

Pyrolysis of waste polypropylene plastics for energy recovery: Investigation of operating parameters and process development at pilot scale

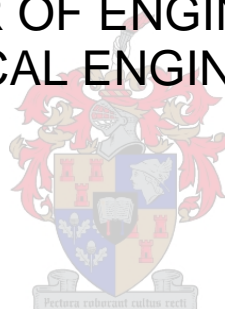
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Abstract

Polypropylene (PP) has been identified as the second most abundant plastic waste in landfills globally and the fastest growing plastic waste in South Africa. The increasing numbers have been attributed to the limitation of conventional mechanical recycling not being able to handle plastic wastes contaminated with other organic wastes. Recycling via pyrolysis has been identified as a promising option to managing these plastic wastes due to its ability to handle significant levels of contamination and also yielding products with huge fuel prospects from plastics. Pyrolysis under vacuum conditions for other organic wastes such as biomass has demonstrated promising yields of condensable products. Unfortunately, pyrolysis of plastics under vacuum has received very little attention. Also, transition from bench to industrial scale applications of pyrolysis processes could be complicated and pilot scale processes to mediate between both levels are very helpful towards attaining the sustainable commercialisation of plastics pyrolysis into fuels.

The aim of the study was to investigate the effects of key process parameters (that include temperature and heating rate) on products yield distribution and quality of condensable products from the pyrolysis of waste PP plastics at bench scale under atmospheric and vacuum conditions. Four temperatures (450, 488, 525 and 600 °C) were investigated at two distinct heating rates of 15 °C/min (slow), 175 °C/min (fast). As part of the aims of the study, a 5 kg/h pyrolysis pilot plant was also designed and commissioned after which tests obtained from atmospheric fast heating rates were scaled-up to the commissioned pilot.

Pyrolysis of PP under atmospheric slow and fast heating rates revealed maximum condensable products (oil and wax) yields of 85.6 and 84.5 wt.% respectively all attained at 488 °C after which further increase of temperature resulted in secondary cracking reactions which promoted yields of permanent gases against condensables. Cracking was however more severe under fast heating rates due to the combined effects of higher temperature and faster heating rate. Gas Chromatography/ Mass Spectrometry (GC/MS) analysis of condensable products obtained under these conditions also revealed that production of gasoline range compounds was favoured mostly under reactions where some cracking reactions occur. Also, Higher Heating Values (HHVs) of condensable products recovered under atmospheric conditions ranged between 41 - 45 MJ/kg. HHVs were however seen to decrease

at severe temperature and heating rate conditions due to the increased production of aromatics.

Maximum yields of condensable products for slow and fast heating rates under vacuum conditions were reported to be 92.7 wt.% (at 525 °C) and 91.8 wt.% (at 488 °C) respectively. Total yields of condensable products under vacuum were observed to be higher than the corresponding yields under atmospheric conditions. Unlike atmospheric conditions, diesel range compounds predominated all condensable products recovered under vacuum pyrolysis. In addition, HHVs of condensable products retrieved under vacuum ranged between 42 - 46 MJ/kg and were seen to remain high even at severe conditions of temperature and heating rate.

Lastly, tests under atmospheric fast heating rates at bench were mimicked on the commissioned pilot plant (because they both employ a pre-heated reactor). Compared to the bench scale test, temperature at which maximum yield of condensable products were retrieved on the pilot decreased by 28 °C with the maximum condensable products yield also decreasing by 6%. These differences were blamed on different reactor length configurations. Physico-chemical properties of oils recovered from the pilot when compared to commercial diesel and gasoline fuels disclosed that PP derived oils contained compositions of both diesel and gasoline range compounds.

Opsomming

Polipropolien (PP) is uitgeken as die plastiek wat wêreldwyd die tweede meeste voorkom in vullisterreine en dit is die vinnigste groeiende plastiekmateriaalafval in Suid Afrika. Die groeiende syfers word toegeken aan die feit dat konvensionele meganiese herwinning beperkte kapasiteit het om afvalplastiekmateriaal wat met organiese afval gekontamineer is, te hanteer. Herwinning via pirolise is geïdentifiseer as 'n belowende opsie om plastiekafval te bestuur, as gevolg van pirolise se vermoë om beduidende vlakke van kontaminasie te hanteer, asook die oplewering van produkte met belowende brandstof eienskappe. Pirolise onder vakuümcondisies van ander organiese afvalmateriaal, soos biomassa, toon belowende opbrengste van kondenseerbare produkte. Ongelukkig, vind pirolise van plastiek onder vakuümcondisies baie min aandag. Verder, kan dit ingewikkeld wees om van banktoetsskaal na industriële skaal oor te gaan en lootskaal prosesse kan hulpvaardig wees om tussen die twee vlakke te bemiddel om volhoubare kommersialisering van plastieksirolise om brandstof te maak, te bekom.

Die doelwit van die studie was om die effekte van sluetel-proses-parameters (insluitend temperatuur en verhittingstempo) op die verspreiding en kwaliteit van kondenseerbare produkte vanaf die pirolise van afval PP-plastiek by banktoetsskaal onder atmosferiese en vakuümdruk kondisies te ondersoek. Vier temperature (450, 488, 525 en 600 °C) was onderoek by twee duidelike verhittingstempo's van 15 °C /min (stadig) en 175 °C /min (vining). As deel van die doelwitte van die studie, is 'n 5 kg/h pirolise lootsaanleg ook ontwerp en opgedra, waarna toetse verkry vanaf atmosferiese vinnige verhittingstempo's, opgeskaleer is na die lootsaanleg.

Pirolise van PP onder atmosferiese stadige en vinnige verhittingstempo's het maksimale kondenseerbare produkte (olie en was) opbrengste gelewer van 85.6 wt.% en 84.5 wt.% onderskeidelik, als verkry by 488 °C, waarna 'n verdere toename in temperatuur sekondêre kraking reaksies tot gevolg gehad het wat opbrengste van permanente gasse teenoor kondenseerbare produkte bevorder. Kraking was egter hewiger onder vinnige verhittingstempo as gevolg van die gekombineerde gevolge van hoër temperatuur en vinniger verhittingstempo. GC/MS-analise van kondenseerbare produkte wat onder hierdie toestande verkry is het ook gewys dat produksie van petrol bestek samestellings is meestal bevoordeel waar sekondêre kraking reaksies voorkom. Verder, was die hoërverhittingswaarde (HHV) van

herwinde kondenseerbare produkte onder atmosferiese kondisies in bestek van 41 - 45 MJ/kg. HHVs het egter verminder by geweldige temperature en verhittingstempo kondisies a.g.v die toenemende vervaardiging van aromatiese verbindings.

Maksimale kondenseerbare produkte opbrengste vir stadige en vinnige verhittingstempo's onder vakuum is gerapporteer as 92.7 wt.% (by 525 °C) en 91.8 wt.% (by 488 °C) onderskeidelik. Totale opbrengste van kondenseerbare produkte onder vakuum was hoër as die ooreenstemmende opbrengste van olies onder atmosferiese toestande. Anders as atmosferiese toestande, het diesel bestek verbindings alle kondenseerbare produkte wat onder vakuum pirolise herwin is oorheers. Verder, het kondenseerbare produkte wat onder vakuum herwin is, HHV's wat in die bestek van tussen 42 - 46 MJ/kg geval het en dit was gevind om hoog te bly selfs onder geweldige kondisies van temperatuur en verhittingstempo.

Laastens, is toetse onder atmosferiese vinnige verhittingstempo's op banktoetsskaal nageboots op die lootsaanleg (want hulle altwee benut 'n voorverhitte reaktor). In vergelyking met die banktoetsskaal toetse, het die temperatuur waarby maksimum opbrengs van kondenseerbare produkte herwin is, met 28 °C verminder. Die maksimum opbrengs van kondenseerbare produkte het ook met 6% verminder. Hierdie verskille is toegeken aan die verskil in lengte konfigurasies van die reaktore. Physico-chemiese eienskappe van olies herwin uit die lootsaanleg, as vergelyk word met kommersiële diesel en petrol brandstowwe, het gewys dat die samestelling van PP afgeleide olies in die bestek van beide diesel en petrol samestellings val.

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Nomenclature

ASTM	–	American Society for Testing and Materials (ASTM)
BTX	–	Benzene, Toluene and Xylene
FBP	–	Final Boiling Point
GC/MS	–	Gas chromatography/Mass spectrometry
HDPE	–	High Density Polyethylene
HHV	–	Higher Heating Value
IBP	–	Initial Boiling Point
IP	–	Institute of Petroleum
LDPE	–	Low Density Polyethylene
MSW	–	Municipal Solid Waste
PE	–	Polyethylene
PP	–	Polypropylene
PS	–	Polystyrene
PUR	–	Polyurethanes
PVC	–	Polyvinyl chloride
RON	–	Research Octane Number
TGA	–	Thermogravimetric Analysis

Definition of Key terms

Aliphatics- A class of saturated or unsaturated carbon compounds, in which the carbon atoms are joined in open or cyclic chains, but the cyclic compounds are not aromatic

Aromatics- They are compounds that consist of one or more rings containing alternating single and double bonds in its chemical structure. In this study, this term will more particularly refer to group of hydrocarbons with benzene as the parent

Aromatisation- It is the formation of aromatic compounds, observed during pyrolysis at high temperatures due to secondary reactions.

Condensation polymers- They are polymers formed through condensation reactions where molecules fuse together, producing much smaller molecules such as water and ethanol as by-products.

Condensable products- Condensable gases which were recovered as both oil and wax

Cyclisation- It is the formation of cyclic/closed ring and aromatic hydrocarbons also caused by secondary reactions

Naphthenes- Any group of cyclic aliphatic hydrocarbons

Olefins- Class of unsaturated hydrocarbons

Paraffins- Saturated hydrocarbons

Recombination reactions- Also a form of secondary reaction but it involves the reaction of two different primary radicals/products into one single final product.

Secondary reactions- The further reaction of primary pyrolysis products into much more stable compounds.

Simulated distillation- It is a chromatographic technique which correlates retention times of hydrocarbons from a GC/MS spectrum with boiling points of the same compounds.

Chapter 1

Introduction

1.1 Background

In today's modern society, plastics provide a basic contribution to many daily activities, ranging from agriculture to packaging (Pinto *et al.*, 1999; Lopez, *et al.*, 2017). However, the build-up of extensive amounts of plastic waste worldwide has raised environment concerns (Siddiqui & Redhwi, 2009; Pinto *et al.*, 2013; Abbas-Abadi *et al.*, 2014; Ahmad *et al.*, 2015). A survey conducted on the flow of plastic materials in 2007 revealed that 260 million tons of plastics were produced worldwide with this figure increasing at a rate of 4 to 5% annually (Al-Salem *et al.*, 2010; Kunwar *et al.*, 2016; Lopez *et al.*, 2017). Also, in 2013, plastic production worldwide has increased to a little below 300 million tonnes (Sharuddin *et al.*, 2016). It is also estimated that about 60% of these generated plastic wastes end up at landfills globally (Valavanidis *et al.*, 2008; Al-Salem *et al.*, 2010). In South Africa, a total of about 1.3 million tonnes of plastic are manufactured out of which only about 20% are recycled with the remaining being landfilled. This is according to a survey conducted by Plastics SA, a representative organisation for all sectors of the South African plastic industry in 2012.

Although more innovative technologies have been used over the past couple of years to recover plastics, there still remains a substantial fraction of plastic wastes which is difficult to recycle mechanically as a result of impurities, lack of markets or the failure to sort and remove the plastics that make recovery unattainable (Panda & Singh, 2013; Heydariaraghi *et al.*, 2016). Most of these non-recycled plastics then become landfilled or incinerated (which is not very prevalent in South Africa) (Williams & Williams, 1997; Demirbas & Taylan, 2015; Heydariaraghi *et al.*, 2016).

Landfilling is not an ideal remedy for plastic waste management because sites for building suitable landfills have been increasingly scarce mainly due to opposition executed by nearby inhabitants and pressures from law-making bodies (Adewole & Wolkowicz, 1999; Achilias *et al.*, 2008; Panda *et al.*, 2010). Secondly, is the poor biodegradability of plastics which promotes soil leaching and impregnation as well as consequent pollution of underground waters. Besides, the lifelong effects of degradation of these plastics have still not been

validated (Pinto *et al.*, 1999; Achilias *et al.*, 2008; Lu *et al.*, 2015) Also, the increasing cost of transport and disposal has caused landfilling of plastic wastes an unpleasant option (Williams & Williams, 1997; Achilias *et al.*, 2008; Al-Salem *et al.*, 2009; Miskolczi *et al.*, 2009; Panda *et al.*, 2010). Lastly, a substantial amount of plastic waste have also ended up in the ocean, and should the current usage and disposal of plastics continue, there will be more plastics than fish in the ocean by 2050 (Geyer *et al.*, 2017; World Economic Forum, 2016).

Presently, plastic recycling can be grouped into four categories; primary or closed-loop, secondary, tertiary and quaternary (Wong *et al.*, 2000; Abbas & Shubar, 2008; Al-Salem *et al.*, 2009; Siddiqui & Redhwi, 2009; Hopewell *et al.*, 2009; Wong *et al.*, 2015). Primary and secondary recycling falls under mechanical recycling processes. Primary recycling involves the conversion of plastics to products with identical properties as virgin plastics (Hopewell *et al.*, 2009; Wong *et al.*, 2000; Achilias *et al.*, 2008). Secondary recycling also known as downgrading is the conversion of plastic wastes into new products of depreciated value (Ali & Siddiqui, 2001; Low, *et al.*, 2001; Lu *et al.*, 2015). Downgrading also refers to a recycling technique where waste plastic material is used to build an object that will usually not be made with virgin plastics. A typical example is plastic lumber that can be used in place of a much more expensive timber (Hopewell *et al.*, 2009). Tertiary recycling is defined as the processing of plastics back into their monomer structures, petrochemicals and/or fuel compounds (Ali & Siddiqui, 2001; Wong *et al.*, 2000). Quaternary recycling employs incineration with or without energy recovery from plastic products (Ali & Siddiqui, 2001; Hopewell *et al.*, 2009; Wong *et al.*, 2000). Primary and secondary recycling have helped in managing waste plastic materials, but they have limitations on properties and uses of final products (Low *et al.*, 2001; Wong *et al.*, 2000; Lu *et al.*, 2015). Quaternary recycling minimizes amount of plastic wastes deposited in landfills and substantial amount of energy can be retrieved on combustion. It nonetheless comes with the release of substantial amount of toxic gases and dusts which are not environmentally friendly. (Pinto *et al.*, 1999; Wong *et al.*, 2000; Larraín *et al.*, 2017). Also, it is very inefficient since considerable cost is incurred in managing the large volumes of flue gases generated.

Since management of plastic wastes via landfill and incineration pose serious threats to the environment with mechanical recycling techniques being limited in terms of feedstock purity and product quality, pyrolysis as a type of tertiary recycling has been acknowledged as

a promising route to managing waste plastics (Lin & Yen, 2005; Lee & Shin, 2007; Miskolczi *et al.*, 2009; Jung *et al.*, 2010; Panda & Singh, 2013). Pyrolysis, a major type of thermochemical conversion, is the degradation of polymers at elevated temperatures in the absence of oxygen to produce valuable products such as char and volatiles, which can be separated into a condensable fraction and permanent gases. Pyrolysis leads to the breakdown of long chain polymers of plastics into shorter chain compounds and monomers, from which the plastics are initially made, and other useful fuels and chemicals (Wong *et al.*, 2015; Miskolczi *et al.*, 2009). It also has the advantage of processing to some extent unwashed and unsorted plastics and multilayer films that are difficult to recycle mechanically thus both clean and contaminated plastics have the potential to be recycled in this fashion (Scheirs, 2006). This implies that polymer mixtures as well as highly contaminated plastics such as mulch film could be processed to yield products with high rate of returns. However, change in composition of feedstock and proportion of contaminants influences product yield and properties (Scheirs, 2006).

Pyrolysis of polypropylene plastics is the focus of this study because, Plastics SA has reported that plastic tubs, punnets, trays, iced cream and yoghurt containers have increased considerably in the South African plastic waste stream. These materials made up of polypropylene (PP) happens to be one of the least recycled post-consumer plastics with only about 18% recycled as at 2012. This is due to the high level of contamination with other non-plastic materials such as food and other organics wastes from domestic streams (Plastics SA, 2015). Also, polypropylene (PP) is the second most manufactured and utilised plastic product worldwide behind Polyethylene (PE) (Al-Salem *et al.*, 2010; Wong *et al.*, 2015). Closed-loop recycling of plastic materials requires that the feed material is free of contaminants, which in real life is often unrealistic (Hopewell *et al.*, 2009; Al-Salem *et al.*, 2010). Therefore, valorisation of waste PP plastics into useful fuels via pyrolysis, has been identified as a promising alternative.

1.2 Motivation for the research

When considering plastics pyrolysis to produce condensable fuel products, several factors affect the yield and quality of products generated from the process. These include temperature, heating rate, residence time of volatiles and solids, among others. A number of works on PP plastics pyrolysis employed only a single condition of heating rate (Heydariaraghi

et al., 2016; Yan *et al.*, 2015; Hájeková and Bajus, 2005) with others (Miskolczi *et al.*, 2009; Zhou *et al.*, 2004; Takuma *et al.*, 2001) not even reporting the heating rate used. This resulted in a wide range of condensable product yields (49 - 83 wt.%) reported for similar heating rate conditions. Also, different reactor configurations employed by the various researchers made the comparison of these studies challenging. The number of studies investigating the influence of heating rate (Encinar & González, 2008; Fakhrhoseini & Dastanian, 2013) are also limited. For a clearer picture of the influence of heating rate and potential interactions with temperature on conversion mechanisms and yields, there is a need to vary both factors.

Moreover, condensable products recovered from PP pyrolysis are sometimes reported as wax (Aguado *et al.*, 2002; Arabiourrutia *et al.*, 2012), liquid (Lu *et al.*, 2015; Owusu *et al.*, 2018) or a mixture of the two (Yan *et al.*, 2015; Hájeková & Bajus, 2005) and in most cases, these are not highlighted. As these properties influence the potential application of the products, it is vital to understand the effects of the process conditions on the physical properties of the condensed product.

Additionally, most pyrolysis experiments reported in literature on PP pyrolysis were conducted under atmospheric conditions (Al-Salem *et al.*, 2017). However, pyrolysis processes can also be conducted under vacuum (below atmospheric) (Miranda *et al.*, 2001). Pyrolysis under vacuum conditions limit secondary cracking reactions since primary products generated are quickly extracted from the hot part of the reactor by the vacuum suction. This process in effect increases the yield of condensable products (oil/wax) and minimises the production of permanent gases. Unlike biomass, pyrolysis of plastics under vacuum conditions received very little attention. From literature, only Miranda *et al.*, (2001) was found to report the vacuum pyrolysis of PP. Their investigation was however conducted at only a single condition of temperature. The effects of how the variation of temperature and heating rate affect the product yield distribution and quality of condensable products under vacuum pyrolysis of PP has been identified as gap.

Also, the scale-up of bench-scale processes to pilot scale on the pyrolysis PP and other plastics is hardly covered in literature. Most scale-ups covered were rather from milligram scale (TGA) to bench scale (Bradfield, 2014; Chomba, 2018). Scale-up to pilot is important because, when laboratory scale pyrolysis experiments look promising and there is the tendency for commercialisation, scaling up helps to further investigate its viability for commercialisation

and also ascertain the validity of bench-scale experiments (Arena & Mastellone, 2006). This will therefore contribute significantly to efforts being made towards the sustainable commercialisation of plastics pyrolysis into fuels since pilot plants bridge the gap between laboratory and industrial scale processes.

This study therefore seeks to investigate the pyrolysis conversion of PP into liquid fuels, with attention given to the effects of key operating parameters, including temperature and heating rate on the yield and quality of obtained fuel oils. Also, to be examined are the effects of vacuum pyrolysis at bench scale on oil yield and quality and how they compare with PP pyrolysis under atmospheric conditions also at bench. Lastly, the design, installation and commissioning of a 5 kg/h pyrolysis pilot plant will also be conducted as part of the study. Bench scale atmospheric tests will then be scaled up to the installed pilot plant.

1.3 Research Aims and Objectives

1.3.1 Aim

The aim of the research was to investigate the effects of key parameters that include temperature and heating rate on the pyrolysis of waste polypropylene (PP) plastics into liquid fuels, at both bench and pilot scale on a pilot plant that will be built as part of the study.

1.3.2 Objectives

To realise this aim, the following objectives need to be performed:

1. To design, install and commission a 5 kg/h pyrolysis pilot plant that converts plastics and non-plastic materials into pyrolysis products.
2. To investigate the effects of temperature and heating rate on yield and quality of PP derived oils under vacuum and atmospheric pyrolysis conditions at bench scale.
3. To scale up atmospheric bench scale processes to the commissioned pilot plant.
4. To characterise oils recovered from the pilot for Physico-chemical properties that include density, viscosity, pour point, cetane index and compare with commercial diesel and gasoline fuels.

I.4 Research Questions

To successfully optimise the conversion of waste polypropylene (PP) plastics into liquid fuels via atmospheric and vacuum pyrolysis at bench and pilot scale, on a pilot plant that will be installed and commissioned, certain key questions need to be addressed. These include;

1. How will factors such as temperature and heating rate affect the yields of condensable products (oil and wax) from PP pyrolysis at bench scale?
2. How does temperature and heating rate affect the quality of condensable products recovered from the bench scale atmospheric and vacuum pyrolysis of PP?
3. How will the investigations for condensable products yield and quality at bench scale under atmospheric conditions compare with those for vacuum?
4. Will the pilot plant that will be used for scale-up study be successfully designed and commissioned?
5. How will factors such as temperature and heating rate affect condensable products yield and quality from the pyrolysis of PP at pilot scale?
6. How will the investigations carried out at pilot scale compare to those for atmospheric conditions at bench?
7. How will condensable products recovered from pilot pyrolysis of PP compare with commercial diesel and gasoline fuels?

I.5 Thesis Overview

This thesis is organized into five major chapters. **Chapter 1** highlights the background, motivation, aims and objectives of the research. **Chapter 2** provides a literature review on the flow of plastic wastes in South Africa, types of pyrolysis, a review on PP pyrolysis, characteristics of commercial fuels and also a review on pilot plant components that was used in designing the pilot plant. All experimental research methods used in this study were explained in **Chapter 3**. Moreover, results obtained from experimental work were discussed in **Chapter 4**. Lastly, key conclusions made from the study were presented in **Chapter 5**. Also presented in that chapter were recommendations for future work.

Chapter 2

Literature review

2.1 Introduction

This chapter considers the various types of plastic waste management, their advantages and disadvantages. Also, the most interesting waste management route was highlighted. The chapter also covers the physical and chemical properties of polypropylene (PP) and why PP is the focus of this research work. Also considered in this chapter is the comparison of the chemical and physicochemical properties of commercial liquid fuels to oils derived from PP pyrolysis. In addition, major factors affecting plastics pyrolysis as well as the types of pyrolysis were highlighted. Finally, overview of the various components associated with typical pilot and commercial scale pyrolysis plants as well as some brief descriptions of some existing pilot pyrolysis plants were also mentioned.

2.2 Flow of Polypropylene in South Africa

Table 2.1. Plastics waste distribution in South Africa as at 2012 reported by Plastics SA

Plastic type	Amount manufactured (tonnes)	Amount recycled (tonnes)	Amount landfilled (tonnes)	percentage recovered (%)	percentage landfilled (%)
PE-LD/LLD	345000	98971	246029	28.69	71.31
PE-HD	200000	45950	154050	22.98	77.03
PP	260000	47080	212920	18.11	81.89
PET	160000	54424	105576	34.02	65.99
PS	63000	3394	59606	5.39	94.61
PVC	159000	16812	142188	10.57	89.43
OTHER	183000	6060	176940	3.31	96.69
Total	1370000	272691	1097309		

PP has been identified as one of the least primary recycled plastic wastes in South Africa by Plastics SA, (2013). As of 2012, out of about 260,000 tonnes of PP manufactured, only about 18% were recycled in a closed-loop (primary) fashion (Chomba, 2018; Plastics SA, 2013). This means that close to 82% of waste PP plastics end up at landfill sites. It was assumed that incinerated plastic tonnages were negligible since very little information is available on the amount of incinerated plastics in South Africa. Based on the HHV of PP (45 MJ/kg), the estimated amount of PP ending up at landfills could generate about 10 Terajoules of energy equivalent to 1,250 barrels of liquid fuel. More detailed flow of PP and other plastics in South Africa have been presented in Table 2.1.

2.3 Plastic Waste Management

Usage and discarding of plastic materials recently nonetheless has given rise to serious environmental concerns since they are not easily biodegradable (Marcilla *et al.*, 2003; Lin *et al.*, 2010; Papuga *et al.*, 2016). Also, a large percentage of plastics produced per annum are used in the manufacture of mainly disposable packaging materials and/or other transitory products which are rejected within about 12 months of their production (see Appendix A) (Hopewell *et al.*, 2009). Due to the durability of the constituents of plastic materials, a huge amount of disposed plastic materials are accumulating in landfills and eventually in the ocean (Panda *et al.*, 2010; Hopewell *et al.*, 2009). Plastics SA reported that, primary recycling (a commonly used recycling technique) of plastics more specifically PP, is problematic since plastic wastes are mostly contaminated with other non-plastic wastes which makes recycling challenging. Pyrolysis, a tertiary recycling technique, tends to be a promising route for recycling plastic materials which are not compatible with primary recycling (Siddiqui & Redhwi, 2009; Rashid & Sarker, 2013). Plastic pyrolysis, yields products composed of mainly hydrocarbon mixtures which can be used as alternate heating/energy sources or as petrochemical feedstock (Low *et al.*, 2001; Wang *et al.*, 2015). Pyrolysis has the following advantages over conventional primary recycling techniques (Low *et al.*, 2001; Miranda, *et al.*, 2001; Scheirs, 2006; Almeida & Marques, 2016);

- i. Its ability to recycle waste commingled plastics which are difficult to be recycled mechanically.
- ii. It can handle to some extent the recycling of unwashed and dirty plastics such as agricultural plastic wastes.

- iii. It allows to a degree, the recycling of plastic laminates, coextrusions as well as multilayer packaging films especially aluminium foil layers which are not easily recycled via the conventional mechanical recycling methods.

2.4 Pyrolysis and factors influencing plastics pyrolysis

Products obtained from the pyrolysis of plastics are mainly composed of volatiles with relatively little amount of char (Walendziewski, 2006; Xingzhong, 2006). The volatile composition is made up of a condensable fraction and a non-condensable gaseous stream (Scheirs, 2006; Williams, 2006). The condensable fraction can be either in the form of oil or wax depending on the reaction conditions and type of plastic material (Hajekova & Bajus, 2005; Scheirs, 2006; Williams, 2006; Gao, 2010). The relative proportion of each product (char, oil and gases) depends on the chemical composition of polymer fed, as well as operating conditions of the pyrolysis process (Buekens, 2006; Jung & Fontana, 2006; Thorat *et al.*, 2013). The mechanism of the degradation of a solid fuel via pyrolysis is shown in Figure 2.1. The solid residue at the end of the conversion is referred as char. As observed from the figure, applying heat in an inert environment to a solid fuel (plastic in this case) sparks the devolatilization of the fuel accompanied with the release of volatiles. Solid residue that remain at the end of the reaction is referred to as the char (negligible amounts are usually obtained from plastics pyrolysis).

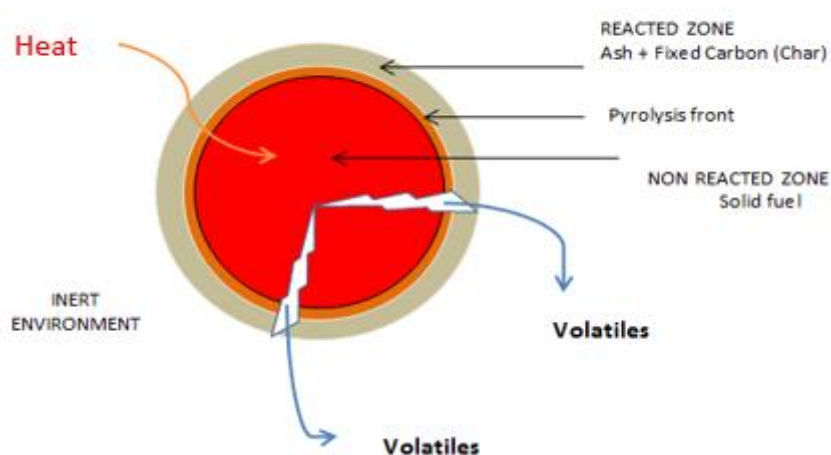


Figure 2.1. Mechanism of Pyrolysis of a solid fuel (Redrawn from Zajec, 2009)

Several factors affect the product stream of all plastics pyrolysis. These include but not limited to; chemical composition of plastic material, pyrolysis temperature, heating rate, solid and vapour residence time (also affected by whether vacuum is applied to the system or not) and operating pressure (Buekens, 2006; Sharrudin *et al.*, 2016; Williams, 2006). These are discussed below. Detailed effects of temperature and heating rate on PP pyrolysis are however discussed in section 2.6.2.

2.4.1 Chemical composition of plastic material

Primary products of pyrolysis are directly related to the chemical structure of the feed polymer. Functional side groups present in polymers as well as the branched structures have substantial effects on the pyrolysis product distribution (Gao, 2010; Scheirs, 2006). Example, the pyrolysis of polystyrene (PS) and condensation polymers such as PET and polyamides, results in the formation of mainly derived compounds of their respective monomer units (styrene for PS and benzoic acid for PET) due to the aromatic ring stability (Karaduman *et al.*, 2001; Scheirs, 2006; Gao, 2010). Also, condensable products generated from PP contains mainly hydrocarbons that are similar to the molecular skeleton of PP (Scheirs, 2006). Practically, waste plastics are contaminated with other materials which may also alter the products obtained from their pyrolysis (Ciliz *et al.*, 2004; Gao, 2010; Adrados *et al.*, 2012).

2.4.2 Temperature and Heating rate

Temperature is the most significant operating parameter in pyrolysis as it dictates the feedstock stability, thermal decomposition rate, as well as reaction products (Buekens, 2006; Scheirs, 2006; Lu *et al.*, 2015; Sharuddin *et al.*, 2016). Conversion temperatures varies with different types of plastics and desired product compositions. Generally, at temperatures above 500 °C, products are mainly composed of mixed fuel gases such as methane and other light hydrocarbons. Thus, increase in temperature increases the yield of gaseous products and light hydrocarbons (C₁-C₆) and decreases the yield of heavy hydrocarbons (C₂₁-C₃₀) (Xingzhong, 2006; Almeida & Marques, 2016). Also, high pyrolysis temperatures of plastics favour the production of stable aromatic compounds (Predel & Kaminsky, 2000; Jung *et al.*, 2010; Obeid *et al.*, 2014; Miandad *et al.*, 2016a). High temperature means high reactivity and recombination until a stable compound is produced. These trends are evident in the work conducted by Jung *et al.*, (2010) when they pyrolysed PP within the temperature range, 668-746 °C in a fluidised bed reactor. They observed a drastic decrease in oil yield from about 43

wt.% to 30 wt.% and a corresponding increase in the yield of permanent gases from about 50 wt.% to 66 wt.% when temperature advanced from 668 to 746 °C. Also, aromatic fractions in the oils recovered increased sharply from about 22 wt.% to 97 wt.% for the same temperature range. They also experienced equivalent trends when PE was pyrolysed under the same set of conditions. Similar conclusion was also drawn by Demirbas, (2004) when he pyrolysed a mixture of PE, PP and PS in a stainless steel batch reactor. For all plastic materials, temperature range for optimising the production of liquid products was reported to be in the range 300 - 500 °C whereas temperatures above 500 °C favoured the production of permanent gases (Buekens, 2006; Xingzhong, 2006; Sharuddin, 2016).

