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Catalytic Pyrolysis of Plastic Waste to Produce Diesel-like Fuel

By
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As the candidate’s supervisor, I have approved this thesis/dissertation for submission

___________________________ **__26 August 2021____**

Dr N.M. Mkhize Date

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Abstract

Over the years, plastic generation and usage have increased due to plastics' favourable properties for domestic and industrial purposes. Plastics are cheap to manufacture, durable, flexible, resistant to moulding and rust, amongst other properties. The diverse application of plastics in the different sectors has led to increased plastic waste and management challenges. Plastic waste management options such as recycling, incineration, and landfilling have been used; however, there are drawbacks to these options.

Plastics are petroleum-based, and a lot of energy is embedded in them. Several waste to energy technologies have been researched and adopted to deal with plastic waste. Among these technologies are gasification, plasma process, pyrolysis, and incineration. Pyrolysis has emerged as the most desirable process since it significantly reduces the volume of waste, produces various high-energy products, and requires lower decomposition temperature. The process is desirable because of its flexibility. Pyrolysis parameters are manipulated to optimise the desired product yield. The process parameters include but are not limited to temperature, heating rate, residence time, particle size, and catalyst. Different types of plastics and biomass can be thermally devolatilised using the process.

In the current study, catalytic devolatisation of polypropylene plastic waste through the pyrolysis process was studied. Key factors affecting the final product, i.e. temperature, feed composition, heating rate and catalysts, were reviewed. The effects of temperature and silica-alumina catalyst on the product yield and quality were investigated. A central composite design was employed for the experimental design. It was observed that increasing the catalyst at lower temperatures impacted on the liquid and solid fraction yield, the liquid fraction yield increased while the solid fraction yield decreased. The use of silica-alumina significantly decreased the process temperature. At 427 °C and 33.9% silica-alumina, an optimum liquid fraction yield of 89.95 wt.% was obtained. It was noted the liquid fraction hydrocarbons in the gasoline range. Shorter hydrocarbons (C_3-C_{18}) were predominant in the liquid oil

Preface

The experimental work described in this dissertation was carried out at the University of KwaZulu-Natal in the College of Agriculture, Engineering and Science (CAES) at the Department of Chemical Engineering, Howard College Campus, Durban, from August 2019 to July 2021, under the supervision of Dr Ntandoyenkosi Malusi Mkhize.

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- My parents and siblings for their support
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Dedications

To my loving and caring parents Mr and Mrs Shumba.

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List of abbreviations

Abbreviation	
ANOVA	Analysis of Variance
BTX	Benzene, Toluene, Xylene
Ca	Calcium
CCD	Central Composite Design
CSBR	Conical Spouted Bed Reactor
DTA-TG	Differential Thermal Analysis
DTG	Differential Thermal Gravimetric
FCC	Fluid Cracking Catalyst
FTIR	Fourier Transform Infrared
GCMS	Gas Chromatography and Mass Spectrometry
GTCC	Gas Turbine Combined Cycle
H_2O	Water
HCl	Hydrochloric acid
HHV	High Heating Value
MPW	Municipal Plastic Waste
Mo/Al-Si	Molybdenum/Aluminium silicate
N_2	Nitrogen
NZ	Natural Zeolite
P	Potassium
PDO	Plastic Derived Oil
PE	Polyethylene
PET	Polyethylene Terephthalate
PP	Polypropylene
PS	Polystyrene
PVC	Poly vinyl chloride
RDF	Refuse Derived Fuel
S	Sulfur
SP	Slow Pyrolysis
VP	Vacuum Pyrolysis

CHAPTER 1: INTRODUCTION

1.1 The rationale for the research

Continual change in living standards has caused an increase in the production and consumption of plastics. Global production of resins and fibres increased from 2 million tonnes in 1950 to 380 million tonnes in 2015 (Liang et al., 2021); the increased plastic consumption has led to a significant increase in the waste plastic generated. An estimate of 300 million tonnes of plastic waste is generated yearly around the world. In 2010 China was the largest plastic waste producer globally, producing almost 60 million tonnes, followed by the United States at 38 million, Germany at 14.5 million, and Brazil at 12 million (Ritchie and Roser, 2018). Figure 1.1 illustrates the total plastic waste generated, discarded, incinerated, and recycled from 1950 to 2020, and projections until 2050. A significant rise in generated and discarded waste plastic is noted from the year 1990 and is a continual increase is predicted in the future. The amount of generated waste plastic continues to rise over the years while discarded waste plastic rises at a slower rate. Total incinerated and recycled waste raised slowly from the year 2000 and is expected to continue rising.

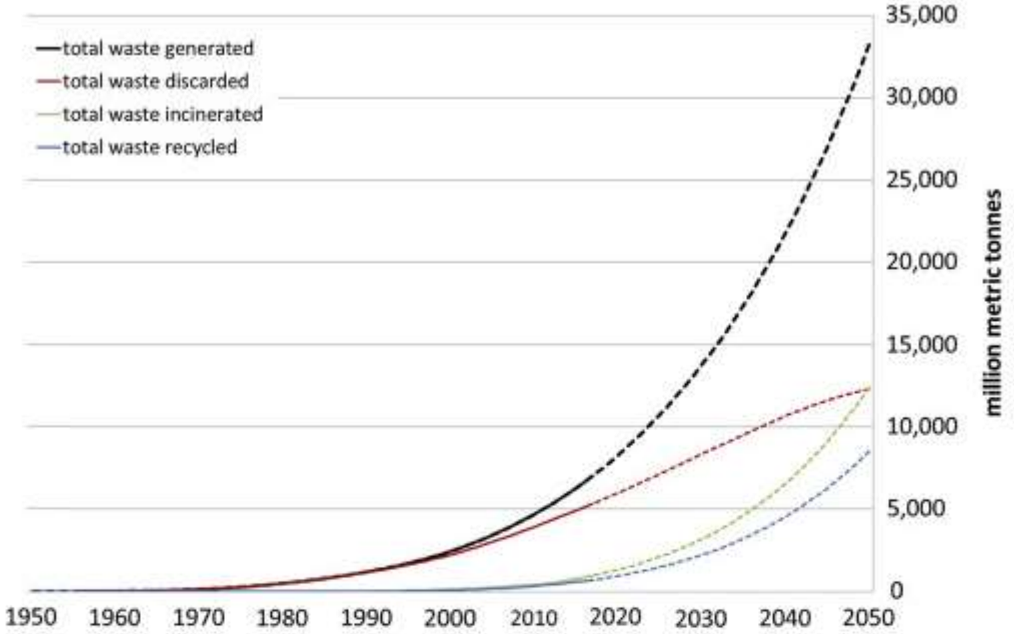

Figure 1 1 Generation and discarding of plastic waste (Geyer et al., 2017)

Most developed countries practice regulated discarding of plastics and proper disposal. However, in developing countries, plastic waste disposal is not controlled. They end up in open dumpsites. The wind blows plastics from these open dumpsites into water bodies. In developing countries, alarming amounts of plastic waste have been observed on the land, in rivers, and oceans because of mismanaged plastic waste. Large volumes of plastic in different forms, for example, packaging and single-use plastic utensils, are exported from developed nations resulting in high amounts of waste accumulation since they have low capacity for recycling and reuse. In developed countries, the amount of mismanaged plastic waste is beginning to decline as they implement waste categorisation at domestic and industrial sources. Waste collection is done regularly. Public awareness campaigns on waste management and the effects of improper disposal of plastics are constantly done in developed countries.

Plastic waste contributes much of the marine litter. An estimated 8 million tons per year of plastic goes into oceans from coastal nations (Parker, 2019). Plastic waste escapes from the environment and landfills, collects and sets in the oceans and finally greys. These plastics later break into small pieces due to pressure from the water. Many fish, seabirds, sea turtles, and other marine mammals die each year after getting entangled in plastics or ingesting them. Under ultraviolet light from the sun, plastic is degraded into fragments that are virtually not possible to claim, disrupting food chains and degrading natural habitats (Liang et al., 2021). Only a small percentage, 1%, of these plastics floats the rest sinks to the floor of the oceans polluting the habitats and food sources of marine life. One in every three fish contains micro plastics in its system.

Plastic SA - South Africa’s representative body for plastic industry, reported that in 2018 South Africa collected 519 370 tonnes of plastic waste, which was recycled, contributing to 46.3% of the total plastic waste generated (Plastics SA Admin, 2019). Only properly managed waste is collected, meaning over half of the generated waste is not handled properly and disposed, causing it to accumulate in the environment and marine. Currently, 34.1% of South Africans have no access to routine waste collection services. Plastic waste is one of the most substantial municipal solid waste contributors.

Different solid waste management strategies have been implemented to deal with plastic waste; however, there are limitations to most of the strategies. These strategies include reuse, recycling, incineration, landfilling, and waste to energy. Incineration is slowly becoming unpopular due to the greenhouse gases produced during the process. The greenhouse gases impose adverse environmental hazards since they affect the ozone Due to legislation pressure discarding plastic waste in landfills is slowly becoming undesirable (landfill waste must be reduced by 35% over the period from 1995 to 2020). The poor biodegradability of plastics and rise in handling and maintenance cost has made the use of landfills unattractive (Geyer et al., 2017). Not all nations were able to meet the mandate leading to it being revised. Of the waste generated, less than 12% is reused and recycled. Plastics do not biodegrade and are bulky; they persist in the environment even after their disposal. Due to their bulkiness, vast amounts of land are required to bury them, thus limiting the use of landfills.

Plastics are petroleum-derived; a lot of energy is embedded in them. They have high energy content than organic waste and biomass, with caloric values ranging from 16-20 MJ/kg. Plastics have caloric values comparable to conventional fuels, as shown in Table 1.1.

Table 1 1 Plastics and fossil fuels calorific values (Williams and Williams, 1997)

Fuel	**Calorific (MJ/kg)**
Gasoline	44
Diesel	43
Heavy fuel oil	41
Coal	24
Polyethylene (PE)	46
Polystyrene (PS)	41
Polypropylene (PP)	46
Polyethylene Terephthalate (PET)	22

Waste-to-energy remains a feasible plastic waste management technology, pyrolysis being one of the options. Plastic can be converted to energy using the pyrolysis process. Thermal pyrolysis requires a lot of energy and produces a wide range of hydrocarbons that require purification before being used as an energy source. Incorporating a catalyst can reduce the energy needed for the process; it also narrows the range of hydrocarbons produced, making the oil/ gas collected useful. Oil, gas, and char obtained can be used for the production of electricity and steam. Gaseous products and char are useful for reheating the process. Hydrocarbons in the oil can be extracted for plastic production, reducing pressure on the existing fossil energy and making the process sustainable. Depleting fossil fuels can be conserved by the recovery of the energy embedded in waste plastic. A lot of plastic lying in dumpsites can be a helpful resource. Figure 1.2 shows the state of open dumpsites in South Africa.

Figure 1 2 South Africa open dumpsites (Bungane, 2019)

1.2 Justification

A lot of energy is embedded in plastics since they are petroleum-derived. Energy can be recovered after the end-use of plastics. Substantial amounts of energy have been lost in landfills and during incineration. Incineration reduces the amount of waste generated but increases greenhouse gas emissions, resulting in air pollution. The ash produced during incineration can be dangerous to both humans and the environment. Installing an incineration plant is expensive, posing a significant challenge to most local authorities. Recycling has emerged as an alternative for controlling plastic waste. However, not all plastic waste can be recycled. Approximately 10% of the total waste goes for recycling. The waste-to-energy recovery process produces liquid fuel and solid fuels. Liquid fuel helps fuel the industrial heating system since it has reduced sulfur and nitrogen content compared to conventional fuels. Extraction of chemicals like hydrogen, styrene can be done from the recovery products. The heating value of the oil produced during the process of energy recovery is approximately 39-42 MJ. Pyrolysis is an upcoming technology used to capture the energy from plastics in liquid, solid, or gaseous form. Thermal pyrolysis has been substantially studied. Researchers obtained oil containing a wide range of hydrocarbons that require refining before use as a fuel. The significant drawbacks of thermal pyrolysis are the yield, quality of oil produced, and extensive energy demand. This study will focus on incorporating a catalyst to increase product yield and quality.

1.3 Aim and objectives

To investigate the use of a catalyst to produce diesel-like oil and other valuable products.

The objectives of this work were:

1. To study the chemical characteristics of plastic waste pyrolysis feedstock
2. Optimise the oil yield using the Central Composite Design
3. To investigate the quality of the oil obtained

1.4 Thesis structure outline

The dissertation lay out is as follows:

Chapter one introduces the research by outlining the increased plastic waste generation and how it is becoming an environmental challenge. The chapter summarizes the use of waste-to-energy technology in dealing with plastic waste. The waste can be used as a feedstock for the recovery of energy embedded in the plastics. The aim of the study and objectives are outlined in this chapter.

Chapter two is a comprehensive literature review on plastic pyrolysis. It focuses on the resins and plastic polymers, their formation and uses in day-to-day activities. Strategies used in mitigating the problem of plastic waste are briefly explained. The process of pyrolysis, differences between thermal and catalytic pyrolysis are well explained. Factors affecting the process of pyrolysis were thoroughly examined. The mechanisms of both the thermal and catalytic pyrolysis process are outlined.

Product yield was investigated in chapter three. Factors that affected product yield were outlined and briefly discussed. The Central Composite Design was used as an experimental tool. Operating conditions were optimised to obtain optimum product yield.

Chapter four focused on improving the quality of condensable products (oil) to produce high-quality fuel, which is diesel-like. The chemical composition and physical properties of the oil were investigated. Chemical analysis was done using the Fourier Transform Infrared (FTIR) and the Gas Chromatography and Mass Spectrometry (GCMS

The main research finding and recommendations were discussed in chapter five.

1.5 Summary Chapter

This chapter outlines the introduction to the aim and objectives of the research work. The study was focused on optimising the oil yield and oil quality using catalytic pyrolysis. This study has been motivated by the enormous quantities of plastic waste in the natural environment and marine bodies containing high quantities of unrecovered energy. Traditional plastic waste management strategies are slowly becoming obsolete; with these methods, a lot of energy embedded in plastic is not recovered.

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CHAPTER 2: LITERATURE REVIEW

2.1 Introduction

The rise in consumption of plastic in modern society is inevitable owing to its versatile utilities, functional values, and a fairly small amount of energy is essential for production compared with other materials (Ng et al., 1995). Plastic polymers are key in different sectors such as transport, communication, shelter, clothing, entertainment and health care. Plastics are essential in day-to-day activities due to their favourable properties, including lightweight, durability, energy efficiency, faster production, and design flexibility. Most plastics are not biodegradable; disposing them after use has become a significant problem worldwide. However, researchers are working on making plastics more useful even after their intended use. Landfilling and incineration are currently used worldwide to manage plastic waste, and their capacities are limited. Incineration is gradually becoming obsolete due to the greenhouse gases produced during the process. Plastic waste is voluminous. Burying plastics in landfills is more expensive since they require immense amounts of land and do not biodegrade. Valuable energy can be extracted from plastic since they are made from petroleum sources. These energy forms have high calorific value. Plastics waste can be transformed into fuels or valuable feedstock for the petrochemical industry.

Various technologies for converting plastic to fuel such as gasification, pyrolysis, refuse-derived fuel (RDF), plasma arc gasification along with chemical recycling approaches such as hydrolysis, methanolysis, glycolysis has received substantial consideration in the management of municipal plastic waste (MPW) (Nizami et al., 2015). Pyrolysis has risen as one of the emerging technologies in addressing plastic waste problems. The process is environmentally friendly with no production of unwanted gases like carbon dioxide. Unlike other processes, solid residue can be used to condition the soil since it comprises of fixed carbon.

The advantage of pyrolysis is that it converts low-density substrates into higher-density liquid, solid, and gas fractions. The pyrolysis process does not result in water pollution and gaseous discharges into the atmosphere. Thus, it is considered a green technology. The process is adjustable, i.e., the process parameters are manipulated to maximise the yield of the desired products. Product yield and quality heavily depend on the set parameters. The main advantage of pyrolysis is handling unsorted and dirty plastics, unlike other processes such as gasification and hydrolysis. The thermal cracking of polymers produces a wide range of hydrocarbons making the oil collected during the process difficult to use as a fuel.

Process efficiency can be improved using a catalyst. In thermal pyrolysis, a catalyst is critical in promoting targeted reactions. The use of a catalyst influences product quality and yield. A catalyst speeds up chemical reactions, with the catalyst remaining unchanged after the process is complete. Catalysts are mainly used to optimise product distribution, reduce activation energy and increase product selectivity (Rahman et al., 2018, Anuar Sharuddin et al., 2016). Since pyrolysis requires large amounts of energy (highly endothermic), a catalyst is critical as it reduces the activation energy speeding the reaction rate. It decreases the process's activation energy, lowering the process temperatures and energy required to complete the process, thus saving energy. Catalytic pyrolysis can produce liquid oil from plastic waste with characteristics comparable to standard diesel fuel (Miandad et al., 2016). Many researchers have used a catalyst to upgrade the condensable products, improving the hydrocarbon distribution to properties similar to normal fuels.

2.1.1 Work done by other researchers

Studies have been done with synthetic and natural catalysts using different types of plastics. Kaolin and red mud are natural catalysts that have been investigated. Artificial catalysts such as zinc oxides, zeolite, spent fluid cracking catalyst (FCC), silica-alumina, and synthesised fly have been studied. The use of catalysts in the thermal decomposition of plastics has resulted in quantitative and qualitative improvement in the liquid fuel yield. High-density HDPE, LDPE, PS, and PP have been investigated both as individual plastics and as mixtures. Polypropylene has been cracked using a 10% natural zeolite (NZ) catalyst. Panda and Singh (2011) cracked polypropylene over kaolin and silica-alumina using a semi-batch reactor in the temperature range 400-500 °C. An oil yield of 91% was reported over silica-alumina catalyst and 89.5% using kaolin. Jantasee et al. (2019) pyrolysed polypropylene with modified molybdenum modified alumina-silica (Mo/Al-Si) catalyst in a batch reactor at 430 °C under atmospheric pressure. A yield of 83.65% pyrolysis oil was obtained with 5% Mo/Al-Si, as the catalyst was increased to 10% oil yield also increased to 86.63%. The oil had properties close to diesel. Polypropylene was also pyrolysed without a catalyst the oil yield for this sample was lower. Pyrolysis oil obtained without a catalyst contained a complex mixture of C_6-C_{25} hydrocarbons. While the oil obtained using a catalyst consisted of C_5-C_{15} hydrocarbons. Moqadam et al. (2015) studied the use of silica-alumina to crack polystyrene in a semi-batch reactor and obtained oil that contained a significant percentage of styrene monomer (> 80 %). Table 2.1 shows the effect of different catalysts on products under various reactor types temperature and feedstock.

Table 2 1 Effect of catalyst

Reference	Reactor type	Catalyst	Feed	Temperature	Effect on product yield		
					Liquid	Gases	Char
Jantasee (2019	Batch reactor	5% Mo/Al-Si	PP	430	83.65	13.79	2.56
		10% Mo/Al-Si	PP	430	86.63	11.99	1.38
Lee et al. (2002)	Semi-batch	10% FCC	HDPE	400	82	16	2
Panda and Singh (2011)		kaolin	PP	500	89.5		
		Silica alumina	PP	500	91		
Luo et al. (2000)	Fluidised bed	Silica alumina	HDPE	500	85	10	5
Lee et al. (2002)	Semi-batch	10% FCC	PS	400	90	6	4
López et al. (2011)		ZMS-5	Industrial Packaging		41.5	8.6	49.9
Lee et al. (2002)	Semi-batch	10% FCC	PP	450	85	13	2
Lerici et al. (2015)	Batch reactor	H-Y Zeolite	PE		42	46	8
			PP		44	52	10
			PS		71	24	5

2.2 Plastics

2.3 Pyrolysis

Pyrolysis is described as controlled thermal degradation of materials in an inert environment (Akovali, 2012). The feed material converts into char and volatiles during the process. Pyrolysis can be done at different temperature levels, reaction times, pressures, with or without reactive gases and catalysts. Unlike combustion, pyrolysis has a low process temperature and low pollutant emissions. Compared to the incineration process pyrolysis is more flexible. Pyrolysis has gained more popularity for its adjustability to produce varying fractions of solid, liquid, and gaseous products by changing the process constraints. Low energy materials are transformed into high energy biofuels during the process leading to the recovery of high-value chemicals. There are different pyrolysis types, including fast, catalytic fast, intermediate, slow, vacuum. These types of pyrolysis vary in process temperatures from 400 to 1000 °C, residence time in the range of 30 minutes to < 1 second and heating rates. The major products differ because of the varied operating parameters.

Pyrolysis has arisen as a preferred waste management technology since it can be used for several various types of wastes such as wood and garden waste, food waste, paper waste, tyres, textiles, and waste plastics. The pyrolysis of wood and garden waste produces bio-oils. Many phenolic compounds have been produced in the intermediate pyrolysis of eucalyptus residue, especially methoxy derivatives from lignin breakdown. For a long time dealing with natural and synthetic rubber waste was a great challenge. Pyrolysis has been widely considered for treating waste tyres or the biggest source of rubber waste. Four products are expected during tyre processing which are pyrolysis oil, steel, solid (char) and gas. The char from tyre pyrolysis is a mesoporous material with an average heating value of 30 MJ/kg. It comprises of reinforced carbon black used in tyre manufacturing and the other organic compounds formed during the pyrolysis process. The oil has xylenes, trimethylbenzenes, dimethylstyrenes, dimethylindenes, and limonenes as the main compounds. In US biomass is anticipated to be developed into a vital energy source in for electricity generation under state-led renewable portfolio standards. The oil is assumed to be converted to electrical power through co-combustion in conventional fossil fuels power plants, gas turbine combined cycle (GTCC), and diesel generators (Nizami et al., 2017).

2.3.1 Pyrolysis of plastic waste

At high temperatures of 400-1000 ˚C and low oxygen polymers are decomposed into important chemicals, fuels and solid residues Pyrolysis volatiles the plastics, and resulting hot volatiles cools to become gasoline, diesel, and heavy oil (Lee et al., 2002). Pyrolysis decreases the volume of waste by 90% or more, causes comparatively lower air pollution, needs small space, and reclaims energy. Plastics pyrolysis occurs at low (< 400 °C), medium (400–600 °C), or high temperature (> 600 °C) under atmospheric pressure. Thermal decomposition of polymers produces gases, distillates, and char of varied amounts. The products are useful as fuels, petrochemicals, and monomers. Product yield is dependent on the polymers or polymer mixtures fed and the operating conditions used. The gaseous and liquid products consist of several different compounds. The pyrolysis process is endothermic and involves bond breaking, it is crucial to supply sufficient heat to the feedstock. The supply of heat is rate-determining during the process.

Volatiles containing fairly low char make up the products obtained from plastic pyrolysis. The volatile composition comprises of condensable fraction and a non-condensable gaseous stream. The condensable fraction can be an oil or wax, subject to the reaction conditions and plastic type. The amount of each product is dependent on the plastic feed chemical composition and the pyrolysis process operating conditions. Heat application in an oxygen free environment to plastics sparks the fuel's devolatisation together with the emission of volatiles. At the end of the reaction there are solid (char) for plastic pyrolysis the amount is usually negligible.

2.3.2 Types of pyrolysis

Pyrolysis can be divided into four types slow, flash, fast and vacuum, according to the reaction time and process temperature (Pawar et al., 2020). The rate at which feed material is heated and volatile removal rate from reactor zone is used to classify the types of pyrolysis.

2.3.2.1 Slow pyrolysis (SP)

Slow or conventional pyrolysis is conducted between 300-600 °C with slow heating rates of 1-100 °C/min and long vapour residence times (1-60 min) (Erdogan, 2020). The heating rate is kept slow, leading to a high char produce and less liquid and gaseous products. Large particle sizes can be used without affecting the heat transfer rate between particles since. low heating rates are employed. The gaseous stream produced comprises mainly of methane and low quantities of hydrogen, propane, ethylene, CO, and CO_2 (Ojha and Vinu, 2015). In the past years, slow pyrolysis has been used for charcoal production.

2.3.2.2 Fast pyrolysis

Fast pyrolysis (FP) reaction proceeds rapidly in a few seconds using much faster heating rates as high as 1000 °C/s (Ojha and Vinu, 2015) for rapid bond breaking. The chemical reaction controls product distribution, heat and mass transfer and phase changes, which are brought about by employing high temperatures (> 500 °C), low vapour residence times (< 3 s). Higher volatiles are produced during the process. A rapid removal of volatiles through cooling reduces secondary reactions. Generally, small particles are utilised to reduce heat and mass transfer restrictions. Typically, fast pyrolysis processes produce 60-75 wt.% of liquid bio-oil,15-20 wt.% of solid char, and 10-20 wt.% of non-condensable gases depending on the feedstock used (Bridgwater, 2012).

2.3.2 3 Flash pyrolysis

Flash pyrolysis is an upgraded version of fast pyrolysis, conducted using high heating rates, > 1000 ^{o}C/s, and short reaction times. Tiny particles are required compared to other processes because of the rapid heating rate and short reaction times.

2.3.2 4 Vacuum pyrolysis

Vacuum pyrolysis (VP) is conducted at temperatures between 300-600C under a vacuum. It is comparable to slow pyrolysis; no fluidising gas is required to purge the pyrolytic vapours. A vacuum between 10-20 kPa is used during the process. It quickly sucks the hot volatiles from the reaction zone to limit secondary reactions, thereby promoting high oil yields. It is a more recent technology.

Table 2.3 shows the operating parameters of different pyrolysis types and the expected liquid yield.

Table 2 3 The operating parameters for pyrolysis types (Erdogan, 2020)

Pyrolysis types	Retention time	Rate of heating	Temperature (°C)	Liquid yield (%)
Slow	5-30 min	Low	300 - 650	< 30
Fast	< 2 s	Very high	450 - 600	50 -70
Flash	< 1 s	High	450– 1000	> 75

2.3.3 Factors affecting the pyrolysis process

Polymer macromolecules are degraded into reasonably smaller molecules during pyrolysis by reactions like depolymerisation, dehydration, decarbonylation, decarboxylation, deoxygenation, oligomerisation, and aromatisation. In addition, pyrolysis product quality and quantity are influenced by feedstock composition, pyrolysis temperature, heating rate, type of reactor, and catalyst effect. The section below discusses in detail these factors and their impact on the process.

2.3.3.1 Chemical composition of feedstock material

Main products of pyrolysis are influenced by the chemical structure of the feed polymer. Feedstock composition affects the product distribution and restricts the operation in terms of products and conversion time. The structure and functional groups in a polymer affect the distribution of pyrolysis products. During the pyrolysis of condensation polymers and polyamides, smaller building blocks (monomers) such as styrene for polystyrene and benzoic acid for PET are formed because of the aromatic ring stability (Scheirs, 2006, Gao, 2010). Liquid oil (condensable) produced in the pyrolysis of PP is characterised by hydrocarbons derived from the molecular skeleton of the polymer. Contamination of plastics by other materials in the waste stream alters the products obtained from their pyrolysis. At 450 °C, the pyrolysis of PE resulted in the production of wax instead of a condensable liquid product. Lee (2012) stated a similar observation that thermal pyrolysis of PE yields wax instead of oil because of its long carbon chain structure. PE produces less amount of oil and high amounts of gas. Many researchers have reported that PS produces large quantities of pyrolytic oil. The simple structure of PS results in maximum devolatilisation. Moreover, the devolatilisation of PS comprises four steps: initiation, transfer, decomposition, and termination (Faravelli et al., 2001).

Miandad et al. (2016) pyrolysed a mixture of plastics at varying ratios. It was observed that adding PS to PP caused a liquid yield reduction to 25% from 80.8% for PS and 42% for PP. Liquid product yield decreased when PS was mixed with PE. Aliphatic and olefin compounds were noted in the oil produced; it was concluded that PE formed these compounds. When PP and PE are blended, gaseous and solid products yield increase while the liquid oil yield decreased. The product yield from different plastics and mixtures of those plastics was presented in Figure 2.10 by Miandad.

