60				1250.00				9.45				7.07			
	21.50				779.00				10.80				6.14			
	21.90				834.00				6.58				7.65			
	12.90				685.00				8.34				4.12			
HR40	25.20	17.78	4.56	25.62	658.00	648.20	75.64	11.67	13.20	10.28	4.07	39.61	6.70	5.80	0.95	16.38
	18.60				739.00				5.43				6.97			
	14.70				696.00				14.60				5.00			
	16.70				549.00				11.60				5.14			
	13.70				599.00				6.56				5.20			

Table B.0.2 Yield (surface area ratios) of chemicals from TG – MS pyrolysis of PS at various heating rates

	Chemical surface area ratios											
Condition	**Styrene/Toluene**	**Average**	**SD**	**RSD (%)**	**Styrene/Ethylbenzene**	**Average**	**SD**	**RSD (%)**	**Styrene/Methylstyrene**	**Average**	**SD**	**RSD (%)**
HR10	44.04	38.77	5.26	13.56	132.47	74.20	50.71	68.33	173.63	154.34	26.93	17.45
	38.74				40.09				165.83			
	33.53				50.05				123.58			
HR20	36.23	40.21	6.36	15.82	72.13	139.09	46.72	33.59	126.87	150.41	26.41	17.56
	38.08				126.75				109.02			
	36.76				124.92				166.26			
	34.35				190.57				172.32			
	47.89				208.59				120.53			
	39.95				181.71				178.95			
	40.95				132.69				160.86			
	34.60				132.28				142.12			
	53.10				82.13				176.80			
HR40	26.11	37.96	8.53	22.46	49.85	74.45	39.19	52.63	98.21	113.09	15.79	13.96
	39.73				136.10				106.03			
	47.35				47.67				139.20			
	32.87				47.33				106.81			
	43.72				91.31				115.19			

Appendix C PS Slow pyrolysis results

Table C.0.3 Slow PS pyrolysis product mass balances

Pyrolysis Conditions		Product Yields (wt %)									Overall Conversion (wt %)		
		Oil Yield			Gas Yield			Char Yield					
Temperature (°C)	Heating rate (°C/min)	Oil	Average	RSD	Gas	Average	RSD	Char	Average	RSD	Conversion	Average	RSD
410	5	64.10	64.55	0.99	26.90	26.90	0.00	9.10	8.60	8.22	90.90	91.25	0.54
410	5	65.00			26.90			8.10			91.60		
410	25	70.30	70.05	0.50	20.70	20.45	1.73	9.00	9.50	7.44	91.00	90.50	0.78
410	25	69.80			20.20			10.00			90.00		
480	5	69.20	69.75	1.12	28.80	28.20	3.01	2.00	2.10	6.73	98.00	97.90	0.14
480	5	70.30			27.60			2.20			97.80		
480	25	73.10	72.85	0.49	24.40	24.45	0.29	2.40	2.70	15.71	97.60	97.30	0.44
480	25	72.60			24.50			3.00			97.00		
550	5	53.00	53.80	2.10	45.30	44.40	2.87	1.80	1.85	3.82	98.20	98.15	0.07
550	5	54.60			43.50			1.90			98.10		
550	25	57.50	57.95	1.10	41.20	40.60	2.09	1.30	1.40	10.10	98.70	98.60	0.14
550	25	58.40			40.00			1.50			98.50		

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Table C.0.4 Slow pyrolysis yield and concentration results for styrene

Pyrolysis Conditions		Styrene yields (wt %)					
		Styrene yield			Styrene concentration		
Temperature (°C)	Heating rate (°C/min)	Yield	Average	RSD	Conc	Average	RSD
410	5	32.29	31.32	4.39	50.54	48.67	5.43
410	5	30.34			46.80		
410	25	43.03	44.63	5.09	61.07	63.81	6.06
410	25	46.24			66.54		
480	5	39.81	38.17	6.07	57.06	54.45	6.76
480	5	36.53			51.85		
480	25	44.41	42.13	7.65	60.57	57.37	7.90
480	25	39.85			54.17		
550	5	19.54	20.03	3.50	36.76	37.44	2.58
550	5	20.53			38.12		
550	25	23.57	24.60	5.88	41.02	42.08	3.56
550	25	25.62			43.14		