2.4.3 Heating rate

Heating rate is also another thermodynamic variable that influences pyrolysis. It is defined in this context of study as the increase in sample temperature per unit of time. Generally, high heating rates augment bond cleavage which facilitates the production of light molecular weight products (Buekens, 2006). In continuous pyrolysis processes, heating rate can be high up to 10,000 °C/min (Gao, 2010; Jung & Fontana, 2006). In slow pyrolysis systems, sample is heated from ambient temperature to the final pyrolysis temperature at a fixed heating rate usually controlled by a programmable temperature controller (Williams & Williams, 1999a; Gao, 2010). Heating rate for such processes is relatively low and ranges between 10 – 100 °C/min (Miranda *et al.*, 2001; Jung & Fontana, 2006; Williams & Williams, 1997b).

2.4.4 Residence Time

Residence time can be found in literature, to describe either vapour residence time or solid residence time in the hot part of the reactor. Solid residence time is defined as the amount of time that solid particles spend in the reactor until they are removed (Gao, 2010; Sharuddin *et al.*, 2016). Vapour residence time is the time spent by vapour products from the time they are produced till the time they exit the reactor. Longer vapour residence time, especially at higher pyrolysis temperatures above 500 °C, favours the cracking of primary products into much more thermally stable light molecular mass hydrocarbons, non-condensable gases and aromatics (Gao, 2010; Arena & Mastellone, 2006; Buekens, 2006; Encinar & González, 2008; Sharuddin *et al.*, 2016; Al-Salem *et al.*, 2017).

2.4.5 Pressure

Most pyrolysis experiments reported in literature were conducted under atmospheric conditions (Al-Salem *et al.*, 2017). Pyrolysis processes can however be conducted under vacuum (below atmospheric pressure), atmospheric or above atmospheric pressure conditions (Pinto *et al.*, 1999; Bilgesü *et al.*, 2006; Williams & Slaney, 2007). Low pressure pyrolysis takes place under vacuum (below atmospheric pressure). Vacuum pyrolysis favours the production of primary products because primary products are quickly removed from the reactor once they are formed, preventing secondary reactions (Miranda *et al.*, 2001a; Karaduman *et al.*, 2003; Li *et al.*, 2004).

2.5 Types of Pyrolysis

Based on the residence time and heating rate in the course of a pyrolysis process, pyrolysis may be categorised as slow, intermediate, fast and vacuum (Gao, 2010). The difference between these processes can be ambiguous and technologies must be defined based on the operating conditions. General definitions of these processes are highlighted below.

2.5.1 Slow Pyrolysis

Slow pyrolysis is characterised by relatively low heating rates, which can be up to but normally below 100 °C/min (Mašek *et al.*, 2016; Williams, 2006; Gao, 2010). In slow pyrolysis processes, feedstock materials are heated progressively from ambient temperature to the desired final temperature (Williams & Williams, 1999; Gao, 2010). Slow pyrolysis usually occurs at temperatures up to 600°C (Williams, 2006) with relatively a longer vapour residence time of few minutes.

2.5.2 Fast Pyrolysis

It usually occurs at temperatures between 500 - 950 °C with rapid heating rate, up to 10,000 °C/min (about 167 °C/s) (Zajec, 2009; Gao, 2010). It also operates under a very short hot volatile residence time, usually less than 1 second with rapid quenching or cooling which leads to the formation of mainly condensable products (Williams, 2006). To sustain the high heating rates in fast pyrolysis, the feedstock needs to be reduced to very small particle sizes normally lower than a few millimetres (Mašek *et al.*, 2016). Keeping the vapour residence time below a few seconds is a key feature of fast pyrolysis, aided by the rapid cooling hence preventing secondary vapour phase decomposition reactions (Jung & Fontana, 2006).

2.5.3 Intermediate Pyrolysis

Intermediate pyrolysis fits between slow and fast pyrolysis. It therefore has a product yield distribution between those typical for fast and slow pyrolysis (Mašek *et al.*, 2016). Intermediate pyrolysis can combine some of the advantages of fast (high yield of liquid products) and slow pyrolysis (ability to use larger particles of feedstock) (Mašek *et al.*, 2016). It happens to be the most recent development in pyrolysis and a number of different technologies have been implemented (Hornung and Seifert, 2006; Henrich *et al.*, 2007; Mašek *et al.*, 2016).

2.5.4 Vacuum Pyrolysis

Vacuum pyrolysis is a comparatively new technique of pyrolysis suitable for biomass, waste plastics, waste tyres and sewage sludge conversion (Rabe, 2005; Lopez *et al.*, 2010). In vacuum pyrolysis, feedstock is thermally disintegrated below atmospheric pressure as low as 2 kPa, absolute (Miranda *et al.*, 2001). The vacuum suction quickly removes vapour products from the reaction chamber reducing the vapour residence time in the process and also minimising secondary reactions (Rabe, 2005; Encinar & González, 2008). This is believed to limit the formation of carbon residue and promotes oil yield.

2.6 Review on PP pyrolysis

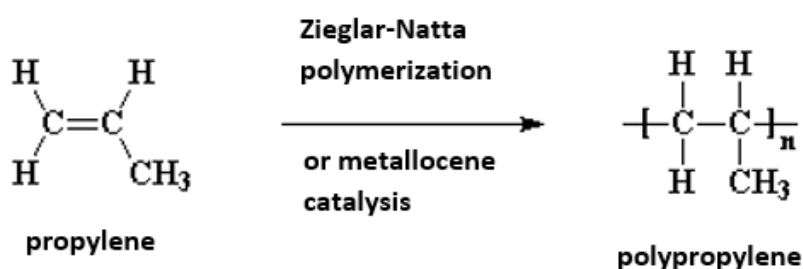


Figure 2.2. Formation of polypropylene polymer from propylene monomer (Adapted from; Polymer Science Learning Centre, 2016)

Polypropylene (PP) is generated by the polymerization of propylene monomers into lengthy chain polymer molecules. Several routes exist towards the polymerization of propylene monomers into PP. However, majority of commercially used PP are manufactured with

catalysts which gives them their semi crystalline characteristic (Kissel *et al.*, 1999; Zorriquetta, 2006). Formation of PP from its monomers is illustrated in Figure 2.2.

2.6.1 Physical Properties of Polypropylene (PP)

Polypropylene is one of the lightest thermoplastic materials with a density ranging between 0.85 - 1.3 g/cm³ (Lin & Yen, 2005; Kaminsky & Zorriquetta, 2007; Gao, 2010; Arabiourrutia *et al.*, 2012; Lu *et al.*, 2015; Wang *et al.*, 2015) and melting point ranging between 150 - 170 °C (Beyler & Hirschler, 2001; Kaminsky & Zorriquetta, 2007; Achilias *et al.*, 2008; Gao, 2010; Lu *et al.*, 2015; Wang *et al.*, 2015; Das & Tiwari, 2018). Higher Heating Value of PP has also been reported to be around 45 MJ/kg (Sorum *et al.*, 2001; Arabiourrutia *et al.*, 2012). The different values of the physical properties reported in literature could be attributed to the different types of PP that might have been used and also the degree of additives or contamination (Lin & Yen, 2005; Yan *et al.*, 2015). Polypropylene has become a significant component of mixed plastic waste stream in recent years due to the exponential increase in the quantity of municipal solid waste (MSW) and with pyrolysis identified as a promising option to managing waste plastic mixtures, the pyrolysis of PP into useful fuel oil is considered in this study.

2.6.2 Pyrolysis of Polypropylene (PP)

2.6.2.1 Thermogravimetric degradation of PP

Table 2.2. Thermal decomposition of PP in TGA experiments

Heating Rate (°C/min)	Degradation temperature Range (°C)	Maximum decomposition temperature (°C)	Carrier gas	References
5	337 - 450	434	Argon	(Chan & Balke, 1997)
5	300 - 500	440	Nitrogen	(Jung <i>et al.</i> , 2010)
5	340 - 481	456	Argon	(Gersten <i>et al.</i> , 2000)

Heating Rate (°C/min)	Degradation temperature Range (°C)	Maximum decomposition temperature (°C)	Carrier gas	References
10	354 - 489	469	Argon	(Gersten <i>et al.</i> , 2000)
10	350 - 500	440	Vacuum	(Miranda <i>et al.</i> , 2001b)
10	400 - 450	500	Nitrogen	(Jung <i>et al.</i> , 2010)
10	400 - 500	455	Nitrogen	(Lee & Shin, 2007)
10*	407 - 458	427	Nitrogen	(Ciliz <i>et al.</i> , 2004)
10**	423 - 472	458	Nitrogen	(Ciliz <i>et al.</i> , 2004)
15	371 - 394	477	Argon	(Gersten <i>et al.</i> , 2000)
20	387- 497	472	Argon	(Chan & Balke, 1997)
20	400 - 525	500	Nitrogen	(Jung <i>et al.</i> , 2010)

*Waste PP **Pure PP

The mechanism of thermal degradation of plastic materials is quite complex (Encinar & González, 2008). Thermogravimetric analysis (TGA) is extensively considered as a very important technique in studying the decomposition processes of solid materials. It can be defined as the measurement of the weight change of a material with the increase of time and temperature. A lot of TGA experiments have been performed on PP under various conditions to assess its thermal behaviour.

Table 2.2 shows some thermal degradation behaviour of PP at various conditions. From the table, it was observed that generally, degradation of PP can begin at temperatures as low as 300 °C and end at about 525 °C. Temperature at which maximum decomposition occurs, also ranged from about 430 - 500 °C. It was also detected that, high heating rates increased the maximum degradation temperature, as can be seen with the experiments performed by Gersten *et al.*, (1997) and Jung *et al.*, (2010). An indication that higher heating rates enhances faster degradation of PP. Single peak temperatures recorded for all data generated signifies that PP degradation is a single-step process. Ciliz *et al.*, (2004), also studied the thermal behaviour of waste and pure PP. They observed that thermogravimetric onset temperature for waste PP was lower than for uncontaminated/pure which could be as a result of impurities interfering with the thermal degradation of PP.

The varying temperature degradation behaviour observed by the various studies was corroborated to the different grades of PP utilised. For instance, Jung *et al.*, (2010) used waste PP for their studies whereas Gersten *et al.*, (1997) and Ciliz *et al.*, (2004) used different grades of virgin PP (E-50-E and MH418 respectively) with obviously varying proportions of additives.

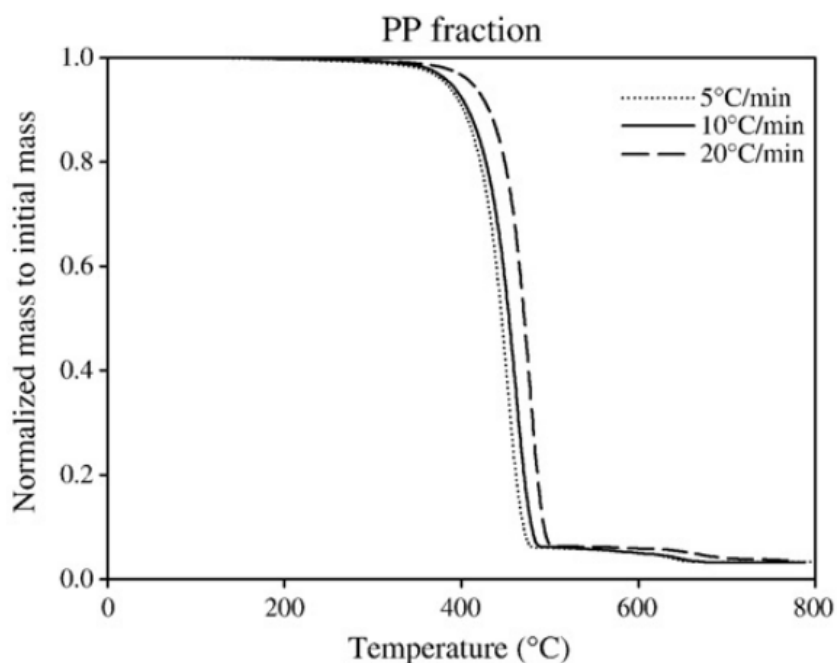


Figure 2.3. TGA curves for PP degradation at heating rates of 5, 10 and 20 °C/min (Reproduced from Jung *et al.*, 2010 with permission from Elsevier)

Typical TGA and DTG curves of PP as obtained by Jung *et al.*, (2010) were represented in Figure 2.3 and Figure 2.4. Tests were conducted at three different heating rates (5, 10 and 20 °C/min) and a final temperature of 800 °C. As highlighted earlier, it was observed from both figures that degradation of PP at all heating rates started at around 400 °C and was virtually complete at 500 °C. It was also noticed that degradation experiments conducted at higher heating rates resulted in slightly higher maximum degradation temperatures (as clearly observed in DTG curves) which is an indication of enhanced thermal degradation of PP at higher heating rates.

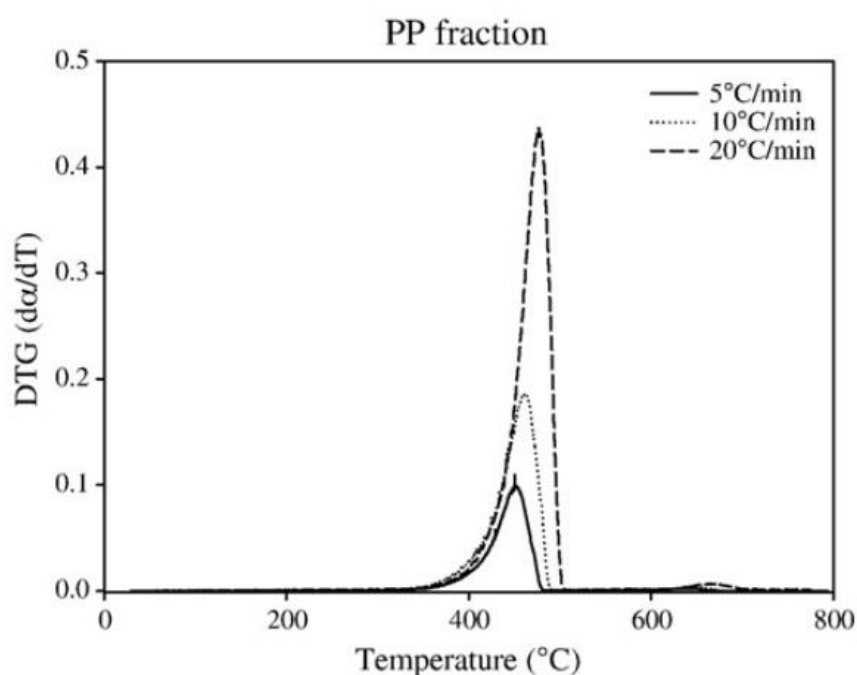


Figure 2.4. DTG curves for PP degradation at heating rates of 5, 10 and 20 °C/min (Reproduced from Jung *et al.*, 2010 with permission from Elsevier)

2.6.2.2 Effects of temperature and heating rate on PP pyrolysis products

Pyrolysis of PP plastics is usually aimed at yielding maximum oil fraction, which preferably should exhibit properties of conventional liquid fuels. The major influencing factors identified from literature are temperature, heating rate and pressure (atmospheric and vacuum). A review on the effects of temperature, heating rate and other key process parameters on product distribution for PP pyrolysis in various process systems have been presented in Table 2.3 and Table 2.4 respectively with focus on condensable fractions (oil and wax). Also, a statistical model was fitted on data gathered from literature to ascertain the effects of

temperature and heating rate on the distribution of condensable products (oil/wax). This followed similar analysis performed on literature data by Neves *et al.*, (2011).

Temperature

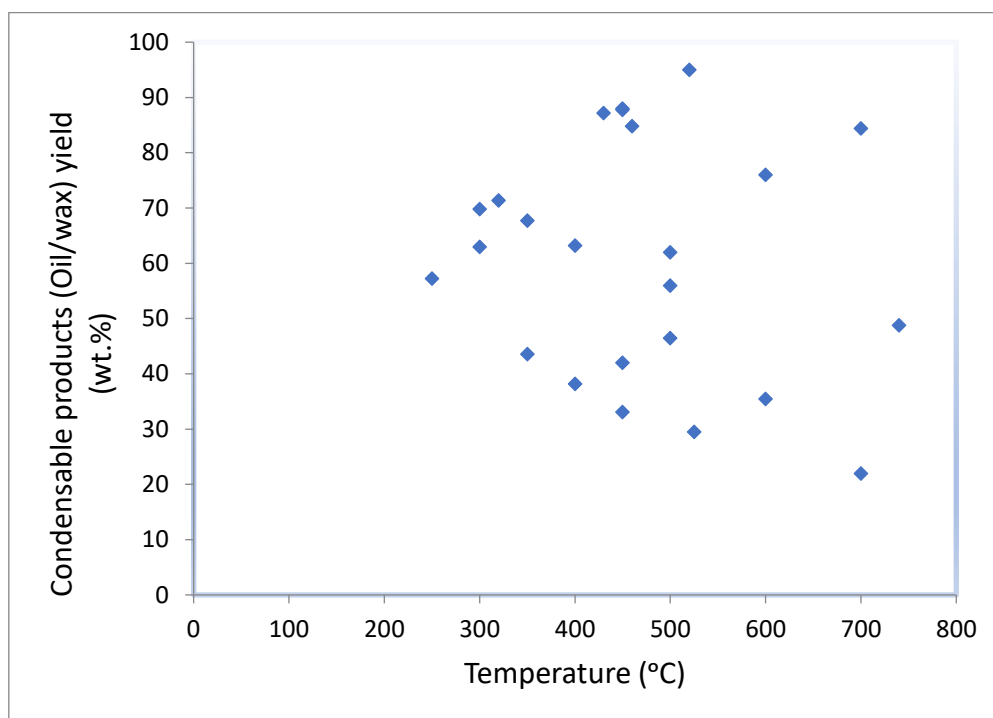


Figure 2.5. Empirical model depicting the effects of temperature on condensable product (oil/wax) yield for slow pyrolysis of PP – Data points from; [Williams & Williams, (1997b), Hájeková & Bajus, (2005), Takuma *et al.*, (2001), Yan *et al.*, (2015), Zhou *et al.*, (2004), Ciliz *et al.*, (2004), Miandad *et al.*, (2016), Uçar, *et al.*, (2016), Heydariaraghi *et al.*, (2016), Koderá *et al.*, (2006), Miskolczi *et al.*, (2009), Ahmad *et al.*, (2015), Lu *et al.*, (2015), Kaminsky & Zorriquetá, (2007) and Demirbas, (2004)]

From the literature data presented in Table 2.3, an empirical model was generated to predict the effects of temperature on condensable products (oil/wax) yield from the slow pyrolysis of PP in batch reactors. The model, represented in Figure 2.5 was generated according to results gathered from the following authors; Williams & Williams, (1997b), Hájeková & Bajus, (2005), Takuma *et al.*, (2001), Yan *et al.*, (2015), Zhou *et al.*, (2004), Ciliz *et al.*, (2004), Miandad *et al.*, (2016), Uçar, *et al.*, (2016), Heydariaraghi *et al.*, (2016), Koderá *et al.*, (2006), Miskolczi *et al.*, (2009), Ahmad *et al.*, (2015), Lu *et al.*, (2015), Kaminsky & Zorriquetá, (2007) and Demirbas, (2004). From the figure, it was observed that correlation between temperature

and yields of condensable products was weak and did not follow any specific trend. This was blamed on the different reactor configurations and process systems used by the various authors. It was however observed that minimum condensable products yield of about 58 - 60 wt.% was obtained in the temperature region of 250 - 300 °C. Peak yields then spanned between 88 - 95 wt.%, obtained in the temperature range of 450 - 500 °C. Temperatures beyond 500 °C saw a general decrease in yields. From the trends, maximum condensable products yield temperature was deduced to be in the region of around 400 - 500 °C. It was also inferred that temperatures beyond 500 °C promoted secondary cracking reactions which lead to the decrease in yields of condensable products.

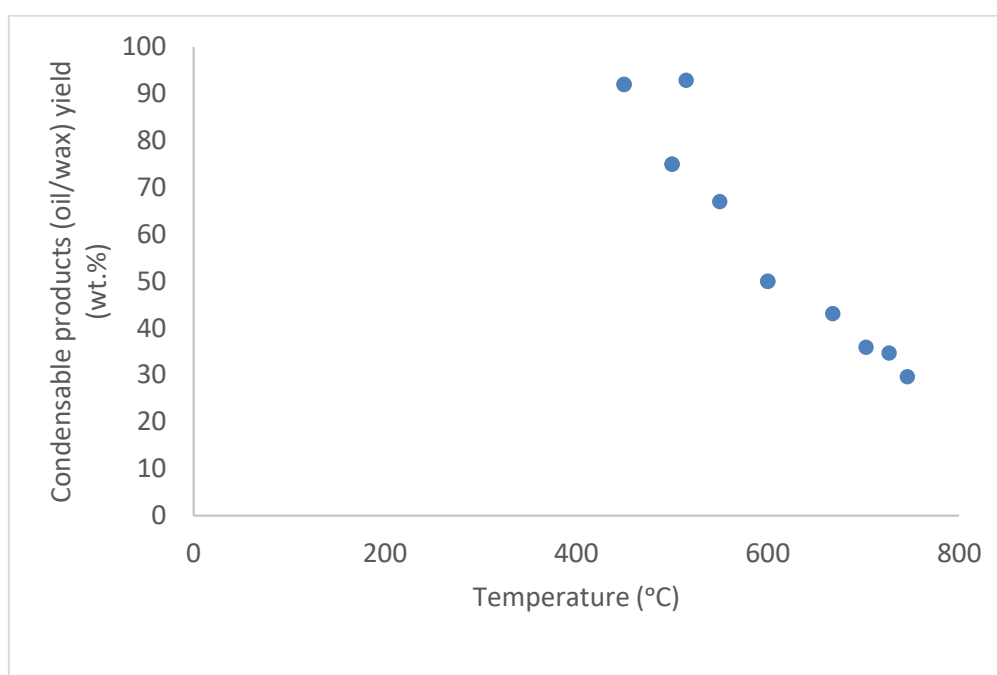


Figure 2.6. Empirical model depicting the effects of temperature on condensable product (oil/wax) yield for fast pyrolysis of PP – Data retrieved from; [Jung *et al.*, (2010), Predel & Kaminsky, (2000) Aguado *et al.*, (2002) and Arabiourrutia *et al.*, (2012)]

Another model was generated to establish the effects of temperature on condensable products (oil/wax) yield for fast pyrolysis of PP (in fluidised bed reactors). The data for this model were retrieved from Jung *et al.*, (2010), Predel & Kaminsky, (2000) Aguado *et al.*, (2002) and Arabiourrutia *et al.*, (2012) all in Table 2.4 and presented in Figure 2.6. From the figure, it was observed that condensable products yield decreased sharply from about 95 to 25 wt.% as temperature progressed from around 450 to 750 °C. This observation showed that at comparatively higher temperatures and faster heating rates, rigorous secondary cracking

reactions occur. The cracking reactions then favour the production of permanent gases and suppresses condensable products yield. The correlation between temperature and oil yield in this instance was very strong as a trend could be observed. The strong correlation is attributed to majority of the data coming from same reactor.

In conclusion, it was observed that condensable products yield for batch pyrolysis of PP under atmospheric pressure conditions generally rose as temperature increased to a point in the region of 450 - 500 °C, after which a further increase of temperature initiates secondary reactions which results in the decrease of condensable products yield and production of more permanent gases. It was also deduced that higher pyrolysis temperatures (above 500 °C) at faster heating rates (above 100 °C) enhances secondary cracking reactions which suppresses the production of condensable products.

Heating rate

Information on heating rate of PP pyrolysis in literature is quite ambiguous. For instance, under batch scale pyrolysis, most of the information on heating rate available were reported in different reactor configurations which made comparison difficult. It was also observed that almost all of these tests were performed under slow heating rates ranging between 5 - 25 °C/min. Moreover, those who varied the heating rate in batch reactors investigated narrow ranges of heating rates which resulted in insignificant trends. Most fast heating rates reported were carried out in fluidised bed reactors which is covered in the previous section under temperature. Therefore, to establish a trend on the effects of heating rate on condensable products yield for batch reactors, all the heating rates reported were collected and fitted to a model. These data points were retrieved from results reported by; Hájeková & Bajus, (2005), Yan *et al.*, (2015), Ciliz *et al.*, (2004), Miandad *et al.*, (2016), Uçar, *et al.*, (2016), Heydariaraghi *et al.*, (2016), (Fakhrhoseini & Dastanian, 2013), Encinar & González, (2008), Demirbas, (2004) and Miranda *et al.*, (2001) all available in Table 2.3. From the model represented in Figure 2.7, it was observed that as heating rate progressed from 5 to 25 °C, yield of condensable products remained virtually constant and did not vary significantly which was corroborated to the rather narrow range of heating rate gathered. However, Lu *et al.*, (2015) who performed their tests in a pre-heated batch reactor however observed a drastic decrease in oil yield from

about 63 to 33 wt.% with the rise of temperature (heating rate in effect). They however did not report the value of the heating rate used.

It was therefore concluded that, narrow ranges of slow heating rate for batch scale pyrolysis of PP had no significant effect on condensable products yield. However, pre-heated batch scale reactors promoted the rapid degradation of PP with this becoming more pronounced at higher temperatures. Similar observations were also made for fluidised bed reactors which substantiates the fact that for pre-heated reactor systems, increase of temperature also means increase in heating rate. Since the effects of wider range of heating rate for batch scale pyrolysis of PP is not entirely addressed in literature, it is worth investigating.

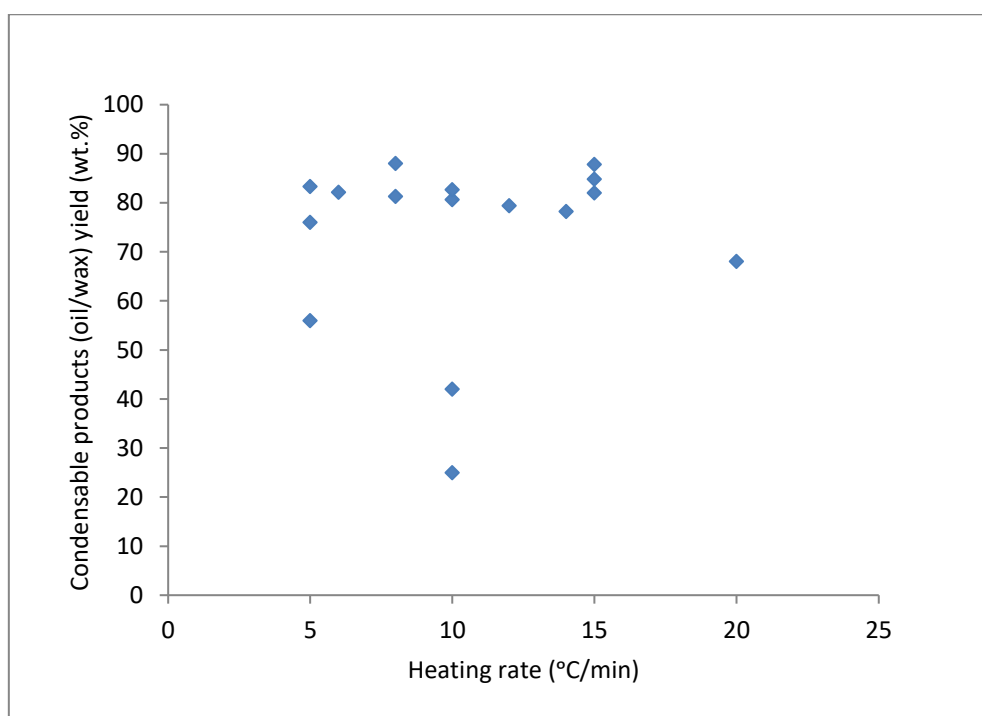


Figure 2.7. Empirical model depicting the effects of heating rate on condensable product (oil/wax) yield for batch scale pyrolysis of PP – Data retrieved from [Hájeková & Bajus, (2005) Yan *et al.*, (2015), (Ciliz *et al.*, 2004), Miandad *et al.*, (2016), Uçar, *et al.*, (2016), Heydariaraghi *et al.*, (2016), (Fakhrhoseini & Dastanian, 2013), Encinar & González, (2008) Demirbas, (2004) and (Miranda *et al.*, 2001)]

2.6.2.3 Vacuum pyrolysis of PP

As mentioned in section 1.2, plastics pyrolysis under vacuum received very little attention as compared to biomass, with virtually nothing reported on how the variation of temperature

and heating rate affects products yield and quality from PP pyrolysis under vacuum conditions. Following literature survey, only Miranda *et al.*, (2001) was found to investigate PP pyrolysis under vacuum. Their test was however conducted at only a single condition of temperature and heating rate. Parameters surrounding their tests are presented in Table 2.3. From the data, they pyrolysed PP at 500 °C temperature and a heating rate of 10 °C/min in a batch reactor under a vacuum pressure of 2 kPa, absolute. Following this, they obtained a combined condensable fraction yield of 95 wt.% of which 70 wt.% was recovered as wax and the remaining 20 wt.% as free-flowing oil. A permanent gas yield of about 3.5 wt.% was recovered with the remaining fraction being char. Comparing the results they obtained to similar conditions under atmospheric pyrolysis as observed with Uçar *et al.*, (2016) and Fakhrhoseini & Dastanian (2013), it was noticed that vacuum conditions generated higher yields of condensable products (oil/wax) with additional yield of up to about 15% observed. This was attributed to the short vapour residence time as a result of quick extraction of volatiles from the hot reactor zone by the vacuum pump, which minimised secondary cracking reactions known to favour the production of permanent gases over condensable products. Following the interesting trend observed for vacuum and the fact that investigation of how process parameters affect products yield and quality for PP pyrolysis is hardly covered in literature, it warrants attention.