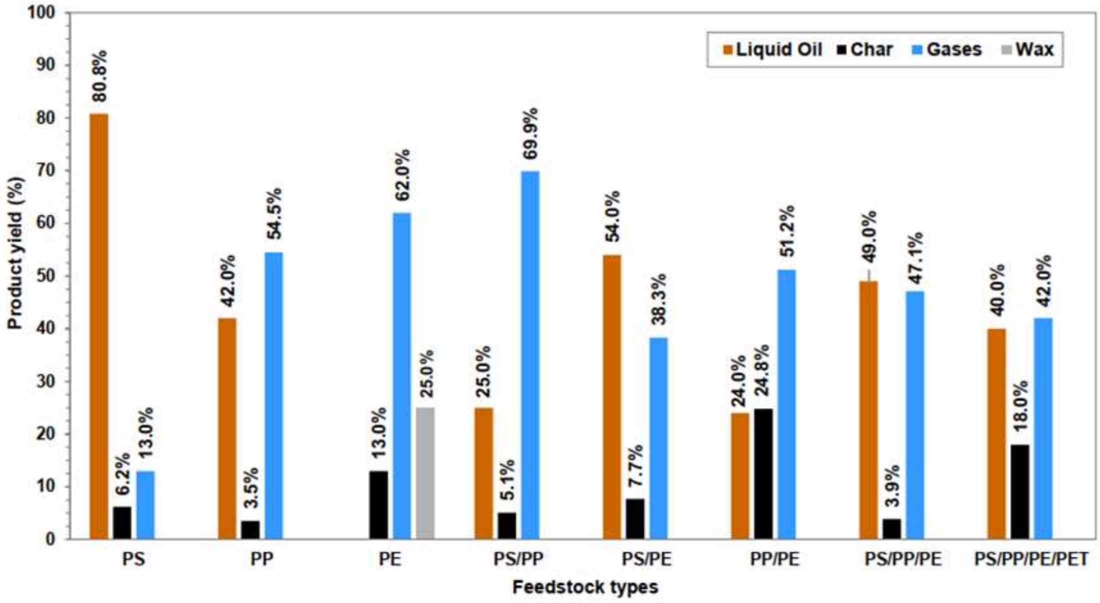

Figure 2 11 Effect of plastic-type on product yield

2.3.3.2 Temperature

Temperature is the key operating parameter in pyrolysis since it indicates the feedstock stability, thermal decomposition rate and reaction products (Buekens, 2006). Conversion temperatures vary with different plastic polymers and anticipated product composition. As a rule of thumb, high operating pyrolysis temperatures and heating rates enhance the polymer’s bond cleavage favouring the production of volatile compounds (Scheirs, 2006). Product compound distribution is influenced by temperature. Higher temperatures favour secondary reactions, resulting in the production of higher gaseous products. Temperature controls the main devolatilisation behaviour and cracking reaction of the plastics. Lopez et al. (2011) suggested that increasing the temperature causes vibration between molecules to increase, resulting in Van der Waals forces holding the polymer molecules to collapse, leading to molecules detaching from the surface, thus breaking the carbon chain.

Westerhout et al. (1998) observed that the effect of temperature on product concentration at higher temperatures was less significant. Polymer chemical composition and residence time influence the product distribution. Mixed fuel gases consisting primarily of methane and light hydrocarbons are produced at temperatures above 500 °C. Increasing the temperature increases the yield of gaseous products and light hydrocarbons (C_1-C_6), thereby decreasing the yield of heavy hydrocarbons (C_{21}-C_{30}) (Xingzhong, 2006)

The formation of stable aromatic compounds is favoured by higher pyrolysis temperatures (Miandad *et al*., 2016a). Excessive energy availed at high temperatures cause high reactivity and recombination leading to the formation of stable compounds. These trends are apparent in work conducted by Jung et al. (2010) during the pyrolysis of PP within the temperature range of 668-746 ˚C in a fluidised bed reactor. Increasing the temperature resulted in the increased gas product. Permanent gases production is favoured at higher temperatures due to the breakdown of larger molecules to smaller hydrocarbons. Secondary reactions are promoted at high temperatures causing a decrease in the oil or wax formation. As the temperature was increased from 668 to 746 °C the amount of aromatics in the oil increased significantly from 27 to 97 wt.%. Nizami et al. (2017) observed a similar trend after pyrolysing a mixture of PE, PP, and PS in a stainless steel batch reactor. In plastic pyrolysis optimum oil yield has been reported in temperatures between 300-500 °C gaseous products are optimised at temperatures above 500 °C (Anuar Sharuddin et al., 2016). Figure 2.11 illustrates the variation of pyrolysis products at different reaction temperatures

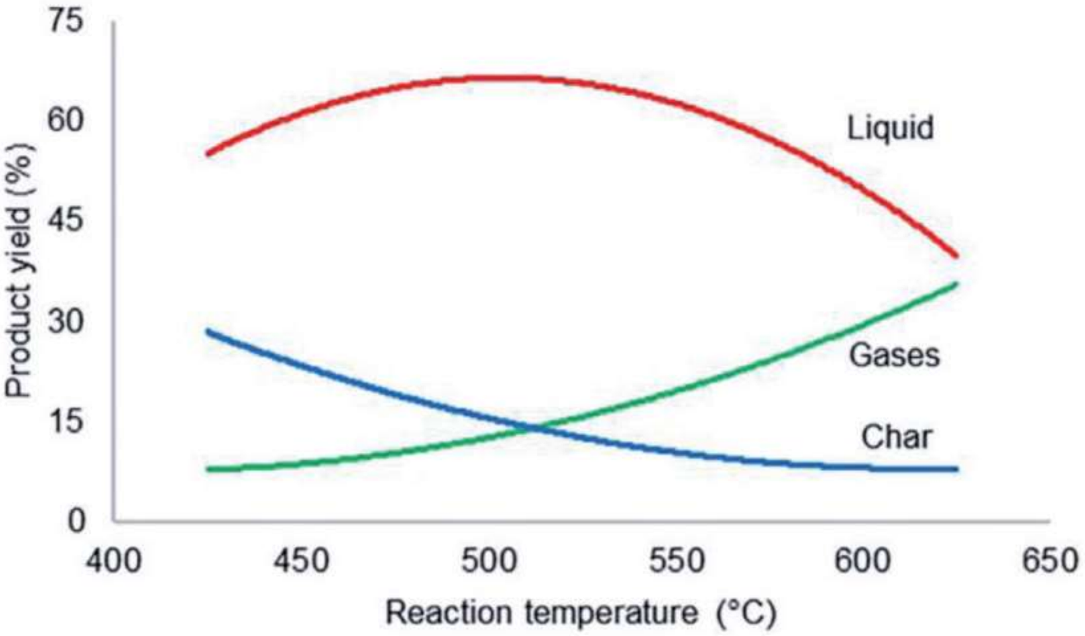

Figure 2 12 Yield of pyrolysis products at various reaction temperatures (Erdogan, 2020)

2.3.3.3 Heating rate (HT)

The heating rate impacts the thermal behaviour of the pyrolysis process and can be defined as the rise in temperature per unit time. High heating rates enhance bond cleavage, facilitating light molecular weight products (Buekens, 2006). The heating rate affects the rate of heat transfer in the sample, thereby varying the product yields. Higher HT promotes the production of volatiles, whereas at low HT, the volatiles remain in the reaction zone for a long time. As the HT rises, the conversion degree of the polymer and the yield of gases increase, while the yields of oil and char decrease (Kabakcı and Hacıbektaşoğlu, 2017). High heating rates of about 10,000 ˚C/min can be used for pyrolysis. During SP, feedstock is heated from room temperature to the anticipated process temperature at a constant rate (Gao, 2010). The HT for such processes is moderately low and ranges between 10 to 100 ˚C/min. Figure 2.12 illustrates the typical change in yield of pyrolysis products at varying heating rates.

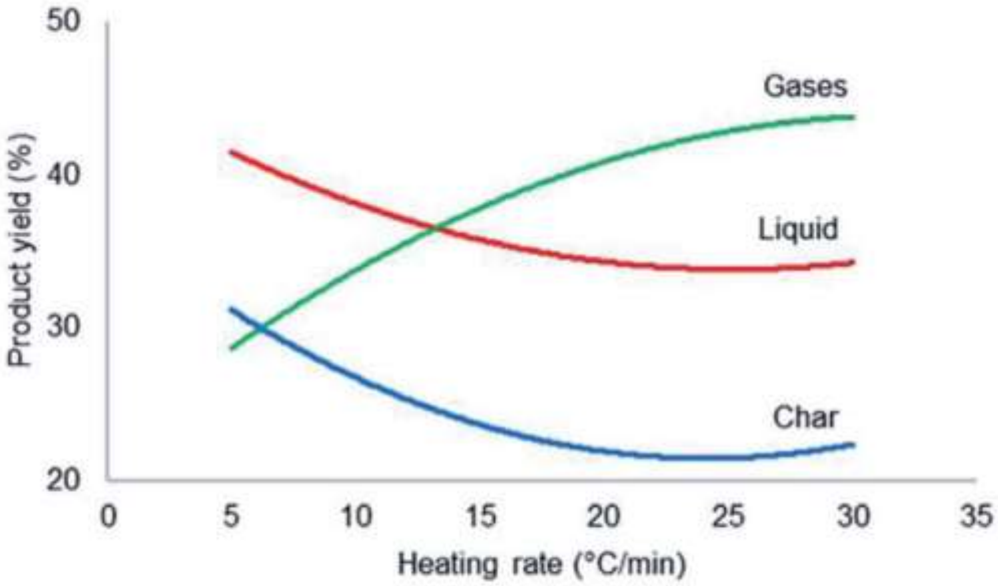

Figure 2 13 The yield of the pyrolysis product at various heating rates (Erdogan, 2020)

2.3.3.1 Retention time (RT)

Retention time is typically the time a sample particle remains in the reactor. The retention time impacts the final product distribution. Retention time can be described as the time spent by volatiles or solids in the reaction zone and can be defined as either volatile RT or solid RT. Longer residence time permits the occurrence of secondary reactions such as thermal cracking, repolymerisation, and recondensation, thereby reducing liquid yield (Onay and Kockar, 2003). The pyrolysis condensable fraction is dependable on the retention time and is not proportional to the increase of reaction temperature. In plastic pyrolysis, secondary reactions are reliant on the time spent in the reaction zone and favours the formation of gases. Moderate temperatures and short volatile residence time are optimum for liquids (Erdogan, 2020). Onwudili et al. (2019) investigated the effect of temperature and residence time on the devolatilisation of LDPE and PS. Longer retention time facilitated the occurrence of secondary reactions resulting in the cracking of oil into gas. At zero residence time and a temperature of 450 °C, LDPE was converted to 91.1 wt.% oil and 8.70 wt.%. An increase in retention time to 120 minutes resulted in the oil yield decrease to 61 wt.%, and gas yield increased to 28.5 wt.%.

2.3.3.5 Particle size

The particle size of the feedstock affects product distribution as a result of the particles' resistance to heat transfer as the size varies (Luo et al., 2005). Generally, as the particle size become larger, the core temperature of the particle is becomes lower than that of the surface resulting in a higher temperature gradient within the particle (Erdogan, 2020). Thus, fine particles promote high mass transfer to the hot vapours leaving the reaction zone, thus inhibiting the secondary reactions favouring increase oil yield. On the contrary, large particles inhibit heat transfer facilitating secondary reactions due to increased resistance to escaping pyrolysis products.

2.3.3.6 Type of reactor

Another factor affecting pyrolysis is the reactor type. The reactor type significantly impacts the products since it influences the mixing of feedstock and catalyst, retention time, cracking reactions, and heat transfer (Wirawan, 2019). Reactor geometry determines the dynamics of the leaving volatiles. Therefore, various reactors give different product quality and quantities. The types of reactors popularly used in plastic pyrolysis research include:

i. Batch reactors

The feedstock is fed in batches when using this type of reactor. After completing the pyrolysis process, the reactor is emptied of products and residues to prepare it for the next batch.

ii. Semi batch reactor

In a semi-batch reactor, the feedstock is fed into the reactor before starting the pyrolysis process. An inert gas is used to remove the volatile products from the reactor zone. Alternatively, the reactor is pressurised with an inert gas while the product is continually withdrawn.

iii. Fixed bed reactor

In a fixed bed reactor, pyrolysis takes place on a stationary bed. It can be classified under continuous reactors as the process is a constant process. Irregular sizes and shapes of the plastic polymer may result in problems in the ongoing process. Fixed bed reactors can be used as a second reactor to crack liquid and gaseous products from primary (Uemichi et al., 1999).

iv. Fluidised bed reactors

Fluidised bed reactors are widely used in commercial plants. In a fluidised bed reactor, feedstock makes up an expanded bed where volatile products or fluidising gas flows through the bed, resulting in bubbles or eddies (Gao, 2010). This type of reactor has homogeneity of both composition and temperature. Therefore, the configuration and bed composition are crucial parameters influencing the pyrolysis process and final products.

2.3.3.7 Catalyst effect

A catalyst accelerates a chemical reaction by reducing the process' activation energy, thus increasing the reaction rate. The catalyst itself is not used up in the course of the reaction. The pyrolysis process consumes high energy, so using a catalyst helps lower the energy required, thus saving energy. The use of the catalyst affects the kinetics and mechanisms of devolatisation, therefore, the product distribution (Patni et al., 2013). The use of catalysts also shortens reaction time. Panda et al. (2010) used 33.3% catalyst to degrade HDPE; the reaction time was reduced to 64 minutes compared to 83 minutes when using no catalyst. Most researchers have reported that catalyst presence impacts the physical and chemical properties of the liquid obtained.

2.4 Types of catalyst

The main catalysts used for catalytic pyrolysis of plastic waste are fluid cracking catalyst (FCC), zeolites and silica-alumina

2.4.1 Zeolites

Zeolites are microporous crystalline alumina-silicates of the elements of groups 1A and 2A (sodium, potassium, magnesium, calcium). The composition can be represented as follows $M_2/nAl_2O_3ySiO_2wH_2O$, y varies from 2 to 10, n is the valence of the cation and w is the amount of structural water (Almeida and Marques, 2016). Zeolites are crystalline aluminosilicate sieves with open pores and ion exchange capabilities (Anuar Sharuddin et al., 2016, Marcilla et al., 2009). A three-dimensional framework with oxygen atoms linking the tetrahedral sides forms the structure of zeolite. The catalyst is made up of different ratios of SiO_2/Al_2O_3, which governs its reactivity that influences the final pyrolysis products. The main characteristics of zeolite catalysts are their ion-exchange abilities and open pores. The ratio of SiO_2/Al_2O_3 determines the reactivity. Zeolite catalysts with high acidity are more reactive in the cracking process, increasing the manufacture of small olefins and decreasing the heavy fractions (Artetxe et al., 2013). A low SiO_2/Al_2O_3 ratio indicates a high acidic catalyst, producing high olefins and lower heavy fractions of C_{12}-C_{20}, while a high SiO_2/Al_2O_3 indicates a low acidic catalyst. Marcilla et al. (2009) investigated the performance of HZSM-5 and HUSY on HDPE and LDPE at a 550 °C and 10% polymer to catalyst ratio using a batch reactor. HUSY produced a higher liquid than HZSM-5. Using HUSY 41 wt.% HDPE, 61.6 wt.% LDPE of liquid was obtained while HZSM-5 produced 17.2 wt.%, 18.3 wt.% respectively. The gas composition for HZSM-5 were 72.6 wt.% for HDPE and 70.7 wt.% for LDPE. The results proved that different catalyst have different product selectivity.

2.4.2 Fluid cracking catalyst (FCC)

FCC consists of zeolite crystals and a non-zeolite acid matrix known as silica-alumina with the binder (Humphries and Wilcox, 1989). The major component of FCC is zeolite Y because of its high product selectivity and thermal stability (Anuar Sharuddin et al., 2016). These catalysts are extensively used in the petroleum refinery industry to break down the heavy oil fractions from crude petroleum to simpler and more favourable liquids and gases. For catalytic pyrolysis process spent FCC is used. It is a waste from the petroleum refining industries. The catalyst contains impurities; however, they are useful in the pyrolysis of plastics. Abbas-Abadi et al. (2014) reported that the 20 wt.% catalyst polymer ratio was optimum for the maximum conversion of HDPE plastic waste into liquid. An increase in catalyst/polymer ratio will favour the production of gases and char. Various thermoplastics from the plastic waste stream were pyrolysed by Kyong et al. (2002) using FCC catalyst and an oil yield of 80-90 wt.% was observed. Degnan (2000) concluded that FCC catalysts increase the liquid oil yield compared to other catalysts. reported

2.4.3 Silica –alumina catalyst

Silica-alumina catalyst is an amorphous acid catalyst containing Bronsted acid sites with an ionisable hydrogen atom and Lewis acid site, an electron-accepting sites (Anuar Sharuddin et al., 2016). The mole ratio of SiO_2/Al_2O_3 determines the acid concentration of the catalyst. Acidity strength has a great impact on the end products of plastic pyrolysis. The high strength of acidity is indicated by a high mole ratio of SiO_2/Al_2O_3, which lowers the production of liquid oil. Luo et al. (2000) obtained 90 wt.% and 85 wt.% from the pyrolysis of PP and HDPE using a silica-alumina catalyst at high temperatures (500 °C).

2.5 Advantages of using a catalyst in pyrolysis

The use of a catalyst improves process performance, quality and products yield. Decomposition reactions are promoted at lower energy consumption. Catalysts promote rapidly cracking reactions resulting in reduced retention times. Cracking reactions promote the formation of liquid oil products with a low boiling point range. Production of undesired products is inhibited in the presence of a catalyst. Process selectivity increases. In polyolefins, a catalyst inhibits the formation of products consisting primarily of cyclic hydrocarbons and aromatics (Almeida and Marques, 2016).

2.6 Effects of catalyst

2.6.1 Effects of catalyst on the pyrolysis liquid oil.

The quality of liquid oil is improved by using a catalyst (Miskolczi et al., 2006, Lopez-Urionabarrenechea et al., 2012). Miskolczi et al. (2013) stated that the mechanism of the pyrolysis process and the conversion of heteroatoms to the gaseous phase is affected by the catalyst. The concentration and distribution of heteroatoms in the liquid oil are dependent on the catalyst used (Brebu et al., 2005). Liquid oil from thermal pyrolysis is of low quality. It can contain contaminants like heteroatoms which arise because of plastic additives or contaminants. Agricultural plastic waste is usually contaminated with the products they carry, such as phosphorous, nitrogen, chlorine, etc. Halogen concentration in liquid oil is decreased by the use of a catalyst. The introduction of silica-alumina catalyst caused a decrease in the bromine content present in pyrolysis liquid oil (Blazso et al., 2002). According to Miskolczi et al. (2009), using ZSM-5 catalyst reduced the nitrogen, phosphorous, and sulfur concentrations in the liquid oil, mainly gasoline. Pollutant degradation occurs in the tiny inner pores of ZSM-5. The presence of a catalyst facilitates the removal of oxygenated species leading to a rise in the HHV of product oil. Some plastics in the plastic waste are contaminated with calcium, sulfur, phosphorus and nitrogen; these contaminants distort the properties of the liquid oil. Liquid oil from catalytic pyrolysis has reduced contaminants concentrations because contaminants attach to the catalyst leading to their removal from the products.

2.6.2. Effect of catalyst on plastic derived oil (PDO) compounds

Oil quality is improved by introducing a catalyst in the process. Thermal pyrolysis leads to the production of large carbon chain compounds ranging between C_5 to C_{28}. At the same time, the use of catalyst decreases the heavy oil and increases the gasoline fraction (C_5-C_{12}) in the pyrolysis liquid (Miandad et al., 2016). The liquid fraction from thermal pyrolysis can be covered by gasoline range (C_4-C_{12}), diesel (C_{12}-C_{23}), kerosene (C_{10}-C_{18}), motor oil (C_{23}-

C_{40}), and BTX (Mastral et al., 2007). There is a wide range of product distribution when using thermal pyrolysis in the absence of a catalyst. The use of catalysts produces a narrow range of liquid products.

2.6.3. Effect of catalyst on physical properties of PDO.

Viscosity is a critical parameter of petroleum products. The presence of a catalyst influences the viscosity of pyrolysis liquid oil, thus its quality and utilisation as fuel. Viscosity plays an essential role in the atomization and subsequent combustion of fuel properties; therefore, PDO with high viscosity can hardly be used for fuels since it is hard to atomise.

Abdullah et al. (2010) stated that the suitable viscosity for fuel at 25 °C $\leq$ 1000 °C. Catalyst crack polymer plastics to give liquid oil of lower molecular weight, thus lowering its viscosity. Miskolczi et al. (2013) concluded that all catalysts demonstrate a high alteration of long-chain aliphatic compounds to aromatic compounds and reduce oxygenated compounds. Since these compounds are thought to cause high molecular weight and viscosity in pyrolysis liquid oil, their reduction means a much better oil is produced. Liquid oil obtained during thermal pyrolysis has a high viscosity. The presence of oxygenated compounds is responsible for the high viscosity. Catalysts allow pyrolysis products to enter, reformulate and exit the catalyst matrix (Miandad et al., 2016). Brebu et al. (2005) explains the increase in oil amount and density resulting from a more pronounced scission of polymer chains into condensable products when using a catalyst. According to Miskolczi et al. (2009), a catalyst reduces the density flash point, boiling range, and HHV of liquid oil. The use of Y-zeolite and natural zeolite (NZ) reduced the pour point of liquid oil from MPW pyrolysis. Moisture content and centane index of liquid oil also decrease during catalytic pyrolysis.

Combining two or more catalyst seems to be more beneficial than when the catalyst is used individually. Miskolczi et al. (2013) noted that the use HZSM-5 in the catalytic cracking of plastics produced gasoline range lower aromatic compound as the major product while the presence of $SiO_2Al_2O_3$ produced a low-quality fuel. However, the combination of the two produced high yields of high octane rating gasoline. Uemichi et al. (1999) also used the dual catalyst and gave almost the same results. Combining the mesoporosity and acidity of two different catalysts results in products of improved octane number.

2.6.4 Effect of catalyst on retention time and temperature

Catalytic pyrolysis promotes the economic feasibility of the pyrolysis process through decreasing the retention time and process temperature (Achilias et al., 2007). The use of a catalyst promotes cracking reactions resulting in reduced retention time. The high rate of carbon cracking reactions accelerates plastics decomposition, resulting in reduced retention time in the reaction hot zone. During catalytic pyrolysis, decomposition requires lower energy to start leading to a reduction in process temperature.

2.6.5 Effect of catalyst on gaseous products

Gaseous products increase with the introduction of a catalyst during pyrolysis. The gases produced comprise CO, CO_2, H_2, and CH_4. A catalyst favours the decarboxylation route, therefore increasing the CO_2 formation reducing CO concentration (Ateş et al., 2013). High cracking rate results in large hydrocarbons being decomposed to smaller chains promoting the production of gases. A catalyst increases hydrogen concentration and carbon frame isomerisation, promoting the i-butane concentration. Miskolczi et al. (2009) observed that the gas produced from the pyrolysis of PP using ZSM-5 catalyst contain mainly C_3 hydrocarbons while C_2 and C_4 hydrocarbons were formed from packaging waste.

2.6.6 Effect of catalyst on char produced

A catalyst reduces residual solids (char), especially catalysts that have high BET surface areas. Separating the catalyst from char is very problematic. The chemical attributes of char are not affected by catalyst (Whyte et al., 2015). However, it increases the ash content since it is not used up during the reaction.

2.7 Mechanism of thermal degradation

Polymer degradation changes the polymer properties because of chemical and physical reactions in bond splitting and successive chemical transformation (Singh and Sharma, 2008). Thermal degradation occurs at high temperatures causing the principal chemical bonds to separate (Van Krevelen and Te Nijenhuis, 2009). The categories of thermal decomposition include chain depolymerisation, random decomposition, and degradation by substituent reactions.

2.7.1 Chain Scission or depolymerisation

Chain depolymerisation involves the sequential release of monomer units from a chain end or a weak link (Van Krevelen and Te Nijenhuis, 2009). Chain depolymerisation is the reverse of chain polymerisation and is known as depropagation or unzipping. Chain splitting begins at one end of the chain, sequentially releasing the monomer units. In this reaction, the molecular mass of the polymer drops gradually, liberating huge amount of the monomer. Chain scission occurs when the polymer backbone bonds become weaker than the side group bonds causing the molecules to carry the active chain ends with the free radical, cations, anions, etc. The depolymerisation process comprises a free radical path. Chain depolymerisation is described by a) the main product, the monomer, b) the reduction of polymerisation degree initially insignificant, and consequently, the mechanical properties do not decline rapidly, and c) the rate of depolymerisation slowly decrease (Welsh,1996)

2.7.2 Random scission

Random scission arises when free radicals are formed at the polymer chain's weakest point (Patni et al., 2013). The process yields a sequence of reduced, replicating oligomers by different carbon chain lengths. The occurrence of random splitting reactions constantly occurs with a change in the molecular weight of the polymer. The scission's primary products decrease continuously until they are adequately tiny to leave the reaction zone to the gas state and are finally withdrawn as volatiles. The decomposed products have a broad range of carbon numbers due to the haphazard nature of the reaction. Addition polymers such as polyolefins (PP and PE) randomly produce fragments when heat is applied to them.

2.7.3 Side chain elimination

Sidechain elimination involves eliminating reactive side groups on the polymer chain, causing the generation of cracked products on the one hand and charring polymer when heated. The process is also called chain stripping and happens in two steps. Firstly, the side groups on the parent chain are eliminated, leaving an unstable polyene macromolecule. Other random scission reactions occur on the polyene macromolecule forming smaller fragments, char, and aromatic compounds. The decomposition of PVC follows the side chain elimination mechanism. Chlorine is eliminated as hydrogen chloride in the first step of PVC thermal degradation (Scheirs, 2006). The residual macromolecule polyene undergoes spitting and cyclisation forming smaller chain and aromatic compounds typically toluene, benzene, and naphthalene (Jung and Fontana, 2006).

2.8 Mechanism of catalytic degradation

The introduction of a catalyst significantly enhances the quality of products produced through the pyrolysis of plastics, reduces the decomposition temperature, and enhances selectivity to certain products. The presence of many acid sites in acid catalysts like zeolite favours hydrogen transfer reactions. However, the accessibility of polymer particles to reactive catalyst sites is restricted to the pore size and the increase of the end products within the pores (Panda et al., 2010). Different mechanisms (carbenium theory, ionic free radical) for waste plastic catalytic decomposition have been studied by numerous researchers and are explained below.

The mechanism of catalytic degradation is explained using the carbonium ion theory (isomerisation, random chain spitting and β cleavage, hydrogen transfer, oligomerisation, aromatisation) Buekens and Huang (1998), Panda et al. (2010) briefly explained the carbonium ion theory using polyethylene as an example. Density, strength and acid active site layout in a catalyst impact the formation of carbonium ions. Therefore, the first stage is the initiation stage.

i. Initiation: This is the initial step of catalytic degradation; it occurs by removing hydride ions or adding a proton. Initiation occurs on the chain’s weak points. For example, adding a proton onto an olefinic linkage results in the formation of a carbonium ion on the chain by adding a proton.

$$-CH_2CH_2CH{=}CHCH_2CH_2- + HX \longrightarrow -CH_2CH_2{}^{+}CH{=}CHCH_2CH_2+X \quad (a)$$

β scission may lead to the breaking of the polymer chain

$$-CH_2CH_2{}^{+}CHCH_2\text{-}CH_2\ CH_2- \longrightarrow -CH_2CH_2CH{=}CH_2+{}^{+}CH_2CH_2 \quad (b)$$

Initiation may occur through haphazard hydride-ion abstraction by low-molecular-weight carbonium ions (R^+):

$$-CH_2CH_2CH_2CH_2CH_2CH_2-+R^+ \longrightarrow CH_2CH_2{}^{+}CHCH_2CH_2CH_2-+RH \ (c)$$

The newly formed on-chain carbonium ion then undergoes β-scission as in Equation (b)

ii. Depropagation: During this step, sequential attacks of the main polymer chains by acidic sites or carbonium ions and chain cleavage reduce the polymer's molecular weight, leading to the yield of oligomer segments approximately C_{30}-C_{80}. The continuous breakup of the oligomer fraction by β-scission of chain-end carbonium ions results in gas formation and a condensable fraction of approximately C_{10}-C_{25}.

iii. Isomerisation: carbonium ion intermediates can undergo rearrangement by hydrogen- or carbon-atom shifts leading to, e.g., a double-bond isomerisation of an olefin

$$CH_2{=}CH\text{-}CH_2\text{-}CH_3 \xrightarrow{H+} CH_3\text{-}^{+}CH\text{-}CH_2\text{-}CH_2\text{-}CH \xrightarrow{H+} CH_3\text{-}CH{=}CH\text{-}CH_2\text{-}CH_3$$

Methyl-group shift and isomerisation of saturated hydrocarbons are other significant isomerisation reaction

iv. Aromatisation: Some carbonium ion intermediates can undergo cyclisation reactions. For instance, when hydride ion removal occurs on an olefin, some carbons are eliminated from the double bond, resulting in the development of an olefinic carbonium ion:

$$R_1^{+}{+}R_2CH\text{—-}CH\text{–}CH_2CH_2CH_2CH_2CH_3 \Longleftrightarrow R_1^{+}{+}R_2CH\text{—-}CH\text{–}CH_2CH_2CH_2CH_2CH_3$$

An intermolecular attack can occur on the carbonium ion double bond.

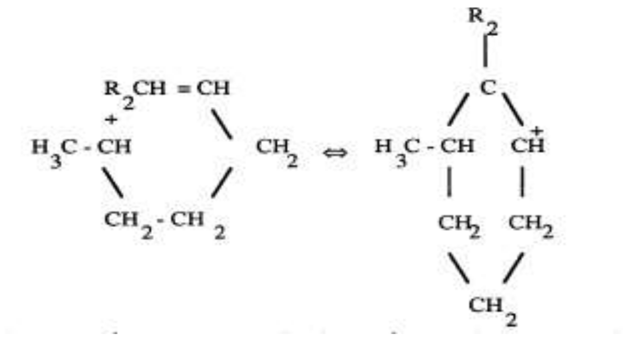

Figure 2 14 The carbonium ion undergoing intramolecular attack (Buekens and Huang, 1998)

Al-Salem et al. (2017) illustrate the reaction mechanism of heterogeneous catalysts using a diagram in Figure 2.6.