Appendix D: PET Slow pyrolysis results

Table D.0.5 Slow PET pyrolysis product mass balances

Pyrolysis Conditions		Product Yields (wt%)									Overall Conversion (wt%)		
		Wax Yield			Gas Yield			Char Yield					
Temperature (°C)	Heating rate (°C/min)	Wax	Average	SD	Gas	Average	SD	Char	Average	SD	Conversion	Average	SD
410	5	35.19	33.89	1.83	29.06	29.28	0.31	35.75	36.83	1.52	64.25	63.17	1.52
410	5	32.60			29.50			37.90			62.10		
410	25	29.90	30.50	0.85	31.80	30.85	1.34	38.30	38.65	0.49	61.70	61.35	0.49
410	25	31.10			29.90			39.00			61.00		
480	5	35.80	35.12	0.83	43.30	43.11	1.39	21.00	21.83	1.04	79.00	78.17	1.04
480	5	35.36			41.64			23.00			77.00		
480	5	34.20			44.40			21.50			78.50		
480	25	36.20	36.90	0.99	44.20	44.00	0.28	19.60	19.10	0.71	80.40	80.90	0.71
480	25	37.60			43.80			18.60			81.40		
550	5	33.00	32.30	0.99	47.00	47.85	1.20	20.00	19.80	0.28	80.00	80.20	0.28
550	5	31.60			48.70			19.60			80.40		
550	25	39.40	39.70	0.42	44.60	44.00	0.85	15.90	16.30	0.57	84.10	83.70	0.57
550	25	40.00			43.40			16.70			83.30		

Table D.0.6 Slow pyrolysis yield and concentration results for TPA and BA

Process conditions		Chemical Yield (wt%)				Chemical concentration (wt%)			
Temperature (°C)	Heating rate (°C/min)	TPA	SD	BA	SD	TPA	SD	BA	SD
410	5	16.55	0.12	20.90	3.48	51.30	3.76	64.79	5.47
410	5	16.37		25.83		45.97		72.52	
480	5	13.83	0.75	24.90	3.61	38.35	1.13	69.04	8.36
480	5	12.35		18.20		36.37		53.61	
480	5	13.00		23.90		36.41		66.92	
550	5	13.16	0.00	20.57	0.23	39.13	1.26	61.14	1.23
550	5	13.17		20.24		40.91		62.88	
410	25	15.29	0.12	18.00	0.55	51.59	0.70	60.74	3.10
410	25	15.46		17.22		50.60		56.35	
480	25	7.32	1.44	27.21	0.81	19.86	3.34	73.86	3.76
480	25	9.35		26.07		24.58		68.55	
550	25	9.42	4.07	27.97	0.43	23.56	10.70	69.98	2.05
550	25	15.18		28.58		38.70		72.87	

Appendix E PS Vacuum pyrolysis results

Table E.0.7 Vacuum PS pyrolysis product mass balances

Pyrolysis Conditions		Product Yields (wt %)									Overall Conversion (wt %)		
		Oil Yield			Gas Yield			Char Yield					
Temperature (°C)	Heating rate (°C/min)	Oil	Average	SD	Gas	Average	SD	Char	Average	SD	Conversion	Average	SD
410	5	53.30	52.01	1.82	44.30	43.66	0.91	2.40	4.33	2.73	97.60	95.67	2.73
410	5	50.72			43.02			6.26			93.74		
410	25	56.50	58.20	2.40	39.80	38.15	2.33	3.70	3.65	0.07	96.30	96.35	0.07
410	25	59.90			36.50			3.60			96.40		
480	5	51.10	51.75	0.92	47.30	46.90	0.57	1.60	1.35	0.35	98.40	98.65	0.35
480	5	52.40			46.50			1.10			98.90		
480	25	65.50	64.80	0.99	33.30	33.85	0.78	1.20	1.35	0.21	98.80	98.65	0.21
480	25	64.10			34.40			1.50			98.50		
550	5	48.90	48.75	0.21	49.00	49.45	0.64	1.10	1.35	0.35	98.90	98.65	0.35
550	5	48.60			49.90			1.60			98.40		
550	25	63.50	64.00	0.71	35.10	34.65	0.64	1.50	1.45	0.07	98.50	98.55	0.07
550	25	64.50			34.20			1.40			98.60		