Table 2.3. Summary on the effects of temperature, heating rate and other key parameters on product distribution in the thermal pyrolysis of PP (batch reactors)

						Yields (wt.%)			
References	Reactor type	Temperature (°C)	Heating Rate (°C/min)	Vapour residence time (s)	Pressure	Gas	Oil	Wax	Residue
Williams & Williams, (1997b)	Fixed bed, batch	700	N/A	25	Atm.	13.6	84.4	N/A	0.15
Hájeková & Bajus, (2005)	Stainless steel batch	450	15	N/A		11	87.8 (oil + wax)	N/A	1.2
Takuma <i>et al.</i> , (2001)	Fixed bed, tubular flow	525	N/A	N/A		10.5	29.5	60	0.1
(Yan et al., 2015)	Fixed bed, batch	460	15	16		13.7	84.8 (oil + wax)	N/A	1.5
Zhou, <i>et al.</i> , (2004)	Fixed bed, batch	430	N/A	13		9.3	87.2	N/A	3.5
Ciliz <i>et al.</i> , (2004)	Fixed bed, batch	600	5	N/A		11	76	N/A	13
Miandad <i>et al.</i> , (2016)	Fixed bed, batch	450	10	N/A		54.5	42	0	3.5
Uçar <i>et al.</i> , (2016)	Fixed bed, batch	500	5	N/A		13	56	30	1
Heydariaraghi <i>et al.</i> , (2016)	Stirred reactor, batch	450	8	N/A		11	88	N/A	1
Kodera <i>et al.</i> , (2006)	Screw kiln, continuous	500	N/A	N/A		6.1	46.5	N/A	2
		600	N/A	N/A		22.5	35.5	N/A	3
		700	N/A	N/A		78	22	N/A	1
Miskolczi <i>et al.</i> , (2009)	Horizontal tube, continuous	520	N/A	N/A		5	95 (oil + wax)	N/A	N/A
(Fakhrhoseini & Dastanian, 2013)	Batch	500	6	N/A		17.76	82.12	N/A	0.12
			8			18.68	81.32		0.09
			10			19.28	80.65		0.07
			12			20.55	79.41		0.04
			14			21.74	78.26		0.00
Encinar & González, (2008)	Cylindrical Stainless-steel	800	5	N/A		16.55	83.34 (oil + wax)	N/A	0.11
			10		17.2	82.67 (oil + wax)	0.13		
			15		17.88	82.02 (oil + wax)	0.1		
			20		31.84	68.06 (oil + wax)	0.1		
Ahmad <i>et al.</i> , (2015)	Batch	250	N/A	N/A	29.05	57.27	N/A	13.68	
		300			28.04	69.82		1.34	
		350			30	67.74		1.56	
		400			31.07	63.23		5.7	
Lu <i>et al.</i> , (2015)	Ceramic batch	300	Pre-heated reactor	N/A	19	63	N/A	18	
		320			19	71.4		9.6	
		350			52.4	43.6		4	
		400			56.1	38.2		5.7	
		450			66.7	33.1		0.2	
(Kaminsky & Zorriqueta, 2007)	Batch	500	N/A	N/A	20	62	18	1	
Demirbas, (2004)	Batch	740	10	N/A	49.6	48.8	N/A	1.6	
Miranda <i>et al.</i> , (2001)	Batch	500	10	N/A	Vacuum (2 kPa, abs.)	3.5	25	70	0.01

N/A – Not reported

Table 2.4. Influence of temperature and other key parameters in product distribution of fast PP pyrolysis in Fluidised bed reactors

		<div>Stellenbosch University https://scholar.sun.ac.za</div> <div><i>Yields (wt.%)</i></div>							
References	Reactor type	Temperature (°C)	Heating Rate (°C/min)	Vapour residence time (s)	Pressure	Gas	Oil	Wax	Residue
Jung <i>et al.</i> , (2010)	Fluidised bed	668	N/A	N/A	Atm.	54.4	43.1	N/A	2
		703				57	35.9		6.9
		727				61.7	34.7		3.1
		746				65.9	29.6		4
Predel & Kaminsky, (2000)	Continuous fluidised bed	515	N/A	5.6		6.8	36.7	56.2	0.26
Aguado <i>et al.</i> , (2002)	Conical Spouted bed	450	N/A	<1		8	N/A	92	N/A
		500				25		75	
		550				33		67	
		600				50		50	
Arabiourrutia <i>et al.</i> , (2012)	Conical Spouted bed	450	N/A	<1		8	N/A	92	N/A
		500				25		75	
		600				50		50	

N/A – Not reported

2.6.3 Condensable products of PP pyrolysis

Production of fuels and chemicals via the pyrolysis of polyolefins appears to be a promising way of plastics recycling (Wang *et al.*, 2015). The calorific value of polypropylene is around 45 MJ/kg which is greater than that of fuel oil (41 MJ/kg) and high-quality coal, 29 MJ/kg (Miskolczi, *et al.*, 2009). Production of liquid fuels via PP pyrolysis can therefore be seen as having a very significant potential.

Condensable products from PP pyrolysis either come in the form of oil or wax. The oil products are chiefly hydrocarbons with carbon number distributions falling in the range, C₅-C₂₀ whereas waxes are composed with higher amounts of long chain hydrocarbons with carbon number distribution greater than C₂₀ (Lopez *et al.*, 2017). The product distribution of these condensable fractions however depends on process parameters; reactor design, temperature, heating rate, residence time and pressure (vacuum). Oils and waxes obtained from PP pyrolysis are essentially made up of aliphatics (paraffins, naphthenes and olefins) and aromatics (Pinto *et al.*, 1999; Demirbas, 2004; Miskolczi *et al.*, 2006; Lee & Shin, 2007). Oil and waxes are mostly reported in literature as one fraction because liquid hydrocarbons are usually dissolved in waxes or the other way around where waxes are dissolved in liquid hydrocarbons. This sometimes brings some ambiguity when comparing literature results (Lopez *et al.*, 2017). Distribution of aliphatic & aromatic hydrocarbons and boiling points of oils obtained from PP pyrolysis have been summarised in Table 2.5 and Table 2.6 respectively.

Ahmad *et al.*, (2015) characterised the oils generated at optimum oil yield temperature of 300 °C of PP pyrolysis. Paraffins, olefins and naphthenic yields observed, were 66, 25 and 7% respectively. No aromatic compounds were produced. Also, the oil obtained was enriched in diesel range hydrocarbons, forming about 46% of the oil fraction, with gasoline range hydrocarbons being 15%. The remaining fractions fell in the wax range. Sakata *et al.*, (1999) also analysed the oils generated from the batch pyrolysis of PP at 380 °C but did not analyse the hydrocarbon types present. They however performed a simulated distillation to group the hydrocarbons present into diesel and gasoline. Simulated distillation is a chromatographic technique which correlates retention times of hydrocarbons from a GC/MS spectrum with boiling points of the same compounds. They concluded that, diesel fractions (56 wt.%) dominated the oil products. The remaining 43 wt.% was found to be gasoline range compounds. From the simulated distillation conducted, they also concluded that boiling point

of oil fell in the range, 36 to 405 °C. Demirbas, (2004) studied the composition of products obtained from PP pyrolysis at different temperatures. It was observed that with an increase in the pyrolysis temperature from 402 to 602 °C, naphthenic and aromatic products increased from 21.5 to 23.5 wt.% and 1.4 to 10.2 wt.% respectively. The increase in aromatic yield was attributed to secondary reactions such as cyclisation and aromatisation of primary products (olefins and paraffins). This is evident in the corresponding decrease in paraffinic and olefinic yields as temperature increased. Bockhorn *et al.*, (1999), studied the pyrolysis of PP in a special type of continuous stirred batch reactor, named the gradient free reactor, at a temperature of 460 °C and recorded an oil composed of 7.6 wt.% and 92.5 wt.% of paraffins and olefins respectively. Furthermore, Pinto *et al.*, (1999), investigated the oil products generated from the thermal pyrolysis of PP in an autoclave at 450 °C. The liquid products comprised of 58 wt.% paraffins, 33 wt.% olefins and 8 wt.% aromatics. Yan *et al.*, (2015) neither reported fractions of hydrocarbons present in their oils however, they grouped the carbon numbers into diesel and gasoline and reported the fractions to be 36 and 58% respectively. Uçar *et al.*, (2016) also reported 50 wt.% paraffins, 45 wt.% olefins and 5 wt.% aromatics as the fractions of hydrocarbons present in their oil when they pyrolysed PP at 500 °C. Predel & Kaminsky, (2000) reported fractions of paraffins, olefins, naphthenes and aromatics in their oil as 12.28, 63.02, 1.95 and 0.06 wt.% respectively when they pyrolysed PP at 515 °C in a fluidised bed reactor. They further reported the boiling point ranges of the oils as 25 to 300 °C. Ciliz, *et al.*, (2004) characterised oils recovered from waste PP pyrolysed at 600 °C and reported aliphatics (paraffins, naphthenes and alkenes) present in the oil to be 17 wt.% with aromatics being 83 wt.%. Miskolczi *et al.*, (2009), pyrolysed PP plastics in a pilot scale horizontal tube continuous reactor, at 520 °C temperature after which the hydrocarbon products obtained were separated via distillation into products, they called gasoline and light oils. Paraffin content contained in the light oil was 61.5 wt.%. Olefins detected was 38.1 wt.% with the remaining 0.4 wt.% being aromatics. The gasoline fraction also contained 59.9, 39.6 and 0.5 wt.% of paraffins, olefins and aromatics respectively. The concluded that the light oils had a boiling point range of 115 to 353 °C and gasoline, 23 to 216 °C. Finally, Kim & Kim, (2004) investigated the effects of heating rate on oil compositions at 500 °C in a stirred batch autoclave and reported that gasoline range hydrocarbons increased significantly as heating rate progressed from 0.5 to 1-2 °C/min. Although the heating rate range examined was narrow, slight decrease in diesel range compounds was observed for the same trend of

heating rate. These trends are evident because increase in heating rate together with temperature promotes cracking and hence increases the yields of light molecular weight compounds.

From the trends presented, it is observed that except for results reported by Bockhorn *et al.*, (1999) and Predel & Kaminsky, (2000), paraffins and naphthenes (alkanes) mostly dominate the oil/wax fractions generated from PP pyrolysis, followed closely by olefins, with aromatics being the least. It is also deduced that, very high pyrolysis temperatures of PP, 600 °C and above promoted the formation of aromatics. Similar conclusions were drawn by Jung *et al.*, (2010) and Westerhout *et al.*, 1998) when they examined PP pyrolysis at very high pyrolysis temperatures (600 to 800 °C). This has been explained as the secondary reactions of paraffins and olefins at elevated temperatures, forming aromatics in the process. The dominant olefinic fractions reported by Bockhorn *et al.*, (1999) and Predel & Kaminsky, (2000) could be corroborated to interaction effects of faster heating rates and fast vapour residence times which might have enhanced beta-scission reactions/intramolecular hydrogen transfer and the swift removal of the resulting alkenes from the reactor.

Furthermore, the carbon number distributions and boiling point ranges, presented in Table 2.6 for almost all the oils reported appear to fall within the ranges defined for both commercial diesel (180 - 380 °C) and gasoline (69 - 180 °C) from literature. The ranges reported stretch from naphtha to fuel oil which stipulates that oils derived from PP pyrolysis might contain compounds belonging to each of these fuels and hence need to be distilled or processed further to obtain pure diesel or gasoline. The boiling point ranges presented by Miskolczi *et al.*, (2009) is a clear indication that PP derived oils contain both diesel and gasoline range compounds, because they obtained two different products similar to diesel and gasoline following distillation of the PP oil. The oil they labelled gasoline had its boiling point range very similar to commercial gasoline and the oil they named light oil had very comparable characteristics in terms of boiling point to commercial diesel.

Table 2.5. Distribution of hydrocarbon types obtained from PP pyrolysis oil

References	Reactor type	Temperature (°C)	Heating rate (°C/min)	Vapour residence time (s)	Pressure	Hydrocarbon fractions (wt. %/ % area of oil)				
						Paraffins	Naphthenes	Olefins	Aromatics	Others
Demirbas, (2004)	batch	402	10	N/A	Atm.	30.40	21.50	44.70	1.40	2
		452				28.20	22.80	42.10	4.50	2.4
		527				24.90	24.40	39.50	2.60	2.6
		602				29.60	23.50	35.50	10.20	1.2
(Predel & Kaminsky, 2000)	Continuous fluidized bed	515	N/A	5.6		12.28	1.95	63.02	0.06	22.70
(Ahmad et al., 2015)*	batch	300	N/A	N/A		66.00	7.00	25.00	0.00	2.00
Pinto <i>et al.</i> , (1999)	Stirred batch autoclave	450	N/A	>20mins		58.00	N/A	33.00	8.00	1.00
Bockhorn <i>et al.</i> , (1999)	Gradient free reactor	460	Pre-heated reactor	N/A		7.60	N/A	92.5	0.00	N/A
Yan <i>et al.</i> , (2015)*	batch	460	15	16		N/A	N/A	N/A	N/A	N/A
Heydariaraghi <i>et al.</i> , (2016)	Stirred batch	450	5	N/A		N/A	N/A	N/A	N/A	N/A
Ciliz, <i>et al.</i> , (2004)*	Fixed bed batch	600	5	N/A		17			83.0	N/A
Kodera <i>et al.</i> , (2006)	Screw kiln, continuous	500	N/A	N/A		N/A	N/A	N/A	N/A	N/A
Uçar <i>et al.</i> , (2016)	Fixed bed, batch	500	5	N/A		50.00	N/A	45	5.00	N/A
Sakata <i>et al.</i> , (1999)*	batch	380	3	N/A		N/A	N/A	N/A	N/A	N/A
Miskolczi <i>et al.</i> , (2009), light oil *	Horizontal tube, continuous	520	N/A	N/A		61.50	N/A	38.10	0.40	N/A
Miskolczi <i>et al.</i> , (2009), gasoline *						59.90	N/A	39.60	0.50	N/A
(Kim & Kim, 2004)	Stirred batch autoclave	500	0.5	N/A		N/A	N/A	N/A	N/A	N/A
			1.0	N/A		N/A	N/A	N/A	N/A	
			2.0	N/A		N/A	N/A	N/A	N/A	

N/A – Not reported; * fractions that were reported in %area

Table 2.6. Carbon number distribution and boiling points of oils recovered from PP pyrolysis

References		Carbon number distribution (wt. %/ %area of oil)			Boiling point range (°C)
		C ₆ -C ₁₀ (Gasoline)	C ₁₁ -C ₂₃ (Diesel)	C ₂₃₊ (Wax)	
Ciliz, <i>et al.</i> , (2004)*		33.00	48.00	18	N/A
(Ahmad et al., 2015)*		15.16	46.03	24.97	N/A
Yan <i>et al.</i> , (2015)*		58.00	36.00	N/A	N/A
Pinto <i>et al.</i> , (1999)		N/A	N/A	N/A	35 - 265
Heydariaraghi <i>et al.</i> , (2016)		N/A	N/A	N/A	50 - 300
Kodera <i>et al.</i> , (2006)		N/A	N/A	N/A	55 - 300
Predel & Kaminsky, (2000)		65.41	34.59	N/A	25 - 300
Sakata <i>et al.</i> , (1999)*		43.00	56.00	N/A	36 - 405
Miskolczi <i>et al.</i> , (2009), light oil *		N/A	95.50	N/A	115 - 353
Miskolczi <i>et al.</i> , (2009), gasoline *		95.50	5.00	N/A	23 - 216
Kim & Kim, (2004)	0.5 °C/min	28.00	59.50	N/A	N/A
	1.0 °C/min	42.00	54.00	N/A	N/A
	2.0 °C/min	42.00	56.50	N/A	N/A

N/A-not reported; *fractions that were reported based on %area

2.7 Chemical composition and distillation behaviour of conventional liquid fuels

Chemical composition of diesel is not definite because over billions of different chemical compounds may be present (Bacha *et al.*, 2007). As a result, it is virtually impossible to characterise diesel for individual compounds (Speight, 2015). However, the large number of compounds present could be easily categorised into paraffins (alkanes), cycloparaffins (cycloalkanes/naphthenes), aromatics and olefins (unsaturated hydrocarbons) (Bacha *et al.*, 2007; Speight, 2015). A key variable which defines diesel is the boiling point range. Boiling point/Distillation range for a mixture of close boiling liquids can be defined as the temperature range over which this mixture exists in vapour liquid equilibrium at atmospheric pressure. Pure liquids have a single boiling point at a given pressure. For a multicomponent liquid mixture, there is no single boiling point to vaporize the complete mixture. Such mixtures have boiling points occurring over a range of temperature, which depends on the components involved, system pressure as well as affinity among the compounds. For such mixtures, the initial boiling point (IBP) at a given pressure is defined as the temperature value when the first bubble of vapour is formed from the liquid mixture. It depends on the mixture composition and pressure (Meks, 2015). Final boiling point (FBP) is defined as the temperature at which the first liquid drop appears in a vaporised mixture (Meks, 2015).

The boiling point range of diesel could be expressed in terms of its distillation temperature range or the corresponding hydrocarbons that get distilled in this temperature range. Distillation range is considered an important property for petroleum crude and its resultant fuel components, since it determines whether fuels possess suitable volatility (Hsu, 2000). Distillation of diesel which defines its boiling point typically falls within but not limited to the temperature range 180 - 380 °C. These temperature limits correspond to the boiling point of the C₁₀ (Decane) and C₂₃ (Tricosane) hydrocarbons respectively. Similarly, boiling point range of gasoline can be defined to be in the range 69 to 180 °C since the limits of the range correspond to C₆ (Hexane) and C₁₀ (Decane) respectively. These ranges are however not limited to the figures stated above and may overlap due to the different grades of diesel and gasoline fuels available. (Pinto *et al.*, 1999; Miskolczi *et al.*, 2006; Li *et al.*, 2004; Laresgoiti *et al.*, 2004; Bacha *et al.*, 2007; Heydariaraghi *et al.*, 2016).

2.7.1 Chemical composition of commercial diesel fuels

Todd *et al.*, (1999), reported the composition of a type of diesel as having mixtures of C₁₀-C₁₉ hydrocarbons with 64% being paraffinic hydrocarbons (straight chain alkanes and cycloalkanes), 1-2% unsaturated hydrocarbons (olefins) and 35% aromatic hydrocarbons. Liang *et al.*, (2005), studied the composition of conventional diesel fuel using Gas Chromatography/Mass Spectrometer (GC/MS). They concluded that diesel fuel contained 90% paraffinic hydrocarbons which included n-alkanes, iso-alkanes and cycloalkanes, no olefins, with the remaining 10% being aromatic hydrocarbons (alkylbenzenes, polyaromatic hydrocarbons and aromatic acids). They also inferred that branched and cyclic alkanes contained in the diesel fuel ranged between C₁₀-C₂₅. Pál *et al.*, (1998) analysed the hydrocarbon groups in diesel range petroleum fractions and concluded that diesel fuel ranged between C₁₁-C₂₃ hydrocarbons with n-alkanes being the prevailing fraction of the hydrocarbon groups. Similar range was also defined by Almeida & Marques, (2016), Yan *et al.*, (2015) and Syamsiro *et al.*, (2014).

Table 2.7. Paraffins, Olefins and Aromatic fractions in different grades of diesel fuel (Adapted from Sjogren *et al.*, 1995)

Type of hydrocarbon	Diesel Fuel Grades										Avg.
	D1	D2	D4	D5	D7	D8	D9	D10	D14	D15	
Paraffins	95.9	83.3	75.4	72.4	79.6	80.4	83.3	77.5	n. a	n. a	64.8
Olefins	1.4	2.0	2.2	1.6	0.9	0.2	0.7	1.8	n. a	n. a	1.1
Aromatics	2.7	14.7	22.5	26	19.8	19.4	16.0	20.7	7.7	3.7	15.3

n. a - not reported; D-diesel grade

Lastly, Sjörge *et al.*, (1995) performed principal component analysis using the composition of ten different grades of diesel fuel as shown in Table 2.7. It was found that the dominating hydrocarbons were paraffins with volume fractions ranging between 72 and 96% (average of 64.8), followed by aromatic hydrocarbons with volume fractions ranging between 2.5 and 26% (average being 15.3%). Very little fraction of olefins was present with the maximum fraction detected being 2.2% and an average fraction of just about 1.1%. From the trends described above, it was evident that paraffins form the majority fraction of diesel fuels followed by aromatics with olefins forming the least. In some cases, olefins were completely

absent. Again, the varying ranges of the hydrocarbons could be attributed to the different grades of diesel available.

2.7.2 Chemical composition of commercial gasoline fuels

Demirbas, (2010) highlighted the major chemical compositions in gasoline fuels which are presented as follows; total amount of alkanes (that includes straight chain, branched and cycloalkanes) amounted to 54.3 wt.%, aromatics had a total fraction of 30.5 wt.% with olefins being the least, having fractions of just 1.8 wt.%.

Squicciarini, (1996) used supercritical fluid chromatography to determine the paraffinic, olefinic and aromatic compositions of six different grades of gasoline. These have been represented in Table 2.8. From the table, it was observed that aromatic compounds were the most dominant fraction of all the gasoline fuels examined, followed closely by paraffins with olefinic hydrocarbons being the least. This is evident in the average composition of all the compounds examined showing paraffinic, aromatic and olefinic yields of about 40.2, 52.4 and 7.4% respectively.

Table 2.8. Paraffinic, Olefinic and Aromatic constituents of different grades of gasoline fuel (Modified from Squicciarini, 1996)

Hydrocarbons (%area)	Gasoline Fuel Grades						Average
	G1	G2	G3	G4	G5	G6	
Paraffins (Alkanes)	32.6	42.9	42.8	48.2	29.7	45.0	40.2
Olefins	1.6	0.7	0.7	1.2	39.2	0.8	7.4
Aromatics	65.8	56.4	56.5	50.6	31.0	54.3	52.4

G- gasoline grade

Tang *et al.*, (2015) used GC/MS to investigate the fractions of alkanes, aromatics and olefinic compounds in five different gasoline fuels collected across five provinces in China. Following their analysis, they observed average compositions of 40.6, 38.1 and 12.9% for alkane, aromatic and olefinic compounds.

It is noticed from the trends that, alkanes and aromatics mostly dominate gasoline fuels. However, the most dominant depends on the type of gasoline fuel. As observed for diesel fuels, olefins in gasoline fuels were also seen to be low. Also, composition of aromatic

compounds in gasoline fuels were seen to be significantly higher than aromatic compounds present in diesel.

2.7.3 Fuel properties of commercial liquid fuels

Based on the mode of application, diesel fuels are usually classified into three main types. These include, land diesel fuels, used in trucks, buses, trains or other land transportation vehicles; marine diesel, used in ships; and plant diesel fuels, used in electric power generation plants, boilers and combustors (Hsu, 2000). The quality of diesel fuels used therefore depends on the performance requirements of the system/engine since land transportation vehicles, ships and power plants have variations in speed and load (Hsu, 2000). Also, commercial fuels and heavy fuel oils, used in compression combustion engines and boilers/combustors respectively, are required to meet certain specifications to ensure acceptable performance (Syamsiro *et al.*, 2014; Ahmad *et al.*, 2015). Standard fuel specifications have been established by Institute of Petroleum (IP) and American Society for Testing and Materials (ASTM) (Sharuddin *et al.*, 2016), and these specifications establish the characteristic ranges for diverse grades of fuels available for different specialised applications (Ahmad *et al.*, 2015; Hsu, 2000). Several ASTM and IP test methods are used to determine fuel properties. The major physico-chemical properties considered when testing fuel properties include, the density/specific gravity, viscosity, calorific/heating values, ash content, boiling point range, octane number (gasoline)/cetane number (diesel), pour point, flashpoint and aniline point (Islam *et al.*, 2010; Miskolczi *et al.*, 2009; Ahmad *et al.*, 2015; Hsu, 2000; Blazso, 2006). These properties are explained below.

Density

Density of a liquid is defined as the mass of liquid per unit of volume at a specific temperature (Kandola *et al.*, 1995). Diesel fuels have much higher density compared to gasoline and other lighter petroleum derived fuels which is an indication of the presence of high molecular weight compounds. Also, it has been established that organic compounds with longer chain lengths have higher density compared to branched organic compounds (Gao, 2010). Density is also correlated to the heating value such that increase in density results in the decrease in heating value. This is because, as the density of a fuel increases, the Carbon to Hydrogen (C/H) ratio increases because the olefinic and aromatic contents tend to dominate which means a lesser amount of C-H will be available per mass of the hydrocarbon hence lower heating

value (American Bureau of Shipping, 2001). The standard density of diesel fuel ranges between 800 - 860 kg/m³ (Li *et al.*, 2005; Miskolczi *et al.*, 2009; Gao, 2010; Islam *et al.*, 2010; Ahmad *et al.*, 2015) whereas that for gasoline ranged between 720 - 780 kg/m³ (Owusu *et al.*, 2018; Fausson, 2017).

Viscosity

Viscosity of a fuel is a degree of its resistance to flow. It is inversely proportional to temperature; that is, the viscosity of a fuel will decrease when fuel temperature increases hence viscosity values are always reported together with the temperature of fuel at which the test was done (American Bureau of Shipping, 2001; Bacha *et al.*, 2007). Also, higher viscosity of liquid fuels implies higher density (American Bureau of Shipping, 2001). Viscosity of fuels is normally measured by the kinematic viscosity since it has proven to be more accurate (American Bureau of Shipping, 2001). Its unit of measurement is mm²/s or centiStokes (cSt). The kinematic viscosity for diesel fuel oils used in heavy-duty low-speed engines ranges from 2.4 to 24 mm²/s at 40 °C (Bacha *et al.*, 2007; Hsu, 2000) whereas that of transportation diesel fuels ranges between 1.3 - 4.5 mm²/s at the same temperature (Bacha *et al.*, 2007; Islam *et al.*, 2010; Hsu, 2000) that for commercial gasoline at the same temperature is around 1.17 mm²/s (Sharuddin *et al.*, 2016; Ahmad *et al.*, 2015).

Pour point

Pour point of a liquid fuel is defined as the minimum temperature at which the liquid stops flowing. Pour point therefore defines the fluidity of liquid fuels at relatively low temperatures (Ahmad *et al.*, 2015). Increase in viscosity and crystallization of waxy compounds are the main parameters that enhance the loss of fluidity of liquid fuels (American Bureau of Shipping, 2001; Ahmad *et al.*, 2015). Although the standard acceptable pour point for fuel oils varies, the pour point for diesel fuel occurs around 6 °C.

Heating Value

Heating value is the amount of energy released on combustion of a fuel. Heating value can be classified as gross (high) or net (lower) (Patel *et al.*, 2000; Bacha *et al.*, 2007). Gross or higher heating value is the quantity of energy generated by absolute combustion of a unit amount of liquid fuel. For higher heating value, the water produced by combustion is condensed to

liquid, whereas for net heating value, the water remains in the gaseous form (Bacha *et al.*, 2007; Kunwar *et al.*, 2016). The standard higher heating value for diesel fuels ranges between 43 - 50 MJ/kg (Ahmad *et al.*, 2015; Islam *et al.*, 2010; Hsu, 2000).

Paraffinic hydrocarbons on combustion releases more energy than their corresponding naphthenic, olefinic and aromatic hydrocarbons (American Bureau of Shipping, 2001; Ahmad *et al.*, 2015). This is because heating value is basically influenced by the carbon/hydrogen ratio present in oil; as the carbon/hydrogen ratio decrease, the heating value increases (American Bureau of Shipping, 2001). More hydrogen per carbon decreases the oxidation state of a hydrocarbon and hence more energy will be released on combustion.

Ash Content

Ash is the residue left after carbonaceous material has been combusted. Higher ash content reduces the combustion efficiency of fuels (Hsu, 2000). It also damages fuel injection system and can cause deposits in combustion chambers. Due to this, ash contents in liquid fuels must be kept to traces. The maximum ash content required in commercial diesel and other liquid fuels is 0.01 wt.% (Syamsiro *et al.*, 2014; Bacha *et al.*, 2007).

Cetane number

Cetane number describes how spontaneously a fuel begins to combust in a diesel engine. High cetane number fuels combust, moments after they have been introduced in a combustion chamber of an engine. Such fuels can be classified as having a short ignition delay period. Contrary, a fuel with low cetane number struggles to auto-ignite resulting in longer ignition delay period.

Two hydrocarbons (n-hexadecane and 1-methylnaphthalene) are used to represent the cetane number scale (Hsu, 2000; Bacha *et al.*, 2007), with 1-methylnaphthalene representing a cetane number of 0 and n-hexadecane representing a cetane number of 100 (Bacha *et al.*, 2007). Cetane number should be at least 40 according to the ASTM requirement for diesel fuel oils (Ahmad *et al.*, 2015; Bacha *et al.*, 2007). Paraffinic hydrocarbons, especially normal paraffins present in diesel fuels improve the cetane number and hence the ignition quality of the fuel (Gao, 2010).

Octane number

Octane number is the measure of the tendency for gasoline fuels to ignite spontaneously. It is used to characterise the anti-knock quality (Sharuddin *et al.*, 2016). High octane number indicates that a fuel possesses a better anti-knock quality (Sharuddin *et al.*, 2016).

Flash Point

The flash point of a liquid fuel is described as the least temperature at which the vapours above the liquid kindle when an external spark is applied (Li *et al.*, 2005; Ahmad *et al.*, 2015). It is considered an important factor in fuel handling to avoid risks of fire during storage. Flash points of transportation diesel fuels are mostly above 40 °C (Ahmad *et al.*, 2015; Hsu, 2000), and that of fuel oils used in boilers and low speed engines are 55 °C (Islam *et al.*, 2010; Hsu, 2010).

Aniline Point

Aniline point is defined as the temperature at which the aniline compound ($C_6H_5NH_2$) forms a single phase with the liquid fuel oil (Sharuddin *et al.*, 2016). Aniline point is used to gauge the content of aromatics present in fuels. Lower aniline point specifies a higher proportion of aromatic compounds whereas higher aniline point indicates the higher amounts of paraffinic compounds present in the oil. Olefins and naphthenes have aniline points between the two extremes of aromatic and paraffin values (Hsu, 2000; Sharuddin *et al.*, 2016). Commercial diesel and gasoline have estimated aniline points of 77.5 and 71 °C respectively (Ahmad *et al.*, 2015; Sharuddin *et al.*, 2016).

2.8 Pilot scale and commercial plastic pyrolysis plants

This section reviews the major components of pilot and commercial pyrolysis plants with discussion on the advantages and disadvantages of the different types available. Most commercial and pilot scale pyrolysis plants operate under continuous processes. The main components of a pyrolysis plant comprise the feeding system, the reactor and the condensers. These are discussed in the sections below. This exercise was conducted to assist in the design of the semi-continuous, kilogram-scale pyrolysis pilot plant that was installed and used in this study.

2.8.1 Feeding System

Feeding of materials into continuous pyrolysis reactors is a common critical challenge. Feeding system has two major functions, i.e. preventing air flowing into the reactor and also controlling the feed-rate (Gao, 2010). They are very susceptible to blockage which prevents smooth flow of feedstock. Smooth and continuous delivery should be the benchmark of an ideal feeding system for a continuous reactor, and be suitable for wide range of materials (Dai *et al.*, 2012). Therefore, for effective operation of continuous pyrolysis processes, it is vital to choose the precise type of feeder. Feeding plays a key role in enhancing continuous, reliable and efficient operation of the process. Varieties of feeding systems exist because of different feedstock properties and process requirements. Common setbacks normally faced in feeding systems include; bridging or blocking, seal failures, fuel specific feeders, noise, high cost, early breakdown service as well as reaction of feedstock occurring in the feeder before entering the reactor. For various thermochemical processes, several feeders have been used. These include; the hopper and lock hopper systems, screw feeders and piston feeders (Wilén & Rautalin, 1993; Dai *et al.*, 2012). Details of these feeders have been discussed below.

2.8.1.4 Screw feeders

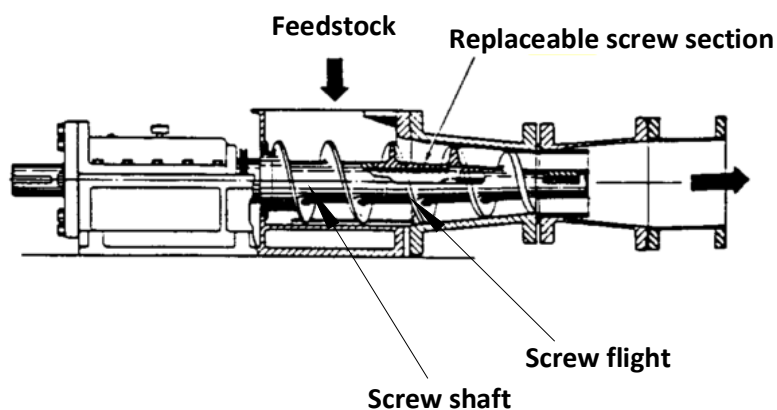


Figure 2.8. Screw feeder (Modified from; Wilén & Rautalin, 1993)

Screw feeders are common feeding equipment capable of delivering bulk solids over extensive feed rate ranges (Bates, 2000; Dai *et al.*, 2012). The commonly used ones include, the single and the twin screw. As shown in Figure 2.8, the screw feeder consists of a shaft on which a helicoidal surface is fitted. This arrangement rotates inside a fixed tube to propel feed materials across the feeder (Bortolamasi & Fottner, 2001). Frictional interaction between

screw flight and adjacent casing, material properties and screw configurations are the factors used to estimate the efficiency of a screw feeder (Dai *et al.*, 2012).