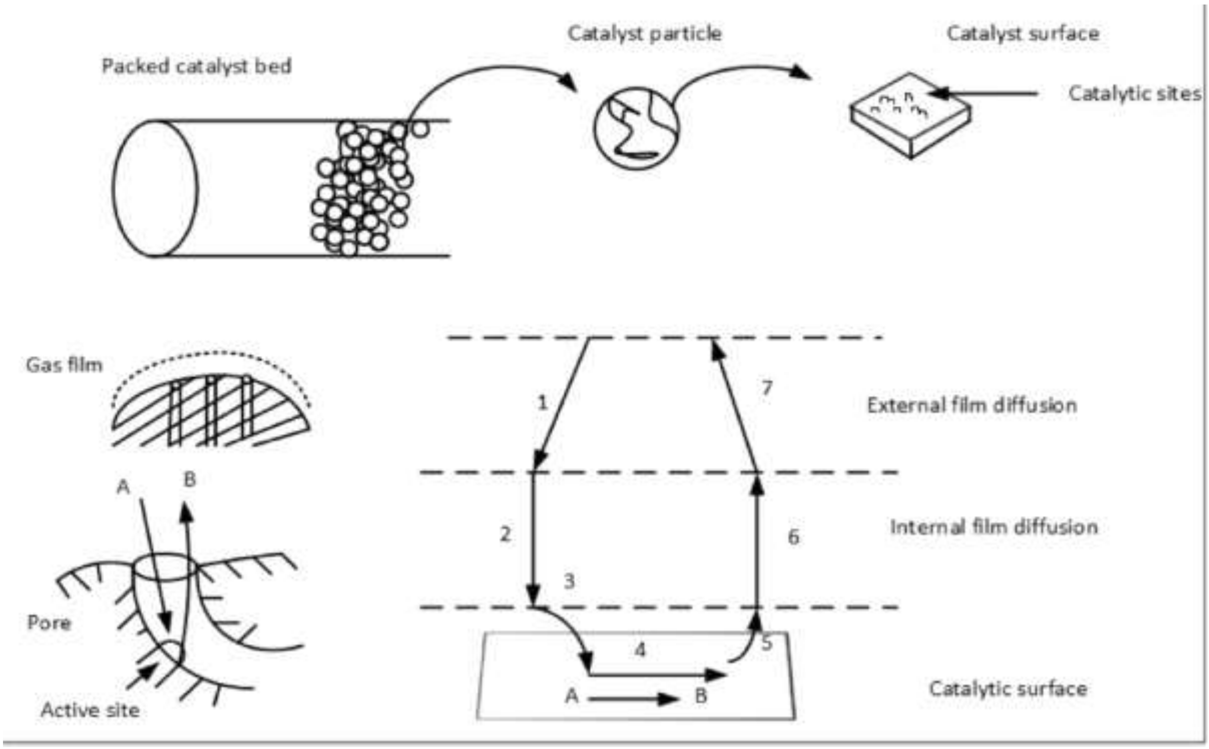

Figure 2 15 The reaction of heterogeneous catalyst as reported by Al-Salem et al. (2017)

2.9 Conclusion

High heating value products are obtained from the pyrolysis of plastic. Various types of plastics have been investigated under different conditions using distinct types of reactors. From the literature surveyed, three important conclusions have been reached.

Firstly, the procedure employed for plastic polymerisation influences the polymer’s macromolecular structure and thermal behaviour. Some of the plastics’ physical properties are temperature dependant. The process used for the formation of plastics polymers has a substantial effect on the application of the plastic polymers in different industries. Plastics have replaced materials like concrete, glass, iron and bamboo in a vast number of industries. The increased use of plastic polymer has caused a significant rise in waste plastics generated globally,

Secondly, the marked increase in a plastic waste generation and other environmental issues led to the review of waste management regulatory rules, resulting in the traditional methods slowly becoming obsolete. Most of the emerging plastics waste management methods are temperature dependant. These methods are favourable with thermoplastics. Thermosetting plastics exhibit undesirable temperature dependant properties making it a challenge to recycle them using some of the emerging technologies. Better recycling methods for the recovery of energy embedded in thermosetting plastics can be employed. The desirability of technology is influenced by the products, operating parameters, etc.

Thirdly, the ease of manipulating pyrolysis process parameters to give desired products has led to attention given to the process by many researchers. The types of pyrolysis processes differ in process temperature, heating rate, retention time and products. Various factors affect the process. Amongst these factors, temperature, feedstock chemical composition and catalyst have the most significant impact on the desired products. Temperature affects the thermal behaviour of plastics and products obtained. The chemical and physical properties of final pyrolysis products are subjective to the chemical composition of the feed and catalyst. Literature does not outline the chemical and physical properties of PDO obtained from different feedstock compositions using different catalysts. The desired product has a significant impact on the parameters and reactor type employed for the process.

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CHAPTER 3: EFFECT OF TEMPERATURE AND CATALYST ON THE PRODUCT YIELD FROM POLYPROPYLENE CATALYTIC PYROLYSIS

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Short Summary

Different factors affecting the process of plastic pyrolysis were reviewed in Chapter 2. The current chapter elaborates on the effect of temperature (400 – 500 °C) and catalyst (4 – 25%) on the product yield. The Central Composite Design is employed to design the experimental method and optimise the process. A semi batch reactor under inert conditions is used to investigate conditions for maximum plastic derived oil yield. The findings from the current chapter contribute significantly to the subsequent chapter.

Declaration by the candidate:

With regard to CHAPTER 3, pages 42 – 69, the nature and scope of my contribution were as follows:

Nature of contribution	Extent of contribution (%)
Planning of experiments	80
Execution of the experiments	95
Interpretation of the results	80
Compilation of the chapter	100

The following co-author have contributed to CHAPTER 3, pages 42 – 69:

Name	e-mail address	Name of contribution	Extent of contribution (%)
Ntandoyenkosi M Mkhize	mkhizeN7@ukzn.ac.za	Planning of experiments	20
		Execution of the experiments	5
		Interpretation of the results	20
		Revision of the chapter	100

Signature of candidate … ……………………..

Date …30/11/2021…………………………..

Declaration by the co-authors:

The undersigned hereby confirm that

1. the declaration above accurately reflects the nature and extent of the contributions of the candidate and the co-authors to CHAPTER 3, pages 42 -69,

2. no other authors contributed to CHAPTER 3, pages 42 -69 besides those specified above, and

3. potential conflicts of interest have been revealed to all interested parties and that the necessary arrangements have been made to use the material in CHAPTER 3, pages 42 -69 of this dissertation

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Effect of temperature and catalyst on the product yield from polypropylene catalytic pyrolysis

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Abstract

Plastics have an essential impact in several sectors such as packaging, automotive, health care, etc. Globally the growing demand for plastics has caused a rise in plastic waste generation since most plastics are thrown away after a single. An investigation on the effect of temperature and silica-alumina catalyst on product yield during the pyrolysis of waste polypropylene plastic was conducted using a semi-batch reactor under temperatures between 400 to 500 °C and catalyst to feed ratio in the range of 10 to 40 wt.%. Liquid and solid products were collected. A two-level full factorial design with three centre points, the central composite design (CCD), was used. An optimum liquid fraction of 89.95 wt.% and solid fraction of 6.90 wt.% were obtained at a temperature of 427 °C at a catalyst to feed ratio of 33.9%. Silica-alumina catalyst promoted liquid fraction production, lowering the char and gaseous products. An increase in catalyst levels had a significant impact on product yield. It was noted that at catalyst levels above 40%, there was an insignificant increase in the oil yield. Also, the temperature had an impact on the liquid fraction.

3.1 Introduction

The utilisation of plastic polymers is extensive and continuously increasing due to their affordability, desirable properties, and ease of manufacture. In 2019 the production of plastics was estimated to be 550 million (Jha et al., 2021). Plastics polymers are petroleum-based; they are produced using petroleum oil mixed with other ingredients such as colourants and antioxidants. However, because of their origin, they can be transformed back to liquid fuel. The process of pyrolysis has been used to recover liquid fuel embedded in plastics. Pyrolysis uses heat to decompose the plastic polymers leading to bonds being broken to form low molecular monomers and oligomers. During pyrolysis, plastics are heated under high temperatures in a reactor without oxygen, producing pyrolysis vapours captured and allowed to cool. Hot volatiles from the process are cooled to produce oil or wax with a higher degree of purity. They can be refined to form a range of petrochemical products, such as virgin plastic (Williams, 2006). Pyrolysis parameters can be manipulated to optimise the preferred product yield. Different variables influence the conversation of plastics to fuel. These variables comprise but are not limited to temperature, feedstock composition, type of reactor, presence of a catalyst, residence time and heating rate. The liquid and gaseous products of pyrolysis are a blend (mixture) of hydrocarbons. At moderate temperatures pyrolysis can yield up to 80 wt.% liquid oil (Anuar Sharuddin et al., 2016).

Temperature is a significant parameter in pyrolysis because it influences the cracking reactions. Cracking is the breaking of large hydrocarbons molecules into smaller hydrocarbon molecules. Subject to the chemical structure of the polymer, devolatilisation occurs at different temperatures. Thermal devolatilisation of ordinary plastics such as polyethylene terephthalate (PET), high-density polyethylene (HDPE), low-density polyethylene (LDPE), polystyrene (PS), and polypropylene (PP) starts at 350 °C. The operating temperatures influence preferred products. A higher temperature of more than 500 °C promotes the production of gaseous products. Low temperatures in the range of 300 to 500 °C promote liquid products. of plastics. Char yield is maximised by employing slow heating rates ending with low maximum temperatures. The slow heating process is mainly for charcoal formation as it reduces oil and gas concentration during the process. Moderate heating rates of 20-100 °C/min and maximum temperatures of 600 °C result in the equal distribution of products (Williams, 2006). This is known as slow or conventional pyrolysis since it employs slow heating rates accompanied by a slow removal of volatiles from the hot reactor region. Fast or flash pyrolysis involves high heating rates of 100-1000 °C/s at temperatures below 650 °C and fast cooling resulting in the formation of a liquid product (Williams, 2006). Rapid quenching of primary pyrolysis vapours prevents the breaking down of gases in the hot reactor reducing char and gas production. Table 3.1 shows typical characteristics of different types of pyrolysis.

Table 3 1 Typical products from different types of pyrolysis (Williams, 2006)

Pyrolysis	Residence time	Heating rate	Reaction environment	Temperature (°C)	Major product
Carbonisation	hours-days	Very low	Combustion products	400	Charcoal
Conventional	10s-10min	Low-moderate	Primary/secondary products	< 600	Gas, char, liquid
Flash liquid	< 1 s	High	Primary products	< 600	Liquid
Flash gas	< 1 s	High	Primary products	> 700	Gas
Ultra	< 0.5 s	Very high	Primary products	1000	Gas, chemical
Vacuum	2-30 s	Medium	Vacuum	400	Liquid

Also, the reactor type influences the cracking reactions, thus the desired product. Batch, semi-batch, or continuous-flow reactors such as fluidised bed, fixed bed reactor, and conical spouted bed reactor (CSBR) are mainly used for research work. Depending on the application, each reactor has its advantages and disadvantages. Based on the easy to control parameters, batch or semi-batch reactors are mostly exploited for thermal pyrolysis. These reactors are not preferred for catalytic pyrolysis due to their potential to form coke on the catalyst surfaces when blended with the polymer, thereby affecting the catalyst performance. Fluidised bed reactors have the essential advantage of uniform heat, mass transfer The fluidised bed can be a mixture of biomass particles and or powdered catalyst. Fluidised bed reactors are preferred during catalytic pyrolysis since catalysts can be reused. The fluidised bed reactor makes the catalytic pyrolysis economical as catalysts are expensive. CSBR facilitates good mixing and can handle particles of large sizes. Elordi et al. (2007) concluded that using CSBR avoids defluidisation problems and makes handling irregular particles easy. However, its complex design involving several pumps, catalyst feeding, and product collection affects its desirability. Hot volatiles produced during devolatilisation reactions is removed from the reaction using a fluidising (carrier) gas.

Apart from the mentioned factors, the rate and type of fluidising gas also influence the pyrolysis product yield. Fluidising gas, also known as a carrier gas, is the inert gas employed to create an inert atmosphere and transportation of vapourised products. The gas takes no part in the cracking reactions. Different types of fluidising gases can be used in the presence of various catalysts, including nitrogen, argon, helium, hydrogen, and propylene. Abbas-Abadi et al. (2014) reported that each fluidising gas's reactivity differs from the molecular weight. Nitrogen is mainly used because it is easy and safer to handle. Hydrogen and propylene are highly reactive and highly flammable.

At a low carrier gas flow rate, the primary products contact time is high, resulting in the production of coke precursor (BTX) to increase as secondary products are recovered despite a low degradation rate. Lin and Yen (2005) observed an instantaneous degradation rate at the lowest fluidising flowrate of 300 ml/min. At a flow rate of 900 ml/min, gasoline and hydrocarbon gases fractions were maximised. Increasing the flow of carrier gas increases the yield of oil by decreasing secondary reactions. By increasing nitrogen flowrate, Cypres and Bettens (1989) improved the removal rate of pyrolysis volatile from the secondary hot zone. Removal of hot vapours from the hot reaction zone using nitrogen purge gas produced high oil or wax yield (Bhaskar et al., 2003). The type of fluidising gas has a substantial influence on the product composition and quality. Melligan et al. (2012) studied the effect of using hydrogen and nitrogen as carrier gases in the catalytic hydro-pyrolysis of biomass. It was observed that bio-oil attained using hydrogen as a carrier gas had a HHV of 24.4 $MJkg^{-1}$ than 17.8 $MJkg^{-1}$ obtained using nitrogen. Literature on the influence of carrier gas type on the product distribution and quality of plastic-derived oil is limited. Fluidising gas flowrate influences the volatiles retention time in the reaction zone.

Residence time is the time taken by hot vapours in the reaction zone. Pressure and residence time also influences pyrolysis product yield. Both pressure and residence time are temperature-dependent factors impacting the products at a lower temperature. High pressure increases gaseous product yield at high temperatures and influences the molecular weight distribution of gaseous and liquid products.

The presence of a catalyst affects the product yield during the pyrolysis process. The catalyst speeds up the reaction rate thus more volatiles are produced. Primarily zeolites, fluid cracking catalyst (FCC), and silica-alumina catalyst are commonly used in the pyrolysis of plastics. The study conducted by Miskolczi et al. (2013) suggested that using zeolite catalyst in the pyrolysis of MPW helps decrease impurities in the oil produced. Employing FCC catalyst improves the plastic conversion. Silica-alumina catalyst is an amorphous acid type whose acidity strength significantly impacts the products from plastic pyrolysis. Sakata et al. (1996) investigated the impact of catalyst acidity using two kinds of silica-alumina catalyst (SA-1 and SA-2) and zeolite catalyst on the product yield of HDPE pyrolysis. SA-2, with the lowest acidity, produced high amounts of liquid oil (74.3 wt.%), followed by SA-

1 (67.8 wt. %) and ZSM-5 (49.8 wt.%). A ZSM-5 had the strongest acid sites, thereby producing more gas product and less liquid oil. Of the three catalysts commonly used in plastic pyrolysis, zeolite catalysts maximise the formation of gaseous hydrocarbons, whereas FCC and silica-alumina maximise the condensable fraction production.

Since plastics produce hydrocarbons as oil or wax, gas, and char when pyrolysed the difference in the condensable fraction, wax/oil is also influenced by condensation collection system, and condensation temperature (Williams, 2006). There is not much literature about the effect of condensing and cooling system on oil yield. (Williams and Williams, 1998).used a fluidised bed pyrolysis process with a condenser cooled water resulting in the production of oil and wax in the ratio of 1.23 for HDPE, 0.540 for LDPE, 0.82 for PP, 4.75 for PP PS, and 1.48 for PET Miandad et al. (2019) incorporated a continuous condensation system using a water bathe and ACDelco Classic coolant to guarantee a cooling rate below 10 °C. This system provided the maximum condensation of vapour to a liquid fraction. An oil collection tank collected the oil produced. Using this setup, the highest oil yield of 70 and 60% were produced using thermal activated natural zeolite (TA-NZ) and acid-activated natural zeolite (AA-NZ) catalyst.

The PDO obtained using catalytic pyrolysis has various applications in furnaces, boilers, turbines, and diesel engines without any treatment required to improve the oil quality (Bridgwater, 2012). Using oil from pyrolysis is more environmentally friendly since the oil produces less CO_2 into the atmosphere. Several researchers observed that the pyrolysis product yield and quality rely on the process parameters. The current study investigates the product yield under catalytic pyrolysis conditions. The influence of a few selected catalysts and their impact on the product yield was reviewed in chapter 2. Other factors such as temperature, heating rate, particle size, retention time affecting liquid oil yield were also presented. Specifically, the study's objective was to investigate the effect of temperature and silica-alumina catalysts on product yield during the catalytic pyrolysis of polypropylene. The central composite design was employed to examine the influence of these two factors on the pyrolysis process. The methodology adopted to fulfil the objectives is described in the following section.

3.2 Materials and methods

3.2.1 Plastic sample acquisition and preparation

Commercial grade silica-alumina catalyst acquired from Sigma Aldrich; South Africa was used in this study. The catalyst is a white powder with a particle size distribution of 100 Mesh. Silica alumina is amorphous; it contains Bronsted (protic) sites and Lewis acid (aprotic)sites. Plastic waste was collected from Bafana Waste Collectors Newlands East, Durban South, Africa. The municipal waste was not sorted at household level. In this investigation, one type of plastic, polypropylene, was used. Approximately twenty kilograms of waste were collected.

The plastic waste stream was contaminated with oil, dirt, and a lot of moisture. Sorting by handpicking method and characterisation was done before cleaning. Liquid soap was used to remove organic waste, oil, and dirt sticking to the plastic. The plastics were left to dry in the open air for three days. The plastic waste stream was mixed sorting was crucial to characterise the different types of plastic present in the plastic waste stream. Handpicking was the most effective method, as it aids in minimising the cost of the sorting and characterisation process.

Plastic samples were reduced into smaller pieces using a hand scissors Size reduction was essential to facilitate efficient heat transfer during the pyrolysis process. A granulator was used to reduce the size of the polymers by shredding the plastic to smaller sizes. After shredding the plastics, the sample was portioned by quartering using a sample divider. The sample was weighed and sieved using a set of IS sieves of sizes 10 mm, 4.75 mm, 2.36 mm, and 1.18 mm. Sieving was done using an electromagnetic sieve shaker. After sieving of the sample on each sieve was weighed. Particles of size in the range of 4.75 mm to 10mm were used for the bench-scale runs. While particles ≤ 2 mm were used for thermos gravimetric analysis (TGA) runs.

3.2.2 Plastic characterisation analysis

3.2.2.1 Proximate analysis

Thermal gravimetric analyser is an analytical instrument used to define the materials' stability and kinetic properties when exposed to regulated heat treatment. For this study, the DTG-60A Simultaneous DTA-TG Apparatus model manufactured by SHIMADZU Japan was used to perform the thermos gravimetric analysis (TGA) and differential thermal gravimetric (DTA). TGA analysed the polymer's devolatilisation rate. Briefly, nitrogen gas (99.999% purity, Afrox, South Africa) was used to purge the furnace to ensure an inert environment by displacing oxygen and air in the furnace, creating inert conditions to avoid oxidation of samples. The TGA measured mass change in the polymer as a function of temperature (time) in a monitored atmosphere. Between 18-20 mg, of sample was heated in a silica crucible at a constant heating rate of 20 °C/min operating in a stream of N_2 atmosphere with a flow rate of 10 ml/min from 30 °C to 600 °C. TGA were used to plot the differential thermal gravimetric (DTA) graphs to determine the transition temperatures of the polymer. The purity composition of the material, drying, and ignition temperatures are determined from the TGA data.

Proximate analysis was done using the ASTM-E1131 method. The proximate analysis was employed to determine the volatile (combustible) matter, moisture content, fixed carbon, and ash present in the feedstock. The combustible content is the quantity of matter that can be thermally degraded in a given substance (Hakeem et al., 2018). The volatile matter is essential; it estimates the potential chemical recovery from pyrolysis (Sharma et al., 2014).

3.2.2.2 Preliminary experiments

Preliminary experiments were done to set up the cooling system. It was observed that keeping the water bathe temperature between 2-3 °C cooled the system effectively. Data from the TGA analysis showed that pyrolysis of PP starts at 400 to 500 °C. Experimental runs to determine the catalyst range were performed at 450 °C. The catalyst to feed range was investigated from 0 to 50%. Nitrogen gas was purged into the reactor to remove oxygen, creating an inert atmosphere. A holding time of 30 minutes was chosen from the literature. A constant heating rate of 20 °C /minute was used for all the runs conducted. The heating rate was determined using the TGA. Temperature and catalyst range from the preliminary experiments were used to design the experimental method.

3.2.3 Experimental design

For the experimental design, a statistical approach was employed. There are many different approaches to design of experiments (DOE), such as the factorial method, Plackett-Buman method, Taguchi method, or response surface method (RSM). A central composite design (CCD) which comprises of a full factorial design with three centre points augmented with star points to permit the estimation of a curvature was employed for the investigation. The

CCD is a response surface method. DOE cost-effectively generates a lot of information and helps in identifying the critical design parameters to control and improve a process. Two factors were investigated temperature and catalyst to feed ratio. Steps followed in creating the design of experiments for this study are shown in Appendix.

Experimental work was carried on based on mixture design obtained from the CCD. The experimental design was blocked; the prescribed run order was followed for the experiments. Two factors, temperature, and catalyst were varied; sample amount and holding time were constant. Oil and char yield were the measured responses. Table 3.2 shows the temperature and catalyst ranges.

Table 3 2 Central composite design (CCD) factors

Factor	Units	Factor type	Lower level (-)	Centre point (0)	Upper level (+)	Lower axial (-α)	Upper axial (+α)
Temperature	°C	Variable	400	450	500	379	520
Catalyst	wt.%	Variable	10	25	40	4	46
Sample amount	g	Constant	40	40	40	40	40
Holding time	min	Constant	30	30	30	30	30
Liquid yield	wt.%	Response					
Solid yield	wt.%	Response					

A numerical response optimiser of CCD was used to obtain the optimum operating condition that gives the optimum products yield. The process temperatures, catalyst range, and centre points were carefully chosen centered on the viability with the pyrolysis equipment and results from the preliminary experiments. Design Expert 11 StatEase was used to do design the experiment. Experiments were performed following the design in Table 3.3.

Table 3 3 Experimental design

	Factor 1	Factor 2	Response 1	Response 2
Run	A: temperature	B:cat:feed	oil yield	Char yield
	C	%	%	%
1	520.711	25		
2	379.289	25		
3	500	10		
4	450	46.2132		
5	450	25		
6	450	3.7868		
7	400	10		
8	500	40		
9	400	40		

3.2.4 Semi-batch pyrolysis reactor

Pyrolysis was conducted using a semi-batch reactor. The pyrolysis equipment comprises of a reactor made of stainless steel from Watford Herts tube (length 60.5 cm, internal diameter 4.00 cm, and outer diameter 4.60 cm) closed at one end and an outlet tube on the other end. A sample holder (length 42 cm, internal diameter 3.3 cm and outer diameter 2.6 cm) made from stainless steel was used to hold the sample. An electric (muffle) furnace externally heats the reactor, with a Cr-Al:K type thermocouple for temperature measurement was secured inside the reactor. An external PID controller controls temperature.

3.2.4.1 Experimental procedure

Initially the empty steel reactor and sample holder were weighed. Samples of 40g of plastics mixed with silica-alumina catalyst were placed in the sample holder, which in turn was placed in the reactor. In turn the reactor was centrally inserted into the electric furnace. The carrier gas, N_2, was purged into the reactor during the experiments. The reactor temperature was measured using a thermocouple and monitored using a. digital control system connected to a monitoring screen to display the operating reactor temperature and the set temperature. Experiments were performed as shown in Table 3.3. Experiments were conducted at various temperatures ranging from 379-520 °C and a constant heating rate of 20 °C/min. Figure 3.2 shows the equipment's set-up.

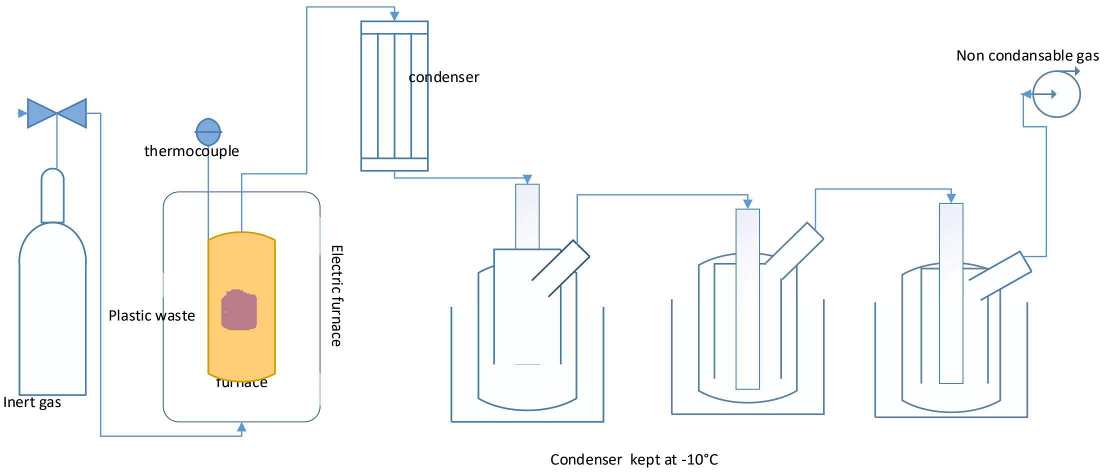

Figure 3 1 Pyrolysis equipment set-up

Condensable products were collected using three condensers. From the reactor, the volatiles flow to a heat exchanger for the condensation of the vapours. Condensation was accomplished using a shell and tube heat exchanger utilizing cold water as the coolant from a water bath followed by a condenser train. The water was maintained at 2-3 °C in a water bath. The condensation train pieces were weighed prior to the experiment and secured together. The condenser train consists of three small condensers maintained below -10 °C using dry ice (wet CO_2). The system components were all weighed on completion of the experiment to establish the quantity of the pyrolysis products. Condensable products (oil) yield was established by the subtracting the masses of the set-up component prior and subsequent to the run. At times, the condensable fraction stuck on to the condenser, which is why the heat exchanger mass was considered for the mass balance.

$$Y_{condensable} = \frac{(R_1 + C_1 + C_2 + C_3) - (R_0 + B_1 + B_2 + B_3)}{M_s} \times 100 \ldots \ldots .3.1$$

Where

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

R_0 = Mass of a heat exchanger before the experiment (g)

R_1 = Mass of heat exchanger after the experiment (g)

B_1 = Mass of condenser 1 before the experiment (g)

B_2 = Mass of condenser 2 before the experiment (g)

B_3 = Mass of condenser 3 before the experiment (g)

C_1 = Mass of condenser 1 after the experiment (g)

C_2 = Mass of condenser 2 after the experiment (g)

C_3 = Mass of condenser 3 after the experiment (g)

Ms = Mass of feed sample (g)

The yield of char was calculated as the fraction of the difference in mass between the sample before and after the experiments as shown in equation 3.2

$$Y_{char} = \frac{(S_1 - S_0)}{M_s} \times 100 \dots\dots\dots 3.2$$

Where

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

S_0 = Mass of the reactor before the experiment (g)

S_1 = Mass of the reactor after the experiment (g)

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

$$Y_{gas} = 100 - (Y_{condensable} + Y_{char}) \dots\dots..3.3$$

The conversion is the fraction of the feed that ends up as products in the pyrolysis process and is determined according to Equation 3.3

$$Conversion\ (\alpha) = \frac{(M_s - M_c)}{M_s} \dots\dots\dots 3.4$$

Where

M_c = Mass of char (g)

3.2.5 Elemental analysis

Characterisation of the char obtained during the pyrolysis was done using a Thermal Scientific Flash 2000 elemental analyser. A sample of 5 mg was combusted for each run to analyse the carbon, hydrogen, nitrogen, and sulfur present in the char. Each sample was analysed in one replicate, and the average was considered.

3.3 Results and Discussion

3.3.1 Plastic characterisation

3.3.1.1 Proximate analysis

Pyrolysis yield can be estimated using the volatile content. The amount of volatile matter gives an approximate expected yield. The waste polypropylene plastic sample was found to have very little highly volatile matter of 0.475%. It was concluded that the high volatile matter comprises of the moisture present in the sample. Polypropylene plastic sample had a low moisture content of less than 1%. The proximate analysis showed a medium volatile matter (combustible matter) of 93%, fixed carbon content of 1.47 wt.% and an ash content of 4.698 wt.%. The combustible matter indicates the quantity of product that could be reclaimed during cracking. Low solid combustible and incombustible remains after the devolatilisation of PP plastic.

The ultimate analysis result demonstrates the suitability of PP as a feed material for the pyrolysis process based on its high carbon value (Hakeem et al., 2018). Results obtained in this work are close to what is expected due to the chemical configuration of polypropylene; C_3H_6. Ideally PP plastics contain 85.71% carbon and 14.29% hydrogen which is approximately the results obtained during this study, 83.99% carbon and 13.98 hydrogen. Differences may result from the presence of other additives. Table 3.4 displays the proximate and ultimate analysis of polypropylene polymer.