Table E.0.8 Vacuum pyrolysis yield and concentration results for styrene

Process conditions		Styrene yields (wt%)					
		Styrene yield			Styrene concentration		
Tempereture (°C)	Heating rate (°C/min)	Yield	Average	RSD	Conc	Average	RSD
410	5	17.90	10.32	103.78	33.43	19.43	101.86
410	5	2.75			5.43		
480	5	14.61	14.09	5.23	28.44	27.05	7.25
480	5	13.57			25.66		
550	5	13.88	16.81	24.66	27.95	34.52	26.93
550	5	19.74			41.10		
410	25	8.24	12.45	47.79	13.72	21.55	51.40
410	25	16.65			29.38		
480	25	26.11	26.25	0.71	40.11	40.63	1.79
480	25	26.38			41.14		
550	25	39.08	36.07	11.82	61.90	56.28	14.14
550	25	33.05			50.65		

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Appendix F: PET Vacuum pyrolysis

Table F.0.9 Vacuum pyrolysis yield and chemical concentration results

Process conditions		Chemical Yield (wt%)				Chemical Concentration (wt%)			
Temperature (°C)	Heating rate (°C/min)	TPA	SD	BA	SD	TPA	SD	BA	SD
410	5	13.68	0.59	19.71	1.49	40.34	3.97	58.10	7.74
410	5	14.52		21.82		45.95		69.05	
480	5	20.25	3.02	16.61	5.70	46.64	8.09	38.26	11.40
480	5	15.97		24.68		35.20		54.38	
550	5	18.60	0.01	22.35	0.20	43.65	1.38	52.44	1.23
550	5	18.58		22.07		45.60		54.17	
410	25	22.46	3.15	19.24	2.96	64.68	9.72	55.41	7.69
410	25	18.00		23.43		50.94		66.29	
480	25	17.64	3.45	22.20	0.85	37.67	7.60	47.40	1.40
480	25	12.76		23.41		26.92		49.39	
550	25	8.95	0.72	21.76	7.86	18.44	1.66	44.84	15.46
550	25	7.93		32.88		16.10		66.71	

Table F.0.10 Vacuum PET pyrolysis product mass balances

Pyrolysis Conditions		Product Yields (wt%)									Overall Conversion (wt%)		
		Wax Yield			Gas Yield			Char Yield					
Temperature (°C)	Heating rate (°C/min)	Wax	Average	SD	Gas	Average	SD	Char	Average	SD	Conversion	Average	SD
410	5	31.52	32.66	1.61	29.54	25.90	2.57	38.94	40.20	0.89	61.06	59.80	0.89
410	5	33.80			25.90			40.20			59.80		
410	25	35.64	34.97	0.95	25.26	21.60	2.59	39.10	44.10	3.53	60.90	55.90	3.53
410	25	34.30			21.60			44.10			55.90		
480	5	43.10	44.30	1.70	38.50	37.50	1.41	18.40	18.20	0.28	81.60	81.80	0.28
480	5	45.50			36.50			18.00			82.00		
480	25	46.40	47.15	1.06	37.50	36.55	1.34	16.10	16.35	0.35	83.90	83.65	0.35
480	25	47.90			35.60			16.60			83.40		
550	5	42.40	41.80	0.85	40.80	41.45	0.92	16.80	16.70	0.14	83.20	83.30	0.14
550	5	41.20			42.10			16.60			83.40		
550	25	48.50	48.63	0.19	39.50	39.96	0.32	12.10	11.28	0.58	87.90	88.72	0.58
550	25	48.77			39.96			11.28			88.72		

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