Screw feeders are volumetric devices, which mean they meter a consistent volume of material controlled by the speed or revolution of the discharge device (Bates, 2000; Dai *et al.*, 2012). The volume of feedstock conveyed in a given period of time is dependent on the following; screw flight, diameters of the shaft, pitch and the roundness of the screw (Dai *et al.*, 2012). Some advantages and disadvantages of the screw feeder include (Wilén & Rautalin, 1993; Bortolamasi & Fottner, 2001; Dai *et al.*, 2012;)

Advantages

- Volumetric feeding. That is their ability to feed in a fixed volume of feedstock into the reactor
- It handles both cohesive and adhesive materials
- It has a flexible arrangement
- Low energy consumption and
- cost effective

Disadvantages

- Limitations in the mass flow rate of feeding for feedstock with low bulk densities
- Blockage which is caused by overload or difficult feed properties such as dense particles.
- Lack of flow which is instigated by bridge or 'rathole' in the case where the screw feeder is preceded by a load hopper
- Feed rate fluctuations which may be caused by screw flight rotation, sporadic bridging in the hopper as well as solid build up in the screw.
- Pressure seal failure
- Particle attrition
- Sticking of materials on flights, shafts and internal casing of the screw.

Screw feeders can be operated single screw or twin screw (positive displacement feeders). Both are equally efficient to use however the single screw is simpler and economical whereas the twin screw can better handle sticky materials (Dai *et al.*, 2012; Rospen Industries Limited).

2.8.1.5 Piston Feeders

Piston feeders normally compress feedstock into an impermeable plug before being transported into the reacting vessel. The plug which usually should be substantially compacted averts the backward flow of gases and reacting feedstock back into the feeding system (Dai *et al.*, 2012). Piston feeders are very good choices for high pressured reactors (Rautalin & Wilen, 1992; Dai *et al.*, 2012).

The mode of operation of a simple piston feeder includes; the charging of their feeding tank with feedstock usually under atmospheric pressure, after which the volume is reduced following the forward movement of the piston. As a result, the pressure within the cylinder increases and the materials moves forward into the reacting vessel (Rautalin & Wilen, 1992). The principle of operation of a simple piston feeder is illustrated in Figure 2.9.

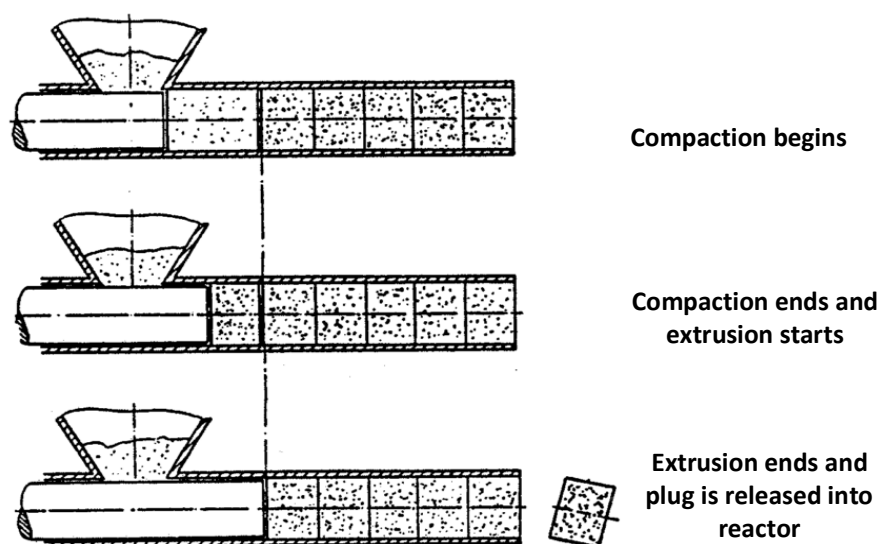


Figure 2.9. The principle of operation of a piston feeder (Adapted from Rautalin & Wilen, 1992)

Some advantages and disadvantages of the piston feeder are listed below (Dai *et al.*, 2012; Rautalin & Wilen, 1992);

Advantages

- They are also positive displacement feeders, i.e. they trap a fixed volume of sample and discharge it into the reactor.
- They can handle sticky and stringy feedstock

- They facilitate short cycling operation and hence a continuous operation is possible with piston feeders
- They enhance uniform moisture content in feedstock materials as a result of the compression
- They have very good pressure sealing due to the compact plug formed
- They handle wide range of materials (plastics, biomass, waste tyres, fibre).

Disadvantages

- Design and operation are quite complicated as compared to other feeding systems
- Wear of piston ring and cylinder since they continuously slide against each other which leads to severe wear (this effect can be reduced by ring coatings and cylinder liners)
- Gas leakage (can be minimised by combining with other feeding systems such as the lock hopper)
- Feeding fluctuations due to intermittent delivery.

2.8.1.6 Lock Hopper feeding systems

Lock hopper systems operate on the principle of intermittent feeding across into reactors, typically by the stepwise opening and closing of valves on the top and bottom of the feed vessel (Swanson *et al.*, 2003).

Mode of operation

The upper valve is opened to receive material into the lock hopper while the lower valve is closed. After the upper valve is closed, a non-reactive gas is used to raise the pressure within the lock-hopper system to or beyond system pressure after which the bottom valve is opened, and the feed material is discharged into the reactor. After the lock-hopper is emptied, the lower valve is closed, and the vessel is depressurized to permit another cycle (Swanson *et al.*, 2003; van der Drift, *et al.*, 2004). Dual and parallel lock hoppers may also be employed, which allows one lock hopper to discharge pressure to the process, while the other lock hopper takes care of filling and pressurizing (Swanson *et al.*, 2003). A lock-hopper feeding system is usually coupled with a piston feeder or a screw feeder to improve sealing and also facilitate smooth and efficient feeding of feedstock into the reactor (Rautalin & Wilen, 1992; Wilen &

Rautalin, 1993). A lock-hopper coupled with a screw feeding system is shown in Figure 2.10. A lock-hopper coupled with a piston feeder is also presented in Figure 2.11. Advantages and disadvantages of the lock hopper system are listed below (Rautalin & Wilen, 1992; Van der Drift *et al.*, 2004);

Advantages

- It is a simple design device with few moving parts
- It handles wide range of feedstock
- It consumes low amount of energy
- It is compatible with other feeding systems such as the screw and piston feeder

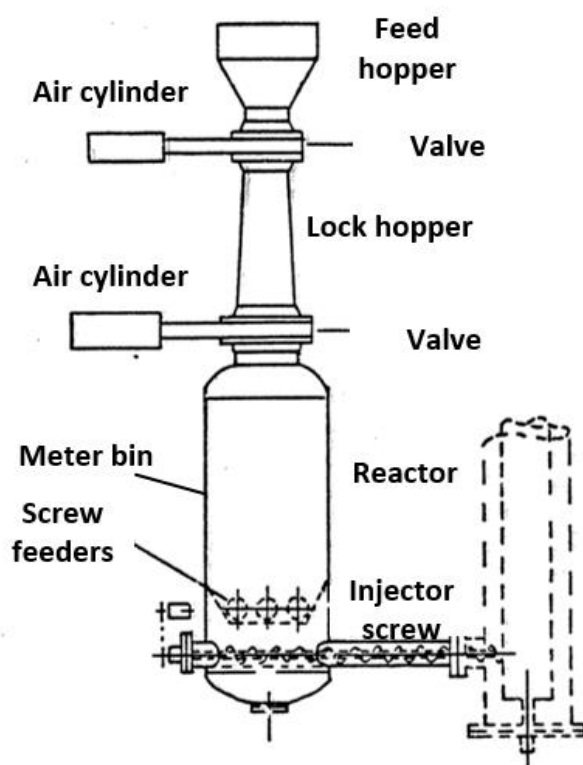


Figure 2.10. Lock-hopper feeding system coupled with a screw feeder (Adapted from Rautalin & Wilen, 1992)

Disadvantages

- It is a complex control strategy which involves valve cycling, pressurization and depressurization.

- Does not really facilitate a truly continuous feed rate, although its typical discrete feeding pattern can be minimized by coupling it with other feeders such as the screw feeders.

The lock hopper feed system is compact and integrated as compared to other feedstock hence it minimizes the amount of oxygen which would enter any reaction system as much as possible (Wilén & Rautalin, 1993).

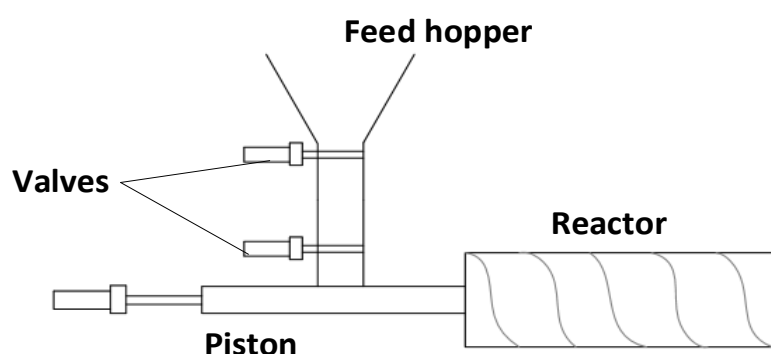


Figure 2.11. Schematic representation of a lock-hopper coupled with a piston feeder.

2.8.2 Reactors

Reactors are critical components in the pyrolysis of plastics since their design and operating conditions directly affect the product type and quality. It is where the mixing, heat transfer and decomposition of plastic materials take place. The reactor type has a significant influence on the plastics mixing, solid and vapour residence time, heat transfer and thus efficiency of the reaction towards achieving the desired final product (Sharuddin *et al.*, 2016). Depending on the heat transfer techniques and flow pattern, reactors may be grouped into fluidised bed, rotary kiln and screw kiln (auger reactors) (Gao, 2010).

Fluidised Bed Reactor

In the fluidised bed reactor, fed plastic materials are suspended in a heating medium composed of gas and a solid material (typically sand when an inert material is needed) in the form of fine particles, and subjected to pyrolysis by means of gas-solid convective heat transfer (Zadgaonkar, 2006). That is, gaseous products or inert gases flow through an

expanded bed of plastic feedstock and other bed materials which is usually sand (Gao, 2010). Its advantages include less temperature gradient and effective heat transfer due to the even turbulent mixage of gases and bed materials (Gao, 2010). It also has excellent heat and mass transfer characteristics hence high thermal conductivity and it is widely accepted and utilised especially in commercial processes (Low *et al.*, 2001; Gao, 2010). Extra advantages of the fluidized bed reactor include its flexibility with catalysts since they mix up very well with the reacting medium (Gao, 2010; Sharuddin *et al.*, 2016). Fast or flash pyrolysis is usually performed with this type of reactor (Jung & Fontana, 2006). The main disadvantage of the fluidised bed reactor is; it requires uniform particles in terms of size and density to allow control of fluidisation, making it suitable for only homogenous feeds and not different kinds of plastic mixtures (Gao, 2010). A schematic representation of a fluidised bed reactor is depicted in Figure 2.12.

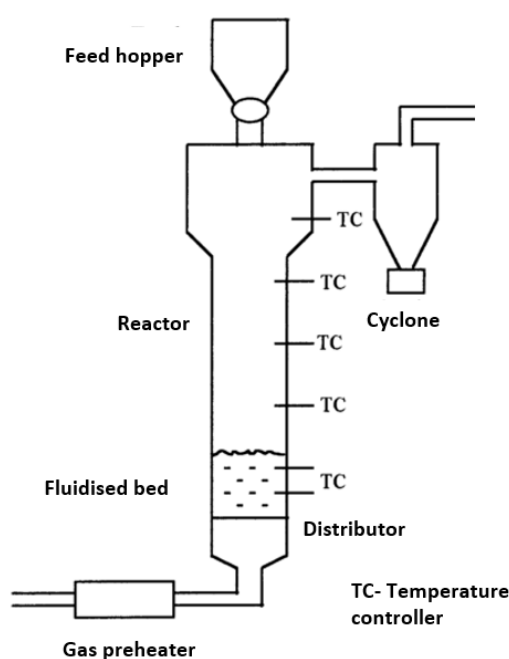


Figure 2.12. Scheme of a fluidised bed reactor (Adapted from Williams & Williams, 1999b)

Screw kiln reactors

The screw kiln reactor is a reaction system that has also been widely used for plastic processing (Serrano *et al.*, 2003; Jung & Fontana, 2006; Koderá *et al.*, 2006; Aguado *et al.*,

2008; Gao, 2010). It comprises of an externally heated extruder that conveys plastic feedstock from the feeding system to the other end of the extruder, and in the process converts feedstock materials into volatiles and residues which are separated and collected (Aguado *et al.*, 2006; Gao, 2010). The screw kiln reactor is driven by an external motor, therefore plastic melts easily flow irrespective of their high viscosity, which is a noteworthy advantage (Aguado *et al.*, 2006). Both melted plastics and plastic solid particles are compatible with the screw kiln reactor. The radial temperature gradient of the extruder is minimised due to its small diameter as well and highly efficient blending of materials (Aguado *et al.*, 2006; Gao, 2010). Residence time is controlled by adjusting the rotation speed of the extruder. A screw kiln reactor system is shown in Figure 2.13.

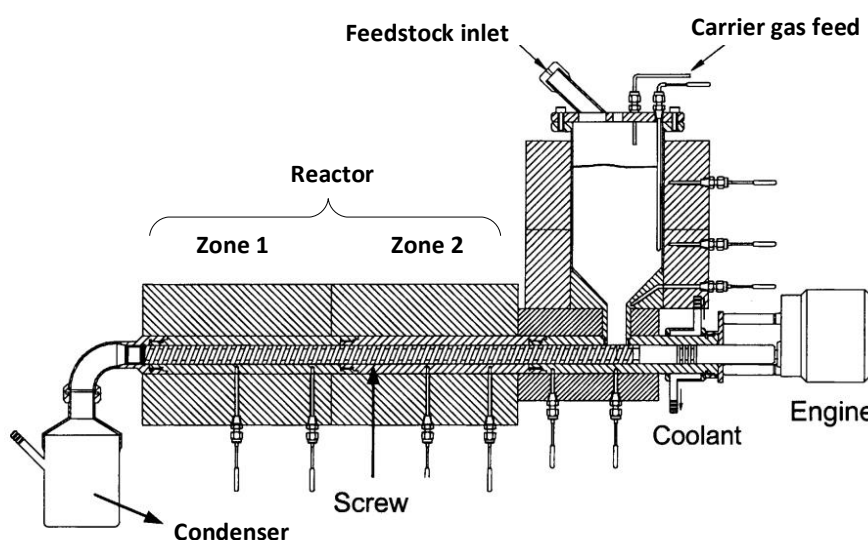


Figure 2.13. Schematic representation of a screw kiln pyrolysis reacting system showing the screw kiln reactor (Adapted from Serrano *et al.*, 2003)

Rotary kiln reactors

The rotary kiln reactor is usually made from steel and normally with an inclination to facilitate the movement of feed materials downstream. Its internal surface is usually sheltered with refractory material to cushion the metal surfaces from extremely high temperatures (Zajec, 2009). In special cases, specific dampers are attached to the inlet section to prevent the entry of oxygen into the reaction chamber or exit of gaseous product into the feeding system during material feeding (Zajec, 2009). Baffles inside the reactor aid with mixing and flow of materials. The main advantage of the rotary kiln reactor is that rotation ensures continuous turning and

blending of plastic materials as the reaction proceeds, such that the mixture is persistently homogenised and mixed with the inert gas, thereby forming uniform pyrolytic products (Li *et al.*, 2004; Zadgaonkar, 2006). Also, it has easily adjustable residence time of solids, which facilitates the control of pyrolysis reactions, and it can process solid waste of varying shapes sizes (Li *et al.*, 2004; Zadgaonkar, 2006). They are relatively cheaper compared to fluidised bed and screw kiln reactors. Due to high degree of mixing that allows efficient heat exchange and considerable flexibility pertaining to the size and type of materials that the rotary kiln reactor can accomodate, it is very much suitable for slow pyrolysis (Zajec, 2009) and possibly, intermediate pyrolysis. Various commercial and pilot scale pyrolysis plants for waste tyres and plastics have been successfully employed, using rotary kiln reactors in their processes. They include the Kobe Steel commercial plant and the Italian ENEA Research Centre Trisaia pilot-scale plant (Li *et al.*, 2004). A schematic representation of a rotary kiln reacting system is shown in Figure 2.14.

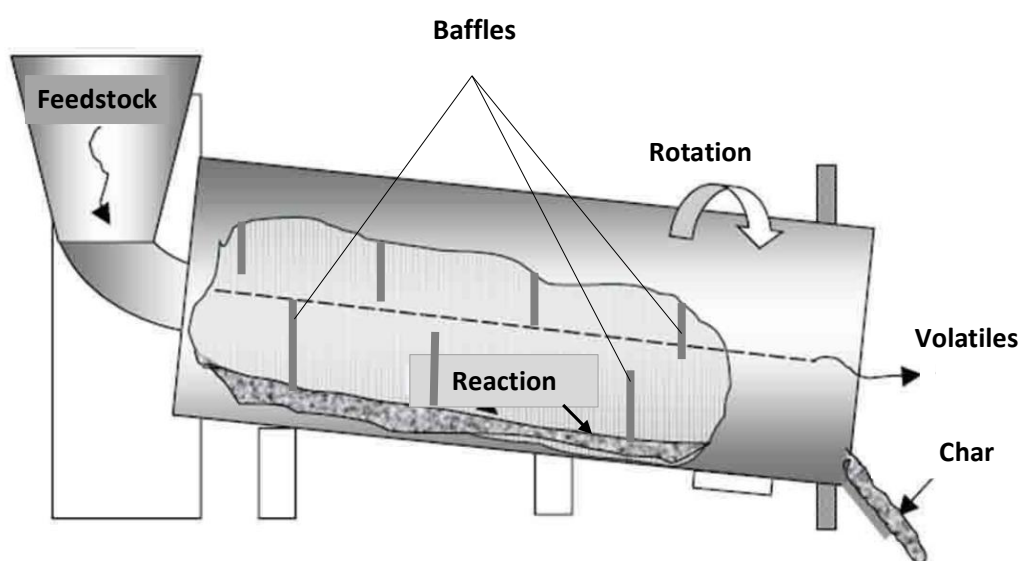


Figure 2.14. Schematic representation of a rotary kiln reactor (Adapted from Zajec, 2009)

Table 2.9 (Arena & Mastellone, 2006) compares some key parameters, features and advantages of the different types of reactors discussed above. These include; operating temperature ranges, suitable particle size, process flexibility, costs and scale-up problems. From the table, all reactors can all operate at temperatures of up to 800 °C. Also, fluidised

bed and screw kiln reactors have more substantial process flexibilities compared to rotary kiln reactors. The process flexibilities include easily adjustable vapour residence time, pressure and temperature. In terms of scale-up complications, the rotary kiln reactor appears to be the best as compared to the other three reactors, giving the least problems when it comes to scale-up issues. The fluidised bed reactor is cheaper and easy to maintain as compared to the rotary kiln and screw kiln reactors. However, it is more difficult to get it into stable operation, especially with heterogeneous waste materials.

Table 2.9. Comparing different types of reactors (Adapted from Arena & Mastellone, 2006)

	Bubbling fluidized bed	Rotary kiln	Extruder/Screw
Temperature profile	Temperature is almost constant in vertical direction but limited variation in radial direction	Longitudinal as well as transversal gradient may be large and not easy to control	Two zones are recommended: one at < 150°C to remove volatile fractions and one > 250°C to extract HCl gas in case of PVC pyrolysis
Temperature range (°C)	500 - 850	450 - 800	200 - 520
Heat exchange and transfer	Very efficient exchange. Large heat transfer activated by solids circulation	Relatively poor exchange. Then there is often the necessity of long cylinder kilns	Degradation occurs by exposure to thermal and mechanical work (shear forces)
Particle size	Narrow size distribution. Mean particle diameter between 0.008 and 3 mm. bed particles attrition and consequent entrainment may be severe	No problem for size. Any size can be treated from fines to large lumps	Plastic feedstock needs to be shredded to the size of side-plates

	Bubbling fluidized bed	Rotary kiln	Extruder/Screw
Residence time of the feed	Particles spend substantial time (mins or hours) in the bed. Gas residence time depends on gas velocity that is below 2 m/s	Very long (1-2 h)	As long as required for full conversion
Conversion	Mixing of solids and gas bypassing can determine performance poorer than other reactors	Conversion can be high	Preferably used as a pre-treatment before feedstock recycling process
Process flexibility	Excellent. Can be used for low- and high-temperature pyrolysis with or without catalyst. Can treat different plastic wastes	Limited. Operating parameters (residence time, temperature, etc.) can be varied in a narrow range.	Permits highly diverse mixed-plastics to be effectively and efficiently converted into a liquid form
Products quality and value	Likely to be high especially in processes for monomer recovery and high temperature situations	The difficulty in temperature control leads to a wide range of products	Either homogeneous liquid or granules are formed depending on the conditions. In very high temperature conditions however, volatiles are produced
Scale-up problems	Must be cautiously considered. Pilot plant is usually important	Generally, not significant	Suitable screw diameter

	Bubbling fluidized bed	Rotary kiln	Extruder/Screw
Costs	Moderate. Low maintenance cost	Moderate cost of investment. Large maintenance cost because of rotating parts and the fouling and erosion of the inner surface	Single screw is less expensive, Double screw are more expensive with counter rotating twin screws being an intermediate in terms of cost

Depending on feeding and product withdrawal technique, reactors can be categorised into batch, semi-batch and continuous. In batch processes, reactor is charged with feedstock, prior to the commencement of the process or after a cycle is complete. In the continuous reactor configuration, feedstock continuously enter and exit the system. In the semi-batch reactor configuration, the feed materials are added continuously but products accumulate and are discharged all at once (Felder & Rousseau, 2005). Batch and semi-batch reactors are used purposely for research because they have simple design and their control parameters are much easier to regulate whereas continuous processes are much suited for commercial operations because feedstock recharging is much cheaper compared to batch processes and also, they increase productivity due to their high efficiency (Williams & Williams, 1997 cited in Gao, 2010; Sharuddin *et al.*, 2016).

2.8.3 Condensers

Pyrolysis hot vapours consist of compounds with different chemical and physical properties. The condensation process therefore helps in collection and segregating the various compounds in the hot volatiles into several fractions. It involves the process where the pyrolysis vapours from the reactor are passed through series of condensers operating at different temperatures and this facilitates the collection of condensed fractions based on their physical and chemical properties. Different types of condensers are employed in pyrolysis processes. These include; the shell and tube heat exchanger and ASTM D86 type (comprises of a tube immersed in a water bath), etc. The most commonly used is the shell

and tube heat exchangers due to their advantages of efficient heat transfer and ease of cleaning/ maintenance (Stonecypher, 2009).

Shell and tube heat exchanger

The shell and tube heat exchanger/condenser for pyrolysis vapours is made up of many tubes, placed within a steel shell as shown in Figure 2.15, with water flowing in the tubes and hot vapours flowing around the tubes. Upon contact with the tube surface, the vapours condense and drop down the condenser. The shell and tube heat exchanger have a very large surface area for heat transfer although in a relatively small confinement, which makes it portable to use (Stonecypher, 2009).

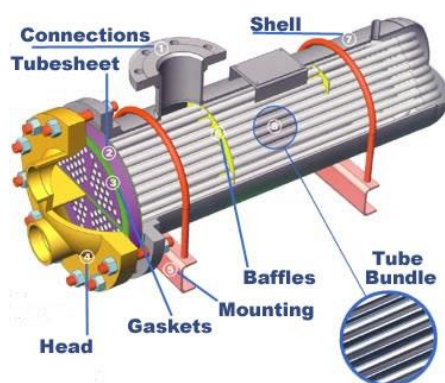


Figure 2.15. Schematic representation of the shell and tube heat exchanger (South west thermal technology, 2016)

2.8.4 Some Pilot and Commercial Scale Plastic Pyrolysis Plants

When experiments performed at laboratory scale looks promising, they are subsequently scaled up to commercial standards. Nevertheless, scale up directly from bench scale to commercial scale is difficult to attain and hence pilot plants are very vital in confirming the validity of laboratory-scale tests and also simulating industrial stage processes (Arena and Mastellone, 2006). A number of pilot plastics pyrolysis plants have been in operation worldwide. Some pilot and commercial plastics pyrolysis plants have been described below.

Hamburg ABB

This plant was established by the University of Hamburg, Germany, as a pilot scale plant operating at 40 kg/h. Their main feedstock was shredded plastic waste with very minimal PVC content (Kaminsky, 2006). They employed a bubbling fluidized bed in converting the plastic materials into high yields of olefins, rather than paraffins and naphthenes, as well as oils rich in benzene, toluene and xylene (BTX) aromatics (Kaminsky, 2006). The reactor operated in the temperature range of 600 to 800 °C, as was purged with steam and nitrogen gas (Arena & Mastellone, 2006).

Veba Oel

Established by Veba Oel AG in Gelsenkirchen, also in Germany, operates at 500 kg/h, using an indirectly heated rotary kiln reactor, preceded by a screw feeder. Operating temperatures were in the range of 650 - 850 °C. The plant converts waste plastic materials and vulcanized elastomers into mainly gas, oil and char. Char produced by this process contains close to 80% elemental carbon, and it is further treated in gasification and hydrogenation plants (Behzadi & Farid, 2006; Ali and Siddiqui, 2006). They also have another plant which operates at 12.5 tons/h in Ruhr area, Germany (Arena & Mastellone, 2006).

Fuji

Fuji Recycle Industries, in collaboration with Mobil Oil, Nippon Steel Corp., and Shinagawa Fuel Corp. operate the Fuji pyrolysis plant. Their technology includes an extruder followed by a fixed bed reactor. Extrusion of feed materials mixed with recycled liquid stream from the reactor takes place at 300 °C, followed by the thermal decomposition in the first chamber of the reactor and then catalytic cracking in the second part of the fixed bed reactor at 400°C (Walendziewski, 2006). Their main feedstock is polyolefin from industrial waste stream with final products being gasoline, kerosene and diesel (Yanik & Karayildirim, 2006). A pilot plant operating at 400 tonnes/year was initially established, which was later scaled up to a demonstration plant operating at 5000 tonnes/year in Okegawa City and Aioi City respectively all in Japan (Arena and Mastellone, 2006).

From the review, the following segments were considered during the design of the pyrolysis pilot plant;

1. Lock hopper coupled with a piston feeder.
2. A rotary kiln reactor and
3. Glass condenser tubes immersed in water

A lock hopper coupled with a piston feeder was chosen because from the mode of operation of the lock-hopper, minimal amount of oxygen enters the system during feeding which is key in every pyrolysis process. Also, the lock-hopper was selected because it can handle a wide variety of feedstock that includes biomass, waste tires, fibres just to mention a few. Moreover, a piston feeder was preferred as an attachment to the lock-hopper because it consumes less amount of energy compared to other feeders such as the screw feeder. It can also handle sticky and stringy feedstock materials. Just like the hopper, the piston feeder is also compatible with wide range of feedstock materials. Unlike the screw feeder, blockage hardly occurs in the piston feeder.

Furthermore, a rotary kiln reactor was selected because compared to the screw kiln and the fluidised bed reactor, it comes with minimal complications resulting from scale-up from bench to pilot scale processes. Also, in terms of slow and intermediate pyrolysis mechanisms, the rotary kiln reactor is very similar to the bench scale reactor that will be used in the study and hence will make results easily comparable. In terms of costs, it is cheaper than screw kiln and fluidised bed reactors. Unlike screw kiln and fluidised bed reactors, the rotary kiln reactor can accommodate wide range of feedstock sizes from fine materials to larger lumps.

Glass condenser tubes immersed in water was preferred because of it is cheaper as compared to the shell and tube heat exchanger. Also, it is easier to operate and maintain.

2.9 Key Conclusions drawn from literature

1. Pyrolysis conversion of polypropylene (PP) begins around 300 °C and ends at about 520 °C. However, 450 - 500 °C was deduced as the temperature range within which optimum condensable products (oil and wax) yield from PP pyrolysis is likely to be attained.
2. For batch processes, secondary cracking reactions tend to dominate PP pyrolysis at temperatures beyond 500 °C which leads to the production of more permanent gases over condensable products. Therefore, to promote yield of condensable products, higher temperatures should be avoided.

3. For fluidised bed processes, it was inferred that heating rate of the process increases with increase of temperature hence compared to batch, secondary cracking reactions begin to occur at a much lower temperature (just after 450 °C).
4. The heating rate trend observed for fluidised bed reactors is similar to batch scale pre-heated reactors where increase in temperature also increases the heating rate, which in effect enhances rapid degradation of PP. It was also inferred that slow heating rates in the range of 5 - 25 °C for batch scale pyrolysis of PP have no significant effect on condensable products yield.
5. Vacuum pyrolysis of PP exhibited promising yield of condensable products when compared to atmospheric pyrolysis. However, the effects of varying temperature and heating rate on condensable products yield and quality under vacuum is barely reported in literature. Therefore, it warrants investigation.
6. At temperatures below 600 °C, paraffins and naphthenes dominated condensable products recovered from PP pyrolysis followed by olefins with aromatics being the least. Nevertheless, at temperatures beyond 600 °C, secondary cracking reactions convert paraffins and olefins into more aromatic products.
7. Boiling point range of oils/waxes recovered from PP pyrolysis revealed that they contain compounds that fall in both diesel and gasoline range.

Chapter 3

Materials and methods

3.1 Introduction

This chapter entails the stepwise approach employed in performing various experiments conducted as part the study, together with a description of all equipment used. Outline includes; feedstock preparation and characterisation, pyrolysis conversion processes (which also entails the description of pyrolysis setups) and products characterisation.

3.2 Feedstock supply and preparation

Industrial waste polypropylene (PP) was obtained from Zibo containers, manufacturers of plastic bowls, punnets and other plastic containers located in Blackheath, Kuils River, South Africa. These plastics were virtually free of other non-plastic contaminants except for additives added during manufacturing. Feedstock was a mixture of chipped black and white pigments of PP with particle size ranging between 4 - 6 mm. The feedstock was mixed up thoroughly followed by sub-sampling using cone and quarter procedure described by Gerlach *et al.*, (2002). In this method, a pile of the thoroughly mixed PP sample was placed on a thin film of plastic spread out on the floor. The pile was then flattened after which a thin, flat piece of cardboard was driven through the middle of the pile perpendicularly, to separate the pile into nearly two equal halves. The cardboard was lifted from the sample and rotated 90 ° from the position that was used to divide the pile initially and driven through the sample once more in the new position resulting in the pile being divided into four separate, nearly equal segments. Piles collected from two diagonal segments were combined (second and fourth quadrants, starting from the upper right in this case) and coned and quartered further in the same manner described above, each time discarding the piles from the other two diagonals and saving them for subsequent quartering. Following sub-sampling, about 10 g of sampled PP was fed into a Retsch mill (ZM 200) which generated much smaller particles with sizes about 2 mm. The milled products were used for characterisation experiments carried out on milligram scale. All samples were kept in air-tight plastic bags to avoid contamination.

3.3 Feedstock characterisation

Proximate analysis of feedstock to determine the moisture, volatiles, fixed carbon and ash, was performed using a Mettler Toledo TGA/DSC 1 Star System Thermogravimetric Analyser in accordance with ASTM E1131. The thermal degradation behaviour of the feedstock was also studied using the Mettler Toledo TGA/DSC 1 Star System where 44 mg of the sample was heated from 30 °C at a ramp rate of 20 °C/min to a final temperature of 600 °C under nitrogen gas running at a flowrate of 80 mL/min.