Table 3 4 The proximate and elemental analysis

Proximate analysis				**Elemental analysis**	
Moisture Content (%)	Volatile matter (%)	Fixed Carbon (%)	Ash Content (%)	C	H
0.475	0.475	1.47	4.698	83.999	13.988

3.3.1.2 Preliminary results

Preliminary experiments were done using a temperature of 450 °C and silica-alumina catalyst to PP plastics range between 0-50 wt.%. At low catalyst to feed ratios of below 10 wt.%, waxy products were attained. No wax product was obtained at 10 wt.% catalyst. Above 40 wt.% catalyst, the oil yield increase was insignificant, indicating the catalyst saturation point. Figure 3.4 shows the effect of catalyst increase on the oil yield.

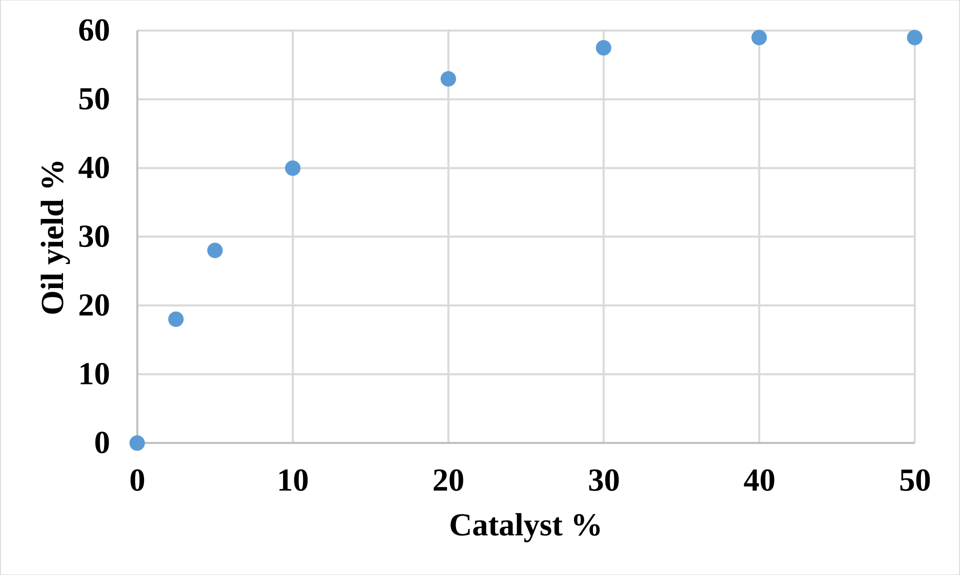

Figure 3 2 Effect of catalyst on yield

Preliminary experiments were done to determine the condensation conditions. Table 3.6 shows the oil yield under different cooling conditions. Initially the volatiles were cooled in a shell and tube heat exchanger which used water maintained at 3 °C as the coolant. A train of three condensers was installed to condense the condensable fractions using dry ice (wet carbon dioxide). All runs were done at 450 °C and 30% catalyst. The use of dry ice for all three condensers promoted the highest oil yield.

Table 3 5 Cooling system determination

Condensers			Product yield	
A	B	C	Liquid	wax
AT	AT	AT	30	
Dry ice	AT	AT	25	
Dry ice	Dry ice	AT	16	38.4
Dry ice	Dry ice	Dry ice	58.5	
AT	Dry ice	Dry ice		42.5
AT	AT	Dry ice	55.25	
Dry ice	AT	Dry ice	53.25	

*AT means at ambient temperature

3.3.2 Thermal behaviour of waste polypropylene

The thermal behaviour of waste PP plastics was studied using the TG curves, which showed the percentage mass loss with temperature and the differential thermos gravimetric (DTG) curves showing the rate of mass loss of PP with temperature. Figure 3.3 shows the thermal behaviour of PP with and without a catalyst. The TG curve shows the presence of highly volatile matter (moisture) when using a catalyst. The high volatile matter might be due to the catalyst absorbing moisture from the environment. The mass-loss rate of waste PP with a catalyst is higher than without a catalyst. After 530 °C the TG curve of plastic waste without catalyst flattens due to the solid residual char. The amount of residual solids when a catalyst waste incorporated is high because the catalyst is not used up during the reaction. At 480 °C in the presence of a catalyst, the TG curve starts to flat, showing the absence of volatile matter.

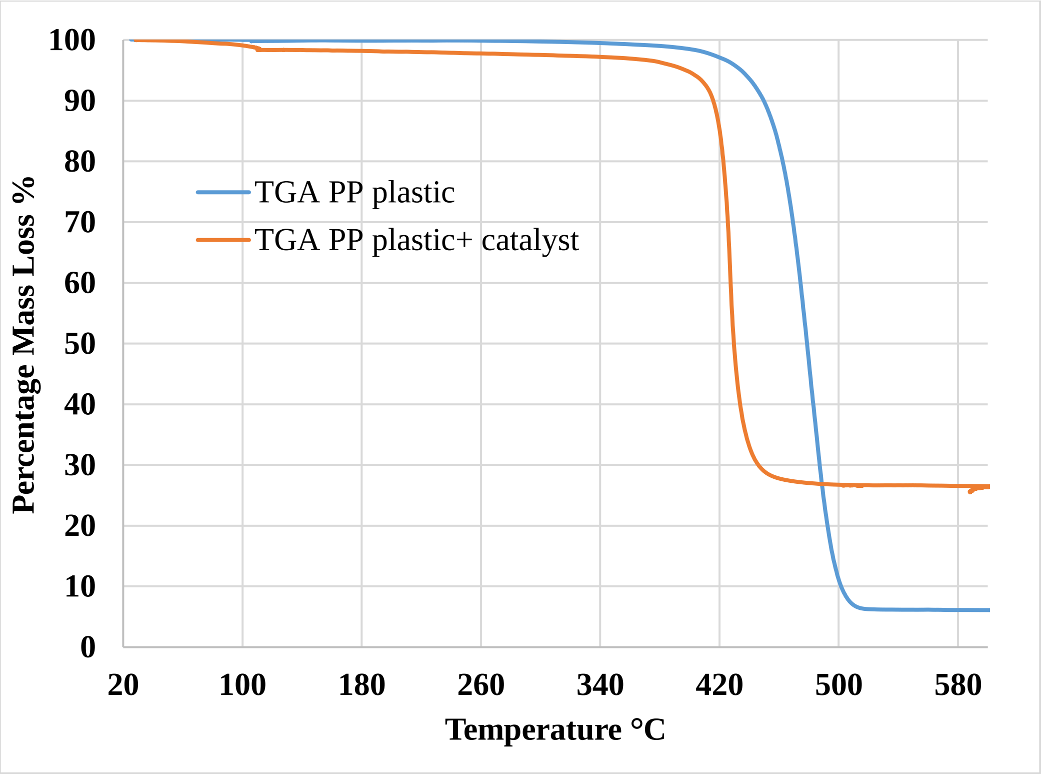

Figure 3 3 PP Thermal gravimetric analysis curves

The DTG profile, Figure 3.4, shows that PP degrades in a single step. Thermal degradation of PP plastic starts at 390 °C and ends at 530 °C, maximum devolatilisation occurs at 486 °C. The presence of a catalyst narrows the devolatilisation temperature range from 390-530

°C to 378-480 °C. The presence of a catalyst reduced the onset, peak, and offset devolatilisation temperatures. Figure 3.4 shows that the onset devolatilisation temperature decreased from 390 to 378 °C. The maximum devolatilisation temperature decreased from 478 to 429 °C as well as the offset devolatilisation temperature dropped from 530 to 480 °C. Catalytic conditions significantly reduce the devolatilisation temperature and reaction time.

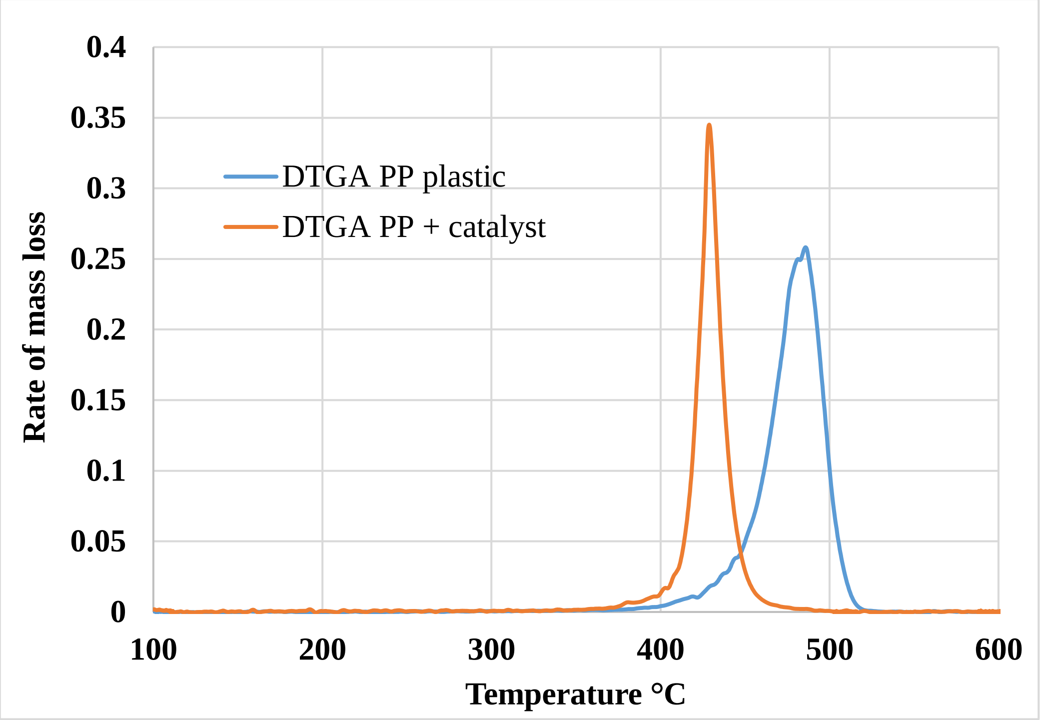

Figure 3 4 PP differential thermal gravimetric curves

Table 3.5 summarises the decomposition temperatures in the absence and presence of a catalyst.

Table 3 6 Thermal characteristic parameters of PP polymer

	Devolatilisation temperature °C		
sample	Onset	Peak	Offset
PP	390	486	530
PP + catalyst	378	429	480

3.3.3 Pyrolysis results

3.3.3.1 Design of experiment results

The effect of temperature and catalyst on the liquid and solid products of pyrolysis were investigated using the CCD experimental tool. The results of the investigation are as given in Table 3.7. After the completion of pyrolysis experiments, the experimental design was used for model selection. Oil and char and yields were recorded on the response section of the experimental tool, and the results were analysed using the design expert software 11.

Table 3 7 PP catalytic pyrolysis product yield of CCD experiments

	Factor 1	Factor 2	Response 1	Response 2
Run	A: temperature	B:cat:feed	oil yield	Char yield
	C	%	%	%
1	520.711	25	90	4
2	379.289	25	85.25	4.75
3	500	10	68.75	28.25
4	450	46.2132	87	2.75
5	450	25	89.5	4.75
6	450	3.7868	55.25	35.5
7	400	10	65	33.25
8	500	40	91.5	6
9	400	40	87	10

Response 1, oil yield was analysed, giving a fit summary which suggested a quadratic model. The model is significant with an insignificant lack of fit. The lack of fit method is used to assess if models are acceptable. For the model to fit well into the experimental design, the lack of fit should be insignificant. The adjusted R^2 value measures the deviation around the mean as described by the model. Predicted R^2 is a measure of the extent of variation in the new data defined by the model. The difference between these two should be within 0.2. The model had a predicted R^2 value of 0.9293 and the adjusted R^2 value of 0.9470, i.e., the difference is less than 0.2. Adequate precision is a signal-to-noise ratio that analyses the predicted values' range at the design points to the average prediction error. Good model discrimination is shown by a ratio greater than 4. The model had a ratio of 25.46, which is desirable. Subject to the experimental results, the subsequent empirical second-order polynomial equation illustrates the interaction of the proposed variables to achieve the oil yield: The coded equation is

$$oil\ yield = 86.90 + 2.33A + 11.74B - 1.06AB = 0.3917A^2 - 9.13B^2 \ldots\ldots 3.5$$

Where A is the temperature, B is the percentage catalyst.

Figure 3.5 shows the actual oil yield from the experimental versus the predicted. The straight line shows the expected yield. There are slight deviations from the expected yield showing that the model is significant.

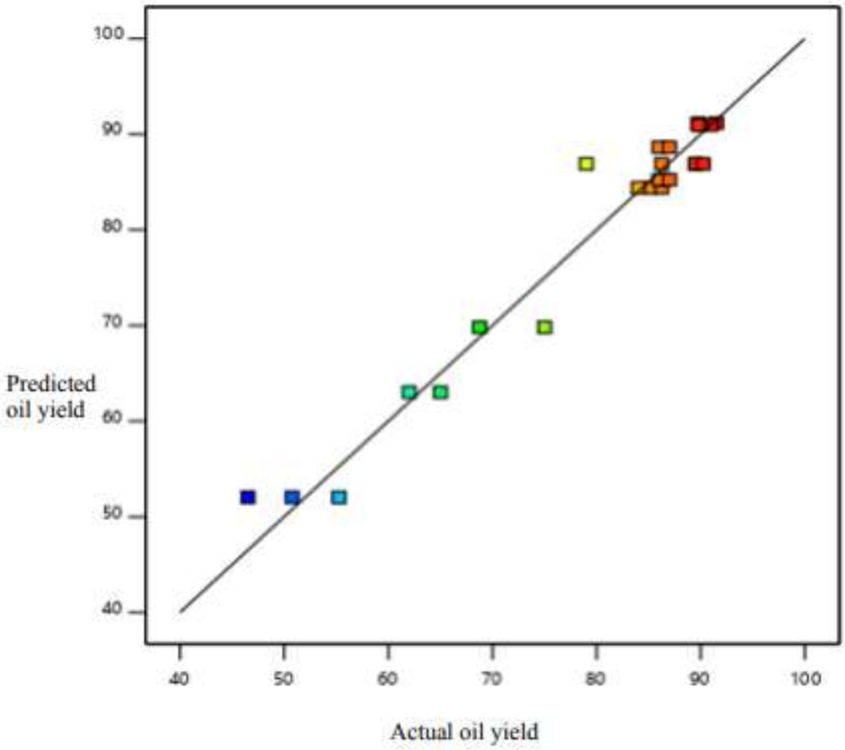

Figure 3 5 Predicted versus actual oil yield

The surface plot in Figure 3.6 shows the liquid yield relative to catalyst effect and temperature. The interaction of temperature and catalyst percentage is revealed on the surface plot. Oil yield increases with an increase in catalyst quantity. At a low catalyst ratio increasing the temperature increased the oil yield from 51.25% to 72%. High amounts of catalyst resulted in higher oil yields. The effect of the catalyst on the liquid fraction yield was quadratic. The highest oil yield was achieved at 25% catalyst at a temperature of 450 °C. Figure 3.6 reveals that oil yield increased linearly with an increase in the amount of catalyst until around 30% catalyst; continuous increase in catalyst had less effect on the oil yield. At high temperatures and high catalyst ratios, oil yield changed slightly.

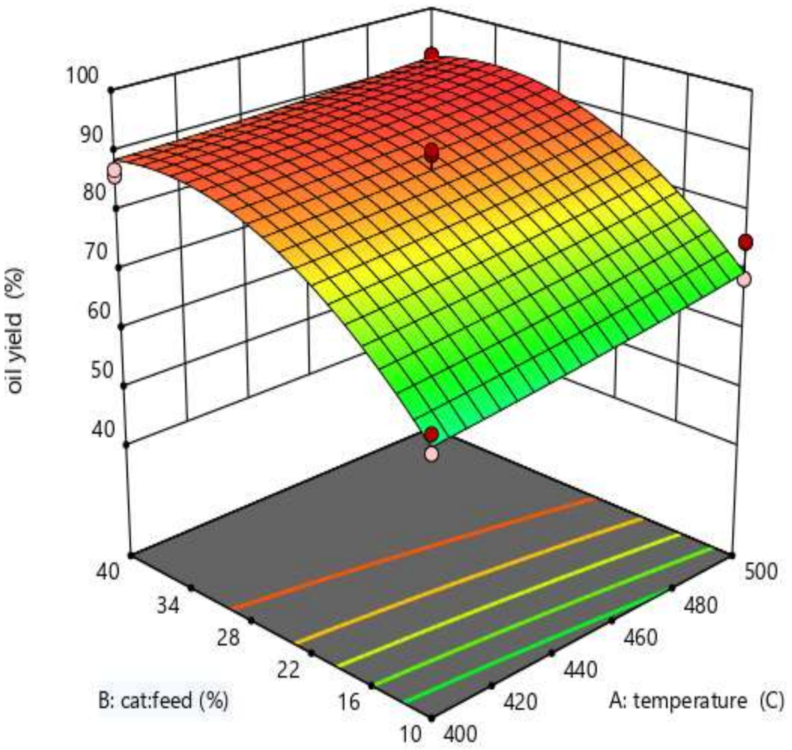

Figure 3 6 Surface plot of oil yield

Figure 3.7 shows the surface plot of char yield in relation to the catalyst to feed ratio and temperature. It is evident from the surface plot that char yield increases at a low catalyst to feed ratio even at high temperatures. The influence of catalyst to feed ratio and temperature on char yield is quadratic. The lowest char amount was noted at 450 °C and 25% catalyst. Subject to the experimental results, a quadratic equation on the interaction of catalyst to feed ratio and temperature was modelled:

$$Char\ yield = 6.95 - 2.31 * temperature - 12.36 * cat{:}feed + 3.06 * temperature * cat{:}feed - 0.4792 * temperature^2 + 8.29 * cat{:}feed^2 \ldots\ldots 3.5$$

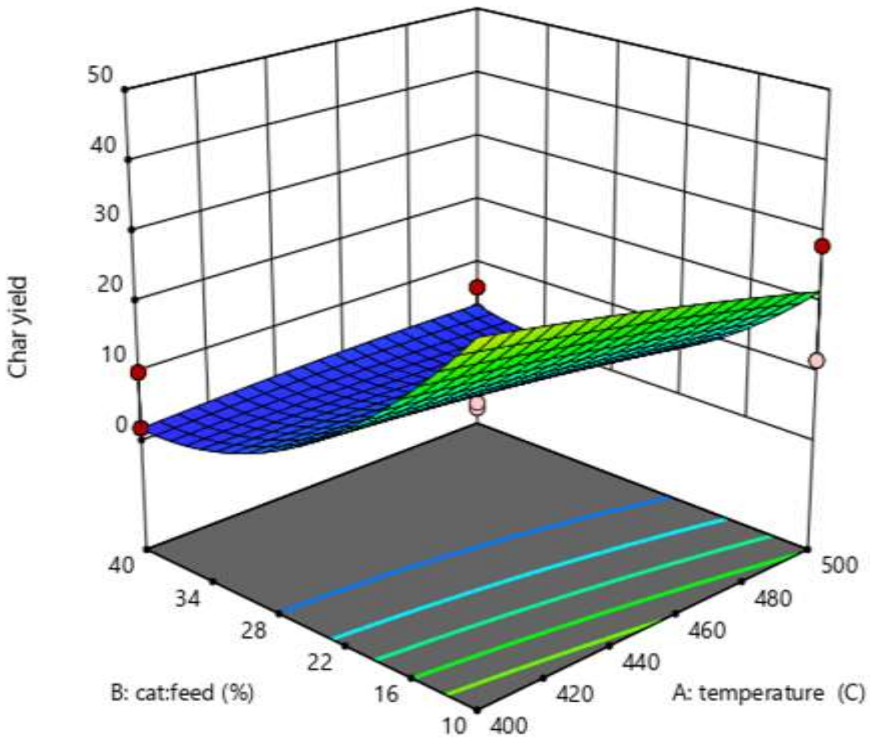

Figure 3 7 Surface plot of char yield

3.3.3.2 Polypropylene PDO pyrolysis results

Two products were collected from the process condensable (oil) and solid (char). The condensable products, which is the oil, was collected in a series of condensers. The char remained in the reactor while the gas was vented in the atmosphere. Catalytic pyrolysis of polypropylene produced liquid oil as the condensable fraction. Figure 3.8 shows the oil yield under different conditions. It was noted that an increase in catalyst amount increases, oil yield. The oil yield increased from 51.25% at 4% catalyst and 450 °C to 91.25% at (25% catalyst) at the same temperature. Further increase in catalyst amount was marked with a reduction in oil yield to 87% at 46% catalyst. The trend of yield increasing as catalyst amount increases were observed at 400 °C and 500 °C. Oil yield increased from 77.5% to 88.5% at 400 °C and from 72% to 89.75% at 500 °C.

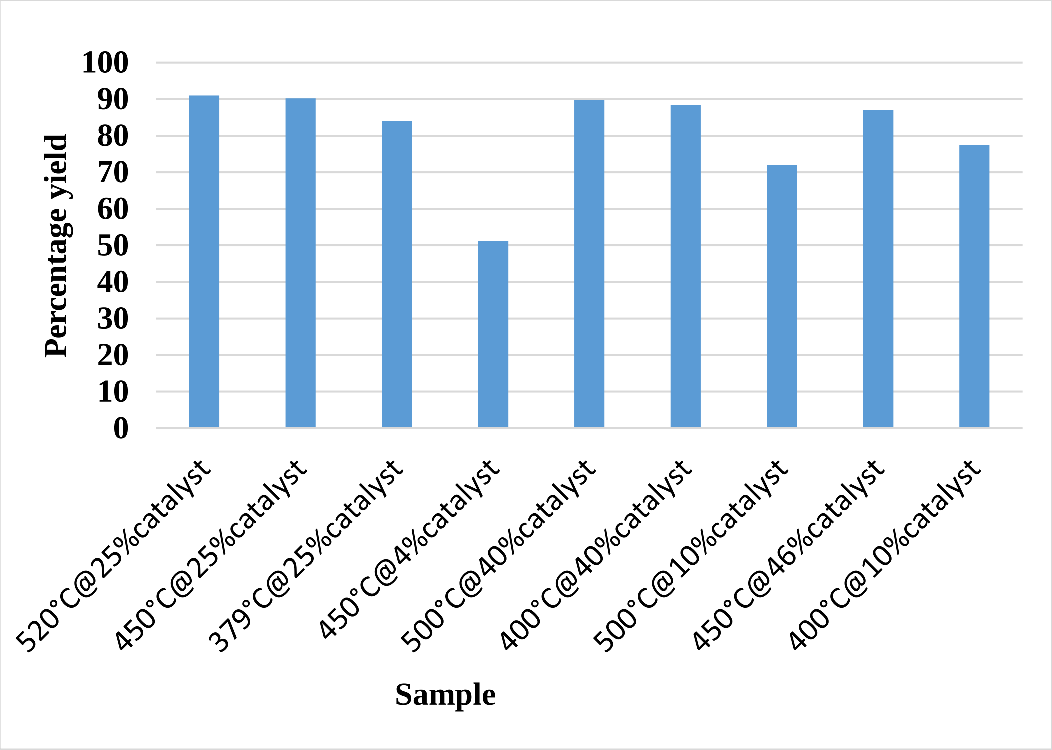

Figure 3 8 Oil yield under different conditions

Effect of temperature on oil yield

At a constant catalyst amount (25% catalyst), increasing the temperature led to a yield increase of 8%. Figure 3.9 shows the oil yield at constant catalyst amount under varying temperatures. It was observed that as temperature increased from 379 to 450 °C the oil yield increased significantly from 84 to 90.25 wt.%. It can be concluded that maximum devolatilisation of waste PP occurs in this temperature range. Under these conditions, the hot vapours are comprised of the condensable volatiles. As the temperature increased to 520 °C, there was a slight increase in the oil yield. Figure 3.9 shows that after 500 °C, the oil yield graph starts to flatten. This shows that higher temperatures promote the formation of non-condensable short carbon chains.

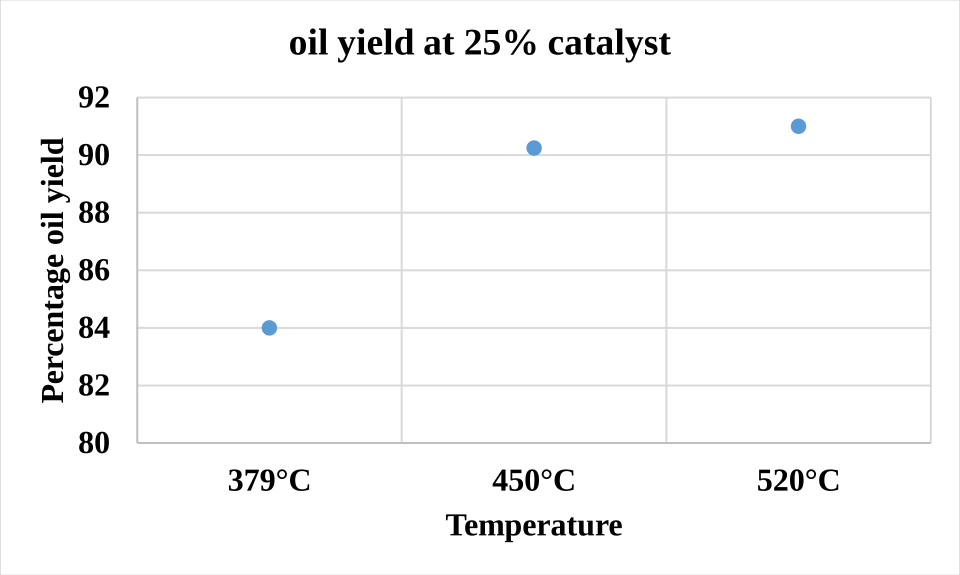

Figure 3 9 Oil yield at 25% catalyst under varying temperatures

Effect of catalyst on yield

Figure 3.10 shows the oil yield at a constant temperature of 450 °C with varying catalyst to feed ratios. At a fixed temperature of 450 °C, it was observed that increasing the amount of catalyst from 4 % catalyst to 25 %, the oil yield increased by 70 %. Further increase in the amount of catalyst to 46 wt.% led to a decline in the oil yield to 88.25 wt.%, corresponding to an approximately 3 wt.% decrease. The increase in catalyst amount promotes the devolatilisation reactions. High amounts of catalysts avail more active sites for devolatilisation, leading to C-C bonds breaking to short carbon chain compounds. As the catalyst increases, shorter carbon chain compounds are promoted, lowering the amount of condensable hydrocarbons, resulting in a decrease in oil yield. The shorter carbon chains hydrocarbons comprise of the gaseous fraction. Panda and Singh (2011) noted that at a feed to catalyst ratio of 20:1there was almost no effect on the oil yield.

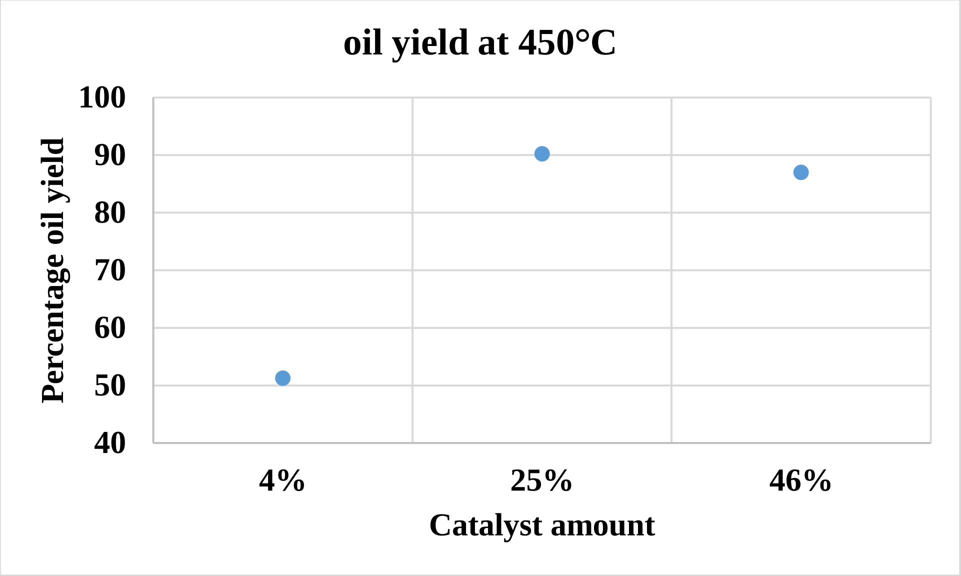

Figure 3 10 Oil yield at 450 °C under varying catalyst to feed ratios

3.3.3.3 Polypropylene plastic pyrolysis solids

The solid residue (char) from the pyrolysis process was collected and weighed. Figure 3.11 shows the char yield under different conditions. A low catalyst amount of 4% produced the highest amount of char of 41.4 wt.%. As the catalyst increased, the solid products were reduced. At a catalyst amount of 46%, a char amount of 4% was obtained. Higher amounts of char indicate incomplete devolatilisation. It was observed that catalytic pyrolysis reduces char production because it promotes devolatilisation reactions. As the temperature increased char amount decreased. The lowest amount of char of 3.5% was obtained at 520 °C.