HHV of the feedstock and condensable products were determined based on ASTM standard D5865-11a using a bomb calorimeter (Cal2K Eco Calorimeter, model 2013) calibrated using benzoic acid.

Elemental analysis was performed using Vario EL Cube Elemental Analyser based on ASTM D 4239 and ASTM D5373. In this method, plastic samples were combusted in a column filled and enriched with Tungsten Trioxide (WO_3) and oxygen at a temperature of 1050 °C. The combustion generated CO_2 , H_2O , NO_x , SO_2 and SO_3 from which the amounts of the various elements were deduced.

3.4 Pyrolysis conversion

3.4.1 Bench scale pyrolysis

The bench scale setup is a gram scale unit and considered as a scale-up version of milligram scale experiments in the TGA.

3.4.1.1 Bench-scale setup description

Figure 3.1 is a graphical representation of the pyrolysis setup used for all bench-scale experiments. The various units of the setup are described below; a nitrogen cylinder from which technical grade nitrogen (99.99% purity, Afrox, South Africa) was supplied, a nitrogen flow controller which regulates the flow of nitrogen gas into the reactor, a well-insulated electric furnace which houses a stainless-steel tubular reactor within which a quartz boat where samples are fed, is placed. The tubular reactor is 1 m long with internal diameter of 60 mm. For fast-insertion tests, the tubular reactor has a feeding chamber attached, where samples are kept while reactor is pre-heated, and samples are introduced into the centre of the reactor only when the final setpoint temperature has been attained. This feeding chamber

is joined to the tubular reactor by a tri-clover fitting. The sample is pushed to the centre of the reactor with the help of a sliding handle. Two K-type thermocouples are placed at the middle of the reactor to monitor the reactor wall and sample temperature (close to the centre).

Next is a set of condensation train where hot volatiles exiting the reactor were condensed. The condensation train consists of an ambient condition condenser made of stainless-steel, positioned at the exit of the reactor. Most heavy molecular weight condensable products (oils containing some wax) were recovered in this condenser (see Appendix D). Following the ambient condenser is a set of four (4) glass condensers connected by thick-walled rubber tubing. These condensers were cooled using dry ice (Afrox, South Africa) which facilitated the capture of most light fractions of condensable products (wax-free oils) (also presented in Appendix D). An auxiliary part of the setup is a vacuum pump which is connected to the exit point of the last condenser in case experiments are to be performed under vacuum conditions.

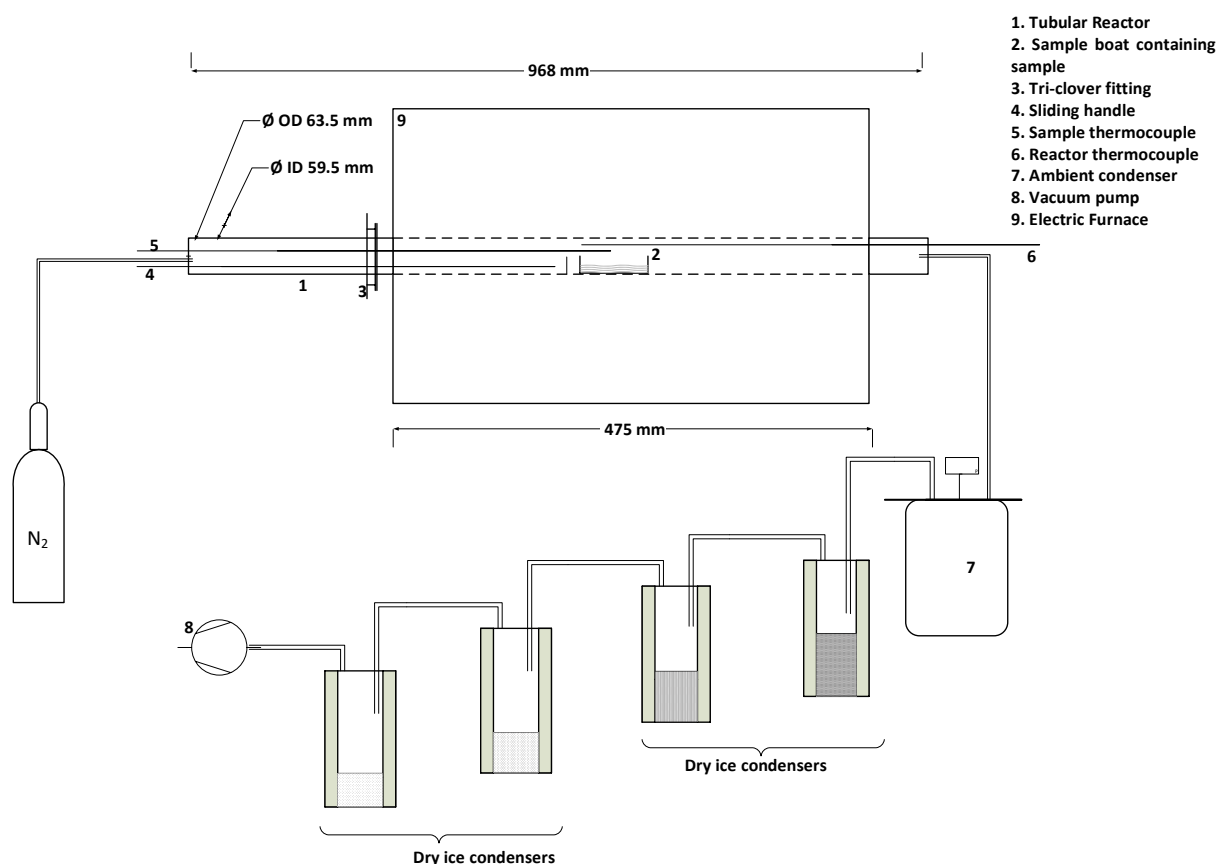


Figure 3.1. Representation of the bench-scale pyrolysis setup

3.4.1.2 Bench-scale experimental procedure

Based on the thermal degradation behaviour of PP studied and described in Section 3.3, four different temperatures were examined at each of the four types of pyrolysis conditions devised. These are; 450 °C, 488 °C, 525 °C and 600 °C. For slow pyrolysis experiments, samples were placed at the centre of the reactor and heated gradually at a rate of 15 °C/min from ambient to the final temperature. For fast-insertion experiments, reactor was pre-heated to the final temperature before samples were introduced to the middle of the reactor hence sample was heated rapidly at estimated heating rates (based on sample thermocouple) ranging between 170 - 180 °C/min. For experiments under ambient conditions, a nitrogen flow of 0.5 L/min was used throughout the course of the experiment to remove any oxygen from the system during reactor purge and to sweep generated volatiles from the hot part of the reactor to condensers. For both heating rates, samples were kept for 60 mins after the maximum temperature has been reached to ensure complete conversion.

For experiments under vacuum, nitrogen supply was disconnected and a two-stage vacuum pump (Instruvac) was connected at the exit point of the last condenser to aid in sweeping volatiles from the hot part of the reactor and to keep the system inert. Vacuum pressure used for all experiments ranged between 90 to 95 kPa below atmospheric.

Permanent gases generated under both atmospheric and vacuum conditions were collected in tedlar bags and analysed using a compact GC described in Section 3.5.2. Char products (usually in small quantities) remain in the sample boat after the conversion. Prior to each experiment, a leak test was performed with the vacuum pump to ensure that no oxygen was present in the system during the tests. For all experiments, 20 g of sample was fed. All experiments were conducted in replicates to ensure consistency of the results.

3.4.2 Pilot conversion

3.4.2.1 Pilot plant setup description

A 5 kg/h pyrolysis pilot plant was installed in the context of this study with the objective to mimic the tests from bench scale experiments at pilot scale. This was necessary because of the different reactor configurations of bench and pilot scale reactors.

With the help of our suppliers, Technotherm Superior Thermal Technologies, the system was designed. It was assembled by Technotherm in Johannesburg, South Africa and commissioned

at Stellenbosch University. As shown in Figure 3.2, the pilot plant comprises the feeding section, the reactor, residue box, a set of condensation train, gas towers, oxygen analyser and a PLC where process parameters such as temperature, and retort rotation speed are controlled.

The feeding system consists of a lock hopper where samples are fed and two pneumatic valves which open and close in a step-wise fashion after samples have been fed. That is, the first valve opens and closes to receive samples after which the second also follows the same mechanism so that the sample is introduced in the piston chamber. This is to minimise the amount of oxygen entering the unit during feeding. The piston, which is the second part of the feeding system, then pushes samples deposited from the hopper into the reactor. This design was based on the lock-hopper and piston feeding system presented by Wilen & Rautalin, (1993) and Dai *et al.*, (2012) respectively.

The reactor is where conversion of materials occurs. It is a rotary kiln within which a spiral screw (baffle) is fitted. The rotation of the reactor enhances efficient heat transfer. Also, the baffle helps in propelling samples across the reactor till the residues are deposited in the residue box. Generated hot volatiles then progress to the condensation train.

The condensers are four glass jars immersed in chilled water. The heaviest oil fractions (oils containing some wax) were recovered in the first with the lightest oil fractions (wax-free oils) recovered in the last. Incondensable gases were sampled after the 4th condenser in regular time intervals using tedlar bags and analysed with the help of the CompactGC 4.0 (Global Analyser Solutions) described in section 3.5.2. The gases were also captured in the gas towers filled with water, after which their volumes were recorded. The towers operate such that, gases displace the water. Volumes of gases together with the concentrations of the main compounds measured by GC, aided in the estimation of the mass of gases generated and subsequently, the mass balance of the process. A vacuum pump with vacuum suction just about 2 kPa, abs (below atmospheric) was connected before the towers to help in the quick extraction of volatiles from the reactor and the gas towers. Nitrogen gas flow of 5 L/min was used to purge the system for 15 minutes before samples were fed. In addition, an average nitrogen gas flow of about 1.5 L/min was used to sweep volatiles from the reactor during conversion.

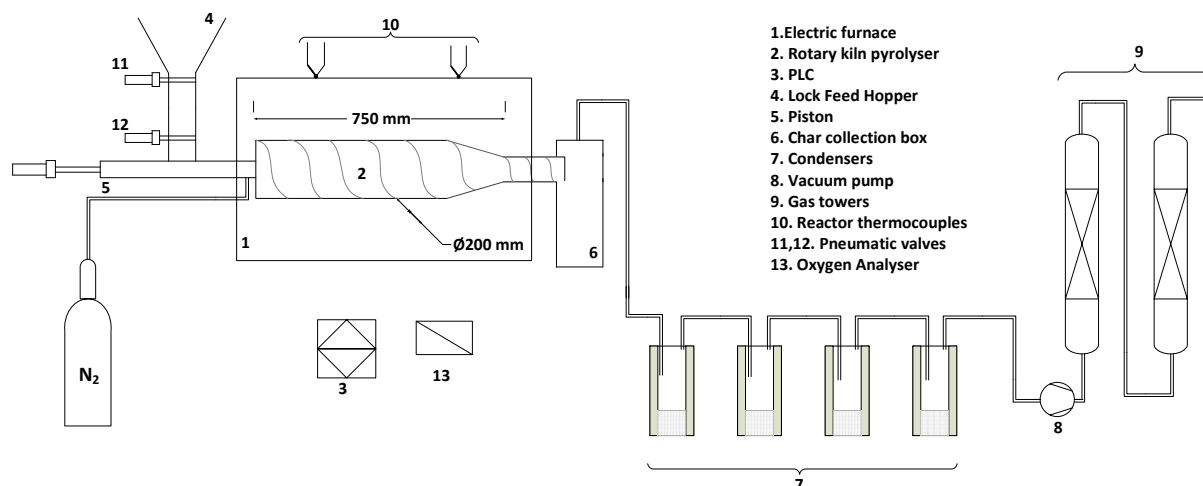


Figure 3.2. Schematic representation of the pilot plant

3.4.2.2 Pilot experimental procedure

Five temperatures were examined at the pilot level. These include, 450, 460, 488, 507 and 525 °C. Modifications to the temperatures examined on the bench were made on the pilot because the pilot's configuration promoted severe cracking reactions when compared to bench scale reactor and hence more permanent gases were likely to be produced at severe temperatures. Since the target was condensable products, attention was given to much lower temperatures on the pilot and hence the inclusion of temperatures, 460 and 507 °C and the exclusion of 600 °C. For each experiment, reactor was pre-heated to the selected temperatures before samples were fed. A total of about 3.6 kg of sample was fed for each run. The pneumatic valves on the lock hopper open every 72 s, and about 50 g of sample is fed per cycle after which the piston moves in the forward direction to convey the samples into the reactor. Following complete feeding, conversion is allowed to progress until there are no more volatiles coming out of the reactor, which is an indication of complete conversion. This is determined based on the results from GC analysis of gases, showing negligible concentrations of gases characteristic of PP conversion. For temperatures 488 to 525 °C, complete conversion took about 2 hours after feeding whereas complete conversion could take up to 4 hours for temperatures, 450 and 460 °C after feeding. The rotation speed of the retort was 25 Hz for all tests, which corresponds to 50% of the maximum retort rotation speed.

Char and solid wax products were recovered in the residue box as two separate layers with char collected at the bottom. These solid products fell upon opening the residue box from bottom after which the char was gently scrapped off and weighed separately. Oils were mostly recovered in the condensers with oils in condenser 1 containing high amounts of wax at the pyrolysis temperatures, 488 - 525 °C. However, oils recovered in the same condenser at temperatures 450 and 460 °C contained relatively low wax fractions. Detailed description of the distribution and appearance of these condensable products have been made at section 4.5.1. Permanent gases were sampled in tedlar bags only when the piston moves forward. This is because, the forward movement of the piston generates some pressure build up that enables efficient movement of volatiles into the tedlar bags. Reverse movement of the piston creates a negative pressure which inhibited gas sampling. Gas towers were switched from one to the other when the gases occupied about three-quarters the total volume of the tower. Volume of gases were then recorded before refilling the towers with water. Like bench scale tests, all tests at different temperatures were conducted in replicates to confirm reliability.

3.5 Products characterisation

The techniques under this section are relevant for oil and gaseous products coming from both bench and pilot tests. Except that for pilot tests, Physico-chemical properties of condensable products (oil and wax) were performed in addition.

3.5.1 Gas Chromatography/Mass Spectrometry (GC/MS)

Simulated distillation (see Appendix C) was used to group the compounds present in oil/wax products into diesel and gasoline fractions. Simulated distillation is a chromatographic technique which correlates retention times with boiling points of compounds (Das & Tiwari, 2018). A standard of known composition was injected and used as a benchmark for grouping compounds into different fractions (Arabiourrutia *et al.*, 2012). A C₇ - C₄₀ mixture of saturated alkane standard (Supelco, USA) was used for grouping detected compounds into gasoline and diesel fractions. Peaks eluting with retention times between those of C₆ and C₁₀ alkanes were grouped as gasoline while C₁₁ and C₂₃ alkanes were grouped as diesel. Chloroform (99% purity, BDH Analytical Chemicals) was used as solvent for all samples. Samples containing mixtures of oil and wax were thoroughly stirred to mix up before analysis to ensure a uniform

representative sample was used. For all tests, peak area was assumed to be the mass of compound detected.

An Agilent Technologies 7890A gas chromatograph coupled with an Agilent Technologies 5975C mass spectrometer (mass-selective detector) was used for the analysis. A Zebron ZB-1701:002 column (length – 60 m; internal diameter – 0.25 mm and film thickness – 0.25 μm) was used for separation. Helium was used as the carrier gas with a steady flowrate of 1.3 mL/min. The process was started by heating the oven at 45 °C and held for 10 minutes, then increased to 100 °C at a heating rate of 2 °C/min. It was finally heated from 100 °C to 260 °C at a heating rate of 7 °C/min and held there for 20 minutes. Injected volume of samples per run was 1 μL and a split ratio of 20:1 was employed.

3.5.2 Gas Analysis

Analysis of the permanent gases for both bench and pilot scale tests, followed the same method used in previous studies by Mundike *et al.*, (2017) and Brown *et al.*, (2019) where a CompactGC (Global Analyser Solutions) was calibrated to quantify concentrations of nitrogen, C₁- C₅ linear hydrocarbon gases, hydrogen, carbon monoxide and carbon dioxide. Mixtures of known concentrations of these gases (Afrox, South Africa) were used for the calibration. N₂ was employed as an internal standard to determine the yield of each gas compound. The CompactGC was made up of three channels. The first channel consisted of a Molsieve 5A column heated at 65 °C and a TCD detector used for the analysis of N₂, H₂, CO and CH₄. The second channel comprised of a PP-Q-bond column at 50 °C and a TCD detector that was used for the analysis of CO₂, C₂H₄ and C₂H₆. The third channel was equipped with a Rtx-1 column at 45 °C coupled with an FID detector used for the analysis of C₂ - C₄ hydrocarbons.

For pilot and atmospheric experiments at bench scale, permanent gases were collected at the end of the 4th condenser in tedlar bags at regular time intervals and fed immediately into the CompactGC 4.0 gas chromatograph. For vacuum conditions at bench-scale, gas sampling was done at the exit point of the vacuum pump. The maximum volume of the bag (5 L) and the time it takes to completely fill the bag (77 sec) were used to estimate the volume of gas that was sampled per minute (about 3.9 L). This volume coupled with volume fractions obtained from the CompactGC were used to calculate the total mass of gases produced and to complete the mass balance of the process.

3.5.3 Fuel Tests

Oil products derived from pilot experiments were subjected to the following fuel tests to verify how they compare with commercial diesel and gasoline fuels.

- i. Density @ 20 °C, in accordance with ASTM D4052. For the procedure, a small volume of about 1 - 2 mL of condensable product (sample) was introduced into an oscillating sample tube and the changes in oscillating frequency (caused by the change in the mass of the tube) in conjunction with calibrated data were used to determine the density.
- ii. Kinematic Viscosity @ 40 °C, in accordance with ASTM D445. This employed the reverse or straight flow viscosity tubes that were immersed in a water bath. About 10 mL of condensable product (sample) was introduced into the viscosity tubes which was clean, dried and already calibrated. The viscosity tube was then immersed in a water bath at a stable temperature of 40 ± 0.02 °C after which a vacuum pump was used to draw samples until it reached the upper meniscus of the viscosity tube. A stopwatch was then used to count the flow time between the upper and lower meniscus. This was repeated for each test sample and Equation 3.1 was used to estimate the kinematic viscosity for each sample.

$$v = Ct \quad 3.1$$

Where,

v - kinematic viscosity (mm^2/s)

C - viscosity calibration constant ($\text{mm}^2/\text{s})/\text{s}$

t - flow time (s)

- iii. Distillation to determine boiling point range, in accordance with ASTM D86. This was performed using atmospheric distillation at ambient pressure. For the process, 100 mL of condensable product was transferred into a flat bottom flask equipped with a thermocouple used for the distillation. The flask was heated to keep a distillation ratio of 4 mL/min and 5 mL/min. The distilled sample was condensed and collected in a measuring cylinder at room temperature. The distillation volume recovered at 250, 350 and 365 °C together with the initial and final boiling point temperatures were recorded. The temperature at which the first

drop of distillate was recovered was identified as the initial boiling point (IBP) whereas the temperature at which all samples in the distillation flask evaporated was recorded as the final boiling (FBP). The temperatures at which the following volumes of condensates were recovered were also recorded. Volumes include 10%, 50%, 90% and 95%.

- iv. Pour point, in accordance with ASTM D97. This test employed cooling samples in a specified glass tube in a bath containing Isopropyl alcohol and Dry ice. The sample was cooled at specific rates and examined at intervals of 3 °C for flow characteristics. The lowest temperature at which sample stops flowing was then recorded to be the pour point.
- v. Aniline point, in accordance with ASTM D611. This was performed by mixing equal proportions of aniline with condensable products after the which the resultant mixture was heated till a complete mixage was obtained. Thereafter, a thermometer was used to check the temperature at which the mixture separated or got hazy and was recorded as the aniline point.
- vi. Cetane Index was estimated by calculation using parameters from density of samples at 15 °C and temperatures at which 10%, 50% and 90% distillation condensates were obtained. Equation 3.2 was used for the estimation and is known as the four variable equation in accordance with ASTM D4737 (Drews, 1998; Owusu *et al.*, 2018).

$$C1 = 45.2 + 0.0892T_{10N} + (0.131 + 0.901B)T_{50N} + (0.0523 - 0.420B)T_{90N} + 0.00049(T_{10N}^2 - T_{90N}^2) + 107B + 60B^2 \quad 3.2$$

Where,

CI- Calculated Cetane Index

$$T_{10N} = T_{10} - 215$$

$$T_{50N} = T_{50} - 260$$

$$T_{90N} = T_{90} - 310$$

$$B = \left[\exp^{-3.5(\rho-0.85)} \right] - 1$$

ρ - Density of sample

A set of tests required about 250 ml of oil sample hence only oils from condensers 1 and 2 have been characterised for fuel. Oils from condensers 3 and 4 were not enough for fuel tests. Also, waxy oils obtained at higher pyrolysis temperatures (488 - 525 °C) could not be characterised for distillation, flash point, cetane index and aniline point due to their high viscosity. All fuel test experiments were performed by Intertek, Cape Town except aniline point, which was performed by Intertek, Durban, all in South Africa.

Chapter 4

Results and discussion

4.1 Introduction

This chapter tackles the effects of temperature and heating rate on condensable products (oil and wax) yield and quality under atmospheric and vacuum pyrolysis of polypropylene (PP) at bench scale. Furthermore, experiments performed at atmospheric conditions at bench level were scaled up to a pilot plant and results obtained were compared. The pilot plant was designed and commissioned as part of the study. Moreover, condensable products recovered from the pilot experiment were subjected to fuel tests that include density, viscosity, flash point and pour point to ascertain how these properties vary with the process parameters examined and also, how they compare with commercial diesel and gasoline fuels.

4.2 Thermodegradation behaviour and Compositional Characterisation of PP

4.2.1 Thermal degradation and Proximate analysis of waste PP

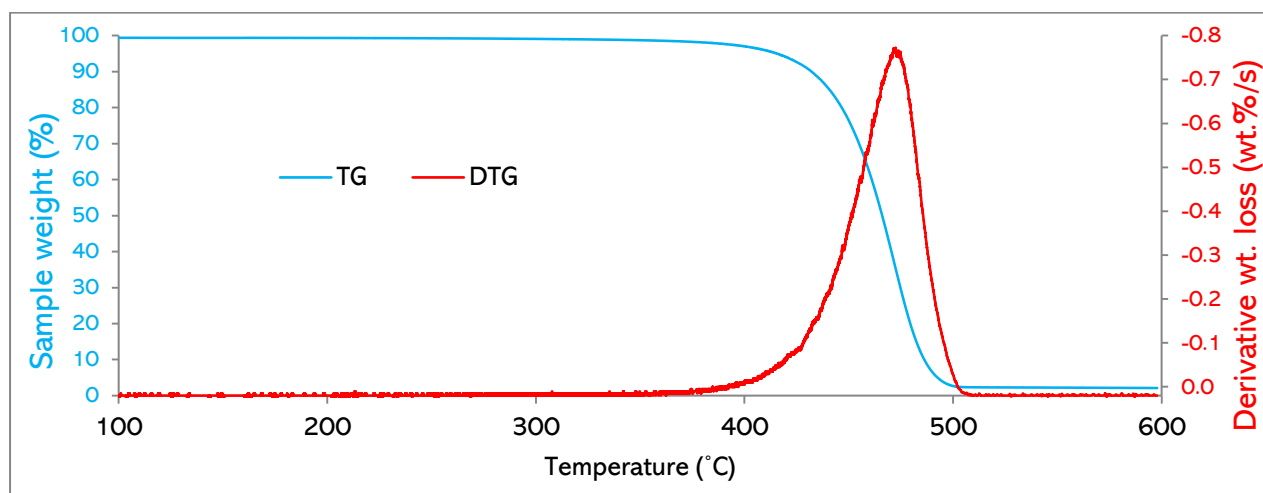


Figure 4.1. TGA/DTG curve for PP degradation at 20 °C/min

PP sample was subjected to Thermogravimetric Analysis (TGA) to determine its degradation with respect to temperature. As shown in Figure 4.1, it was observed that degradation of PP began and was completed at temperatures of about, 400 °C and 500 °C respectively with maximum degradation occurring at 475 °C. The single peak detected indicates that

degradation of PP is a single-step mechanism. Similar observations were reported by Chan & Balke, (1997), Lee & Shin, (2007), Jung *et al.*, (2010) and Yan *et al.*, (2015) which possibly suggests that PP used in this study had identical chemical composition to most PP used in literature. The degradation temperature range was used as a basis to define temperature range for bench-scale experiments.

Table 4.1. Proximate Analysis of PP

Compound	wt.% (average)
Moisture	0.05 ± 0.01
Volatiles	97.49 ± 0.14
Fixed Carbon	2.00 ± 0.25
Ash	0.46 ± 0.1

TGA was used to conduct proximate analysis on PP samples. As shown in Table 4.1, it was deduced that the volatile matter was the major component of PP with fraction of about 97.5 wt.% followed by the fixed carbon content with traces of ash and moisture. Volatile matter represents the possibility of how much volatiles (condensable and permanent gases) can be harnessed when a material is subjected to pyrolysis. The relatively small amount of fixed carbon signifies that for conversion under optimal conditions, very little amount of char is expected. The figures obtained were pretty consistent with those reported by Uçar *et al.*, (2016) and Jung *et al.*, (2010) suggesting that chemical composition of PP examined in this study was similar to those reported in literature. The relatively low content of ash of about 0.5 wt.% obtained as compared to those reported by Uçar *et al.*, (2016) (2.2 wt.%) and Jung *et al.*, (2010) (3.55 wt.%) signifies that PP examined in this study contained minimal amounts of additives/contaminants.

4.2.2 Elemental analysis of waste PP

Elemental analysis of PP in Table 4.2 revealed that PP is mainly composed of carbon and hydrogen with traces of nitrogen, sulphur and oxygen. Fraction of Carbon present was recorded to be 85.07 wt.% with Hydrogen being 14.16 wt.%. Nitrogen, Sulphur and Oxygen were present in trace amounts with fractions of 0.05, 0.10 and 0.16 wt.% respectively present. The C/H ratio of PP waste used in this study (6.0) was very close to those reported by

Heydariaraghi *et al.*, (2016) and Miranda *et al.*, (2001) who all reported C/H ratios of about 6.1 and 5.6 respectively. Since these studies employed pure PP, it implies that PP waste used in this study is consistent in elemental composition with pure PP. HHV of PP waste used in the study was recorded to be 45.3 MJ/kg. Sorum *et al.*, (2001) reported very close figure of HHV (46.4 MJ/kg) for pure PP.

Table 4.2. Elemental Composition of PP

Element	wt.%
C	85.07 ± 0.41
H	14.16 ± 0.18
N	0.05 ± 0.00
S	0.10 ± 0.00
O (by difference)	0.16 ± 0.23
HHV (MJ/kg)	45.30 ± 0.12

4.3 Atmospheric pyrolysis of PP at bench-scale

Tests under atmospheric pyrolysis of PP at bench scale were performed at four temperatures (450, 488, 525 and 600 °C) at slow and fast heating rates under atmospheric conditions. This followed PP characterisation discussed under section 4.2.1. 400 °C was not included in the temperatures to be investigated because initial screening tests showed highly incomplete conversion of PP waste at this temperature (see Appendix D). Condensable products derived were characterised for Higher Heating Value (HHV) and Gas Chromatography/Mass Spectrometry (GC/MS) to determine their energy contents and compositions respectively. Finally, analysis of permanent gases using a CompactGC was conducted at all conditions to ascertain gaseous composition and also complete the mass balance of the processes.

4.3.1 Product yield distribution (Atmospheric conditions)

The condensable products recovered in the first condenser at room temperature were waxier than those recovered under dry ice (next set of condensers) (Appendix D). This could possibly suggest that condensables recovered in the first condenser, under ambient conditions contained heavier molecular weight compounds compared to those recovered under dry ice.

Hence condensables recovered under ambient and dry ice were referred to as heavy oil and light oil fractions respectively.

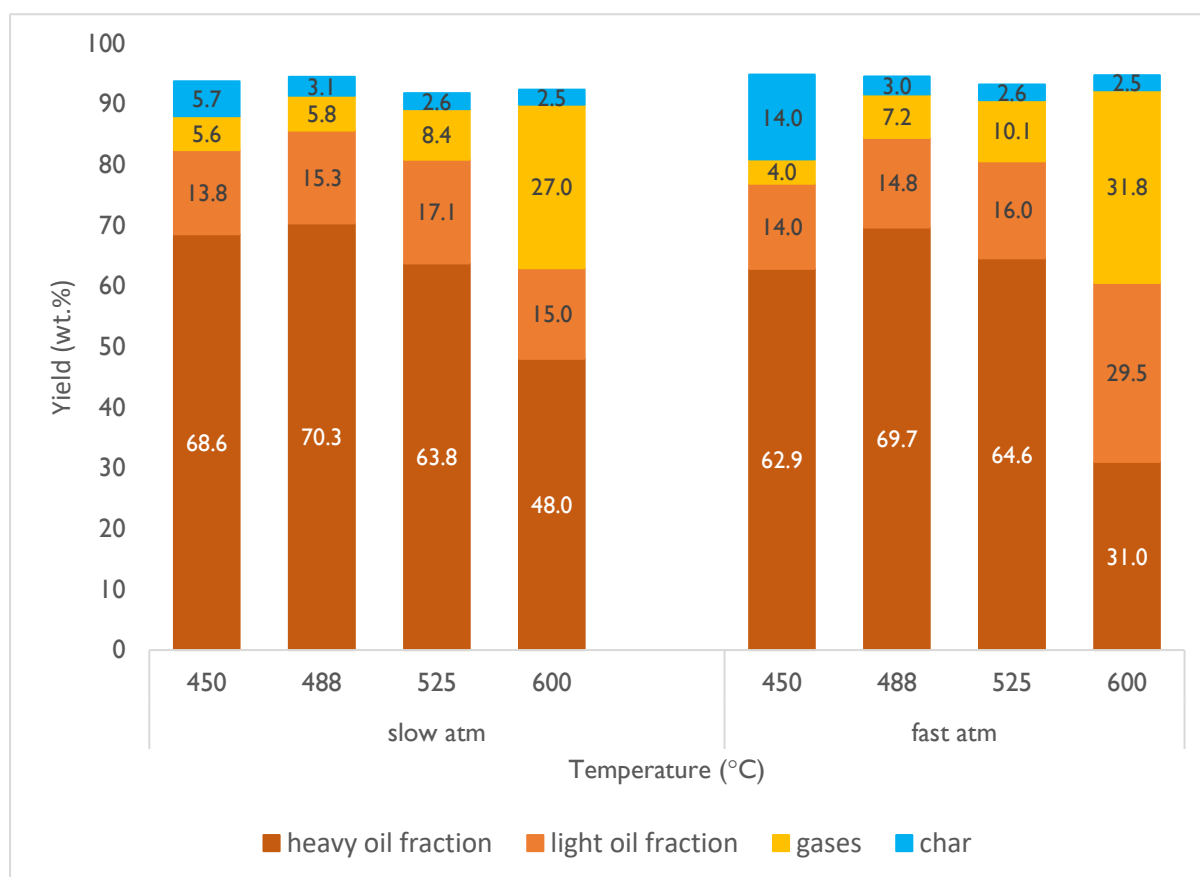


Figure 4.2. Effects of Temperature and heating rate on product yield distribution (Atmospheric conditions)

The yields of products for pyrolysis of PP under atmospheric conditions have been presented in Figure 4.2. The mass balances for all the process conditions ranged between 91 - 95 wt.% which is typical for pyrolysis processes as observed with Owusu *et al.*, (2018). Standard deviation of char, permanent gases, light and heavy condensable products under slow heating rates were less than 1.5 wt.%, 1.0 wt.%, 1.1 wt.% and 2.0 wt.% respectively whereas that for fast insertion processes were less than 0.9 wt.%, 3.2 wt.%, 0.6 wt.% and 6.4 wt.% in the same order (Appendix B).