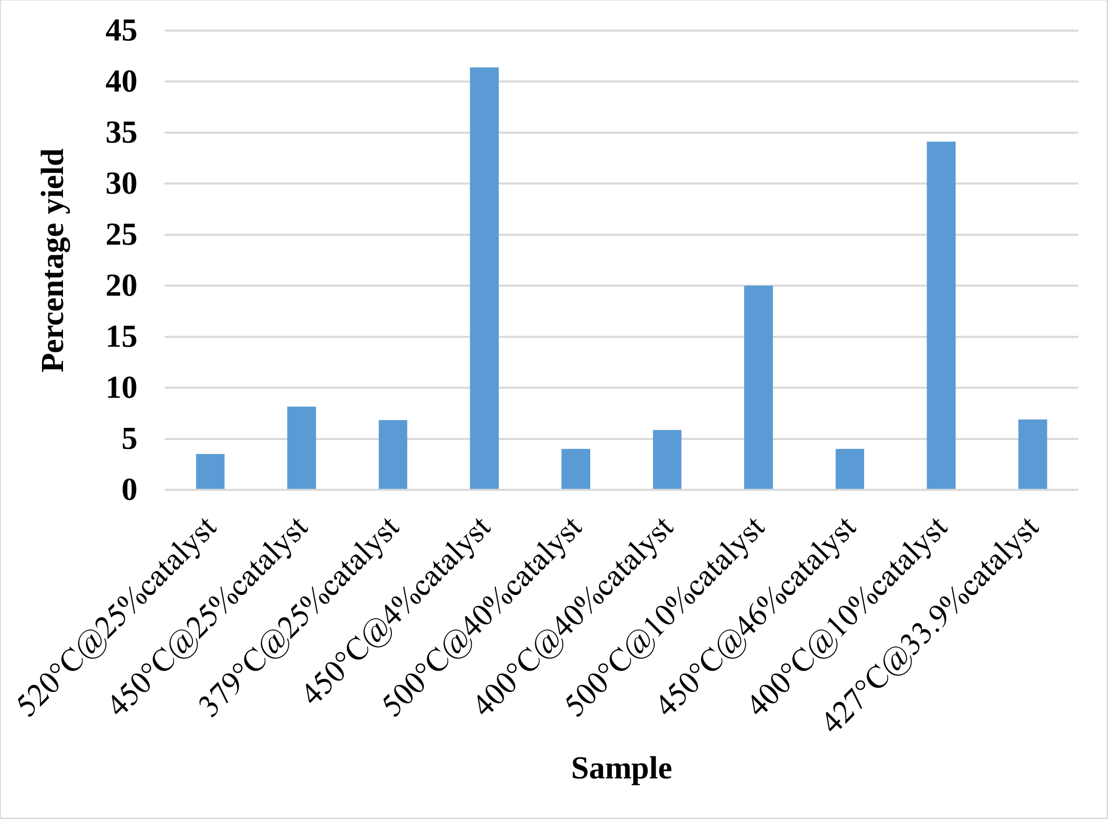

Figure 3 11 Pyrolysis char yield under different operating conditions

Char characterisation

Elemental analysis on the char was done to investigate the elements present in the residue after devolatilisation. Figure 3.12 shows the elements present in the char obtained during this investigation. At lower temperatures and low catalyst levels, the amount of carbon present in the char was high. This observation shows that there was incomplete devolatilisation of the plastic polymer. Char obtained at 450 °C, and 4% catalyst contains the highest carbon content of 24.3%. An increase in catalyst decreases the carbon content in char as noted under 379 °C and 25% catalyst. The carbon content was reduced to 17.8%. Low carbon amounts in char were observed at a high catalyst percentage. High amounts of the catalyst lead to high polymer degradation; thus, all volatile matter is changed to pyrolysis vapours.

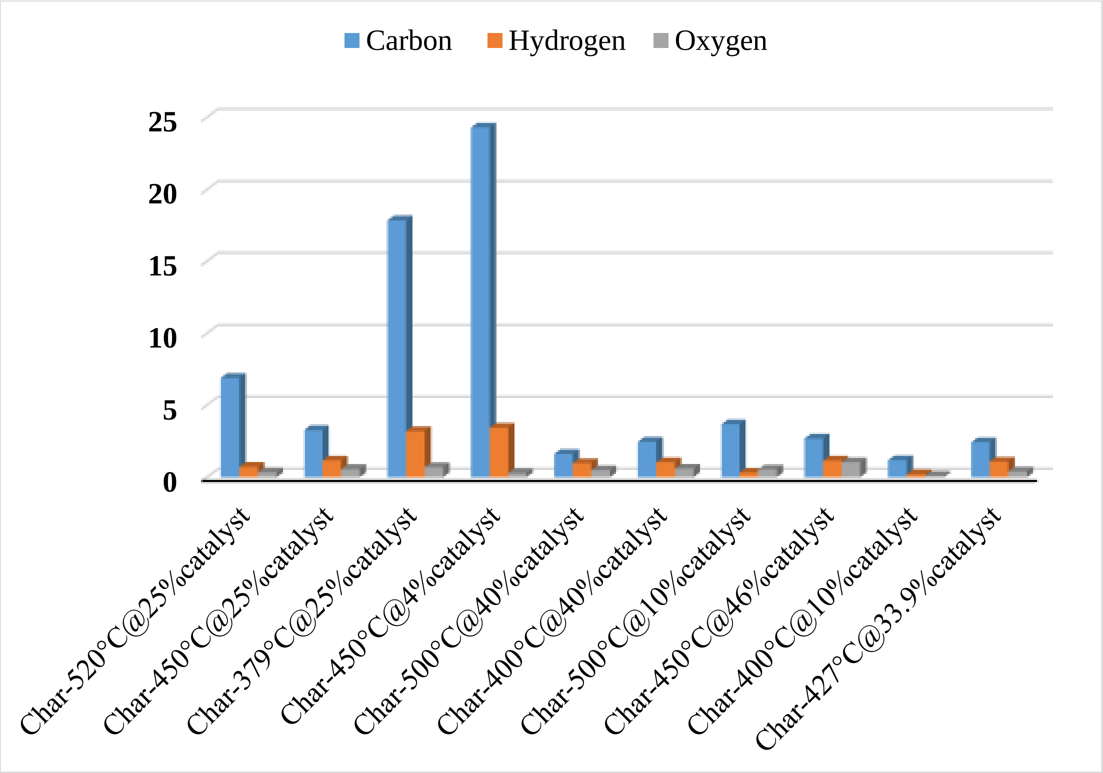

Figure 3 12 Char elemental composition

3.3.4 Optimisation of operating parameters

The Central Composite Design was used to optimise the experimental results by maintaining the responses within the desired ranges. This study was targeted at finding the parameters that optimise the process in order to maximise the oil yield. The developed model indicates that the optimum yield can be obtained at a temperature of 427 °C and a catalyst to feed ratio of 33.9%. The model predicted an oil yield of 89.954. The optimum parameters were tested in the laboratory. Confirmation experiments were done in duplicate. Oil yields of 90.2% and 89.6% were obtained using the optimum conditions predicted. Table 3.7 shows the optimum parameters predicted using the model.

Table 3 8 Optimum operating parameters

Temperature °C	Cat:feed %	Oil yield %	Char yield %	Desirability
427	33.9	89.954	6.90	0.966

3.5 Conclusions

In this work the effect of temperature and catalyst on product yield was studied using a semi-batch reactor. Waste polypropylene plastic was mixed with the silica-alumina catalyst (in-situ). The experiments conducted showed that both temperature and catalyst significantly affected the waste polypropylene plastic pyrolysis process. The PDO yield increased significantly while the solid product (char) decreased significantly. High catalyst amounts caused a decrease in the oil yield, promoting gas yield. The silica-alumina catalyst lowered the process temperature. Increasing the reactor temperature above the process temperature had less effect on the PDO yield since the volatiles were removed from the hot zone as the process progressed. The cooling system had a positive influence on the oil yield. Regeneration of the catalyst was difficult since the solid residue was deposited on the catalyst's active site. To overcome the challenge two-stage catalytic pyrolysis can be incorporated.

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CHAPTER 4: EFFECT OF TEMPERATURE AND CATALYST ON POLYPROPYLENE PYROLYSIS OIL QUALITY.

Manuscript

Title: Effect of temperature and catalyst on polypropylene pyrolysis oil quality.

Targeted Journal: Fuel Processing Technology

Issue: xxx

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Short Summary

The quality of plastic-derived oil under optimal conditions temperature 427 °C and catalyst (33.9%) from objective 2 (Chapter 3) is elaborated in the current chapter (CHAPTER 4). This chapter aims to expand the findings regarding plastic-derived oil's physical and chemical properties compared to conventional diesel. A Gas Chromatogram and mass spectrometer, density and viscometer are used to investigate the physio-chemical properties of the oil.

Declaration by the candidate:

With regard to CHAPTER 4, pages 71 – 97, the nature and scope of my contribution were as follows:

Nature of contribution	Extent of contribution (%)
Planning of experiments	80
Execution of the experiments	95
Interpretation of the results	80
Compilation of the chapter	100

The following co-author have contributed to CHAPTER 4, pages 71 – 97:

Name	e-mail address	Name of contribution	Extent of contribution (%)
Ntandoyenkosi M Mkhize	mkhizeN7@ukzn.ac.za	Planning of experiments	20
		Execution of the experiments	5
		Interpretation of the results	20
		Revision of the chapter	100

Signature of candidate …   ……………………..

Date …30/11/2021…………………………..

Declaration by the co-author:

The undersigned hereby confirm that

1. the declaration above accurately reflects the nature and extent of the contributions of the candidate and the co-authors to CHAPTER 4, pages 71 -96,

2. no other authors contributed to CHAPTER 4, pages 71 - 91 besides those specified above, and

3. potential conflicts of interest have been revealed to all interested parties and that the necessary arrangements have been made to use the material in CHAPTER 4, pages 71 - 96 of this dissertation

Signature	**Institutional affiliation**	**Date**
	University of KwaZulu-Natal	

Effect of temperature and catalyst on polypropylene pyrolysis oil quality.

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Abstract

Rapid industrialisation and population growth have come along with different challenges, such as the energy crisis and environmental destruction. Natural energy sources are depleting; therefore, there is a need for an alternative energy source. Biomass and plastic waste have emerged as potential sources of energy. Plastics are petroleum-based; energy is embedded in waste plastics. The energy can be reclaimed in liquid, solid, or gaseous form. This study investigated the effect of temperature and catalyst on the liquid product quality obtained during catalytic pyrolysis. of waste polypropylene. The oil obtained was yellow with a choking smell consisting of hydrocarbons in the gasoline range. Cyclopropane,1,2-dimethyl-, trans dominated the oil. The silica-alumina catalyst had a significant effect on the liquid oil hydrocarbons distribution. The oil contained a few compounds in the diesel range and a significant percentage of paraffinic compounds due to the molecular skeleton of PP. The physical properties of the oil resembled gasoline.

4.1 Introduction

A continual diminish in fossil fuel supplies has seen the development of many technologies for the generation of alternative fuel sources. Extensive research on the use of plastic waste and biomass as sources of fuels has been conducted. Thermochemical conversion has emerged as the most attractive method among the methods developed due to its compatibility with the current industrial chemical process. Pyrolysis is a method of polymer devolatilisation using high temperatures without oxygen to generate a range of products, i.e., char, gases, and volatiles (condensed to attain pyrolysis oil). Plastic derived oil (PDO) is a complex mixture of various compounds (Johansson et al., 2017). Oil from thermal pyrolysis has a wide range of carbon number distribution making it a challenge to use the oil as a fuel. The carbon number distribution affects the quality of the oil. Physio-chemical properties such as viscosity and density are critical parameters of fuels; thus, improving and monitoring the quality of resultant pyrolysis PDO is essential. Plastic oil quality is affected by the feedstock composition and technology incorporated during the process. The technological aspect includes the pyrolysis process parameters, reactor type, product condensation, and collecting.

The plastic feed composition directly affects the quality of resultant products during the pyrolysis process. Plastic feedstock composition affects plastic oil properties such as flash point, low-temperature properties, and heteroatom content (S, Cl, and N_2). Fuel derived from PE contains high amounts of linear paraffins and 1-olefins, paraffins typical in diesel (Scheirs, 2006). The fuel has a low cetane rating. Liquid condensable from PP comprises mainly primary olefins resembling the molecular configuration of PP, i.e., branched hydrocarbons. The major production of a specific C_9 olefin identified as 2,4dimethylhept-1-ene is a characteristic distinctive to polypropylene pyrolysis. Less coke residue and more liquid oil are produced during the pyrolysis of PP plastics. Fuel from polystyrene is high in aromatics. Polystyrene depolymerises, predominantly giving the styrene monomer. Ethyl benzene, toluene, trimethylbenzene, and benzene are produced during the cracking process of PS. Under mild conditions, pyrolysis of PET results in the formation of terephathalic acid. The pyrolysis of PET yields no liquid products (Sakata et al., 1996). PVC is not favoured as a feed for pyrolysis because it comprises 57% chlorine (Wirawan, 2019).

Pyrolysis oil is a complicated mixture of various compounds, including carboxylic acids, water, aldehydes, ketones, aromatics with a broad molecular weight and boiling point. Often plastic pyrolysis products need to be modified because of their wide range of carbon numbers among the products (Xue et al., 2017). Because of the many hydrocarbons, some have undesirable properties incompatible with conventional fuels; thus, they require upgrading. Catalytic pyrolysis is used for upgrading the oil to improve its properties. The final products will have a narrow carbon number distribution and better selectivity (Elordi et al., 2011). The oil fraction can be utilised in chemical extraction apart from upgrading the oil to improve its fuel properties. Phenols can be extracted for use in the resin industry. (Kim, 2015). The technology used to condense and collect pyrolysis products affects the chemical composition and properties of the products.

A catalyst is used for the acceleration of the chemical reaction. The activation energy of the process is reduced, resulting in decreased e reaction rate. The use of a catalyst lowers the operating temperature required for the process. Pyrolysis is affected by its high energy usage. The introduction of a catalyst helps in reducing the amount of energy required for the process (Erdogan, 2020). The catalytic pyrolysis of polyolefins rises the selectivity of volatile products by altering the product distribution (Anuar Sharuddin et al., 2016). Many researchers have used a catalyst to upgrade the pyrolysis liquid hydrocarbon distribution to match the properties of conventional fuels such as diesel and gasoline. Catalyst causes a decrease in temperature and retention time improving the quality of pyrolysis products. Catalyst can change the energy barrier of the existing reaction in the non-catalytic pathway or completely alter the reaction mechanism to follow a different path (Zhou et al., 2016)

Catalysts are classified into two groups depending on the structure, homogenous and heterogeneous catalysts. Homogenous catalysts have the similar phase as the reactants, while heterogeneous catalysts are in a different phase. Heterogeneous catalysts are mainly used for pyrolysis because they can be recovered from the reactant mixture. There are many types of catalyst that can be used for pyrolysis such as zeolites (HZSM-5, HUSY, Mordenite, and Beta), silica-alumina, activated alumina, mesoporous aluminosilicates, and metal-based catalyst

Catalyst can be applied for several reasons: lower pyrolysis temperature, a higher chemical, physical stability, high yield of target components, and improved miscibility with refinery streams (Matayeva et al., 2019). The catalyst might be used at different stages in the pyrolysis process, mixed with the plastic waste in the pyrolysis reactor (in-situ operation), and built-in the process after the pyrolysis reactor for the reforming of prime pyrolysis vapours (ex-situ operation). The catalyst and polymer feed are mixed in the pyrolysis reactor for the in-situ operation, and the catalytic upgrading happens in the same reactor. During the in-situ process when the plastics liquefies and spreads around the catalyst. The liquefied plastic is drawn into gaps between particles and therefore to active sites at the outer surface of the catalyst (Marcilla et al., 2009). In-situ catalytic pyrolysis is easy; mechanical alteration of existing reactors is not necessary. The decomposition temperature is lowered; thus, there is a potential reduction of energy when using in-situ configuration. However, catalyst recovery is difficult since solid residue is deposited on the catalyst active sites.

The catalyst is put in a second reactor upgrade the pyrolysis vapours for the ex-situ operation. It is also known as stage pyrolysis since it consists of the a thermal step and catalytic step (Xue et al., 2017). The plastics are thermally pyrolysed, releasing pyrolysis vapours that are sent downstream to the catalytic bed. Moderate high temperatures are required in the pyrolysis unit to ensure the formation of the vapours to be upgraded.

Regeneration of catalyst is more superficial for ex-situ catalytic pyrolysis. The configuration is attractive for high ash content feedstock

Pyrolysis plastic derived oil (PDO) is very complex made up of different compounds groups. An effective fractionation of the PDO may be favourable method to produce different liquid fuels fractions compared to treating the whole oil (Westerhof et al., 2011). To collect different liquid fractions, hot volatiles can flow past an array of condensers maintained at different and gradually decreasing temperatures. PDO tends to have a higher density and viscosity as it passes through several condensers due to the diverse condensation times (Prurapark et al., 2020). The density and viscosity of oil increase as the collecting time increases since shorter molecular hydrocarbons condense earlier than longer chains. Prurapark et al. (2020) used a mobile type of pyrolysis equipment which consisted of the main condenser and four other condensers afterward. Water was used as the coolant in the condensers. Pyrolysis vapours flowed to the gas separator to enter the main condenser then proceed to the first, second, third, and fourth condensers. Oil was collected at the bottom of every condenser. Using this cooling and collecting system improved the density and viscosity of the oil obtained. Johansson et al. (2017) used fractional condensation to separate pyrolysis oil components into a useful fraction using biomass feedstock. The fractional condensation system consisted of three condensing cyclones with gradually decreasing coolant temperature. Cyclones were used to collect the first three fractions as collecting bottles were set at each condenser's bottom. The fourth fraction was collected using two coalescing filters. Pyrolysis vapours were further cooled in a cold trap using dry ice (carbon dioxide ice) and ethanol; this fraction was denoted as fraction 5. Figure 4.1 shows the fractional condensation system.

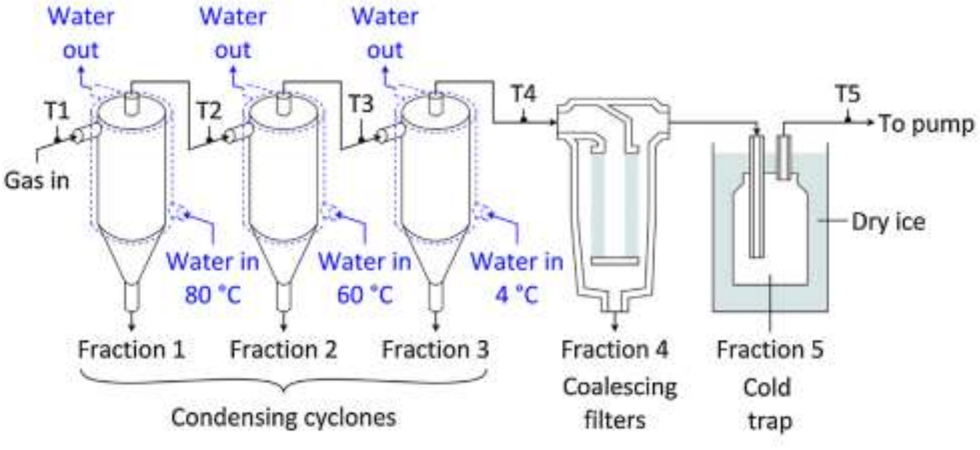

Figure 4 1 Fractional condensation system schematic set-up (Johansson et al., 2017)

In this investigation, an in-situ catalytic configuration was adopted using a semi-batch reactor. A shell and tube heat exchanger with water as the coolant and a series of condensers with gradually decreasing coolant temperature were adopted to enhance the quality of the PDO. Materials used and methods followed used to fulfil the objective are discussed in the following section.

4.2 Materials and methods

Sample acquisition, preparation and analysis are the same as in the previous chapter section 3.2.1 to 3.2.3. Briefly, a bulky sample of 20 kg waste plastics acquired from Bafana Waste Controllers, Newlands east of Durban, South Africa was sorted and characterised into different types of plastics. Polypropylene plastics samples were manually cut using a pair of scissors into small manageable pieces, which were shredded using a granulator to particle sizes of 10mm. Sample particles size ranging between 2-10 mm were isolated through sieving. Particles of ≤ 2 mm were used for TGA runs.

Silica alumina catalyst secured from Sigma Aldrich; South Africa was used for the study. The thermal behaviour of waste PP and the mixture of waste PP plastics and silica-alumina catalyst was analysed using the DTG-60A Simultaneous DTA-TG Apparatus model manufactured by SHIMADZU Japan. Proximate analysis was conducted on particles between 2-3.5 mm using ASTM-E1131 method to estimate the expected yield. The volatile matter is essential; it gives an estimate of the potential chemical recovery from pyrolysis (Sharma et al., 2014). The results for the proximate analysis and waste polypropylene composition are shown in Table 4.1.

Table 4 1 Proximate analysis and waste PP plastic composition

Proximate analysis (wt.%)	Moisture Content	Volatile matter	Fixed Carbon	Ash Content
	0.475	0.475	1.47	4.698
Waste PP plastic composition			Carbon	Hydrogen
			83.999	13.988

Experimental work was carried on based on mixture design in Table 4.1 as obtained from central composite design (CCD). The experimental design was blocked; the prescribed run order was followed for the experiments. Two factors, temperature, and catalyst were being varied; sample amount and holding time were constant. Oil yield was the response. The pyrolysis temperature range, catalyst range, coolant, and were carefully chosen based on the pyrolysis equipment capacity and preliminary experiment results. Table 4.2 shows the temperature and catalyst ranges. A numerical response optimiser of CCD was used to obtain the optimum operating condition that yields oil with the best quality, carbon distribution, and physio-chemical properties.

Table 4 2 Central composite design (CCD) factors

Factor	Units	Factor type	Lower level (-)	Centre point (0)	Upper level (+)	Lower axial (-α)	Upper axial (+α)
Temperature	C	Variable	400	450	500	379	520
Catalyst	wt.%	Variable	10	25	40	4	46
Sample amount	g	Constant	40	40	40	40	40
Holding time	min	Constant	30	30	30	30	30
Liquid yield	wt.%	Response					

4.2.1 Semi-batch pyrolysis reactor

Pyrolysis was conducted using a semi-batch reactor. The pyrolysis equipment comprises of a stainless steel reactor manufactured by Watford Herts tube (length 6.05 cm, internal diameter 4.00 cm, and outer diameter 4.60 cm) closed at one end and an outlet tube on the other end. A sample holder (length 42 cm, internal diameter 3.3 cm and outer diameter 2.6 cm) made from stainless steel is used to hold the sample. An electric (muffle) furnace externally heats the reactor, with a Cr-Al:K type thermocouple fixed inside the reactor measuring the temperature. An external PID controller controls the temperature. A digital control system was used to monitor the reactor temperature. The system included a monitoring screen that displayed the operating reactor temperature and the set temperature. Samples of 40-55 g of polypropylene were loaded for each experiment.

4.2.1.1 Experimental procedure

Initially the empty steel reactor and sample holder were weighed Samples of 40-55 g of plastic mixed with silica-alumina catalyst were placed in the sample holder, which in turn was placed in the reactor. N_2 was purged into the reactor as a carrier gas during the experiments. Experiments were performed under conditions shown in Table 4.2. Experiments were conducted at different temperatures ranging from 379-520 °C. For this study, a constant heating rate of 20 °C /min was employed. The amount of catalyst is reported as a fraction of the feed. Figure 4.2 shows the equipment's set-up.

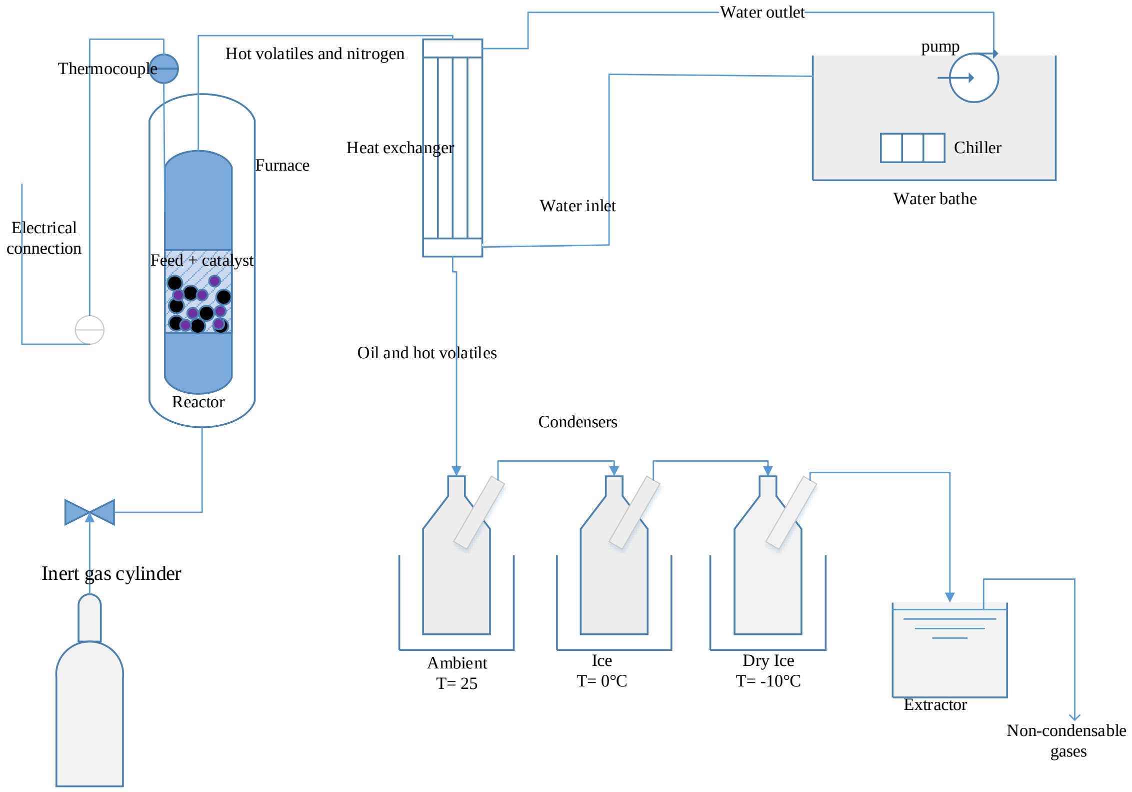

Figure 4 2 Pyrolysis equipment set-up

Condensation of the hot volatiles was accomplished using a shell and tube heat exchanger utilising cold water as the coolant from the water bathe followed by a condenser train. The water bath was maintained at 3-5 °C. The condensation train pieces were weighed before the experiment and secured together. It consists of three small condensers kept at a gradually decreasing temperature. The first condenser is kept at ambient temperature, the second was maintained at 0 °C using ice, while the third condenser was maintained at a temperature of -10 °C using dry ice (wet CO_2). Condensable fractions were collected in the condensers. On completion of the experiment, the set-up pieces were all weighed to determine the quantity of the pyrolysis products. The condensable products (oil) yield was calculated as in chapter three, section 3.2.4.1.

4.2.2 Plastic derived oil (PDO) analysis

Experiments were done in duplicate and a representative of the plastic derived oil (PDO) was characterised using chemical and physical stages. The Fourier Transform Infrared

(FTIR) and Gas Chromatography-Mass Spectrometry (GCMS) were used for chemical characterisation, while Athon Paar Density and viscosity meter was used for physical characterisation.

4.2.2.1 Fourier Transform Infrared (FTIR)

The chemical and physical characteristics of the liquid fraction obtained from the pyrolysis experiment were analysed using different methods. The Fourier Transform Infrared (FTIR) analyser measured the wavelengths in the infrared region that was absorbed by materials. This technique was used to obtain the infrared spectrum of absorption, emission, and photoconductivity of liquids, gas, and solid. It detects various functional groups present in different materials. The identification of compounds is mastered by applying infrared radiation to a sample of the material being tested. The sample's infrared light absorbance at different wavelengths is measured and used to determine the sample's molecular composition and structure. An interferometer is used to identify samples by producing an optical signal with all the IR frequencies encoded. The mathematical technique of Fourier transform is used to translate raw data into an actual spectrum, which is then searched against NIST reference libraries for identification. The infrared absorption frequency ranges from 400 to 4000 cm^{-1}.

An IRSpirit Fourier Transform Infrared Spectrophotometer QATR-S Single Reflection Accessory model SHIMADZU Japan was used for this study to analyse functional groups present in each pyrolytic oil obtained at different temperatures and catalyst to feed ratio. The KBr technique was implemented. A small amount (approximately a drop or two) of liquid oil sample was mounted on a potassium bromide (KBr) disc and covered to avoid the sample vapourisation. The KBr disc is first scanned as the background. A similarity search was completed from the NIST spectral library. Direct assessment of sample spectrum could be done.