For slow pyrolysis processes, it was observed that char yield at all temperatures was rather insignificant and was seen to decrease slightly with the rise of temperature. Significantly low yields (below 3.2 wt.%) were obtained at temperatures beyond 450 °C. Based on the total

content of fixed carbon and ash (2.5 wt.%, Table 4.1), it can be deduced that sample conversion was almost complete. Total yield of condensable products (heavy and light) increased slightly from about 82 wt.% to a maximum of 86 wt.% as temperature progressed from 450 to 488 °C. It however dropped to 80 wt.% when temperature augmented to 525 °C and further decreased drastically to 63 wt.% when temperature reached 600 °C. From the trends, 488 °C was deduced to be the temperature at which maximum condensable products yield of 86 wt.% was recovered, after which further increase of temperature resulted in a corresponding decrease in condensable products yield. The decrease in yield of condensables observed after the optimum temperature was blamed on the occurrences of secondary cracking reactions to produce much lighter products to the detriment of oils. This is evident in the corresponding increase in the yields of permanent gases detected. Permanent gas yields were observed to increase sharply from about 6 to 27 wt.% as temperature rose from 450 to 600 °C with the latter temperature producing the highest yield of permanent gases. This shows that secondary cracking reactions become more pronounced at the higher temperatures. Ahmad *et al.*, (2015) reported similar trends when they pyrolysed PP in a batch reactor in the temperature range 250 - 400 °C. They reported maximum condensable products yield of about 70 wt.% after which a further rise in temperature resulted in a decrease in yield of oil to about 63 wt.% with a corresponding increase in gas yield. Mechanism of secondary cracking reactions occur when two or more unstable primary volatile products generated from the devolatilization of PP further react to produce much more stable compounds. This mechanism is facilitated at severe temperatures and heating rates.

Results for experiments under fast-insertion pyrolysis followed almost the same trend observed for slow pyrolysis. Yield of char was also observed to decreased with the increase of temperature. Considerable amount of char was however generated at 450 °C. While increasing heating rate usually results in reduced char yield, the reverse trend was observed in this case. This was blamed on the incomplete conversion of PP due to the relatively shorter solid residence time when compared to slow pyrolysis conditions. Trends observed for condensable products yield followed similar path as slow pyrolysis with maximum condensable products yield of about 85 wt.% attained at 488 °C. A further increase of temperature resulted in reduced condensable products yield and promoted the formation of

permanent gases which again was attributed to secondary cracking reactions. Similar observations to these trends were made by Lu *et al.*, (2015) who also investigated the pyrolysis of PP in a pre-heated batch reactor where they recorded a maximum condensable products yield of about 72 wt.% after which a further increase of temperature resulted in the increase of permanent gas yield at the expense of oil. A permanent gas yield of about 67 wt.% was generated as against an oil yield of 33 wt.% at their highest temperature investigated. At 600 °C, compared to slow pyrolysis, it was seen that yields of light oil fractions and permanent gases became more pronounced to the detriment of heavy oil fractions, with light oil fraction shooting by about 15 wt.% and permanent gases by close to 5 wt.%. It was then inferred that when comparing slow and fast heating rates, significant difference in the distribution of yields of volatiles (oil and gas) was only observed at the highest temperature examined, 600 °C. This observation was interpreted as consequence of interaction between temperature and heating rate. At slow heating rate, most of the volatiles were released before the reactor temperature reached 500 °C (with respect to TGA curve in Figure 4.1). At fast heating rate, the volatiles were released in a reactor already at 600 °C, which facilitated severe cracking reactions to produce lighter compounds.

In conclusion, for both slow and fast pyrolysis of PP under atmospheric conditions, secondary reactions known to suppress oil yield occurred beyond the temperature at which maximum condensable products were obtained, 488 °C. However, interaction between temperature and heating rate at 600 °C led to significant secondary cracking reactions at this temperature which promoted the formation of lighter products.

4.3.2 Condensable products characterisation (Atmospheric conditions)

4.3.2.1 GC/MS analysis (Atmospheric Conditions)

Each product recovered under atmospheric pyrolysis of PP was analysed by GC/MS which gave the proportions of compounds found in diesel and gasoline fractions based on surface area. As a first approach, assuming similar response factors of the compounds as generated by the GC/MS, the proportions of diesel (respectively gasoline) was multiplied by the yield (wt.%) of the product to estimate the yield of diesel (respectively gasoline) in each product.

Figure 4.3, illustrates how the process parameters (temperature and heating rate), affected the proportions of diesel (C₁₁-C₂₃) and gasoline (C₆-C₁₀) range compounds under atmospheric

slow and fast insertion processes. For slow pyrolysis, it was observed that, total diesel composition (in both heavy and light condensable products) decreased steadily from around 42 to 34 wt.% as temperature progressed from 450 to 600 °C. The gradual decrease in diesel yield observed with the increase of temperature was corroborated to secondary cracking effects at higher temperatures that lead to the conversion of heavy molecular weight compounds (diesel) into lighter ones (gasoline and permanent gases). Total yield of gasoline range compounds correspondingly increased with the rise of temperature and were generally predominant as temperature rose except at 600 °C where the yield was observed to decrease. This was blamed on the further conversion of gasoline compounds into more permanent gases. This is evident in the sharp increase in yield of permanent gases observed as temperature progressed from 525 to 600 °C as reported in the previous section, 4.3.1.

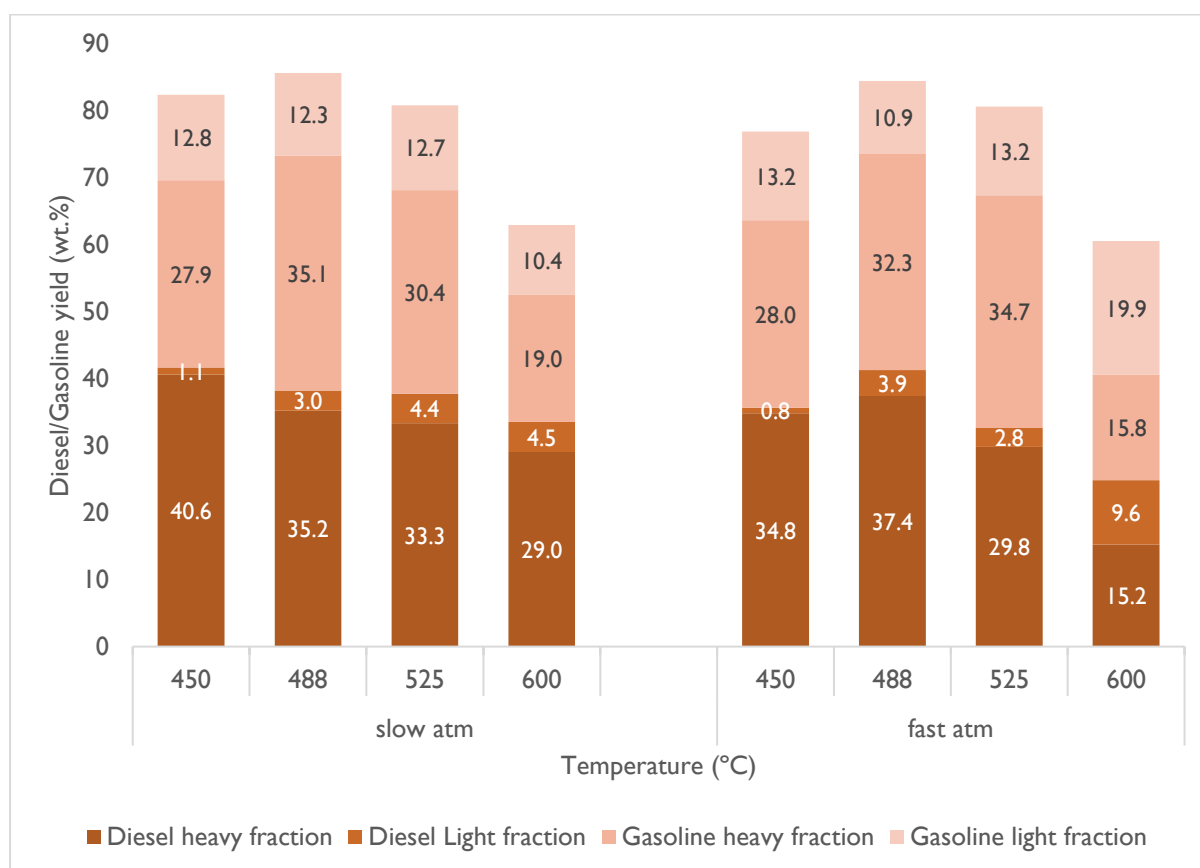


Figure 4.3. Proportions of Diesel and Gasoline present in oils obtained from atmospheric pyrolysis of PP (Diesel and Gasoline proportions in each product was based on GC/MS surface area and yields of oil)

For fast-insertion pyrolysis, also depicted in Figure 4.3, it was observed that, the total diesel fraction (in both heavy and light oil) increased somewhat from about 36 to 41 wt.% when temperature rose from 450 to 488 °C. It then decreased to around 33 wt.% at 525 °C and further to 25 wt.% when temperature reached 600 °C. Compared to slow pyrolysis, it was noticed that yields of diesel compounds were mostly lower especially at the highest temperature tested (600 °C), which further ascertains the fact that secondary cracking reactions became more severe at higher temperatures and faster heating rates. This is evident in the comparatively improved yield of gasoline compounds under fast heating rate conditions compared to slow heating rate. It was also observed that gasoline range compounds were prevalent over diesel range compounds at all temperatures under fast heating rates.

These observations were enough to conclude that, production of gasoline range compounds from PP pyrolysis is favoured mostly under reaction conditions where some secondary cracking occurs.

Surprisingly, physical observation of condensable products revealed that heavy condensable product recovered under ambient conditions (condenser 1) tended to become waxier or more viscous in nature with the rise of temperature (high temperature is known to decrease the number of carbon atoms of the compounds through cracking reactions) (Appendix D). This unforeseen phenomenon was explained as; - at relatively lower pyrolysis temperatures, although both lower molecular weight (MW)/lower boiling points and heavy MW/higher boiling point compounds were produced, the heavier compounds were not released because pyrolysis temperature was lower than their boiling points. Heavy MW/Higher boiling point compounds were only released at elevated pyrolysis temperatures and hence the formation of waxy compounds at these temperatures. This observation was also identified to be novel with respect to what has been currently reported in literature. Physical observations for light condensable products (recovered from condensers 2-5) however did not change with the variation of temperature. These products were clear, free-flowing and did not contain wax. They were stable and never solidified even after months of storage.

4.3.2.2 Higher Heating Value (HHV) analysis (Atmospheric conditions)

The HHV of condensable products (oil and wax) obtained from the atmospheric pyrolysis of PP have been presented in Table 4.3. From the table, it was observed that HHV of all heavy

condensable products were greater than corresponding HHVs of light condensables which is expected because heavy condensable products contained higher number of carbon atoms. Moreover, it was noticed that HHV for each type of oil generally decreased with the upsurge of temperature which was corroborated to the increased production of aromatic compounds. Aromatics were found to be present in higher amounts in gasoline compounds than diesel (refer to section 2.7.2) hence increased production of gasoline compounds at higher temperatures (from GC/MS results in the previous section) implies higher aromatic contents and therefore the lower HHVs recorded at higher temperatures. Lastly, the range of HHV for all the condensable products (41 - 46 MJ/kg) were consistent with the HHVs of commercial heavy fuel oil, diesel and gasoline having HHVs ranging between 41 - 46 MJ/kg.

Table 4.3. HHV of PP derived oils under atmospheric pyrolysis of PP

Temperature (°C)	HHV(MJ/kg)			
	Slow		Fast insertion	
	Heavy oil fraction	Light oil fraction	Heavy oil fraction	Light oil fraction
450	45.28	43.79	45.67	45.24
488	45.46	43.13	45.45	44.46
525	44.15	42.42	45.82	45.67
600	41.56	41.60	44.45	42.97

4.3.3 Gas analysis (Atmospheric Conditions)

The gaseous product yield distributions with reference to the feedstock for atmospheric pyrolysis of PP have been presented in Figure 4.4 and Figure 4.5. The description focussed on the hydrocarbon gases and hydrogen because of their promising energy potential. CO and CO₂ detected were attributed to the presence of trace amounts of oxygen gas in the reactor. Their yields were seen to increase with the upsurge of temperature since reactivity of oxygen gas increased with increasing temperature. As depicted in the figures, it was observed that C₃ gases were the most dominant produced at all process conditions. This is expected because polypropylene is made from propylene monomer units and pyrolysis is known to breaking down polymer structures back into their monomers hence the dominating amounts of C₃ (polypropylene monomers) in the gas stream. Similar observations were made by Yan *et al.*,

(2015) and Das & Tiwari, (2018) who all reported C₃ (propane, propadiene and propylene) to be the most dominant of all the gases generated with yields representing around 45 and 35 wt.% of the total gas yield respectively. Hydrogen gas (H₂) production largely increased with increase of temperature, but its production remained relatively low at all process conditions.

Under slow heating rates, yields of gases C₁-C₅, generally increased with the rise of temperature, with 600 °C observed to be the temperature at which maximum yield of all gases were produced. This showed that increase in temperature under slow heating rates generally enhanced some level of cracking reactions that promoted yields of the permanent gases with the rise of temperature.

Under fast-insertion pyrolysis, yields of all the gases, C₁ - C₄ were seen to increase sharply with the upsurge of temperature while for C₅, yield increased from 0.70 to 1.27 wt.% when temperature rose from 450 to 488 °C after which the yields were seen to decrease at the subsequent higher temperatures (525 - 600 °C). The increase in yield of the comparatively lighter hydrocarbon gases (C₁ - C₄) to the detriment of the heavier hydrocarbon C₅ gas with temperature rise also confirms the higher intensity of cracking reactions at higher temperatures under faster heating rates.

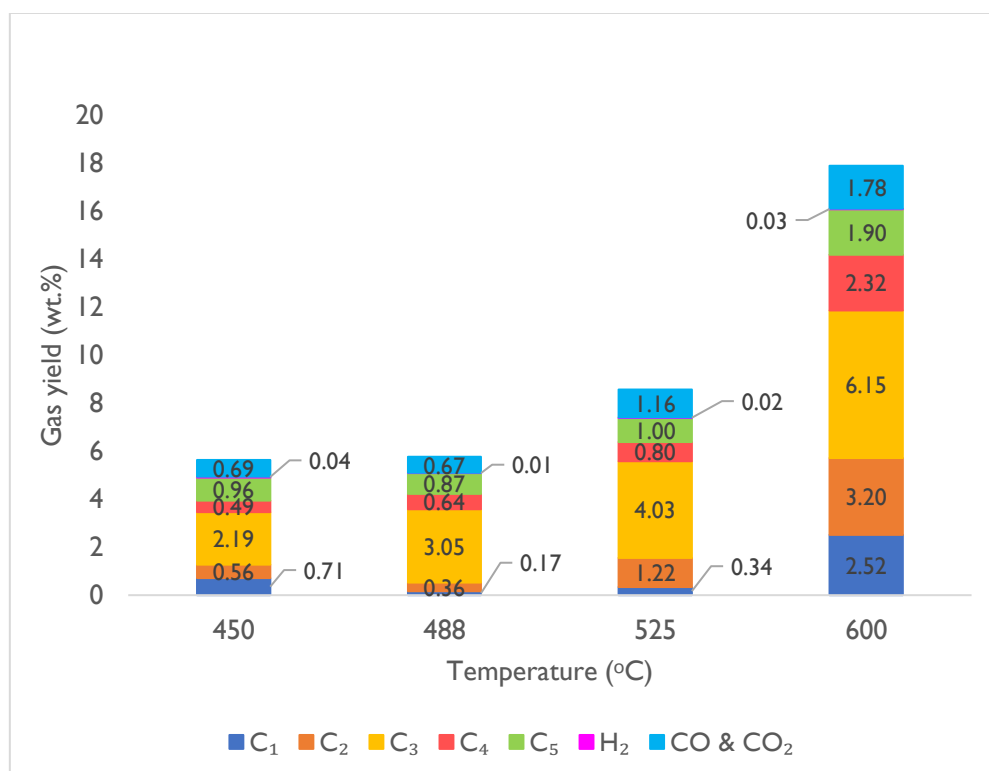


Figure 4.4. Effects of temperature on gaseous product distribution (Atmospheric slow condition)

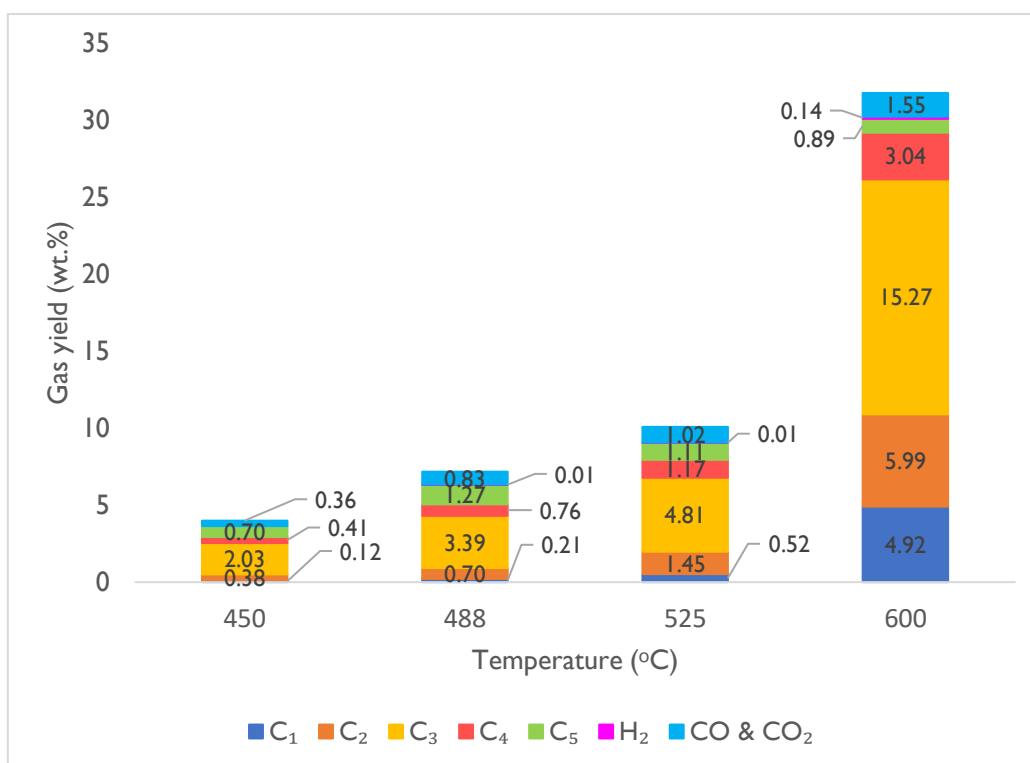


Figure 4.5. Effects of temperature on gaseous product distribution (Atmospheric fast insertion condition)

4.4 Vacuum pyrolysis of PP at bench-scale

Tests under vacuum pyrolysis of PP followed similar approach as atmospheric conditions. Experiments at bench scale were also performed at same temperatures (450, 488, 525 and 600 °C) used for atmospheric pyrolysis at slow and fast heating rates. Condensable products obtained were also characterised for HHV and GC/MS. Permanent gases were characterised using a CompactGC that aided in closing the mass balance. All results obtained under vacuum pyrolysis were compared to atmospheric conditions.

4.4.1 Product yield distribution (Vacuum pyrolysis)

For tests under vacuum conditions, all condensable fractions recovered in the ambient condition condenser were recovered in the form of solid wax (Appendix D). Compared to the waxes recovered in the same condenser under atmospheric conditions, these waxes appeared relatively dry and sticky. These waxes were also referred to as heavy oil products. Condensable products recovered from dry ice condensers, however, were free-flowing liquids

and had similar appearances to those retrieved from same condensers under atmospheric pyrolysis, hence the name light oil fraction was still maintained in this context.

Mass balance at all process conditions ranged between 89 - 98 wt.%. Maximum standard deviation for char, permanent gases, light and heavy condensable products under slow heating rates were 0.6 wt.%, 1.2 wt.%, 3.8 wt.% and 4.6 wt.% respectively whereas that for fast insertion heating rates were 0.5 wt.%, 1.2 wt.%, 2.5 wt.% and 2.4 wt.% respectively (Appendix B).

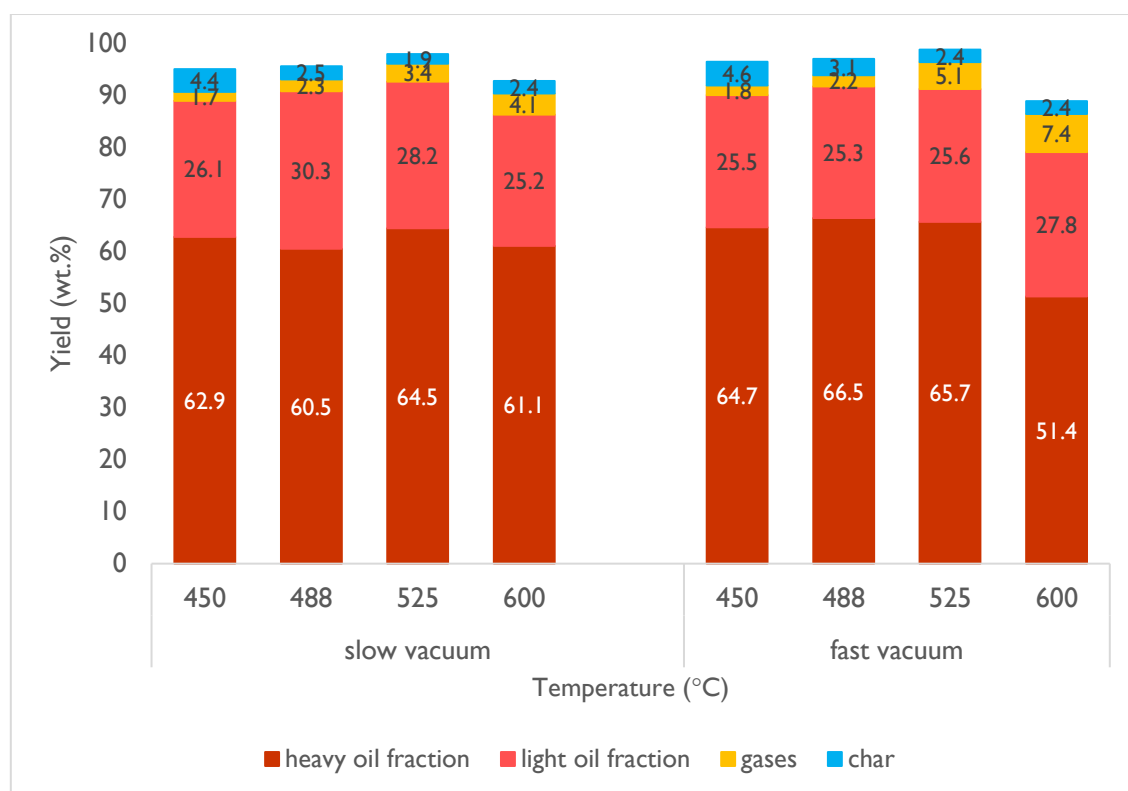


Figure 4.6. Effects of temperature and heating rate on product yield distribution (Vacuum conditions)

Product yield distribution depicted in Figure 4.6 showed that char yields under vacuum slow conditions were lower than 5 wt.%, demonstrating that PP conversion was also nearly complete. It further substantiates the negligible amount of fixed carbon obtained from the proximate analysis of PP. Yield of total condensable products (oil and wax) increased progressively from about 89 wt.% and peaked at 93 wt.% when temperature rose from 450 to 525 °C. It then decreased to 86 wt.% when temperature reached 600 °C, the highest

temperature examined. The decrease in yield of total condensable products after the temperature where peak amounts of condensables were recovered was blamed on cracking reactions. When comparing with experiments under atmospheric conditions, total condensable products under vacuum were higher at similar temperature and at optimal temperature. This was corroborated to the limited cracking effects under vacuum conditions since volatiles generated were quickly removed from the hot part of the reactor. This is consistent with the relatively lower yields of permanent gases generated under vacuum. Between the temperature range, 450 - 525 °C, permanent gas yields under vacuum were at least twice lesser than their corresponding yields under atmospheric conditions. At 600 °C, the highest temperature examined, permanent gas yield recovered under vacuum conditions was about four times even lesser than corresponding yields under atmospheric pyrolysis.

For vacuum fast pyrolysis of PP, insignificant yields of char were also observed. Total yield of condensable products (oil and wax) remained virtually constant (increasing from 90 - 91 wt.%) as temperature progressed from 450 to 525 °C but decreased sharply to about 79 wt.% at 600 °C. Total condensable products yield under vacuum conditions were again observed to be higher than corresponding yields under atmospheric conditions. As observed for atmospheric conditions, significant difference in condensable products yield distribution between slow and fast heating rates under vacuum pyrolysis was also observed only at 600 °C. These differences were however not as pronounced as atmospheric conditions.

In conclusion, at all the process conditions examined, vacuum pyrolysis of PP generated higher yields of condensable products compared to the pyrolysis of PP under atmospheric conditions. This ascertains the promising potential of vacuum pyrolysis in harnessing higher yields of condensable products. Compared to atmospheric pyrolysis, secondary cracking reactions were minimal under vacuum conditions because volatiles were quickly extracted from the reactor by the vacuum suction. This led to the production of significantly high yields (about 80 wt.% at least) of condensable products even at severe temperature and heating rate conditions under vacuum. Only limitation with vacuum pyrolysis of PP is that, majority of the condensable fractions were recovered in the form of wax with over 60% of total condensable fractions recovered as wax at all process conditions.

4.4.2 Condensable products characterisation (vacuum conditions)

4.4.2.3 GC/MS Analysis (Vacuum conditions)

Figure 4.7 illustrates how temperature and heating rate affected the proportions of diesel and gasoline range compounds present in the heavy and light condensable products. Estimation of the proportions followed same procedure as used for atmospheric conditions described in section 4.3.2.1.

It was observed that diesel range compounds predominated at all process conditions which is corroborated to the majority of condensable products being recovered as wax.

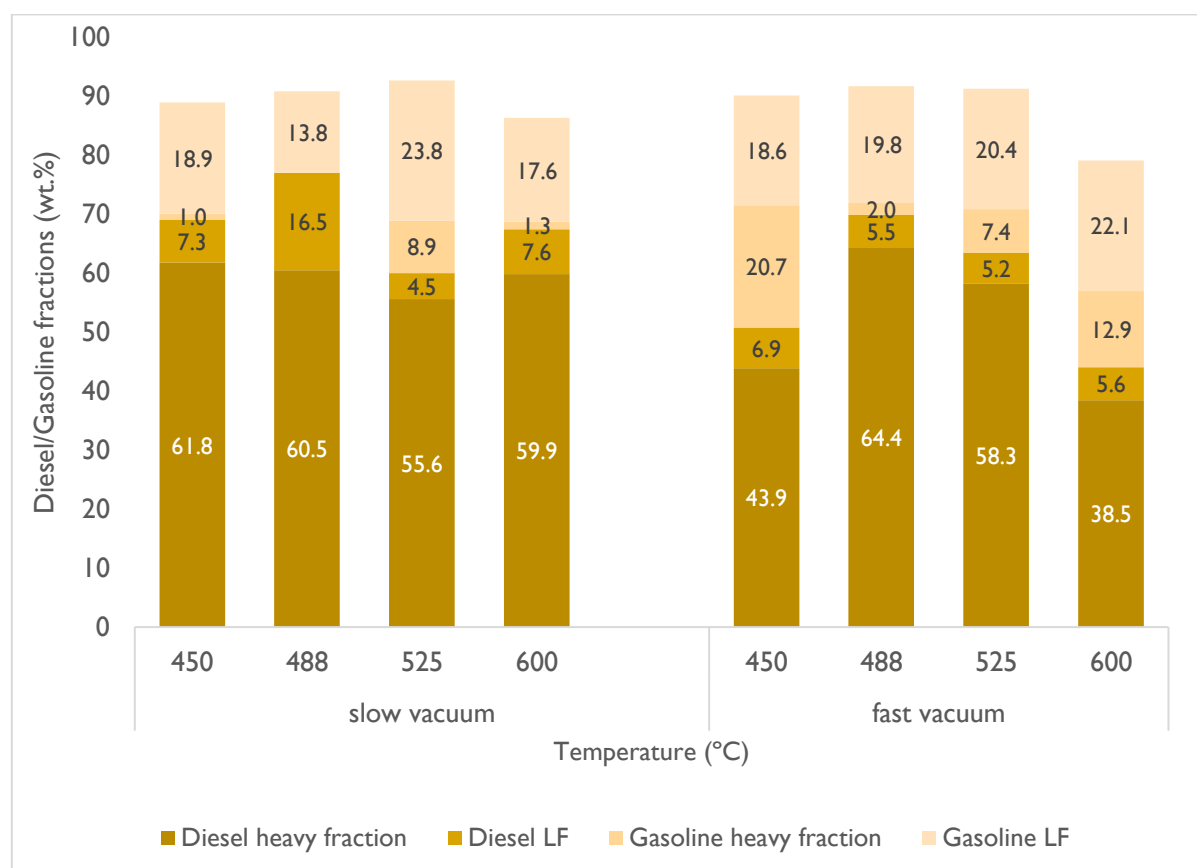


Figure 4.7. Proportions of diesel and gasoline in condensable products (oil and wax) recovered under the vacuum pyrolysis of PP (Diesel and gasoline proportions in each product was based on GC/MS surface area and yields of oil)

For slow heating rate conditions, it was observed that total diesel composition rose from around 69 to 77 wt.% as temperature increased from 450 to 488 °C after which a further increase of temperature resulted in decreases in yields of diesel range compounds. It appears that production of diesel and gasoline range compounds did not follow any definite trend,

but diesel range compounds recovered at much higher temperatures (525 and 600 °C) were lower than the first two initial temperatures (450 and 488 °C), with the converse being true for gasoline range products. This signifies that cracking reactions at higher temperatures somewhat suppressed the production of diesel compounds.

For fast insertion processes, total yield of diesel compounds increased from about 51 to 70 wt.% (maximum yield) as temperature progressed from 450 to 488 °C. Further increase of temperature then resulted in a sharp decrease in diesel yield to around 63 wt.% at 525 °C and 44 wt.% at 600 °C. This observation was attributed to the rapid cracking reactions of heavy compounds (diesel) into lighter ones (gasoline and permanent gases) which is consistent with the corresponding increase in gasoline range compounds observed.

The relatively higher yield of total diesel range compounds (respectively lower gasoline yield) observed at the highest temperature tested (600 °C) under slow heating rates confirms the observation made for the occurrences of feeble secondary cracking reactions under slow heating rates when compared to fast. This is in accordant with the comparatively lower diesel yield (respectively higher gasoline yield) observed at the same temperature under fast insertion conditions.