4.2.2.2 Gas Chromatography-Mass Spectrometry (GCMS)

Gas Chromatography-Mass Spectrum is an analytical technique that uses a combination of two techniques to analyse chemical mixtures. This technique can be used for quantitative and qualitative evaluation of a solution containing numerous chemicals. The gas chromatography separates the mixture's components using the principle that a mixture will separate into individual substances when heated. An inert gas (helium) is used to carry the heated gases through the column. The mass spectroscopy characterises the components of the mixture individually by the mass of the components. The NIST library has a mass spectrum of thousand compounds stored in the computer and is used to match the resulting compounds.

The polypropylene pyrolysis condensable products were qualitatively and quantitatively analysed using the GCMS-QP2010 SE model with an AOC-201 auto injector and AOC-20S auto sampler SHIMADZU model manufactured in Japan. The GC oven temperature profile was set as below:

1. Started at 30 °C and hold time of 5 min
2. The temperature was increased to 35 °C at a heating rate of 0.7 °C/min and hold time of 1 min
3. The temperature was continuously increased to 45 °C at a heating rate of 2 °C/min
4. After that, the temperature was ramped to 80 °C at a heating rate of 5 °C/min and hold time of 2 min
5. The temperature was ramped again to 210 °C
6. Temperature ramping at a heating rate of 5 °C/min continued till 280 °C and hold time of 2 min

Oil samples were injected at a split ratio of 1:70 at an injection temperature of 150 °C using a 30 m x 0.25 mm ID x 0.25 µm film thickness Zebron ZB-1701 capillary column. Helium was used as a carrier gas at a constant linear velocity of 0.6 ml/min. The sample was injected at a volume of 0.5 ml with a split ratio of 70. The method employed for the chemical analysis of the oil using the GCMS is summarised in Table 4.3

Table 4 3 GCMS analysis method

Parameter	
Injection temperature °C	150
Column oven temperature °C	30
Injection mode	Split (70:1)
Injection volume	0.5 µL
Carrier gas flow	Helium at 0.6ml/min (linear flow)
Oven program	30 °C (5 min) to 35 °C (1 min) at a rate of 0.7 °C/min 45 °C at a rate of 2 °C/min, 80 °C (2 min),at a rate of 5 °C/min, 210 °C at a rate of 10 °C/min finally 280 °C (2 min) at a rate of 5 °C/min
Mass Spectrometer	
MS temperature (°C)	200 (ion source) 250 (interface)
Threshold	0
Solvent delay (cut-time) (min)	6
Duration (min)	6-56

4.2.2.3 Density and viscosity of plastic derived oil

Athon Paar Density and viscosity meter DSA 5000M model was used to measure the density and viscosity of the PDO. DSA 5000M measures density, viscosity, and sound velocity simultaneously. It allows measurements in the temperature range 0-100 °C. The sample is introduced into a U-shaped capillary tube using a syringe and automatically flows to measuring cells. For each run, a sample of 3.5 mL is required. DSA 5000M has two features to check that samples are filled correctly. FillingCheck^{TM} detects filling errors automatically and gives a warning when the sample contains bubbles or particles. The U-View ^{TM} camera displays live images of the filled U-tube. Figure 4.3 shows the density and viscosity meter DSA 5000M.

Figure 4 3 Athon Paar Density and viscosity meter DSA 5000M

4.3 Results and Discussion

4.3.1 Pyrolysis results

Table 4.4 shows the oil yield obtained from the experiments. It was noted that as the catalyst amount increase, the oil yield is increased significantly. Increasing the temperature at a constant catalyst amount has less effect than catalyst effect. The change is associated with a change in the devolatilisation reaction, thus impacting the quality of the oil. The optimum yield was obtained at 427 °C and 33.9% catalyst; this oil was used as a representative for analysing the oil quality.

Table 4 4 Central Composite Design (CCD)

	Factor 1	Factor 2	Response 1
Run	A: temperature	B:cat:feed	Oil yield
	°C	%	±2%
1	520.711	25	88.5
2	379.289	25	81.5
3	500	10	69.5
4	450	46	84.5
5	450	25	87.75
6	450	4	48.75
7	400	10	75
8	500	40	87.25
9	400	40	86

The functional group composition and the chemical composition of the oil are discussed in the subsequent section.

4.3.2 FTIR results for PDO

Figure 4.5 shows the spectrum from the FTIR analysis. The peak at 3740 cm^{-1}indicates the presence of O-H stretching vibrations typically of alcohol functional groups. The spectrum shows several peaks between 3000 cm^{-1} and 2800 cm^{-1}indicates the presence of $–CH_3$, $-CH_2$, and C-H functional groups, signifying aliphatic species such as alkenes and alkanes. The peak at 1645.43 cm^{-1} indicates the C=C absorbance present in the oil. The presence of the peak at 1457.57 cm^{-1} shows the C-H bending interactions indicating alkanes functional groups Peaks in the region of 1350-1500 cm^{-1} are due to the deformation vibrations of C-H bonds confirming the presence of aliphatic groups. A sharp peak at 1377.83 cm^{-1} attributed to O-H bending interactions signifying phenol functional groups. The peaks at 967.90 and 888.19 cm^{-1} represent C=C bending vibrations illustrating alkenes functional groups.

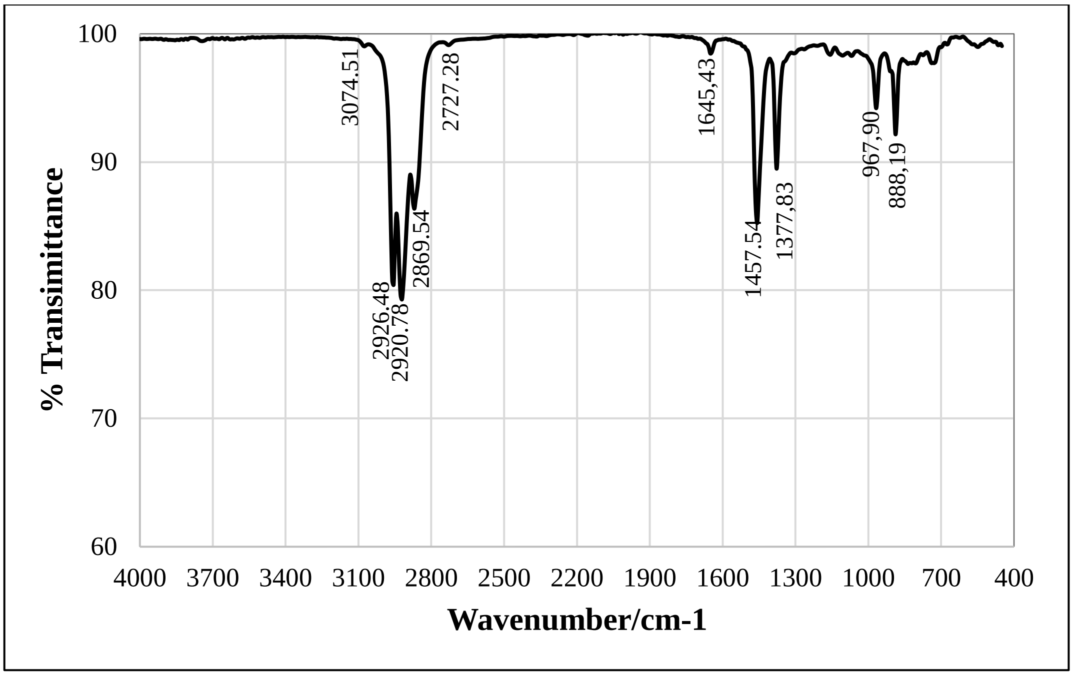

Figure 4 4 Oil FTIR spectrum

Table 4.5 indicates the wavenumber, types of vibrations, and nature of functional groups present in the oil.

Table 4 5 FTIR functional group composition of pyrolysis oil

Wavenumber (cm^{-1})	Type of vibration	Nature of functional group
3740	O-H stretching	Alcohol
2926	C-H stretching	Alkane
2920	C-H stretching	Alkane
2869	C-H stretching	Alkane
2727	C-H stretching	Aldehyde
1645	C=C stretching	Alkene
1457	C-H bending	Alkane
1377	O-H bending	Phenol
967	C=C bending	Alkene
888	C=C bending	Alkene

4.3.3 GCMS results for PDO

Figure 4.6 illustrates the resultant chromatogram of the sample. The chromatogram shows that it is a complex mixture of various compounds. Peaks on the chromatogram were not uniformly distributed throughout the chromatogram. Most of the peaks were congested during the first five minutes. Congestion of the peaks may be concluded as the presence of short carbon chains with close boiling points. The oil consists of alkenes and alkanes due to the branched structure of PP

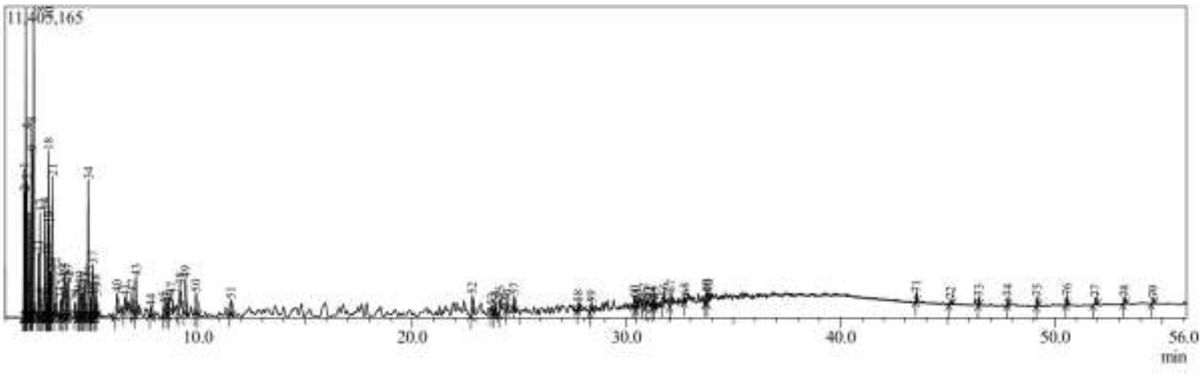

Figure 4 5 PDO chromatogram

Most of the hydrocarbons were mainly paraffinic and olefin in nature. The identified compounds were typically unsaturated hydrocarbons such as 3-methyl-3-hexene, 1-Butene,2,3-dimethyl-, cyclopropane,1,2-dimethyl, trans-, 2-pentene,3-methyl- etc. The chromatogram spectrum consisted of eighty-eight peaks. Cyclopropane,1,2-dimethyl-, trans was the dominating compound in the PDO. Table 4.6 shows the ten major compounds in the sample oil.

Table 4 6 Major oil compounds

Peak number	R Time	Area%	Similarity	Name
3	1.971	5.14	98	1-Propene,2- methyl-
4	1.999	2.78	97	E-Butene-(E)-
5	2.031	2.35	99	E-Butene-(Z)-
8	2.239	3.36	97	2-methy-1-butene
10	2.345	8.41	97	Cyclopropane,1,2-dimethyl-,trans
14	2.849	2.36	96	1-Pentene,2-methyl-
15	3.000	2.90	92	2-Hexene- (E)
16	3.033	3.58	94	1-Butene,2,3-dimethyl
19	3.214	3.52	97	2-Pentene,3-methyl-
31	4.894	4.77	96	3-Methy-3-Hexene

Literature survey reported that catalytic pyrolysis of PP narrows the carbon distribution, thus increasing the gasoline fraction. A liquid fraction can be covered by gasoline range (C_4-C_{12}), diesel (C_{12}-C_{23}), kerosene (C_{10}-C_{18}), motor oil (C_{23}-C_{40}), and BTX. Hydrocarbon compounds present in the PDO are primarily in the gasoline range. The compounds from the chromatogram were reported as a fraction of the total hydrocarbons according to the carbon numbers. Table 4.7 shows the carbon number distribution of the compounds obtained during thermal and catalytic pyrolysis.

Table 4 7 Carbon number distribution and petrochemical ranges

	Thermal pyrolysis	**Catalytic pyrolysis**
Carbon number	**Percentage (%)**	**Percentage (%)**
C_3-C_6	2.05	22.72
C_7-C_9	6.16	42.04
C_{10}-C_{12}	20.48	23.86
C_{13}-C_{15}	30.44	9.06
C_{16}-C_{18}	12.32	1.14
C_{20+}	21.55	1.13
Petrochemical ranges		
Gasoline	28.69	88.64
Diesel	66.24	35.22
Kerosene	63.24	30.00

Table 4.7 illustrates that the catalyst increased the oil compounds to gasoline fraction. The heavy oils that were produced during thermal pyrolysis were reduced to lighter oils. PDO obtained through thermal pyrolysis is composed of hydrocarbons in the diesel and kerosene range while catalytic PDO consists mainly of gasoline range hydrocarbons. It can be concluded that short carbon chains are produced during catalytic pyrolysis thus improving the oil quality by narrowing the hydrocarbon distribution range Figure 4.7 illustrates the distribution of hydrocarbon compounds in oils obtained under different conditions studied in this investigation.

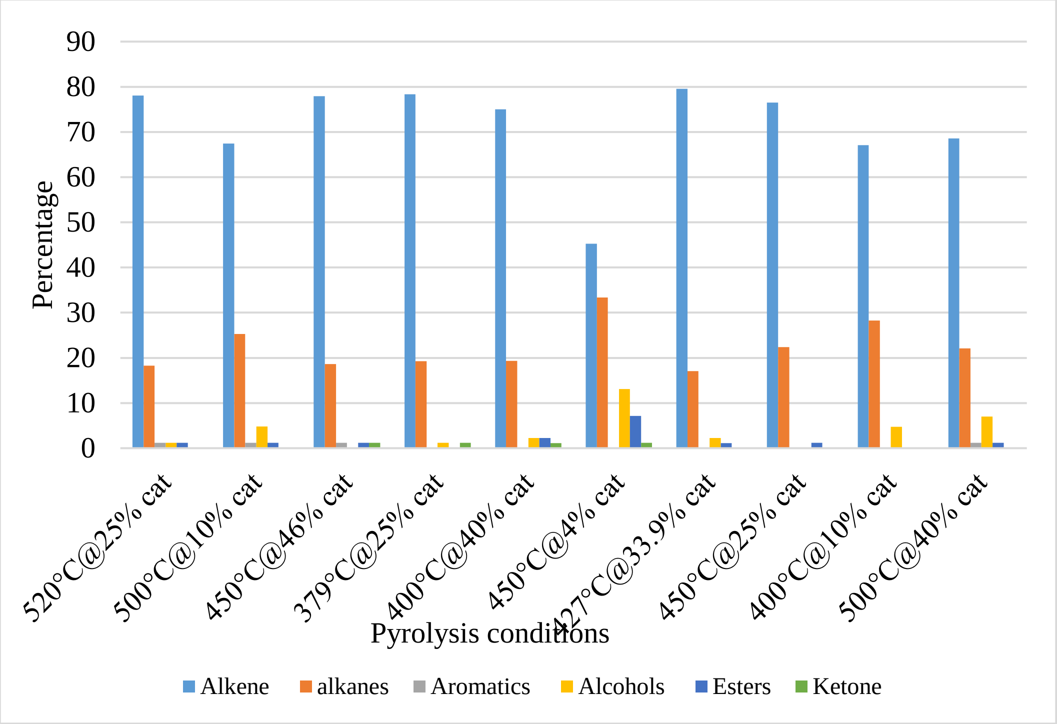

Figure 4 6 Hydrocarbon compounds

Alkenes make up the significant part of the oil, followed by alkanes. Alcohols and aromatic compounds were present in some oils but not in all samples collected. Minimal amounts of esters and ketones were noted in oils

4.3.3.1 The effect of catalyst on the oil compounds

Figure 4.8 shows the effect of catalysts on the oil compounds. It can be noted that a rise in catalyst amount causes an increase in the number of alkenes, decreasing the number of alkanes. The catalyst effect was investigated at a constant temperature of 450 °C. As the catalyst increased from 4 to 25 wt.% a significant increase in alkenes from 45 to 76 wt.% was observed. Alkene amount increased slightly when catalyst amount increased to 46 wt.%.

Consequently, the number of alkanes decreased from 33 to 22 and 18 wt.%, respectively. The number of alcohols and esters decreased with an increase in catalyst amount. This observation maybe because of more catalyst active sites present leading to the formation of simpler molecules.

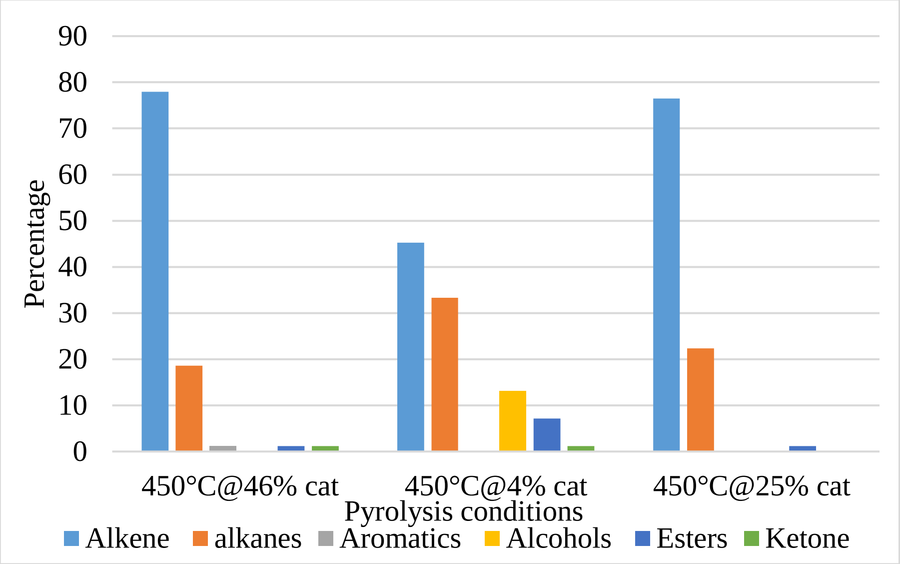

Figure 4 7 Effect of catalyst on oil compounds

4.3.3.2 The effect of temperature on PDO compounds

Figure 4.9 shows the effect of temperature on PDO compounds from catalytic pyrolysis. It was noted that an increase in temperature does not affect the PDO compounds. At a constant catalyst amount of 25%, the temperature increase is insignificant to the oil compounds.

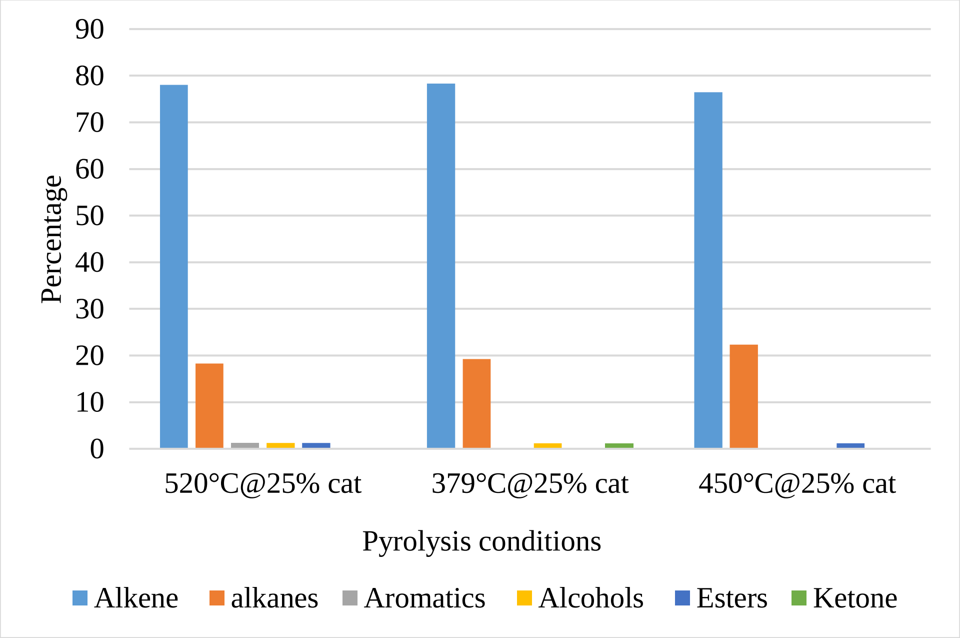

Figure 4 8 Effect of temperature on oil compounds

4.3.4 Physio-chemical properties of the oil

Physio-chemical properties of the oil were determined using the density and viscosity meter. These properties were described to define polypropylene PDO’s suitability for use as a fuel.

Table 4.8 shows the physical properties of PDO illustrating that the oil exhibit properties similar and comparable to petrol fuels. The oil properties were compared to gasoline and diesel. The oil obtained was of low viscosity, yellowish in colour with a choking smell. Sonawane et al. (2015) observed similar oil colour using 10% NZ catalyst in the pyrolysis of PP. The liquid product from thermal cracking is highly viscous, dark brown, and contains wax, while catalytic pyrolysis oil is highly volatile and light yellow in colour (Hakeem et al., 2018). Similar observations were made in this study. Bubbles were observed when the oil was poured.

Table 4 8 Physical properties of the oil

Physical property	**Catalysed PP oil**	**Gasoline**	**Diesel oil**
Colour	Light yellow		
Odour	Choking smell		
Density @25°C (g/cm^3)	0.763	0.72-0.78	0.82-0.90
Kinematic viscosity @40°C (cSt)	1.02	1.0-2.1	2.0-4.5

The oil density influences the injection and ignition quality of a fuel. The densities of the oil were investigated at a range of temperatures from 15 to 40 °C. It was observed that the density of the oil decreased linearly with an increase in temperature. Figure 4.8 illustrates the change in viscosity of the PDO at different temperatures. At 25 °C, the density of the oil was 0.763 g/cm^{3,} which is comparable to the density range reported for gasoline of 0.72-0.78 g/cm^3. Panda and Singh (2011) noted a density of 0.7702 gm/cc at 15 °C after pyrolysing polypropylene with silica-alumina catalyst at 500 °C with plastic to catalyst ratio of 3:1. A similar result was observed in this study. The density of oil obtained from thermal pyrolysis is higher than that of oil obtained using a catalyst. Hakeem et al. (2018) noted a density of 1.060 g/ml after thermally pyrolysing PP. The difference in the densities indicates that catalytic pyrolysis narrows the compound distribution and produces lighter hydrocarbon compounds.

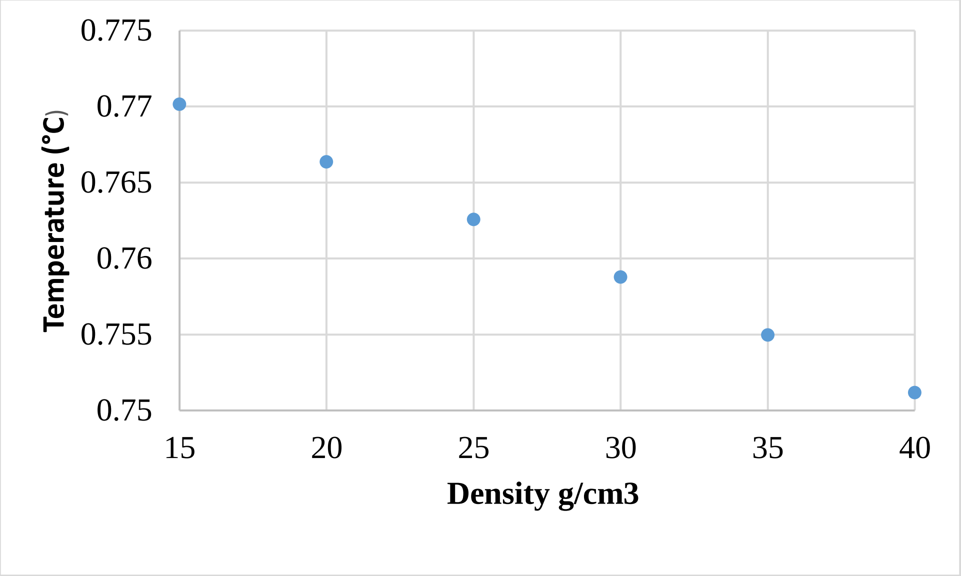

Figure 4 9 Density of polypropylene PDO

Viscosity is a vital property for fuel oil. It indicates how well the fuel can flow in the engine. High viscous oil is not suitable for automobile engines as it can result in mechanical inefficiency; low viscous oils drain away faster thus are not recommended. The viscosity of the polypropylene PDO was investigated at different temperatures as shown in Figure 4.9. Figure 4.9 shows that the oil viscosity decreases as temperature increases. The oil had a viscosity of 1.02 cSt at 40 °C, comparable to the viscosity range of gasoline at the same temperature.

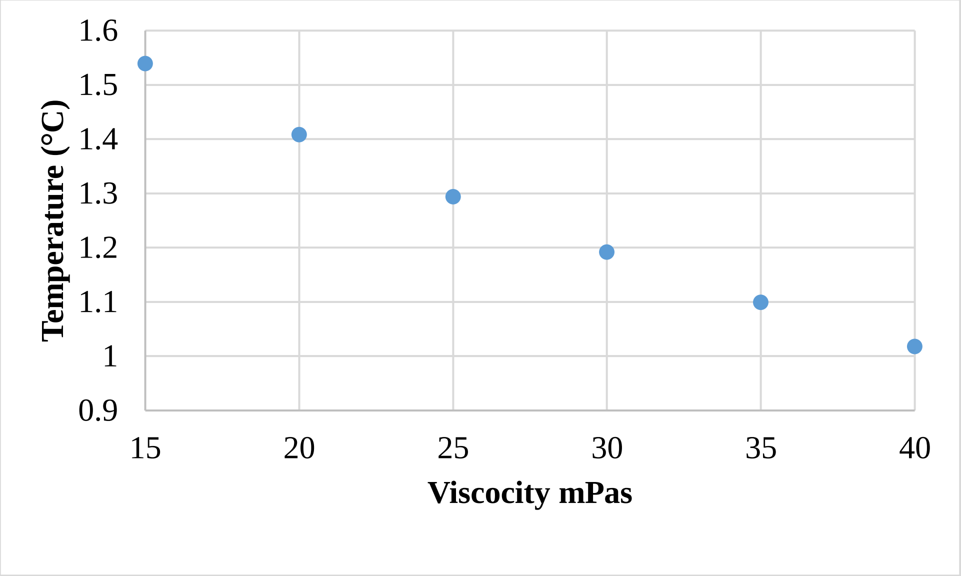

Figure 4 10 Polypropylene PDO viscosity

4.4 Conclusion

From the investigation, it can be concluded that the quality of waste plastic oil is affected by the presence of a catalyst. Silica-alumina catalyst narrows the hydrocarbon range promoting the production of light oil. The cooling and collecting system employed during the pyrolysis process positively affected the quality of the oil. Collecting pyrolysis oil in different fractions helped separate the hydrocarbons; thus, the oil can be more useful since it would be compounded in the same petrochemical range. Limited or no purification might be required after pyrolysis. The viscosity and density of the sample oil fall within the gasoline range. Catalytic pyrolysis of polypropylene produces oil in the gasoline range hydrocarbons. The oil contains a few compounds in the diesel range and a more significant percentage of paraffinic compounds due to the molecular skeleton of PP.

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CHAPTER 5: MAIN RESEARCH FINDINGS

5 .1 Conclusions and Future work

The polypropylene plastic obtained from the plastic waste stream had less than 1% moisture content and very high volatile matter of 93 wt.%. No heteroatoms such as sulphur were present in the sample plastic used during the investigation. The thermal decomposition temperatures of PP with a catalyst is lower than without a catalyst. Use of a catalyst lowers the energy consumption by reducing the decomposition temperatures.

It was observed from the results that the catalyst increased the oil yield lowering the char and gases yields. Preliminary results experiments revealed that increasing the amount of catalyst has a significant impact on the liquid yield until the catalyst saturation point. After this point, increasing the catalyst amount will not cause a substantial increase in oil yield. At a constant temperature increasing the catalyst amount causes a decrease in oil yield. Increasing the temperature at constant catalyst amount does not increase the yield when using a semi batch reactor. This is because decomposition would have completed therefore no or limited reactions occurs in the reaction zone since the product are collected as they are being produced.

Low temperature and catalyst amount results in incomplete thermal degradation as observed from the char elemental analysis showing a higher percentage of carbon and hydrogen present in char obtained under these conditions. An optimum oil yield of 89.95 wt.% was obtained at 427 °C and 33.9 wt.% catalyst. An increase in the liquid oil yield lowers the yield of char and gas. The condensing and collecting system employed during the pyrolysis process has an impact on the yield of the oil. Wax or oil can be obtained from the pyrolysis of PP depending on the cooling system used to cool the pyrolysis vapours as observed from the preliminary experiments results.

Temperature and catalyst have a quadratic relation with the oil yield. The predicted model is significant for the process as observed from the ANOVA. A higher signal to noise ratio signified the at the oil yield was affected more by temperature and catalyst amount other than other factors.