4.4.2.4 HHV Analysis (Vacuum)

Table 4.4. HHV of PP derived oils (Vacuum conditions)

Temperature (°C)	HHV(MJ/kg)			
	Vacuum Slow		Vacuum Fast insertion	
	Heavy oil fraction	Light oil fraction	Heavy oil fraction	Light oil fraction
450	45.24	42.79	46.03	45.84
488	45.01	42.90	45.58	45.01
525	45.53	43.01	45.96	44.94
600	45.22	42.78	45.53	45.60

HHVs of condensable products recovered under vacuum pyrolysis of PP have been presented in Table 4.4. Unlike atmospheric conditions where HHVs were observed to decrease with the increase of temperature, HHVs of each type of condensable product recovered under vacuum stayed high even at higher temperatures under all process conditions. This was attributed to

the limited formation of aromatics under vacuum pyrolysis, which is consistent with the predominant yield of diesel range compounds observed at all process conditions (from GC/MS tests presented in previous section, diesel compounds were identified to contain lower amounts of aromatic compounds compared to gasoline). Similar to what was observed under atmospheric conditions, it was also noticed that under vacuum conditions, HHVs of heavy condensable products were greater than HHVs of corresponding light condensables, which was attributed to the higher number of carbon compounds present in the heavy products. HHVs of all condensables reported under vacuum were consistent with the HHVs of commercial liquid fuels. HHVs obtained ranged between 42 - 46 MJ/kg and were comparable with commercial diesel and gasoline fuels.

4.4.3 Gas Analysis (Vacuum conditions)

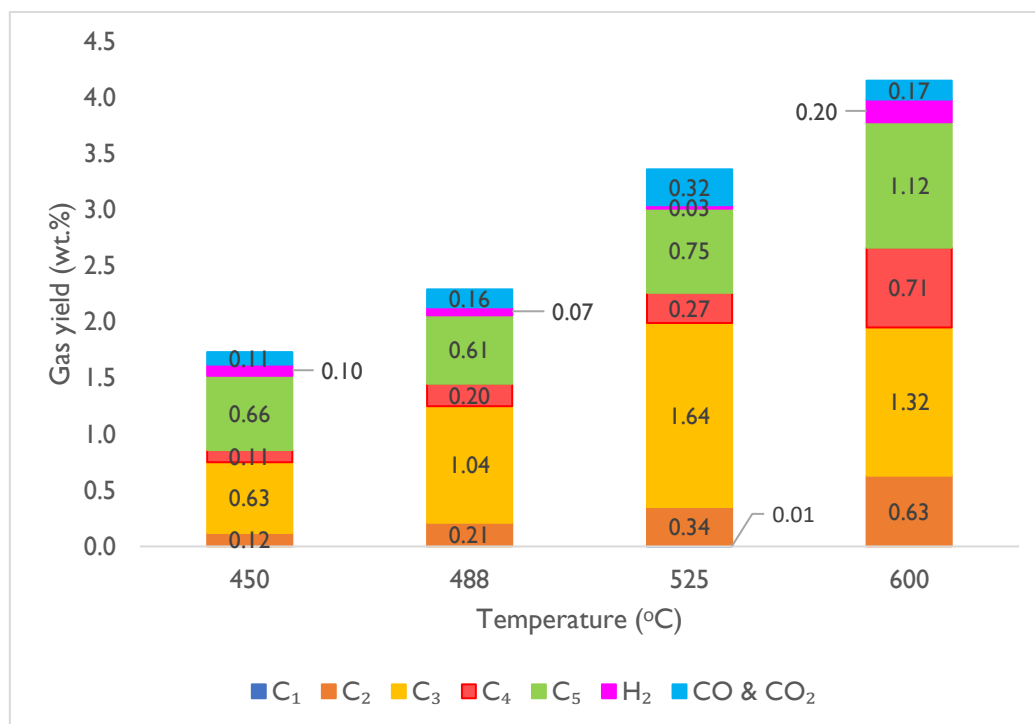


Figure 4.8. Effects of temperature on gaseous product distribution (Vacuum slow conditions)

Figure 4.8 and Figure 4.9 illustrate the yields of permanent gases generated from the pyrolysis of PP under vacuum conditions. Unlike the spectrum of gases generated under atmospheric conditions, total amount of CO and CO₂ detected under vacuum pyrolysis were comparatively low, demonstrating that, very little amount of oxygen was present in the reactor under vacuum. Similar to atmospheric conditions, C₃ gases were the most prevalent at all the

process conditions showing that significant amounts of depolymerisation of PP back into its monomer compounds also occurs in PP conversion under vacuum. Also, a combined C_1 yield of only 0.02 wt.% was produced under both slow and fast heating rates, confirming that minimal cracking reactions occurred under vacuum conditions. Yields of hydrogen gas (H_2) retrieved under vacuum were also noticed to be comparatively higher than corresponding yields recovered under atmospheric conditions.

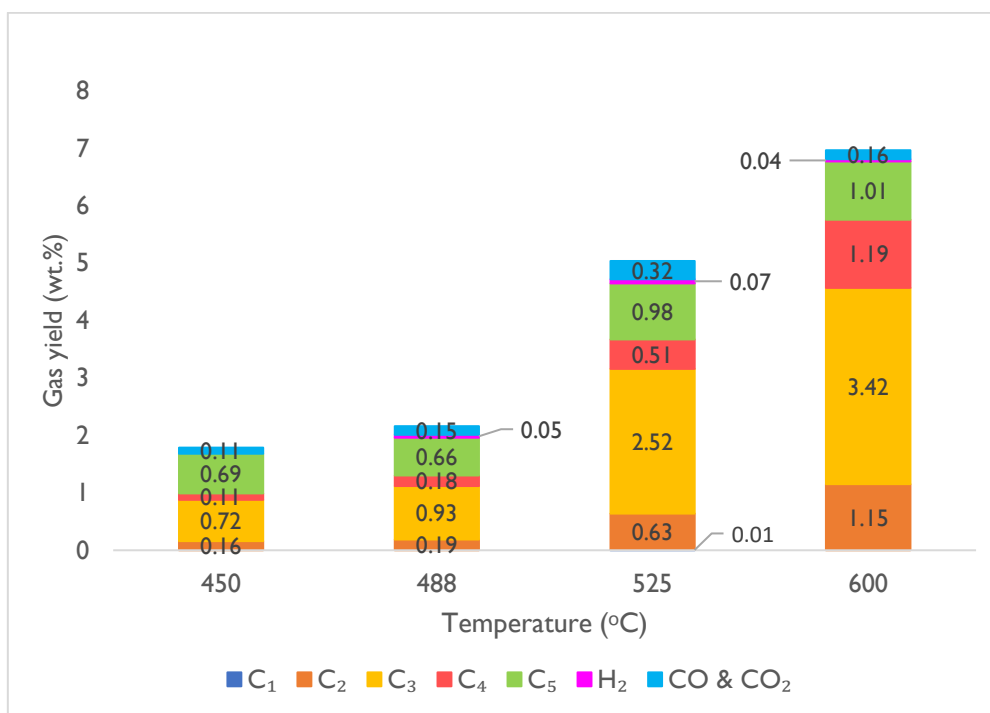


Figure 4.9. Effects of temperature on gaseous product distribution (Vacuum fast insertion conditions)

Under both slow and fast insertion processes, it was observed that the yields of the gases C_2 - C_5 generally increased with the upsurge of temperature with none of the heavier gases cracking further to produce lighter ones at higher temperatures. This ascertains the fact that pyrolysis under vacuum conditions (even at severe conditions of temperature and heating rate) significantly suppressed cracking reactions. Compared to atmospheric conditions, it was observed that total gas yields under vacuum conditions were significantly lower. At all process conditions, total gas yields under atmospheric conditions were at least twice that of the corresponding yields obtained under vacuum. This further validated the reduced degree of cracking reactions under vacuum.

4.5 Process Development at Pilot Scale

This section tackles the pilot scale pyrolysis of PP. As stated in section 3.4.2.1, the objective of the pilot scale study was to mimic bench-scale atmospheric pyrolysis tests to ascertain how they both compare (since they have different configurations). Pilot study was also performed to address any industrial scale prospects. As fast insertion and slow pyrolysis gave similar yields, it was decided to mimic fast insertion, due to the similarity of the two processes. Indeed, with the pilot, sample is introduced in a pre-heated reactor just like for fast insertion processes. While as in the case of fast insertion test at bench scale, the heating rate could not be set, the heating rate was influenced by the reactor temperature on the pilot: An increase in temperature automatically resulted in an increase in the heating rate of the sample particles.

This section therefore encompasses, the effects of temperature on product yield distribution and quality of condensable products. Effects of the process parameters on composition of permanent gases were also investigated. Also addressed are the Physico-chemical properties (density, viscosity, pour point, boiling point range etc.) of condensable products recovered and how they compare with commercial diesel and gasoline fuels.

4.5.1 Product yield distribution (Pilot scale pyrolysis)

A 5 kg/h pyrolysis pilot plant was designed and commissioned after which bench-scale experiments were projected to the pilot plant. Pilot scale tests were performed at five different temperatures (450, 460, 488, 507 and 525 °C). The selection was based on temperatures used for bench-scale tests but saw the inclusion of temperatures, 460 and 507 °C and exclusion of 600 °C. As mentioned at section 3.4.2.2, the latter temperature was excluded from pilot tests because, conversion was quite severe as observed with bench scale tests and promoted the formation of significant amount of permanent gases which is not of interest in this study. The former temperatures were included to increase the chances of easily identifying the most suitable temperature at which maximum condensable products were attained. The vacuum pump on the pilot had a maximum suction capacity of about 2 kPa below atmospheric pressure which is relatively close to ambient pressure compared to the vacuum pressure on bench (90 - 95 kPa below atmospheric). Standard deviations of char, oils, waxes and permanent gases were less than 0.3, 2.6, 2.6 and 2.2 wt.% respectively (Appendix B).

Table 4.5. Summarised description of oil labels

Oil label	Description
C1A	Top oil fraction of condenser 1
C1B	Bottom oil fraction of condenser 1
C2	Oil recovered from condenser 2
C3	Oil recovered from condenser 3
C4	Oil recovered from condenser 4
CF	Oil collected at reactor and feeder joint
CW	Wax recovered from char collection box

Based on the pilot design, contrary to what was expected, significant amount of wax was collected in the char collection box as can be seen in Figure 4.10. As highlighted earlier under section 3.4.2.2, the wax was recovered together with char samples as two separate layers with the char at the bottom. The char was then carefully scraped off the wax and weighed separately. For each temperature, oils were recovered in all four condensers with the first condenser recovering the most. Two different types of oil based on physical observations were recovered from Condenser 1 at all temperatures. At relatively lower temperatures, 450 and 460 °C, a more viscous and opaque oil was recovered at the bottom whereas a clear, less viscous oil was recovered on top. At relatively higher temperatures (488 - 525 °C), oil fractions recovered in Condenser 1 were both highly waxy in nature but differed in colour. These are depicted in Figure 4.11 & Figure 4.12 respectively. The lighter oil fractions which were always recovered on top of condenser 1 were labelled C1A while those recovered at the bottom were labelled C1B. Furthermore, at temperatures 450 and 460 °C, an extra dark coloured oil was collected at the joint of the reactor inlet duct and the piston feeding system due to the release of volatiles during the back and forth movement of the piston feeder. This oil was labelled as CF. Oils from condensers 2, 3 and 4 were labelled as C2, C3 and C4 respectively. Unlike condenser 1, these oils were all single-phase in nature. Waxes recovered from char collection box were labelled as CW. Devised labels of oil and wax products have been summarised in Table 4.5. Waxy oils recovered in condensers 1 were categorised as oil together with all other

oils retrieved from the condensers. Waxes recovered from the char collection box were tagged as wax.



Figure 4.10. Sample of product recovered from char collection box showing layers of char (in black) and wax (in gold). (A) View showing both layers of char and wax, (B) View showing mainly char, (C) view showing mainly wax



Figure 4.11. Oil samples obtained in condenser 1 at 460 °C. (A) Top light fraction, (B) Bottom waxy fraction. Samples physical appearances are similar to those recovered at 450 °C.

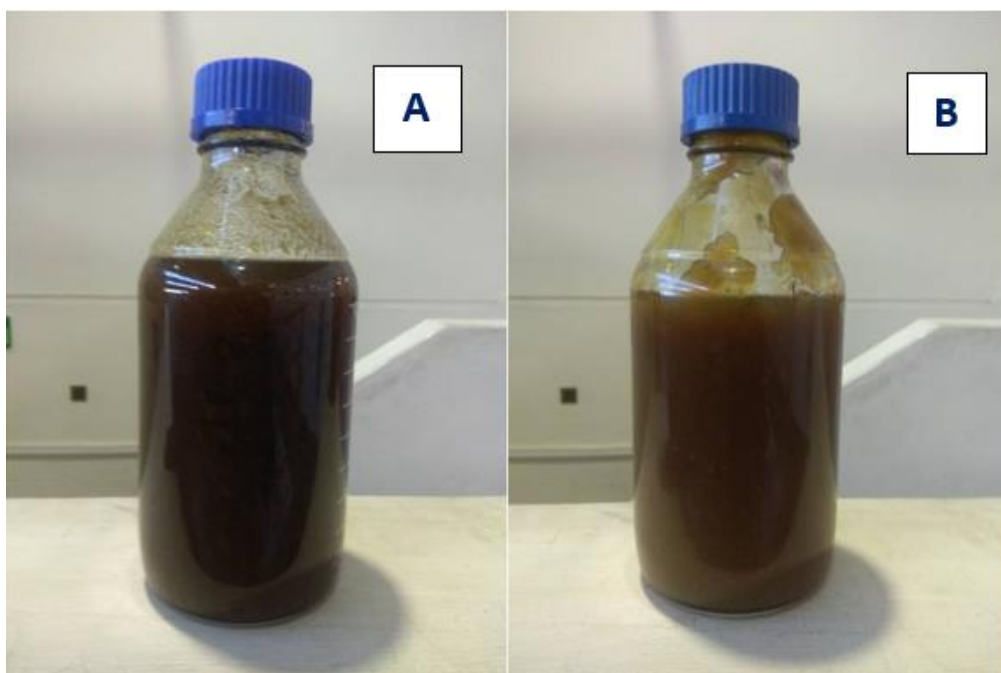


Figure 4.12. Oil samples recovered in condenser 1 at 488 °C. (A) Top dark waxy oil fraction, (B) Bottom brownish waxy oil fraction. Physical appearance of samples is similar to those obtained at temperatures, 507 and 525 °C.

Figure 4.13 represents the effects of temperature on products distribution at pilot scale pyrolysis of PP. Mass balance at all temperatures ranged between 83 to about 88 wt.% which is quite promising considering how challenging it was to completely keep the system air tight. For instance, during the continuous closing and opening of pneumatic valves in the feeder, some smoke released evidenced the loss of volatiles.

Product distribution revealed that, char yield was relatively negligible, with the highest and lowest yields (1.29 and 0.55 wt.%) obtained at the lowest and highest temperatures respectively. Total condensable products (oil and wax) yield of about 77 wt.% was recovered at 450 °C which rose gently to about 80 wt.% when temperature reached 460 °C. This temperature was observed to be the temperature where maximum yield of condensable products were recovered. A further increase of temperature to 488 °C, resulted in a sharp decrease in condensable products yield to about 70 wt.%, which is attributed to the incidence of secondary cracking reactions. This is consistent with the increase in the yield of permanent gases from around 6.8 to 10.6 wt.% for the same temperature rise. This suggests that, conversion at 488 °C on the pilot is already high enough temperature for significant

occurrence of cracking reactions. Condensable products yield was found to remain virtually constant (at about 70 wt.%) as temperature progressed from 488 to 525 °C. The trend infers that the degree of secondary cracking reactions remained unchanged for the temperature range 488 to 525 °C, which was not expected when compared to bench scale tests.

The evolution of permanent gas yield was observed to increase steadily from about 5.6 to 15.5 wt.% as temperature rose from 450 to 525 °C. As observed for bench scale tests, the gradual increase in permanent gas yield to the detriment of oil yield observed, could be attributed to the occurrence of more cracking reactions of the partially converted plastics and volatiles in the hot part of the reactor. It is likely that oil at 488 °C was slightly underestimated (consistent with its lowest mass balance), probably due to more volatile loss, which means that oil yield at 488 should probably intermediate between yields obtained at 460 °C and 507 °C. Though oil yield at 488 °C was probably underestimated, the optimum at temperature around 460 °C appears reliable based on the lower gas yield, when compared to 488 °C.

Comparing the optimum yield of oil (about 85 wt.%) attained at 488 °C under atmospheric fast insertion at bench scale (similar to the pilot process since reactor is pre-heated in both cases) to the pilot's 80 wt.% obtained at 460 °C, it was detected that maximum yield on the pilot decreased by about 6% with optimum temperature decreasing by 28 °C. Part of the difference could be due to lower mass balance due to more product loss on the pilot. The fact that lower temperature was required for the conversion at pilot scale was probably due to more extensive cracking in the pilot reactor. The reason for a lower maximum condensable products yield obtained at a lesser temperature on the pilot level is ascribed to the following;

1. It was assumed that, the much more elongated length of the pilot reactor compared to the bench scale reactor increased the residence time of the volatiles in the pilot reactor which promoted secondary cracking reactions that reduced the oil yield in effect. Conversion of PP on the pilot occurred across the whole length (750 mm) of the reactor whereas conversion on bench took place only at a segment of the reactor (heated segment) with length of around 475 mm. Also, the volume of the pilot far supersedes that of the bench scale reactor hence the higher residence time of the volatiles.

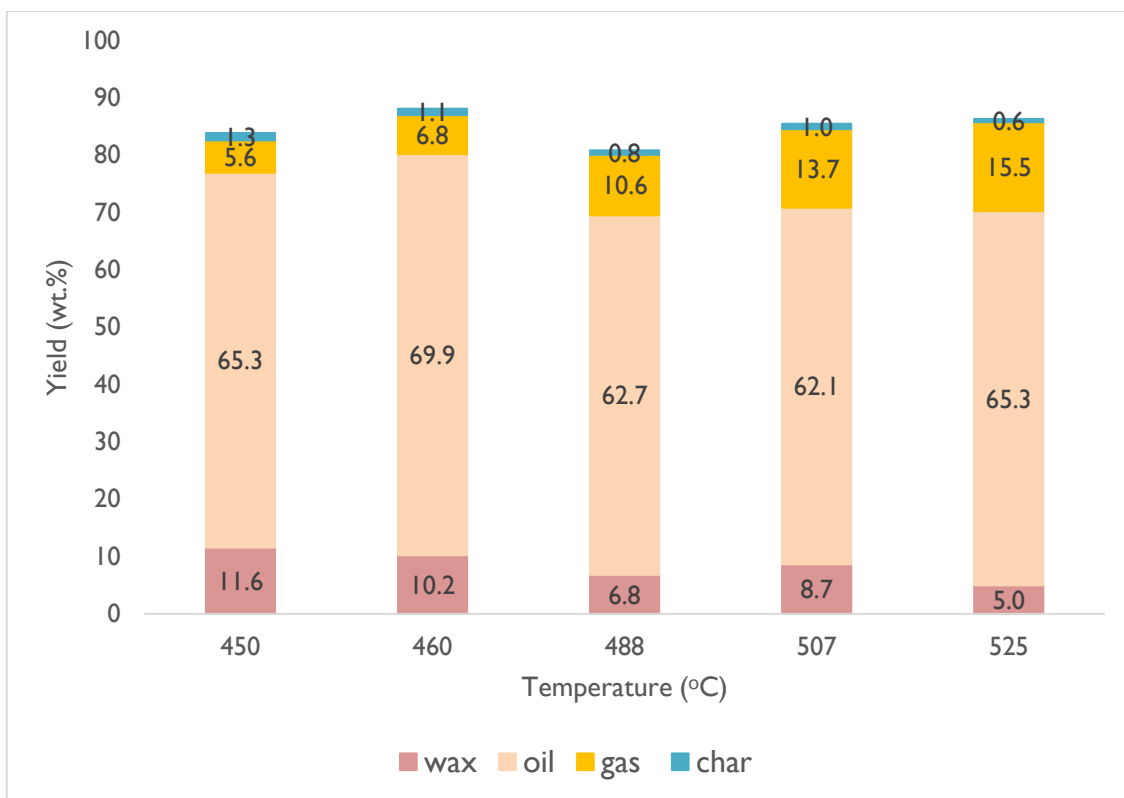


Figure 4.13. Effects of temperature on product yield distribution (Pilot scale pyrolysis of PP)

4.5.2 Liquid product analysis (Pilot scale process)

4.5.2.5 GC/MS Analysis (Pilot scale process)

GC/MS characterisation and analysis of condensable products recovered from pilot runs followed similar process as described for bench scale, where the proportions of diesel (respectively gasoline) was multiplied by the yield (wt.%) of the condensable products to estimate the yield of diesel (respectively gasoline) in each product fraction. The yields of diesel (C₁₁-C₂₃) and gasoline (C₆-C₁₀) are presented in Figure 4.14 and Figure 4.15 respectively.

From the figures, it was observed that diesel range product dominated in oils recovered in the first condenser which is expected because the heavier molecular weight compounds (diesel) get condensed ahead of the light compounds (gasoline). That is, the higher boiling point molecules will condense at a higher temperature, which is the first condenser (beginning of the condensation system). These trends are consistent with those obtained for bench scale tests (atmospheric fast insertion) where diesel range compounds dominated oils recovered in the first condenser. Diesel range compounds were also the most prevalent at all

temperatures examined. This is contrary to what was observed at bench (atmospheric fast insertion) where gasoline range compounds were the most prevalent. This differing phenomenon was attributed to the presence of slight vacuum conditions on the pilot, which might have aided in somewhat extracting volatiles faster from the hot reactor zone, thereby limiting cracking which has been established to favouring the production of gasoline.

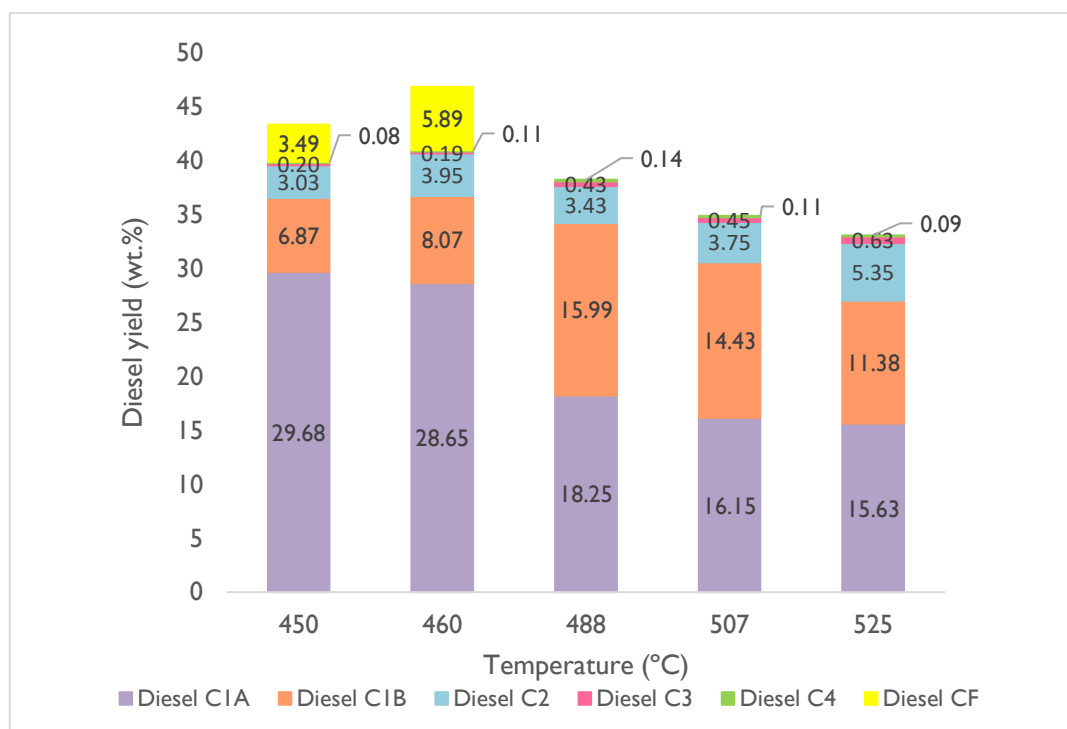


Figure 4.14. Yields of Diesel present in all oil products from pilot scale pyrolysis of PP (Proportions in each product was based on GC/MS surface area and yield of oil)

As represented in Figure 4.14, it was observed that total diesel yield increased somewhat from about 43 wt.% to 47 wt.% when temperature rose from 450 to 460 °C after which a steady decrease in yield (from 38 to 33 wt.%) was observed with the subsequent increase of temperature (488 - 525 °C). Maximum yield of diesel was obtained at 460 °C. On the other hand, 525 °C was the temperature at which minimum yield of diesel was recovered. Decrease in diesel yield at higher temperatures was expected because higher temperatures promoted cracking of heavy compounds (diesel) into lighter ones (gasoline and permanent gases). From Figure 4.15 total gasoline range compounds rose slightly from about 21 to 23 wt.% as temperature progressed from 450 to 460 °C. Yield then dropped to about 17 wt.% at

temperatures, 488 and 507 °C and was seen to rise slightly again to 18 wt.% at the final temperature tested, 525 °C. Gasoline compounds had comparatively higher yields at the first two initial temperatures (450 and 460 °C) when cracking reactions were still minimal. Their yields however reduced substantially at the subsequent higher temperatures investigated (488 - 525 °C). This was blamed on the further loss of gasoline compounds into more permanent gases arising from the much more severe cracking on the pilot. This is in agreement with the sudden increase in yields of permanent gases observed for the same temperature range.

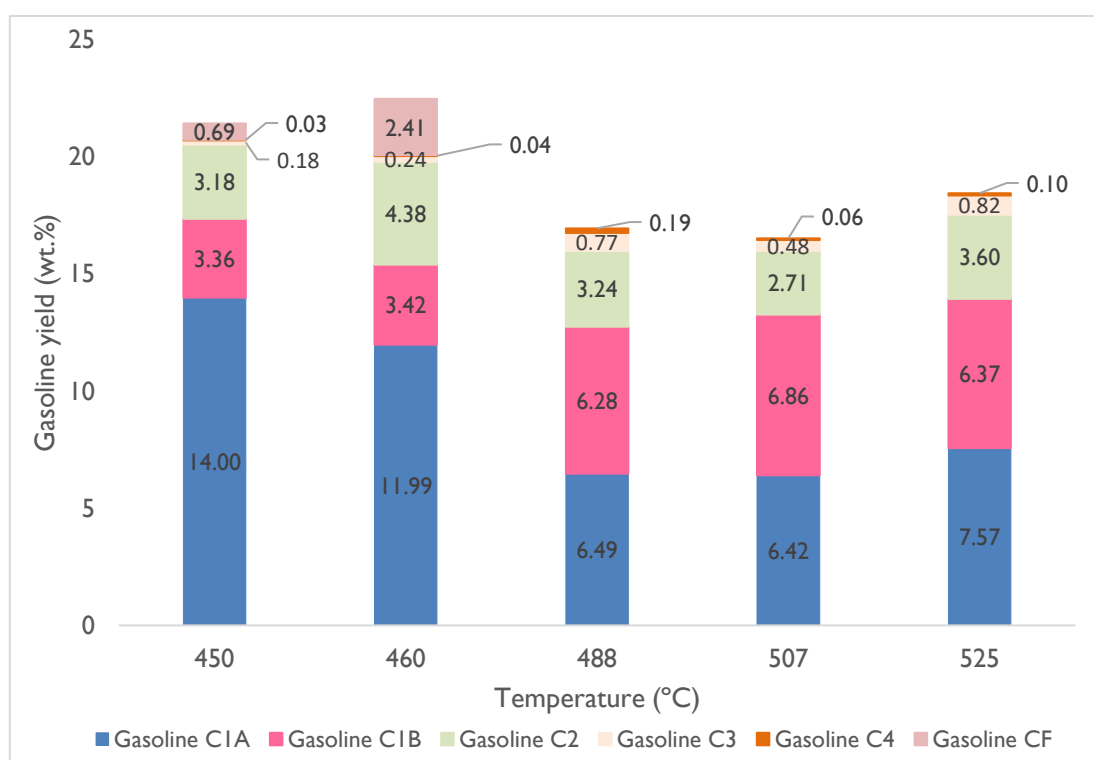


Figure 4.15. Yields of Gasoline present in all oil fractions from pilot scale pyrolysis of PP (Proportions in each product was based on GC/MS surface area and oil yield)

4.5.2.6 HHV of condensable products oils (pilot study)

The HHV for all oil samples are presented in Table 4.6. It can be seen that all oil samples had HHV ranging between 44 to 46 MJ/kg which is equivalent with commercial diesel and gasoline fuels. Unlike bench scale atmospheric fast insertion process where HHVs for each type of oil were observed to generally decrease with the upsurge of temperature, HHVs on pilot stayed high at higher temperatures and did not change with the rise of temperature. This difference

observed is consistent with the diesel and gasoline proportions obtained for each set of tests. Pilot scale products had diesel range compounds dominating at all temperatures, which means comparatively lower aromatics were present and hence the higher HHVs of condensables even at higher temperatures. For bench scale tests, gasoline range compounds predominated and that means increased aromatics with temperature rise and hence the lower HHVs observed with the upsurge of temperature.

Table 4.6. HHV of PP oils recovered from pilot pyrolysis of PP

Temperature (°C)	HHV (MJ/kg)						
	C1A (liquid)	C1B (liquid + wax)	C2 (liquid)	C3 (liquid)	C4 (liquid)	CF (liquid)	CW (wax)
450	45.75	45.37	45.49	45.42	45.36	45.83	46.33
460	45.94	44.91	45.16	46.24	45.86	45.91	45.55
488	45.92	45.38	45.56	45.12	45.41	N/A	45.24
507	44.59	44.45	44.98	45.75	45.79	N/A	46.78
525	44.25	44.61	45.11	45.00	44.54	N/A	45.79

N/A- No sample available at that condition; C1A- Top oil fraction from condenser 1; C1B; Bottom oil fraction from condenser 1; C2- Oil from condenser 1; C3- Oil from condenser 2; C4- Oil from condenser 4; CF- Oil from feeder/reactor inlet joint; CW- Wax from char pot

4.5.3 Gas Analysis (Pilot scale process)

Distribution of yields of gaseous products generated from the pyrolysis of PP at pilot scale is presented in Figure 4.16. Like bench scale processes, the description played emphasis on the hydrocarbon gases and hydrogen because of their huge energy potential. As observed from the plot, C₃ was the predominant fraction at all temperatures which is consistent with what was reported from bench scale in section 4.3.3. Also, like bench scale processes, presence of CO and CO₂ was blamed on traces of oxygen present in the reactor. Reactivity of oxygen increases with the increase of temperature which could explain the increasing yield of CO and CO₂ with the rise of temperature.

From the graph, C₃ yield rose slightly from 2.07 to 2.59 wt.% when temperature progressed from 450 to 460 °C. Yield further increased appreciably at subsequent temperatures (488 - 525 °C) and peaked at 525 °C, where a yield of 8.30 wt.% was attained for C₃. Just as observed at bench scale, the domination of C₃ in the gas stream, is an indication that cracking of PP back to its monomer structure also happens during conversion on the pilot. This trend is consistent with what was reported by Das and Tiwari, (2018) and Ciliz *et al.*, (2004) who all reported C₃ as the predominant product in their gas stream.

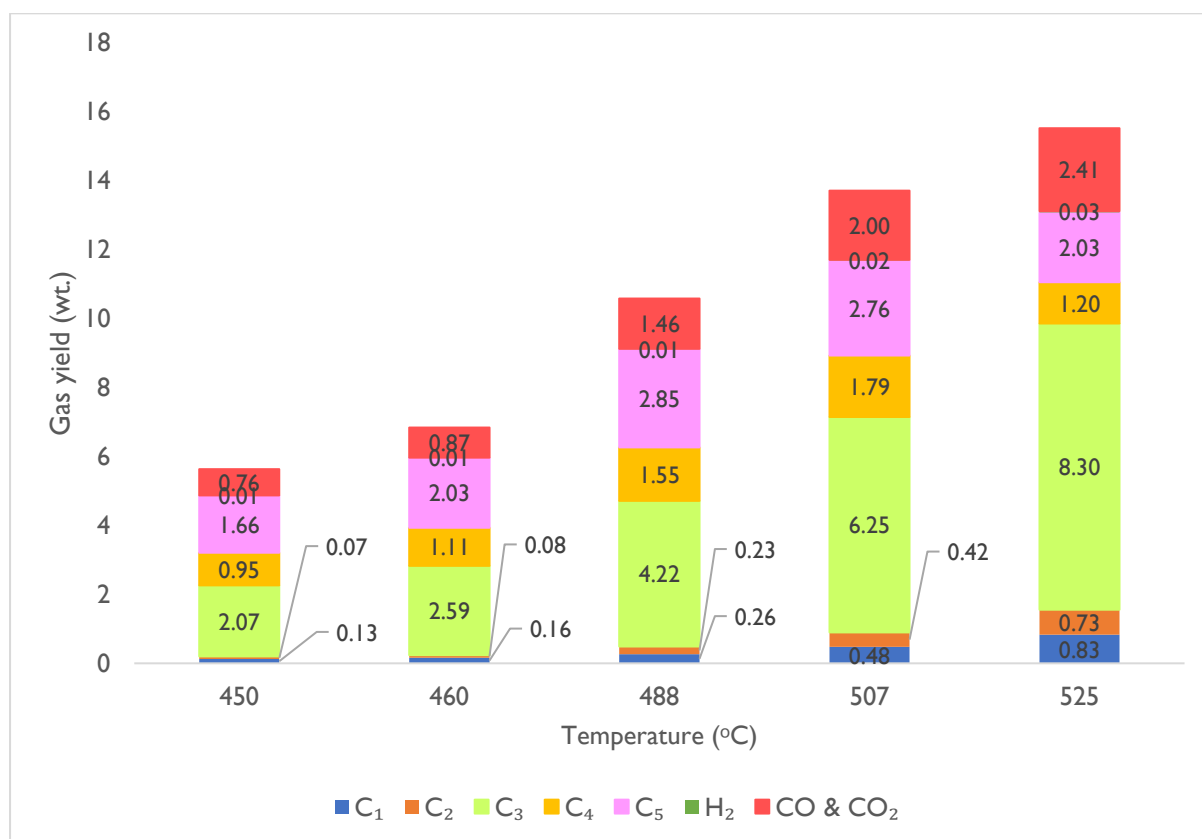


Figure 4.16. Effects of temperature on gaseous product distribution (Pilot scale pyrolysis of PP)

Moreover, C₁ and C₂ gases followed similar trend observed for C₃ but their yields were comparatively lower. They were also seen to increase steadily with the rise of temperature with their highest yields (0.83 and 0.73 wt.% respectively) obtained at 525 °C. Also, C₄ and C₅ gases increased steadily as temperature progressed from 450 to 507 °C but decreased abruptly when temperature reached 525 °C. The increase in yield of the lower molecular weight gases (C₁ - C₃) to the detriment of the heavier molecular ones (C₄ and C₅) as

temperature intensified further validates the occurrences of cracking reactions at higher temperatures. Like bench scale tests, yield of hydrogen gas was relatively negligible and was seen to increase with the rise of temperature.

4.5.4 Comparing fuel properties of PP pyrolysis oils with commercial fuels

Oil products derived from pilot scale experiments were subjected to the following fuel tests and compared to commercial diesel and gasoline fuel specifications; Density @ 20 °C, Kinematic Viscosity @ 40 °C, Pour Point, Distillation to determine boiling point range and Cetane index. The methods followed to performing these tests have been highlighted in section 3.5.3. Flash point was not examined because initial boiling point of all oils were quite low which implies that their flash points could be around ambient temperature, 20 °C. Also, only oils obtained from condenser 1 (C1A and C1B), C2 and CF were characterised for fuel tests. C3 and C4 could not be tested because their volumes were not enough for the tests. A set of tests required a minimum of 250 ml of sample. Moreover, waxy oils especially for those obtained from 488 to 525 °C could not be characterised for distillation, flash point and cetane index because they could not be distilled. All these tests require that samples can be distilled. Also, CF oil obtained at 450 °C could not be characterised for these tests for similar reason.

Fuel tests for the oils characterised have been presented in Table 4.7. with specifications for commercial diesel and gasoline fuels also depicted in Table 4.8.

At 450 °C, Density @ 20 °C for all oils remained virtually constant. Density for oils C1A, C1B and C2 ranged between 0.77 to 0.78 kg/L with CF having the highest density of 0.79 kg/L. Also, compared to the other oil fractions, CF had the highest viscosity of 2.53 mm²/s with C2 being possessing the least, 0.96 mm²/s. These observations ascertain the dominance of heavier molecular weight compounds (diesel) in CF and light molecular weight compounds (gasoline) in C2 as observed with GC/MS tests. Similar observations were made for oils recovered at 460 °C. CF had the highest density (0.80 kg/L) and viscosity (1.95 mm²/s) whereas C2 had the lowest density and viscosity of 0.76 kg/L and 1.71 mm²/s respectively. Also, at subsequent temperatures (488 - 525 °C) it was observed that C1A and C1B had higher densities than C2 which is also as a result of the presence of different molecular weight compounds. It was however noticed that for all the oil fractions, pyrolysis temperature had no substantial effect on their density. Moreover, compared to commercial diesel and gasoline fuels, only CF (460 °C) and C1A (at 488 °C) had density comparable with diesel. All the other oils had density

values between diesel and gasoline which is consistent with the fact that compounds belonging to both ranges of diesel and gasoline are present in oils. Except for oils CF (at 450 °C) and C1A (at 488 °C) which have viscosities falling in the diesel range, all other oils had viscosities falling between that for diesel and gasoline range. Pour point, the minimum temperature at which the oil ceases to flow, for all oils were less than 18 °C which implies that all the oils obtained have pour point consistent with the specification required for commercial liquid fuels. Furthermore, it was noticed that the initial boiling points for all oil products were in the range of the initial boiling point for commercial gasoline fuels whereas their final boiling points lied in the region of the final boiling point for commercial diesel. This buttresses the fact that all oil products that could be analysed from the pilot pyrolysis of PP contained both compounds in the diesel and gasoline range. Also, except for oil C2 (at 450 °C), all oils characterized for cetane index, had cetane indices above 40 (which is the minimum requirement according to ASTM). This implies that majority of the oils recovered will readily combust in a diesel engine (Bacha *et al.*, 2007). Lastly, aniline point is a measure of the proportions of aromatic compounds present in the oil. Compared to the commercial standards of aniline point, it appears that for the oils tested, CF (at 460 °C) had the highest aniline point which implies that the oil contained lower amounts of aromatics and higher amounts of paraffinic compounds. C1A (at 450 °C), C2 (at 450 °C) and C1A, C2 (at 460 °C) however had comparatively lower aniline points which indicates that they contained higher amounts of aromatic compounds.

Table 4.7. Fuel properties of PP pyrolysis oils

Sample	Fuel Properties						
	Density @ 20 °C (Kg/L)	Kinematic Viscosity @ 40 °C (mm ² /s)	Pour point (°C)	IBP (°C)	FBP (°C)	Cetane Index	Aniline Point (°C)

450 °C

C1A	0.77	1.27	<-40	63	349	52	63
C1B	0.78	1.70	<-40	67	359	50	N/A
C2	0.77	0.96	<-40	56	340	38	58
CF	0.79	2.53	-33	N/A	N/A	N/A	N/A

N/A- Sample not compatible with test

460 °C

C1A	0.78	1.81	<-40	69	357	56	60
C1B	0.79	1.71	<-40	69	362	57	N/A
C2	0.76	0.91	<-40	66	342	56	58
CF	0.80	1.95	-36	92	306	56	71

N/A- Sample not compatible with test

488 °C

C1A	0.80	2.14	-10	N/A	N/A	N/A	N/A
C1B	0.79	1.93	-7	N/A	N/A	N/A	N/A
C2	0.77	1.09	<-40	60	342	41	N/A

N/A- Sample not compatible with test

507 °C

C1A	0.79	1.88	-5	N/A	N/A	N/A	N/A
C1B	0.79	1.97	-2	N/A	N/A	N/A	N/A
C2	0.78	1.58	-6	87	354	55	N/A

525 °C

C1A	0.79	2.09	-5	N/A	N/A	N/A	N/A
C1B	0.79	1.76	-6	N/A	N/A	N/A	N/A
C2	0.78	1.36	-6	N/A	N/A	N/A	N/A

N/A- Sample not compatible with test

Table 4.8. Specifications for commercial diesel and gasoline fuels

Fuel	Fuel Properties						
	Density @ 20 °C (Kg/l)	Kinematic Viscosity (m ² /s)	Pour point (°C)	IBP (°C)	FBP (°C)	Cetane Index	Aniline Point (°C)
Diesel	0.8 ^[1]	2.2 - 5.3 ^[1]	≤ 18 ^[4]	172 - 196 ^{[2] [5]}	350 - 362 ^{[1] [2]}	min, 40 ^[3]	77.5 ^[3]
Gasoline	0.71 - 0.79 ^{[1] [8]}	1.17 ^{[1] [9]}	N/A	27 -40 ^{[2] [6] [7]}	215 - 225 ^{[1] [2] [8]}	N/A	71 ^[3]

N/A -Not applicable

Sources: ^[1]SANS, 2014a; ^[2]Owusu *et al.*, (2018); ^[3]Ahmad *et al.*, (2015); ^[4]Miandad *et al.*, (2016); ^[5]Kalargaris *et al.*, (2018); ^[6]Heydariaraghi *et al.*, (2016);^[7]Pinto *et al.*, (1999); ^[8]SANS 2014b; ^[9]Sharuddin *et al.*, 2016

Chapter 5

Conclusions and recommendations

5.1 Conclusions

This study focused on the bench-scale optimisation of temperature and heating rate which appeared to be the key process parameters that affect PP pyrolysis, with the aim of improving oil yield and fuel properties. Also, pyrolysis processes at bench-scale were conducted under atmospheric and vacuum conditions and compared to ascertain which of the two scenarios yielded the most condensable products with most promising fuel characteristics. Finally, optimum conditions from bench-scale experiments were scaled up to a 5 kg/h pilot plant (that was designed and commissioned as part of the study) to simulate industrial processes and also validate the results from bench.

Following bench scale experimental work, the following conclusions can be drawn:

1. Under atmospheric pyrolysis of PP (both slow and fast insertion), optimum condensable fractions (oil/wax) were attained at 488 °C after which a subsequent increase of temperature initiated secondary cracking reactions known to promote the yields of permanent gases over condensable products. Therefore, to maximise oil yield under atmospheric pyrolysis of PP, higher temperatures above 488 °C need to be avoided.
2. Yields of condensable products under vacuum pyrolysis of PP were higher than their corresponding yields recovered under atmospheric conditions. This is due to the short residence time of volatiles under vacuum conditions limiting cracking. Limitation of vacuum is the recovery of high amounts of wax from the condensable products.
3. Higher Heating Values (HHVs) of all condensable products (oil/wax) recovered from the atmospheric and vacuum pyrolysis of PP ranged between 41 - 46 MJ/kg and were comparable with commercial liquid fuels. Severe secondary cracking reactions were found to decrease HHVs of condensable products due to the increased production of aromatics.

4. Production of more gasoline range compounds in condensable products retrieved from the pyrolysis of PP was favored mostly under reaction conditions where some secondary cracking occur with the converse being true for diesel range compounds.

From the process development at pilot scale, the following conclusions were drawn:

1. The 5 kg/h pyrolysis pilot plant was successfully designed and commissioned. The plant operated successfully in converting both plastics and non-plastic wastes into final pyrolysis products.
2. Compared to the results obtained from bench scale, optimum oil yield temperature of 460 °C obtained on the pilot decreased by 28 °C with the optimum yield decreasing by 6%. This was attributed to the elongated length of the reactor which increased the volatile residence time thereby enhancing more secondary cracking reactions.
3. HHVs of oils retrieved from the pilot scale tests were consistent with those recovered from bench scale tests. The HHVs were also similar to commercial diesel and gasoline fuels.
4. Production of more diesel range compounds was preferred at lower pyrolysis temperatures whereas that for gasoline range compounds is favored at higher pyrolysis temperatures. This conclusion is consistent with what was observed at bench scale.
5. Gases generated from PP pyrolysis are composed primarily of the hydrocarbon gases ranging from C₁ to C₅ with traces of hydrogen which is an indication that gases generated from the process have promising energy content that can be used to sustain the pyrolysis process or channeled for other energy activities.
6. Physico-chemical properties showed that compositions of all oil products tested fell in both diesel and gasoline range. Cetane indices of the wax-free oils also proved that they can readily burn in a diesel engine.

5.2 Recommendations

Despite the presence of the vacuum pump, working under pressures significantly lower than ambient was not possible without major modifications of the pilot setup. It is therefore recommended that modification on the pilot to improve the level of vacuum should be considered since vacuum pyrolysis on bench scale provided promising yields of oil.

Moreover, most of the condensable products generated under vacuum were recovered as wax. Also, some of the products retrieved on the pilot were waxy in nature and could not be distilled to help ascertain their boiling point range, meaning a fraction of the wax is possibly made up of hydrocarbons with molecular weight greater than diesel. Further cracking of these waxes into saleable oils is recommended.

It was concluded that, oils and waxes recovered under the pyrolysis of PP at both bench and pilot scale comprised of compounds that fall in both diesel and gasoline range. To obtain pure diesel or gasoline product, it is recommended that the oils should be distilled to obtain pure compositions.

Also, the reaction kinetics behind all the process conditions especially vacuum pyrolysis, should be investigated to better understand the mechanisms.

Finally, a techno-economic study should be considered to help ascertain the economic viability of the pyrolysis of PP into liquid fuels at commercial scale.

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Appendices

Appendix A: *Uses and flow of plastics*

Table A.1. Some useful applications of commonly used plastic materials

Material	Applications	
	Packaging	Non-packaging
PET	Carbonated drink bottles, mineral water bottles, clear bottles used for dishwashing liquids and edible oils, Jars, Biscuit trays, Punnets, Salad domes	Carpeting, fibres for apparel and industrial applications. Engineering components such as sewing machine parts
HDPE	Milk bottles, fruit juice bottles, drums, packaging films, carrier type shopping bags, tubs, closures, cosmetic bottles, crates, pallets, bins	Irrigation pipes, water reticulation, shade-cloth, netting, shopping trolleys, refuse bins, toys, medical implants such as hip replacement components
PVC-P (Flexible)	Industrial cling film, pouches	Cable insulation, gum boots, shoe soles, flooring, matting, medical cloth and tubing, tarpaulins, hoses, safety gloves, soft toys, rain wear, erasers, banners, see-through 'vinyl curtains, tents and upholstery etc.
PVC-U (Rigid)	Clear bottles and jars (limited use) Blister packaging, food packaging, inserts such as chocolate trays	Pipes for water reticulation and sewage, conduit profiles, cladding, stationery foils, plumbing etc.
LDPE	Packaging films, domestic cling film, stretch wrap, shrink wrap, bags, shrouds, dust covers, peel-able lids, cosmetic tubes, boutique shopping bags	Irrigation pipes, cable insulation, agricultural films, rational moulded products such as tanks
PP	Yoghurt tubs, margarine tubs, ice cream containers, wrappers, packaging films, bottles, caps and	Coat hangers, battery cases, reels, automotive components such as bumpers, furniture, bowls, buckets, carpeting, hair extensions,

Material	Applications	
	Packaging	Non-packaging
	closures, canisters, strapping tape, woven bags, crates	appliances including toasters and kettles, toilet seats, ropes, fishing nets
PS-HI (High impact)	Yoghurt and other dairy product tubs, display boxes, cake domes, punnets	Coat hangers, take away cutlery, take away crockery, toys, cups, plates, audio and video cassette housings, CD and DVD covers, cell phone covers, stationery items including pens and rulers, toys, watch glasses, shower doors, office drawers, stationery trays etc.
PS-E (Expanded)	Protective packaging, take-away food containers, clamshell packaging, meat and vegetable trays, punnets	Vending cups, insulation panels, suspended ceiling panels
Others, Polycarbonate (PC)		Baby bottle, housings for cameras, video equipment, light covers, traffic light covers, safety glasses, visors, crash helmets

Appendix B: *Standard Deviation*

Table B.1. Raw data showing standard deviations of products yields (Atmospheric slow)

Temperature (°C)	Product yields and standard deviations (wt.%)			
	Heavy oil	Light oil	gas	char
450	68.6 ± 0.2	13.8 ± 0.5	5.6 ± 0.4	5.7 ± 1.5
488	70.3 ± 0.2	15.3 ± 0.8	5.8 ± 0.3	3.1 ± 0.4
525	63.8 ± 1.7	17.1 ± 1.1	8.4 ± 0.2	2.6 ± 0.2
600	48.0 ± 2.0	15.0 ± 1.0	27.0 ± 1.3	2.5 ± 0.1

Table B.2. Raw data showing standard deviations of products yields (Atmospheric fast-insertion)

Temperature (°C)	Product yields and standard deviations (wt.%)			
	Heavy oil	Light oil	gas	char
450	62.9 ± 2.0	14.0 ± 0.4	4.0 ± 1.0	14.0 ± 0.9
488	69.7 ± 0.8	14.8 ± 0.0	7.2 ± 0.5	3.0 ± 0.1
525	64.6 ± 0.5	16.0 ± 0.2	10.1 ± 1.9	2.6 ± 0.1
600	31.0 ± 6.4	29.5 ± 0.6	31.8 ± 3.2	2.5 ± 0.1

Table B.3. Raw data showing standard deviations of products yields (Vacuum slow)

Temperature (°C)	Product yields and standard deviations (wt.%)			
	Heavy oil	Light oil	gas	char
450	62.9 ± 1.9	26.1 ± 3.3	1.7 ± 0.1	4.4 ± 0.6
488	60.5 ± 4.6	30.3 ± 3.8	2.3 ± 0.6	2.5 ± 0.2
525	64.5 ± 3.0	28.2 ± 3.6	3.4 ± 0.1	1.9 ± 0.4
600	61.1 ± 0.8	25.2 ± 1.5	2.9 ± 1.2	2.4 ± 0.0

Table B.4. Raw data showing standard deviations of products yields (Vacuum fast insertion)

Temperature (°C)	Product yields and standard deviations (wt.%)			
	Heavy oil	Light oil	gas	char
450	64.7 ± 0.9	25.5 ± 1.0	1.8 ± 1.0	4.6 ± 0.2
488	66.5 ± 1.8	25.3 ± 0.0	2.2 ± 0.5	3.1 ± 0.5
525	64.5 ± 3.0	28.2 ± 3.6	5.11 ± 1.2	1.9 ± 0.4
600	61.1 ± 0.8	25.2 ± 1.5	7.36 ± 0.5	2.4 ± 0.0

Table B.5. Raw data showing standard deviations of products yields (Pilot tests)

Temperature (°C)	Product yields and standard deviations (wt.%)			
	Oil from condensers	Wax from char box	gas	char
450	76.90 ± 0.5	11.57 ± 0.9	5.63 ± 0.5	1.29 ± 0.1
460	80.14 ± 0.2	10.21 ± 2.6	6.83 ± 0.9	1.13 ± 0.3
488	69.49 ± 0.9	6.80 ± 0.4	10.57 ± 1.4	0.78 ± 0.0
507	70.81 ± 2.2	8.68 ± 1.0	13.71 ± 0.1	0.96 ± 0.1
525	70.22 ± 2.6	4.98 ± 1.1	15.52 ± 2.2	0.55 ± 0.1

Appendix C: Simulated distillation used for GC/MS characterisation of oils

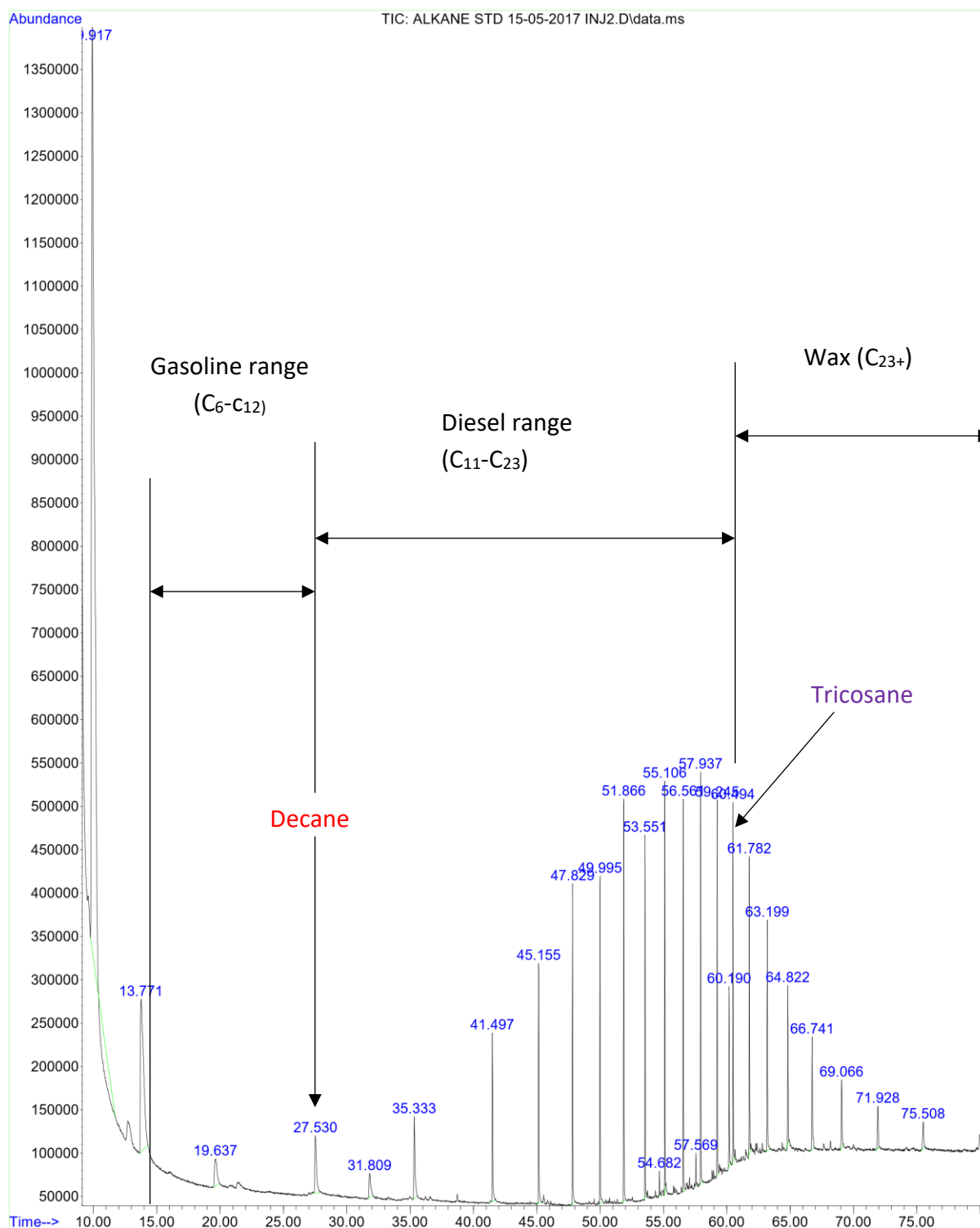


Figure C.1. GC/MS Chromatogram of Alkane standard used in simulated distillation showing the retention time ranges for gasoline, diesel and wax range compounds used to characterise oils.

Appendix D: Images of condensable products and char obtained from bench

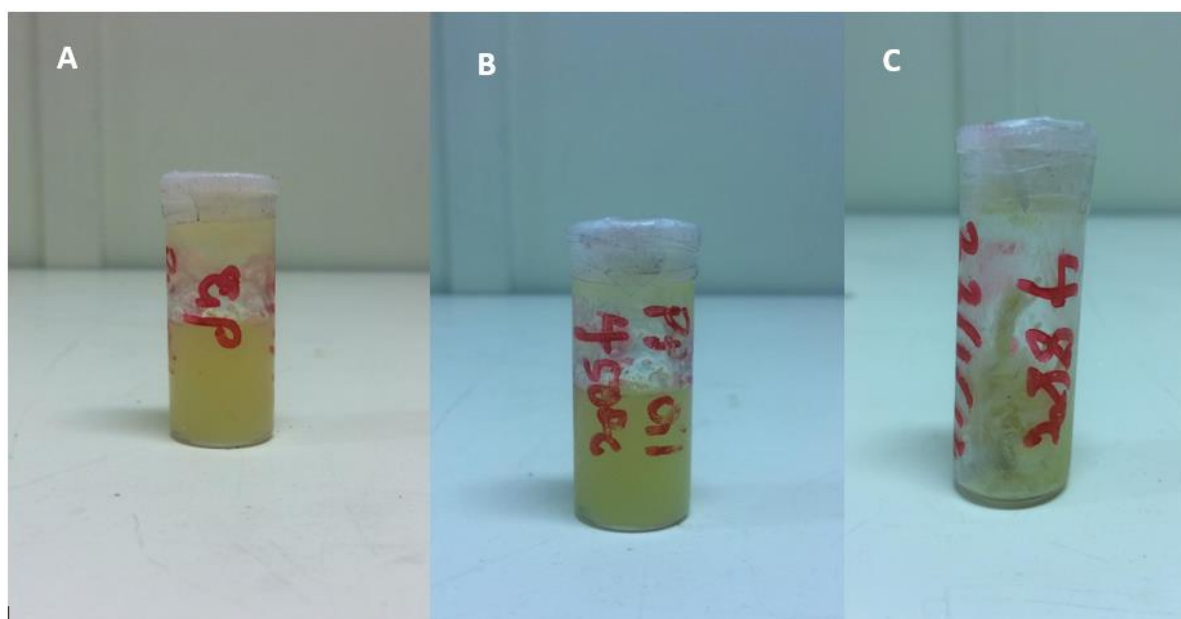


Figure D.1. Heavy condensable products obtained from ambient condition condenser. (A) Oils recovered at 600 °C under atmospheric conditions showing its viscous nature (wax-containing), (B) Oils recovered at 450 °C under atmospheric conditions showing its less viscous wax nature, (C) Condensable product obtained in ambient condition condenser under vacuum showing its completely solid wax nature.

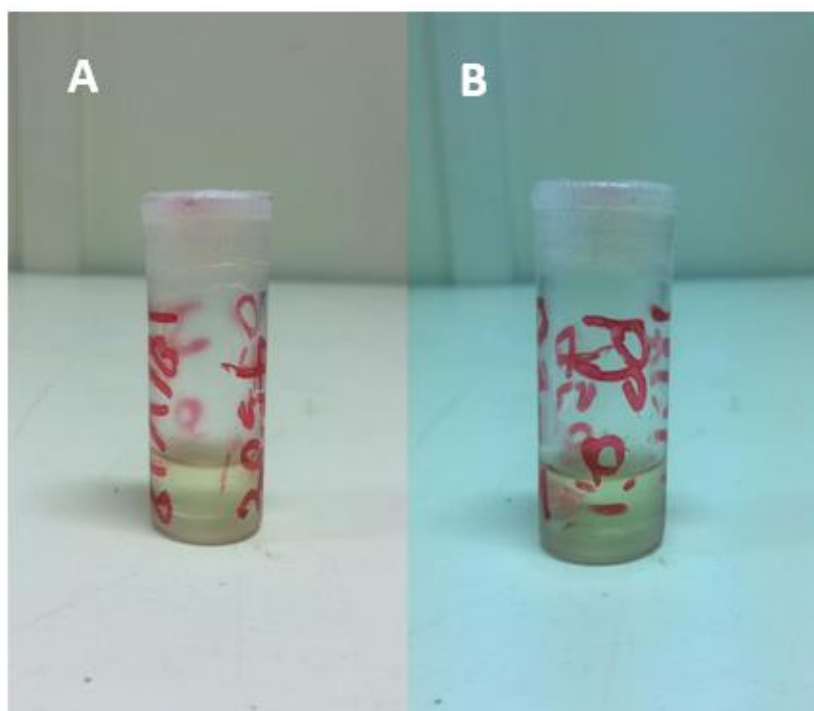


Figure D.2. Light condensable products obtained under dry ice condensers showing their clear, free-flowing and wax-free nature. (A) From ambient, (B) From vacuum.

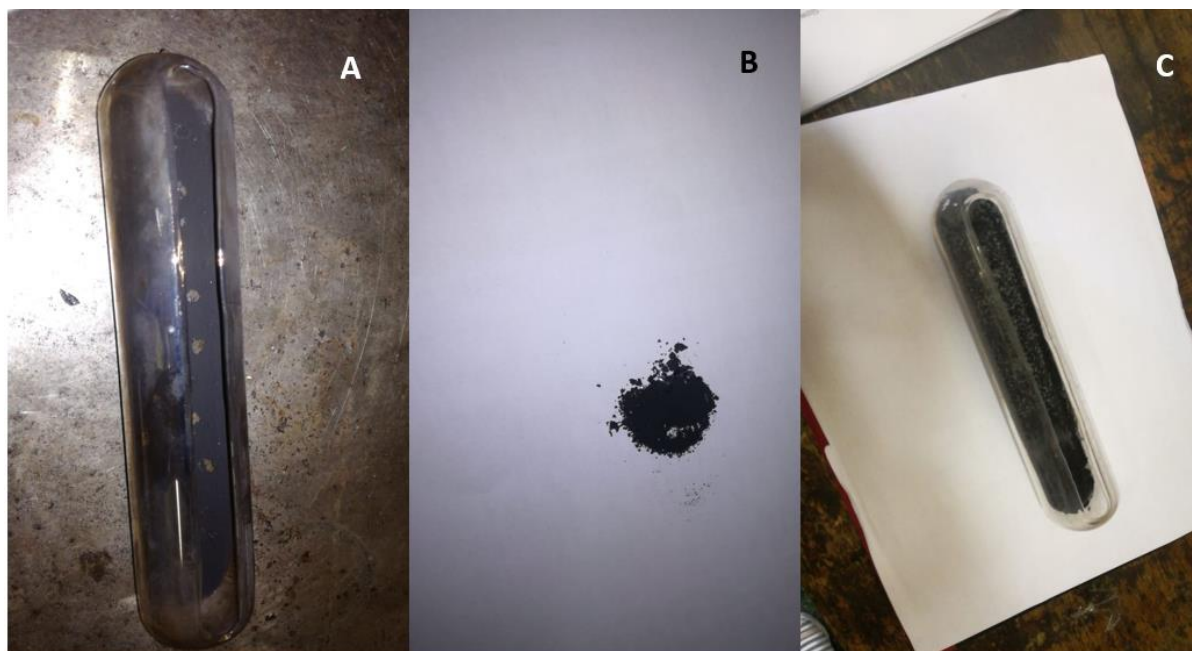


Figure D.3. Images of char showing complete and incomplete conversions of PP. (A) Sample boat showing char remains after complete conversion of PP at 600 °C under atmospheric condition, (B) Char sample obtained from the pyrolysis of PP at 600 °C, (C) Sample boat showing incomplete conversion of PP at 400 °C.