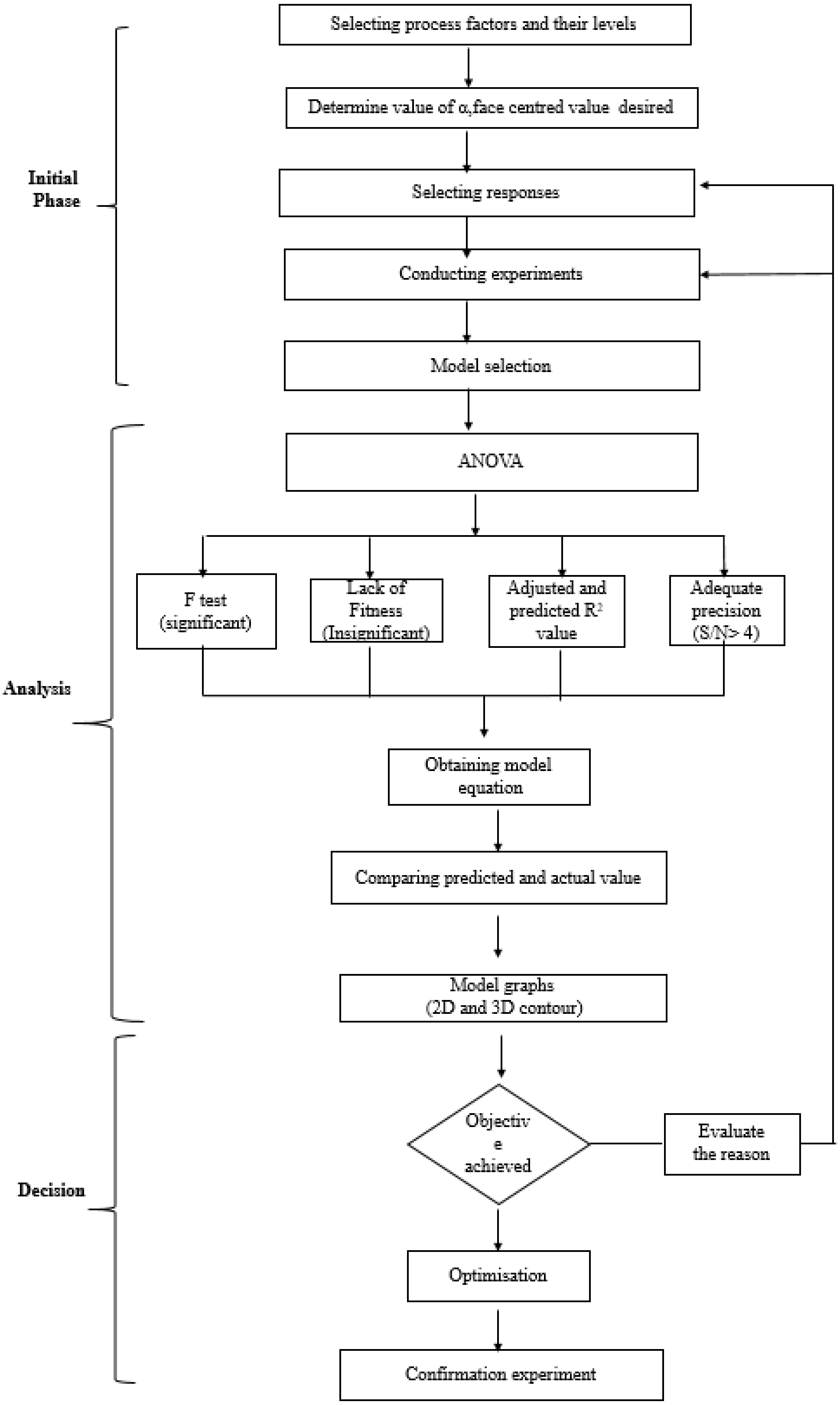
The oil obtained through the catalytic pyrolysis of PP using silica-alumina catalyst comprised mainly of alkenes and alkanes with little aromatics. The use of silica –alumina catalyst narrowed the carbon distribution range on the oil. Collecting the oil as different fractions aids in separating the hydrocarbons into different petrochemical ranges. It reduces the cost of purifying the oil making it more useful. Gasoline range compounds were dominant in the oil followed by diesel range and the kerosene range of compounds.

Oil from the catalytic pyrolysis of PP contains hydrocarbons in the range C_3-C_{18}. Cyclopropane,1,2-dimethyl-, trans, 1-Propene,2- methyl- and 3-Methy-3-Hexene are the dominant hydrocarbons in the oil. The oil has a low viscosity and density similar to gasoline range hydrocarbons. No heteroatoms were present in the oil. The oil contains fewer compounds in the diesel range and a more significant percentage of paraffinic compounds due to the molecular skeleton of PP.

Polypropylene plastics produce paraffinic compounds under catalytic pyrolysis. The quality of oil obtained is affected by the condensing and collecting system employed during the process. I recommend that more work be done on how the condensing and collecting system affect the quality of oil obtained from plastic pyrolysis.

APPENDICES

A: Central Composite Design flow diagram



B. Proximate analysis

- High volatile matter (Moisture content)

The highly volatile matter content may be determined by the following equation:

$$V = \frac{W - R}{W} \; X\, 100 \qquad (2)$$

Where:

V = highly volatile matter content, as received basis (%)

W = original specimen mass (mg) and

R = mass measured at Temperature X (mg)

W = 20.69544 mg, R = 20.59705 mg and V = 0.4754%, T_x = 110 °C

- Medium volatile matter

The medium volatile content can be determined using the following equation

$$O = \frac{R - S}{W} X100 \qquad (3)$$

Where:

O = medium volatile matter content, as received basis, %

R = mass measures at Temperature X, (mg)

S = mass measured at Temperature Y, (mg)

W = original specimen mass, (mg)

R = 20.59705 mg, S = 1.2761 mg, W = 20.69544 mg, O = 93.358%, T_y = 670 °C

- Combustible material content

The combustible material can be determined using the following equation:

$$C = \frac{S - T}{W} X100 \qquad (\,4)$$

Where:

C = combustible material content, as-received basis, (%),

S = mass measured at Temperature Y, (mg),

T = mass measured at Temperature Z, (mg) and

W = original specimen mass, (mg).

S = 1.2761 mg, T = 0.97057 (mg), W = 20.69544 mg and C = 1.467% T_z = 800 °C

- Ash content

$$A = \frac{T}{W} X100 \qquad (4)$$

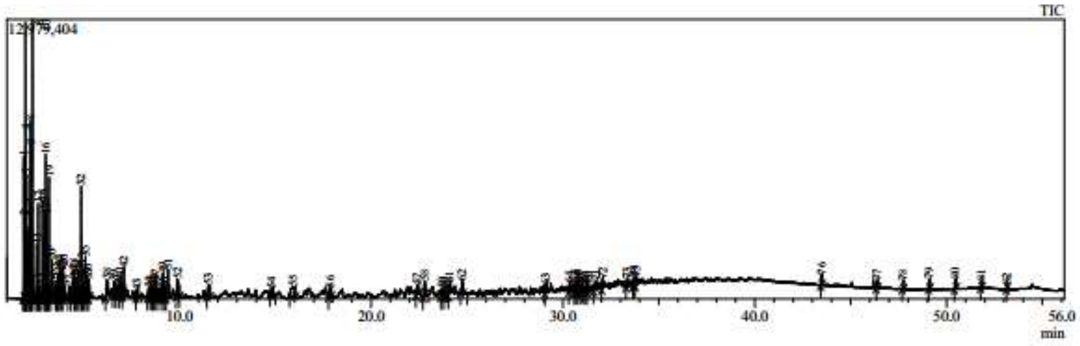
Where:

A = ash content, as-received basis, (%),

T = mass measured at Temperature Z, (mg)

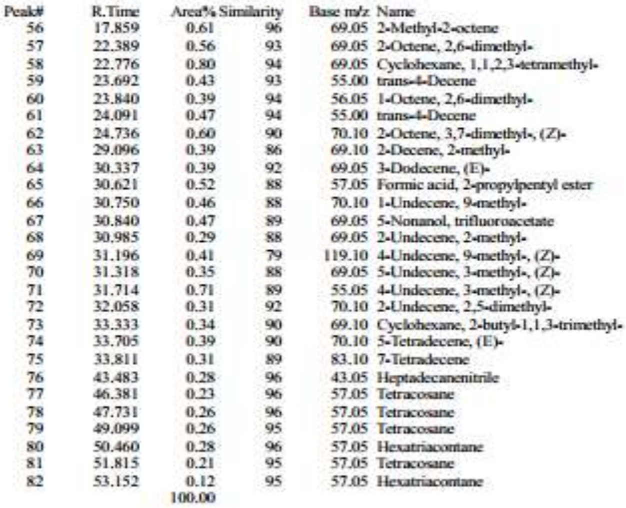
W = original specimen mass, (mg).

, T = 0.97057 (mg), W = 20.69544 mg and A = 4.6897%

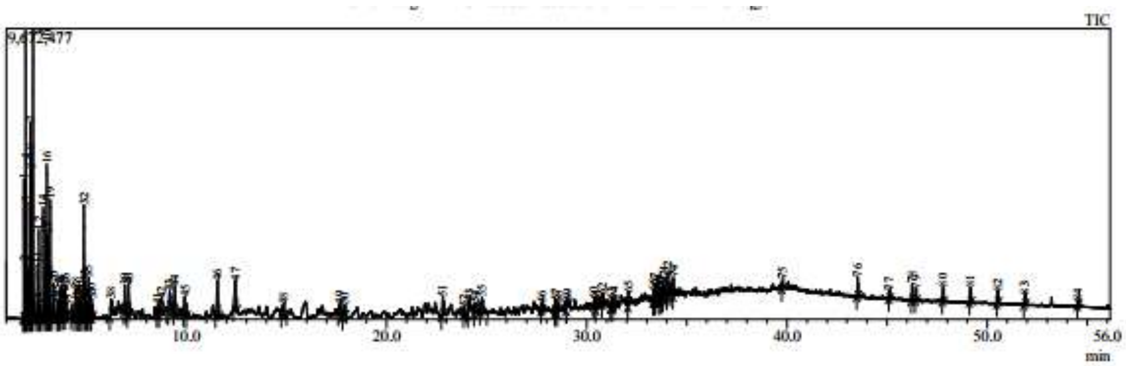


Peak Report TIC

Peak#	R.Time	Area%	Similarity	Base m/z	Name
1	1.878	2.37	97	41.05	Propene
2	1.922	1.28	98	43.05	Isobutane
3	1.966	5.49	98	41.05	1-Propene, 2-methyl-
4	1.995	2.69	99	41.05	2-Butene, (E)-
5	2.027	2.10	98	41.05	2-Butene, (Z)-
6	2.116	1.72	96	43.05	Butane, 2-methyl-
7	2.203	1.61	91	42.05	Butane, 2,3-dimethyl-
8	2.233	3.41	96	55.05	2-Methyl-1-butene
9	2.272	3.03	97	55.00	2-Pentene
10	2.339	8.06	97	55.05	Cyclopropane, 1,2-dimethyl-, trans-
11	2.554	1.46	90	43.05	1-Pentene, 4-methyl-
12	2.631	2.31	98	69.05	1-Butene, 2,3-dimethyl-
13	2.685	0.29	97	57.05	Pentane, 3-methyl-
14	2.841	2.41	96	56.05	1-Pentene, 2-methyl-
15	2.992	3.28	87	55.05	1H-Tetrazole, 1-methyl-
16	3.025	3.54	94	69.05	1-Butene, 2,3-dimethyl-
17	3.075	2.04	98	41.05	2-Pentene, 3-methyl-
18	3.133	1.07	96	55.00	2-Hexene, (Z)-
19	3.204	3.38	97	41.05	2-Pentene, 3-methyl-
20	3.353	1.13	98	41.05	2-Butene, 2,3-dimethyl-
21	3.576	0.40	96	56.05	1-Pentene, 2,4-dimethyl-
22	3.620	0.30	87	69.05	1-Pentene, 3,3-dimethyl-
23	3.659	0.77	95	83.10	2-Pentene, 4,4-dimethyl-, (E)-
24	3.758	1.69	88	41.05	3-Hexene, 2-methyl-, (E)-
25	3.877	1.15	95	69.05	4-Methyl-2-hexene,c&t
26	3.950	1.27	90	43.05	5-Methyl-2-hexene,c&t
27	4.256	0.52	93	56.05	5-Methyl-2-hexene,c&t
28	4.480	1.50	96	56.05	1-Hexene, 2-methyl-
29	4.556	0.82	88	70.05	2,3-Dimethyl-1-hexene
30	4.641	0.74	94	69.05	4-Methyl-2-hexene,c&t
31	4.704	1.01	96	41.05	3-Heptene
32	4.877	4.88	96	69.10	3-Methyl-3-hexene
33	4.940	1.03	93	56.05	(Z)-2-Heptene
34	5.001	0.58	96	69.05	3-Methyl-3-hexene
35	5.099	1.57	96	69.05	2-Hexene, 3-methyl-, (Z)-
36	5.215	0.94	93	83.10	2-Pentene, 2,4-dimethyl-
37	5.260	0.52	88	56.05	2-Heptene
38	6.219	0.80	95	83.10	2-Hexene, 2,3-dimethyl-
39	6.591	0.86	94	55.00	3-Hexene, 2,3-dimethyl-
40	6.764	0.67	92	69.05	2-Heptene, 4-methyl-, (E)-
41	6.907	0.99	88	43.05	1-Octene
42	7.100	1.35	92	69.05	2-Methyl-2-heptene
43	7.784	0.40	94	56.05	2-Heptene, 5-methyl-
44	8.399	0.60	94	55.05	3-Hexene, 2,3-dimethyl-
45	8.548	0.63	95	56.05	1-Heptene, 2-methyl-
46	8.675	0.79	88	55.00	3-Ethyl-3-hexene
47	8.750	0.93	93	69.10	3-Heptene, 4-methyl-
48	8.998	1.08	88	55.05	2-Hexene, 2,3-dimethyl-
49	9.146	1.66	94	55.05	2-Hexene, 2,3-dimethyl-
50	9.250	0.49	88	70.10	Heptane, 3-methylene-
51	9.409	1.84	94	69.05	2-Methyl-2-heptene
52	9.895	1.16	91	70.10	2-Heptene, 3-methyl-
53	11.514	0.81	91	83.10	2,3-Dimethyl-2-heptene
54	14.803	0.48	89	69.05	1-Hexene, 3,3,5-trimethyl-
55	15.916	1.27	92	55.05	5-Undecene, 4-methyl-

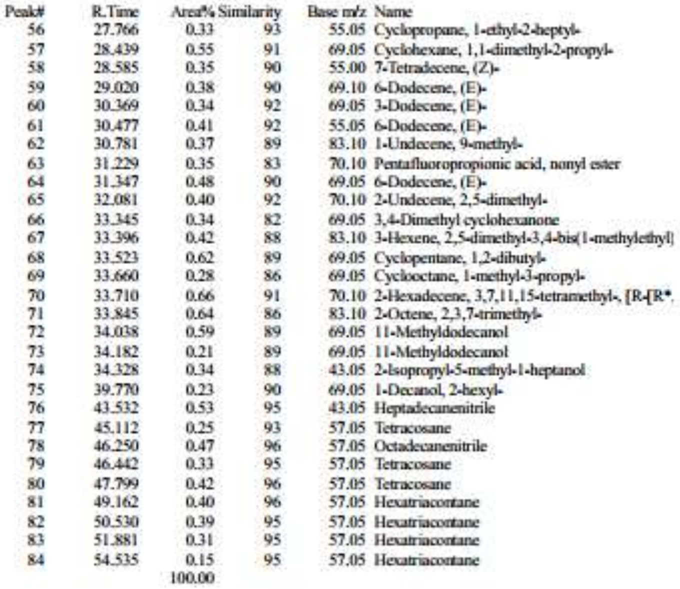


Peak#	R.Time	Area%	Similarity	Base m/z	Name
56	17.859	0.61	96	69.05	2-Methyl-2-octene
57	22.389	0.56	93	69.05	2-Octene, 2,6-dimethyl-
58	22.776	0.80	94	69.05	Cyclohexane, 1,1,2,3-tetramethyl-
59	23.692	0.43	93	55.00	trans-4-Decene
60	23.840	0.39	94	56.05	1-Octene, 2,6-dimethyl-
61	24.091	0.47	94	55.00	trans-4-Decene
62	24.736	0.60	90	70.10	2-Octene, 3,7-dimethyl-, (Z)-
63	29.096	0.39	86	69.10	2-Decene, 2-methyl-
64	30.337	0.39	92	69.05	3-Dodecene, (E)-
65	30.621	0.52	88	57.05	Formic acid, 2-propylpentyl ester
66	30.750	0.46	88	70.10	1-Undecene, 9-methyl-
67	30.840	0.47	89	69.05	5-Nonanol, trifluoroacetate
68	30.985	0.29	88	69.05	2-Undecene, 2-methyl-
69	31.196	0.41	79	119.10	4-Undecene, 9-methyl-, (Z)-
70	31.318	0.35	88	69.05	5-Undecene, 3-methyl-, (Z)-
71	31.714	0.71	89	55.05	4-Undecene, 3-methyl-, (Z)-
72	32.058	0.31	92	70.10	2-Undecene, 2,5-dimethyl-
73	33.333	0.34	90	69.10	Cyclohexane, 2-butyl-1,1,3-trimethyl-
74	33.705	0.39	90	70.10	5-Tetradecene, (E)-
75	33.811	0.31	89	83.10	7-Tetradecene
76	43.483	0.28	96	43.05	Heptadecanenitrile
77	46.381	0.23	96	57.05	Tetracosane
78	47.731	0.26	96	57.05	Tetracosane
79	49.099	0.26	95	57.05	Tetracosane
80	50.460	0.28	96	57.05	Hexatriacontane
81	51.815	0.21	95	57.05	Tetracosane
82	53.152	0.12	95	57.05	Hexatriacontane
		100.00			



Peak Report TIC

Peak#	R.Time	Area%	Similarity	Base m/z	Name
1	1.881	2.33	97	41.05	Propene
2	1.925	0.84	97	43.05	Isobutane
3	1.970	5.30	98	41.10	1-Propene, 2-methyl-
4	2.000	2.13	99	41.05	2-Butene
5	2.030	2.12	98	41.05	2-Butene, (Z)-
6	2.119	1.29	96	43.05	Butane, 2-methyl-
7	2.206	3.22	97	43.05	Pentane
8	2.236	3.22	94	55.05	2-Methyl-1-butene
9	2.276	2.78	97	55.05	2-Pentene, (E)-
10	2.344	7.75	97	55.05	Cyclopropane, 1,2-dimethyl-, trans-
11	2.560	1.42	90	43.05	1-Pentene, 4-methyl-
12	2.636	2.12	98	41.05	1-Butene, 2,3-dimethyl-
13	2.690	0.27	96	57.05	Pentane, 3-methyl-
14	2.846	2.66	96	56.05	1-Pentene, 2-methyl-
15	2.995	2.93	86	55.05	1H-Tetrazole, 1-methyl-
16	3.030	3.59	95	69.10	1-Butene, 2,3-dimethyl-
17	3.081	2.00	98	41.05	2-Pentene, 3-methyl-
18	3.139	1.07	95	55.05	3-Hexene, (Z)-
19	3.210	3.20	98	41.05	2-Pentene, 3-methyl-
20	3.360	0.96	98	41.05	2-Butene, 2,3-dimethyl-
21	3.584	0.44	95	56.05	1-Pentene, 2,4-dimethyl-
22	3.625	0.25	88	69.10	3,3'-Bifuran, 2,2',3,3'-tetrahydro-
23	3.667	0.86	95	83.10	2-Pentene, 4,4-dimethyl-, (E)-
24	3.766	1.51	89	41.05	3-Hexene, 2-methyl-, (E)-
25	3.884	1.04	94	69.10	4-Methyl-2-hexene,c&t
26	3.959	1.08	91	43.05	5-Methyl-2-hexene,c&t
27	4.266	0.41	94	56.05	2-Hexene, 5-methyl-, (E)-
28	4.490	1.48	96	56.05	1-Hexene, 2-methyl-
29	4.564	0.82	88	70.10	2,3-Dimethyl-1-hexene
30	4.650	0.67	94	69.10	3-Methyl-3-hexene
31	4.714	0.94	96	41.05	3-Heptene, (E)-
32	4.885	4.69	96	69.10	3-Methyl-3-hexene
33	4.950	1.10	93	56.05	2-Heptene
34	5.012	0.54	95	69.10	3-Methyl-3-hexene
35	5.109	1.48	96	41.05	2-Hexene, 3-methyl-, (Z)-
36	5.227	0.89	93	83.10	2-Pentene, 2,4-dimethyl-
37	5.275	0.54	87	56.05	2-Heptene
38	6.235	0.75	95	83.10	2-Hexene, 2,3-dimethyl-
39	6.933	1.39	90	43.05	Heptane, 4-methyl-
40	7.116	1.37	92	69.10	2-Methyl-2-heptene
41	8.568	0.40	95	56.05	1-Heptene, 2-methyl-
42	8.768	1.43	94	55.05	3-Heptene, 4-methyl-
43	9.165	0.90	93	55.05	2-Hexene, 2,3-dimethyl-
44	9.428	1.47	94	69.10	2-Methyl-2-heptene
45	9.924	1.17	90	70.10	2-Heptene, 3-methyl-
46	11.557	2.24	90	83.10	Cyclohexane, propyl-
47	12.446	1.90	97	43.05	2,4-Dimethyl-1-heptene
48	14.843	0.73	89	69.05	1-Hexene, 3,3,5-trimethyl-
49	17.661	0.66	90	55.05	2,3-Dimethyl-3-heptene, (Z)-
50	17.893	0.66	96	69.05	2-Methyl-2-octene
51	22.812	0.93	94	69.05	2-Octene, 2,6-dimethyl-
52	23.878	0.34	95	56.05	1-Octene, 2,6-dimethyl-
53	24.125	0.53	94	55.05	trans-4-Decene
54	24.425	0.66	95	69.05	2-Nonene, 2-methyl-
55	24.773	1.00	91	70.05	2-Octene, 3,7-dimethyl-, (Z)-



Peak#	R.Time	Area%	Similarity	Base m/z	Name
56	27.766	0.33	93	55.05	Cyclopropane, 1-ethyl-2-heptyl-
57	28.439	0.55	91	69.05	Cyclohexane, 1,1-dimethyl-2-propyl-
58	28.585	0.35	90	55.00	7-Tetradecene, (Z)-
59	29.020	0.38	90	69.10	6-Dodecene, (E)-
60	30.369	0.34	92	69.05	3-Dodecene, (E)-
61	30.477	0.41	92	55.05	6-Dodecene, (E)-
62	30.781	0.37	89	83.10	1-Undecene, 9-methyl-
63	31.229	0.35	83	70.10	Pentafluoropropionic acid, nonyl ester
64	31.347	0.48	90	69.05	6-Dodecene, (E)-
65	32.081	0.40	92	70.10	2-Undecene, 2,5-dimethyl-
66	33.345	0.34	82	69.05	3,4-Dimethyl cyclohexanone
67	33.396	0.42	88	83.10	3-Hexene, 2,5-dimethyl-3,4-bis(1-methylethyl)
68	33.523	0.62	89	69.05	Cyclopentane, 1,2-dibutyl-
69	33.660	0.28	86	69.05	Cyclooctane, 1-methyl-3-propyl-
70	33.710	0.66	91	70.10	2-Hexadecene, 3,7,11,15-tetramethyl-, [R-[R*,
71	33.845	0.64	86	83.10	2-Octene, 2,3,7-trimethyl-
72	34.038	0.59	89	69.05	11-Methyldodecanol
73	34.182	0.21	89	69.05	11-Methyldodecanol
74	34.328	0.34	88	43.05	2-Isopropyl-5-methyl-1-heptanol
75	39.770	0.23	90	69.05	1-Decanol, 2-hexyl-
76	43.532	0.53	95	43.05	Heptadecanenitrile
77	45.112	0.25	93	57.05	Tetracosane
78	46.250	0.47	96	57.05	Octadecanenitrile
79	46.442	0.33	95	57.05	Tetracosane
80	47.799	0.42	96	57.05	Tetracosane
81	49.162	0.40	96	57.05	Hexatriacontane
82	50.530	0.39	95	57.05	Hexatriacontane
83	51.881	0.31	95	57.05	Hexatriacontane
84	54.535	0.15	95	57.05	Hexatriacontane
		100.00			

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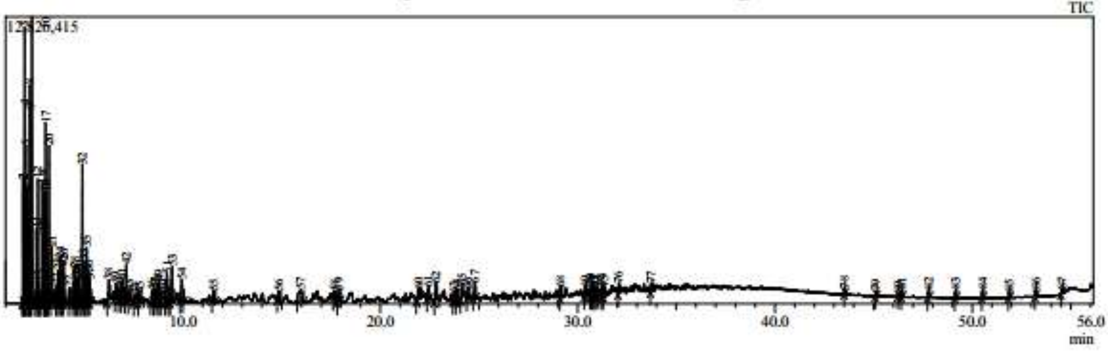
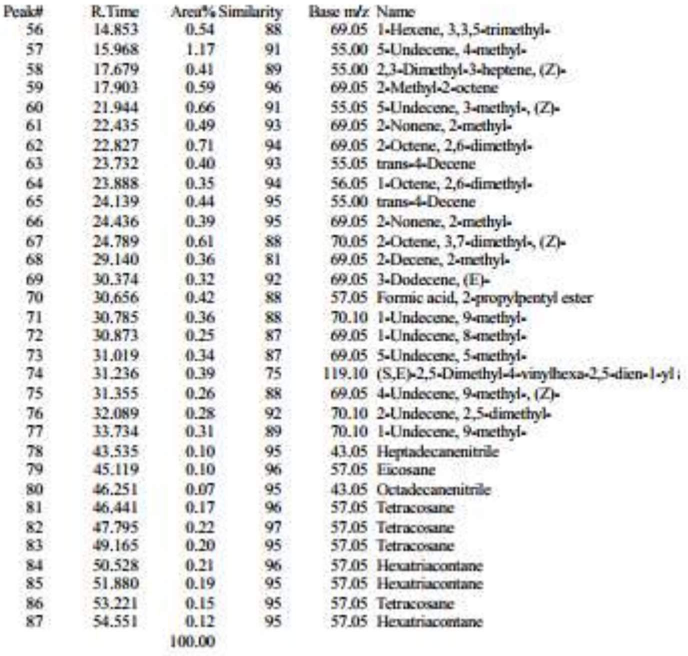


Peak Report TIC

Peak#	R.Time	Area%	Similarity	Base m/z	Name
1	1.881	1.62	97	41.05	Propene
2	1.924	1.52	98	43.05	Isobutane
3	1.968	4.55	98	41.10	1-Propene, 2-methyl-
4	1.997	2.71	97	41.05	2-Butene, (E)-
5	2.030	2.28	99	41.05	2-Butene, (Z)-
6	2.119	2.19	96	43.05	Butane, 2-methyl-
7	2.206	1.11	92	42.05	Cyclopentane
8	2.236	3.68	96	55.05	2-Methyl-1-butene
9	2.276	3.08	97	55.05	2-Pentene
10	2.343	7.75	97	55.05	Cyclopropane, 1,2-dimethyl-, trans-
11	2.560	1.66	90	43.05	1-Pentene, 4-methyl-
12	2.636	2.48	98	69.10	1-Butene, 2,3-dimethyl-
13	2.691	0.39	96	57.05	Pentane, 3-methyl-
14	2.847	2.47	96	56.05	1-Pentene, 2-methyl-
15	2.965	1.20	95	41.05	3-Hexene, (E)-
16	2.999	2.02	88	55.05	1H-Tetrazole, 1-methyl-
17	3.032	3.75	93	69.10	1-Butene, 2,3-dimethyl-
18	3.083	2.25	98	41.05	2-Pentene, 3-methyl-
19	3.141	1.16	95	55.05	3-Hexene, (Z)-
20	3.212	3.62	97	41.05	2-Pentene, 3-methyl-
21	3.362	1.32	98	41.05	2-Butene, 2,3-dimethyl-
22	3.586	0.40	96	56.05	1-Pentene, 2,4-dimethyl-
23	3.670	1.10	95	83.10	2-Pentene, 4,4-dimethyl-, (E)-
24	3.771	1.79	87	41.05	3-Undecene, (Z)-
25	3.888	1.21	94	69.05	4-Methyl-2-hexene,c&t
26	3.963	1.29	90	43.05	5-Methyl-2-hexene,c&t
27	4.269	0.54	93	56.05	5-Methyl-2-hexene,c&t
28	4.494	1.51	96	56.05	1-Hexene, 2-methyl-
29	4.571	0.80	89	70.10	2,3-Dimethyl-1-hexene
30	4.656	0.75	95	69.10	3-Methyl-3-hexene
31	4.720	1.00	96	41.05	3-Heptene
32	4.898	4.98	96	69.10	3-Methyl-3-hexene
33	4.959	1.01	94	56.05	2-Heptene
34	5.021	0.59	95	69.05	3-Methyl-3-hexene
35	5.118	1.63	96	69.05	2-Hexene, 3-methyl-, (Z)-
36	5.233	1.02	93	83.10	2-Pentene, 2,4-dimethyl-
37	5.280	0.51	82	56.05	2-Heptene
38	6.241	0.82	95	83.10	2-Hexene, 2,3-dimethyl-
39	6.615	0.83	94	55.05	3-Hexene, 2,3-dimethyl-
40	6.792	0.65	91	69.05	2-Heptene, 4-methyl-, (E)-
41	6.929	0.86	85	41.05	3-Decyn-2-ol
42	7.127	1.34	92	69.05	2-Methyl-2-heptene
43	7.278	0.51	93	55.05	2-Hexene, 2,3-dimethyl-
44	7.579	0.59	96	83.10	3,4-Dimethyl-2-hexene
45	7.812	0.41	94	56.05	2-Heptene, 5-methyl-
46	8.429	0.58	94	55.05	3-Hexene, 2,3-dimethyl-
47	8.579	0.58	95	56.05	1-Heptene, 2-methyl-
48	8.715	0.83	88	55.05	3-Ethyl-3-hexene
49	8.785	0.84	94	69.05	3-Heptene, 4-methyl-
50	9.027	1.05	87	55.05	2-Hexene, 2,3-dimethyl-
51	9.183	1.61	94	55.05	3-Ethyl-3-hexene
52	9.280	0.50	88	70.10	Heptane, 3-methylene-
53	9.447	1.81	94	69.05	2-Methyl-2-heptene
54	9.936	1.22	91	70.10	2-Heptene, 3-methyl-
55	11.548	0.50	91	55.05	2,3-Dimethyl-2-heptene



Peak#	R.Time	Area%	Similarity	Base m/z	Name
56	14.853	0.54	88	69.05	1-Hexene, 3,3,5-trimethyl-
57	15.968	1.17	91	55.00	5-Undecene, 4-methyl-
58	17.679	0.41	89	55.00	2,3-Dimethyl-3-heptene, (Z)-
59	17.903	0.59	96	69.05	2-Methyl-2-octene
60	21.944	0.66	91	55.05	5-Undecene, 3-methyl-, (Z)-
61	22.435	0.49	93	69.05	2-Nonene, 2-methyl-
62	22.827	0.71	94	69.05	2-Octene, 2,6-dimethyl-
63	23.732	0.40	93	55.05	trans-4-Decene
64	23.888	0.35	94	56.05	1-Octene, 2,6-dimethyl-
65	24.139	0.44	95	55.00	trans-4-Decene
66	24.436	0.39	95	69.05	2-Nonene, 2-methyl-
67	24.789	0.61	88	70.05	2-Octene, 3,7-dimethyl-, (Z)-
68	29.140	0.36	81	69.05	2-Decene, 2-methyl-
69	30.374	0.32	92	69.05	3-Dodecene, (E)-
70	30.656	0.42	88	57.05	Formic acid, 2-propylpentyl ester
71	30.785	0.36	88	70.10	1-Undecene, 9-methyl-
72	30.873	0.25	87	69.05	1-Undecene, 8-methyl-
73	31.019	0.34	87	69.05	5-Undecene, 5-methyl-
74	31.236	0.39	75	119.10	(S,E)-2,5-Dimethyl-4-vinylhexa-2,5-dien-1-yl
75	31.355	0.26	88	69.05	4-Undecene, 9-methyl-, (Z)-
76	32.089	0.28	92	70.10	2-Undecene, 2,5-dimethyl-
77	33.734	0.31	89	70.10	1-Undecene, 9-methyl-
78	43.535	0.10	95	43.05	Heptadecanenitrile
79	45.119	0.10	96	57.05	Eicosane
80	46.251	0.07	95	43.05	Octadecanenitrile
81	46.441	0.17	96	57.05	Tetracosane
82	47.795	0.22	97	57.05	Tetracosane
83	49.165	0.20	95	57.05	Tetracosane
84	50.528	0.21	96	57.05	Hexatriacontane
85	51.880	0.19	95	57.05	Hexatriacontane
86	53.221	0.15	95	57.05	Tetracosane
87	54.551	0.12	95	57.05	Hexatriacontane
		100.00			

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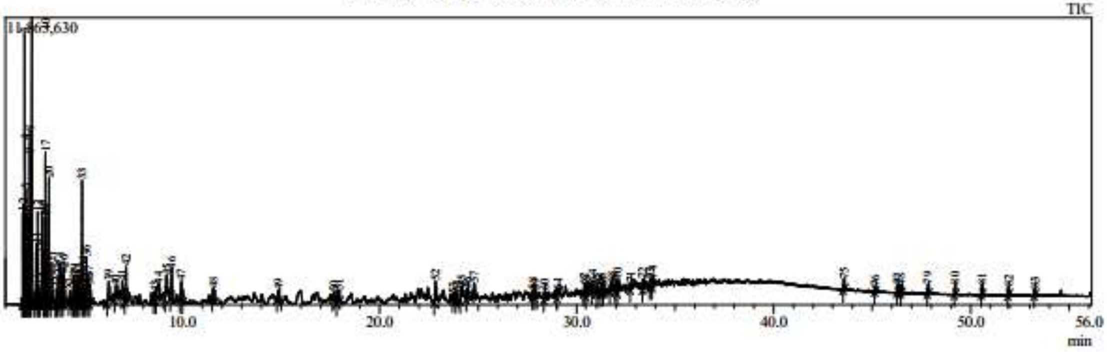

Peak Report TIC

Peak#	R.Time	Area%	Similarity	Base m/z	Name
1	1.884	1.53	97	41.05	Propene
2	1.927	1.73	98	43.05	Isobutane
3	1.972	5.35	98	41.05	1-Propene, 2-methyl-
4	2.000	2.70	98	41.05	2-Butene, (E)-
5	2.033	2.14	99	41.05	2-Butene
6	2.122	2.24	96	43.05	Butane, 2-methyl-
7	2.209	1.43	91	42.05	Butane, 2,3-dimethyl-
8	2.240	3.38	96	55.05	2-Methyl-1-butene
9	2.279	3.07	97	55.05	2-Pentene
10	2.346	8.81	97	55.05	Cyclopropane, 1,2-dimethyl-, trans-
11	2.565	1.69	91	43.05	1-Pentanol, 2-methyl-
12	2.639	2.31	98	41.05	1-Butene, 2,3-dimethyl-
13	2.693	0.46	97	57.05	Pentane, 3-methyl-
14	2.850	2.45	96	56.05	1-Pentene, 2-methyl-
15	2.965	1.21	94	41.05	3-Hexene, (E)-
16	3.001	1.71	92	55.05	2-Hexene, (E)-
17	3.034	4.12	94	69.05	1-Butene, 2,3-dimethyl-
18	3.085	2.22	98	41.05	2-Pentene, 3-methyl-
19	3.144	1.10	96	55.05	3-Hexene, (Z)-
20	3.215	3.69	97	41.05	2-Pentene, 3-methyl-
21	3.364	1.22	98	41.05	2-Butene, 2,3-dimethyl-
22	3.588	0.44	95	56.05	1-Pentene, 2,4-dimethyl-
23	3.672	1.18	96	83.10	2-Pentene, 4,4-dimethyl-, (E)-
24	3.773	1.96	88	41.05	Ethanone, 1-(1,2,2,3-tetramethylcyclopentyl)-,
25	3.890	1.21	95	69.05	4-Methyl-2-hexene,c&t
26	3.965	1.43	89	43.05	5-Methyl-2-hexene,c&t
27	4.273	0.50	94	56.05	2-Hexene, 5-methyl-, (E)-
28	4.450	0.45	90	83.10	2-Pentene, 3,4-dimethyl-, (E)-
29	4.496	1.16	92	56.05	1-Hexene, 2-methyl-
30	4.573	0.78	88	70.10	2,3-Dimethyl-1-hexene
31	4.658	0.78	95	69.05	3-Methyl-3-hexene
32	4.722	1.08	96	41.05	3-Heptene
33	4.897	5.61	95	69.05	3-Methyl-3-hexene
34	4.960	1.07	93	56.05	2-Heptene
35	5.021	0.60	95	69.05	3-Methyl-3-hexene
36	5.119	1.80	96	41.05	2-Hexene, 3-methyl-, (Z)-
37	5.235	1.09	93	83.10	2-Pentene, 2,4-dimethyl-
38	5.285	0.56	82	56.05	1-Hexene, 2-methyl-
39	6.245	0.97	95	83.05	2-Hexene, 2,3-dimethyl-
40	6.620	0.78	95	55.05	3-Hexene, 2,3-dimethyl-
41	6.937	0.78	87	43.05	1-Octene
42	7.133	1.69	92	69.05	2-Methyl-2-heptene
43	8.583	0.43	95	56.05	1-Heptene, 2-methyl-
44	8.788	1.53	96	55.00	3-Heptene, 4-methyl-
45	9.183	1.05	94	55.05	3-Ethyl-3-hexene
46	9.450	1.78	94	69.05	2-Methyl-2-heptene
47	9.939	1.31	91	70.10	2-Heptene, 3-methyl-
48	11.561	0.71	91	83.10	2,3-Dimethyl-2-heptene
49	14.862	0.62	89	69.05	1-Hexene, 3,3,5-trimethyl-
50	17.683	0.53	91	55.00	2,3-Dimethyl-3-heptene, (Z)-
51	17.920	0.77	96	69.05	2-Methyl-2-octene
52	22.841	0.98	94	69.05	2-Octene, 2,6-dimethyl-
53	23.740	0.24	92	55.05	trans-4-Decene
54	23.903	0.35	95	56.05	1-Octene, 2,6-dimethyl-
55	24.157	0.53	94	55.00	trans-4-Decene

Peak#	R.Time	Area%	Similarity	Base m/z	Name
56	24.445	0.33	95	69.05	2-Nonene, 2-methyl-
57	24.801	0.37	91	70.05	2-Octene, 3,7-dimethyl-, (Z)-
58	27.791	0.29	93	55.05	Cyclopropane, 1-pentyl-2-propyl-
59	27.904	0.22	90	70.05	2-Decene, 3-methyl-, (Z)-
60	28.378	0.26	93	55.05	1-Decene, 5-methyl-
61	29.035	0.36	90	69.05	4-Undecene, 9-methyl-, (Z)-
62	30.387	0.41	92	69.05	6-Dodecene, (E)-
63	30.501	0.43	92	55.00	6-Dodecene, (E)-
64	30.801	0.62	91	83.05	1-Undecene, 9-methyl-
65	31.034	0.38	92	69.05	2-Undecene, 2-methyl-
66	31.250	0.38	79	119.10	4-Undecene, 9-methyl-, (Z)-
67	31.368	0.25	88	70.05	4-Undecene, 9-methyl-, (Z)-
68	31.764	0.42	89	55.00	4-Undecene, 3-methyl-, (Z)-
69	31.971	0.08	89	69.05	Cyclopentane, 1,2-dibutyl-
70	32.102	0.42	91	70.05	2-Undecene, 2,5-dimethyl-
71	32.758	0.15	90	69.05	7-Tetradecene, (E)-
72	33.374	0.38	88	70.05	Cyclohexane, 2-butyl-1,1,3-trimethyl-
73	33.748	0.36	90	70.10	1-Undecene, 9-methyl-
74	33.855	0.34	90	83.05	7-Tetradecene
75	43.561	0.29	95	43.05	Heptadecanenitrile
76	45.150	0.13	95	57.05	Tetracosane
77	46.289	0.21	96	57.05	Octadecanenitrile
78	46.480	0.25	96	57.05	Tetracosane
79	47.837	0.30	97	57.05	Tetracosane
80	49.204	0.31	95	57.05	Hexatriacontane
81	50.570	0.29	95	57.05	Nonacosane
82	51.924	0.25	96	57.05	Tetracosane
83	53.260	0.19	95	57.05	Tetratriacontane
		100.00			

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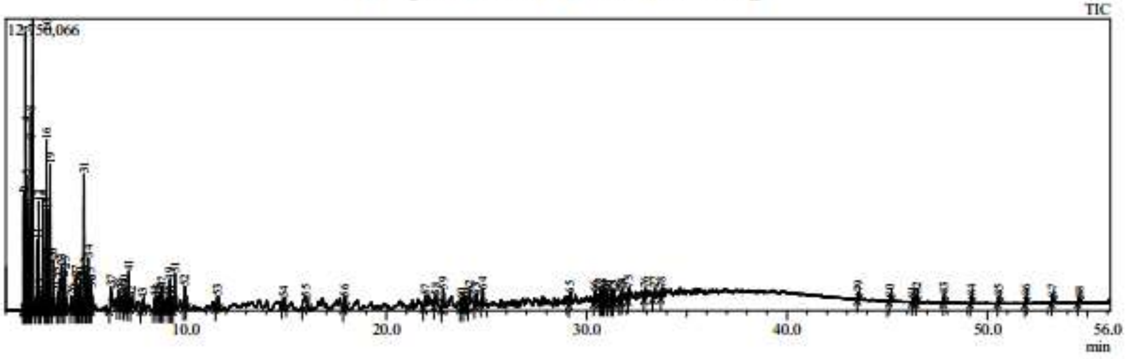
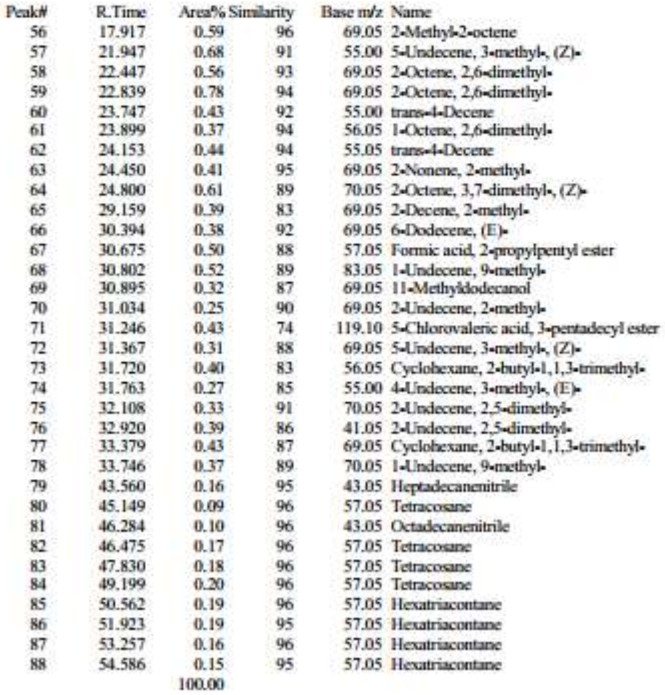


Peak Report TIC

Peak#	R.Time	Area%	Similarity	Base m/z	Name
1	1.883	1.57	97	41.05	Propene
2	1.927	1.63	98	43.05	Isobutane
3	1.971	4.78	98	41.05	1-Propene, 2-methyl-
4	2.000	2.49	98	41.05	2-Butene, (E)-
5	2.032	1.94	99	41.05	2-Butene, (Z)-
6	2.122	2.07	96	43.05	Butane, 2-methyl-
7	2.209	1.13	89	42.05	Cyclopentane
8	2.239	3.21	96	55.05	2-Methyl-1-butene
9	2.278	2.90	97	55.05	2-Pentene
10	2.346	7.73	97	55.05	Cyclopropane, 1,2-dimethyl-, trans-
11	2.565	1.64	91	43.05	1-Pentanol, 2-methyl-
12	2.639	2.25	98	41.05	1-Butene, 2,3-dimethyl-
13	2.694	0.41	95	57.05	Pentane, 3-methyl-
14	2.850	2.36	96	56.05	1-Pentene, 2-methyl-
15	3.002	2.83	93	55.05	2-Hexene
16	3.035	3.86	94	69.05	1-Butene, 2,3-dimethyl-
17	3.085	2.09	98	41.05	2-Pentene, 3-methyl-
18	3.144	1.08	95	55.05	2-Hexene
19	3.215	3.44	97	41.05	2-Pentene, 3-methyl-
20	3.365	1.25	98	41.05	2-Butene, 2,3-dimethyl-
21	3.590	0.41	96	56.05	1-Pentene, 2,4-dimethyl-
22	3.673	1.09	95	83.10	2-Pentene, 4,4-dimethyl-, (E)-
23	3.774	1.83	87	41.05	Ethanone, 1-(1,2,2,3-tetramethylcyclopentyl)-,
24	3.892	1.14	95	69.05	4-Methyl-2-hexene,c&t
25	3.966	1.35	88	43.05	5-Methyl-2-hexene,c&t
26	4.273	0.54	93	56.05	5-Methyl-2-hexene,c&t
27	4.497	1.50	96	56.05	1-Hexene, 2-methyl-
28	4.574	0.76	88	70.10	2,3-Dimethyl-1-hexene
29	4.659	0.74	94	69.05	3-Methyl-3-hexene
30	4.724	0.98	96	41.05	3-Heptene
31	4.901	5.06	96	69.05	3-Methyl-3-hexene
32	4.962	0.98	92	56.05	2-Heptene
33	5.024	0.58	95	69.05	3-Methyl-3-hexene
34	5.122	1.64	96	41.05	2-Hexene, 3-methyl-, (Z)-
35	5.238	0.97	93	83.05	2-Pentene, 3,4-dimethyl-, (Z)-
36	5.280	0.55	82	56.05	1-Hexene, 2-methyl-
37	6.247	0.86	95	83.10	2-Hexene, 2,3-dimethyl-
38	6.620	0.85	94	55.05	3-Hexene, 2,3-dimethyl-
39	6.802	0.73	90	69.05	2-Heptene, 4-methyl-, (E)-
40	6.938	0.89	87	41.05	1-Octene
41	7.133	1.41	92	69.05	2-Methyl-2-heptene
42	7.281	0.55	90	55.00	2-Hexene, 2,3-dimethyl-
43	7.817	0.42	94	56.05	2-Heptene, 5-methyl-
44	8.435	0.60	94	55.00	3-Hexene, 2,3-dimethyl-
45	8.585	0.60	95	56.05	1-Heptene, 2-methyl-
46	8.715	0.78	88	55.05	3-Ethyl-3-hexene
47	8.794	0.93	93	69.05	3-Heptene, 4-methyl-
48	9.034	1.09	86	55.05	2-Hexene, 2,3-dimethyl-
49	9.188	1.64	94	55.05	3-Ethyl-3-hexene
50	9.290	0.53	88	70.05	Heptane, 3-methylene-
51	9.452	1.89	94	69.05	2-Methyl-2-heptene
52	9.941	1.23	91	70.05	2-Heptene, 3-methyl-
53	11.559	0.64	91	55.00	2,3-Dimethyl-2-heptene
54	14.865	0.53	89	69.05	1-Hexene, 3,3,5-trimethyl-
55	15.973	1.31	92	55.00	5-Undecene, 4-methyl-



Peak#	R.Time	Area%	Similarity	Base m/z	Name
56	17.917	0.59	96	69.05	2-Methyl-2-octene
57	21.947	0.68	91	55.00	5-Undecene, 3-methyl-, (Z)-
58	22.447	0.56	93	69.05	2-Octene, 2,6-dimethyl-
59	22.839	0.78	94	69.05	2-Octene, 2,6-dimethyl-
60	23.747	0.43	92	55.00	trans-4-Decene
61	23.899	0.37	94	56.05	1-Octene, 2,6-dimethyl-
62	24.153	0.44	94	55.05	trans-4-Decene
63	24.450	0.41	95	69.05	2-Nonene, 2-methyl-
64	24.800	0.61	89	70.05	2-Octene, 3,7-dimethyl-, (Z)-
65	29.159	0.39	83	69.05	2-Decene, 2-methyl-
66	30.394	0.38	92	69.05	6-Dodecene, (E)-
67	30.675	0.50	88	57.05	Formic acid, 2-propylpentyl ester
68	30.802	0.52	89	83.05	1-Undecene, 9-methyl-
69	30.895	0.32	87	69.05	11-Methyldodecanol
70	31.034	0.25	90	69.05	2-Undecene, 2-methyl-
71	31.246	0.43	74	119.10	5-Chlorovaleric acid, 3-pentadecyl ester
72	31.367	0.31	88	69.05	5-Undecene, 3-methyl-, (Z)-
73	31.720	0.40	83	56.05	Cyclohexane, 2-butyl-1,1,3-trimethyl-
74	31.763	0.27	85	55.00	4-Undecene, 3-methyl-, (E)-
75	32.108	0.33	91	70.05	2-Undecene, 2,5-dimethyl-
76	32.920	0.39	86	41.05	2-Undecene, 2,5-dimethyl-
77	33.379	0.43	87	69.05	Cyclohexane, 2-butyl-1,1,3-trimethyl-
78	33.746	0.37	89	70.05	1-Undecene, 9-methyl-
79	43.560	0.16	95	43.05	Heptadecanenitrile
80	45.149	0.09	96	57.05	Tetracosane
81	46.284	0.10	96	43.05	Octadecanenitrile
82	46.475	0.17	96	57.05	Tetracosane
83	47.830	0.18	96	57.05	Tetracosane
84	49.199	0.20	96	57.05	Tetracosane
85	50.562	0.19	96	57.05	Hexatriacontane
86	51.923	0.19	95	57.05	Hexatriacontane
87	53.257	0.16	96	57.05	Hexatriacontane
88	54.586	0.15	95	57.05	Hexatriacontane
		100.00			

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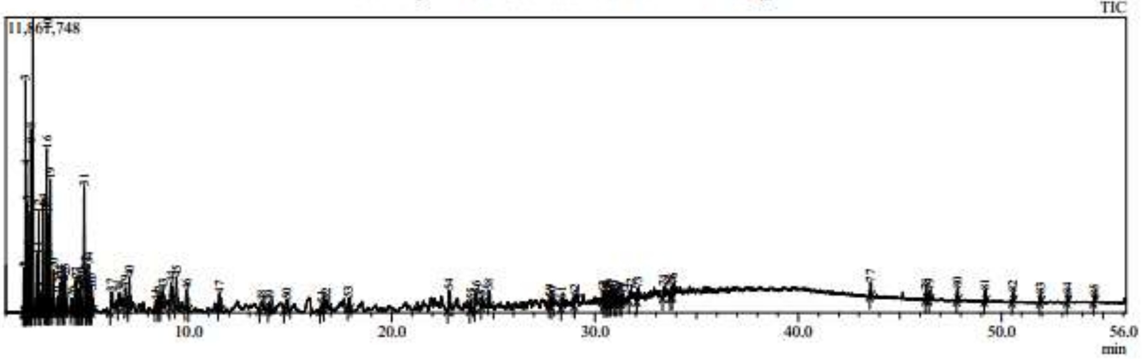

Peak Report TIC

Peak#	R.Time	Area%	Similarity	Base m/z	Name
1	1.884	0.70	97	41.05	Propene
2	1.927	0.71	98	43.05	Isobutane
3	1.971	4.21	99	41.05	1-Propene, 2-methyl-
4	2.000	2.03	99	41.05	2-Butene, (E)-
5	2.031	2.14	99	41.05	2-Butene
6	2.120	1.70	96	43.05	Butane, 2-methyl-
7	2.205	1.49	91	42.05	Butane, 2,3-dimethyl-
8	2.236	3.43	96	55.05	2-Methyl-1-butene
9	2.274	3.34	98	55.05	2-Pentene
10	2.341	9.09	97	55.05	Cyclopropane, 1,2-dimethyl-, trans-
11	2.555	1.56	90	43.05	1-Pentene, 4-methyl-
12	2.630	2.46	98	41.05	2-Pentene, 4-methyl-
13	2.685	0.40	94	57.05	Pentane, 3-methyl-
14	2.838	2.68	96	56.05	1-Pentene, 2-methyl-
15	2.987	3.15	92	55.05	2-Hexene, (E)-
16	3.019	4.27	94	69.05	1-Butene, 2,3-dimethyl-
17	3.069	2.38	98	41.05	2-Pentene, 3-methyl-
18	3.127	1.27	96	55.00	3-Hexene, (Z)-
19	3.197	3.86	97	41.05	2-Pentene, 3-methyl-
20	3.345	1.17	98	41.05	2-Butene, 2,3-dimethyl-
21	3.567	0.39	95	56.05	1-Pentene, 2,4-dimethyl-
22	3.648	1.18	95	83.10	2-Pentene, 3,4-dimethyl-, (E)-
23	3.749	1.81	88	41.05	3-Hexene, 2-methyl-, (E)-
24	3.865	1.23	95	69.05	4-Methyl-2-hexene,c&t
25	3.939	1.42	91	43.05	5-Methyl-2-hexene,c&t
26	4.243	0.51	94	56.05	2-Hexene, 5-methyl-, (E)-
27	4.466	1.60	96	56.05	1-Hexene, 2-methyl-
28	4.540	0.93	87	70.05	2,3-Dimethyl-1-hexene
29	4.625	0.81	94	69.05	3-Methyl-3-hexene
30	4.689	1.16	96	41.05	3-Heptene
31	4.862	5.50	96	69.05	3-Methyl-3-hexene
32	4.925	1.18	92	56.05	2-Heptene
33	4.990	0.64	94	69.05	2-Pentene, 3-ethyl-
34	5.083	1.74	96	41.05	2-Hexene, 3-methyl-, (Z)-
35	5.200	0.96	93	83.05	2-Pentene, 2,4-dimethyl-
36	5.245	0.67	82	56.05	1-Hexene, 2-methyl-
37	6.207	0.83	95	83.10	2-Hexene, 2,3-dimethyl-
38	6.580	0.74	94	55.05	3-Hexene, 2,3-dimethyl-
39	6.899	0.88	88	43.05	1-Octene, 3,7-dimethyl-
40	7.090	1.40	92	69.05	2-Methyl-2-heptene
41	8.380	0.35	93	55.05	3-Hexene, 2,3-dimethyl-
42	8.541	0.40	96	56.05	1-Heptene, 2-methyl-
43	8.748	1.49	95	55.05	3-Heptene, 4-methyl-
44	9.143	1.03	93	55.05	2-Hexene, 2,3-dimethyl-
45	9.406	1.58	94	69.05	2-Methyl-2-heptene
46	9.895	1.18	92	70.05	2-Heptene, 3-methyl-
47	11.517	0.84	91	83.10	2,3-Dimethyl-2-heptene
48	13.595	0.68	91	55.00	4-Nonene
49	13.982	0.51	92	70.05	4-Decene, 8-methyl-, (E)-
50	14.816	0.81	88	69.05	1-Hexene, 3,3,5-trimethyl-
51	16.572	0.37	96	55.00	3-Heptene, 4-ethyl-
52	16.789	0.75	93	56.05	Cyclopropane, 1,2-dimethyl-3-pentyl-, (1.alph
53	17.885	0.47	96	69.05	2-Methyl-2-octene
54	22.826	0.90	94	69.05	Cyclohexane, 1,1,2,3-tetramethyl-
55	23.887	0.40	94	56.05	1-Octene, 2,6-dimethyl-

Peak#	R.Time	Area%	Similarity	Base m/z	Name
56	24.141	0.52	94	55.00	trans-4-Decene
57	24.435	0.28	95	69.05	2-Nonene, 2-methyl-
58	24.789	0.50	93	70.05	2-Octene, 3,7-dimethyl-, (Z)-
59	27.783	0.27	93	55.00	Cyclopropane, 1-pentyl-2-propyl-
60	27.895	0.22	90	70.05	2-Decene, 3-methyl-, (Z)-
61	28.371	0.21	93	55.00	1-Decene, 5-methyl-
62	29.030	0.33	90	69.05	4-Undecene, 9-methyl-, (Z)-
63	30.386	0.34	92	69.05	3-Dodecene, (E)-
64	30.494	0.41	93	55.05	6-Dodecene, (E)-
65	30.605	0.32	86	69.05	Cyclopropane, 1,2-dimethyl-1-pentyl-
66	30.655	0.66	89	57.05	Formic acid, 2-propylpentyl ester
67	30.796	0.82	90	83.05	3-Dodecene, (E)-
68	30.940	0.30	90	70.05	4-Undecene, 9-methyl-, (Z)-
69	31.029	0.38	91	69.05	2-Undecene, 2-methyl-
70	31.241	0.35	82	70.05	4-Undecene, 9-methyl-, (Z)-
71	31.364	0.34	90	69.05	4-Undecene, 9-methyl-, (Z)-
72	31.758	0.42	89	55.00	4-Undecene, 3-methyl-, (Z)-
73	32.099	0.36	92	70.05	2-Undecene, 2,5-dimethyl-
74	33.372	0.40	91	69.05	Cyclohexane, 2-butyl-1,1,3-trimethyl-
75	33.741	0.46	90	70.05	5-Tetradecene, (E)-
76	33.855	0.43	87	83.05	5-Tetradecene, (E)-
77	43.560	0.34	95	43.05	Heptadecanenitrile
78	46.288	0.27	96	43.05	Octadecanenitrile
79	46.472	0.26	95	57.05	Tricosane
80	47.834	0.30	96	57.05	Tetracosane
81	49.200	0.29	96	57.05	Tetracosane
82	50.567	0.27	96	57.05	Tetracosane
83	51.919	0.22	96	57.05	Hexatriacontane
84	53.256	0.19	96	57.05	Hexatriacontane
85	54.585	0.19	95	57.05	Tetracosane
		100.00			

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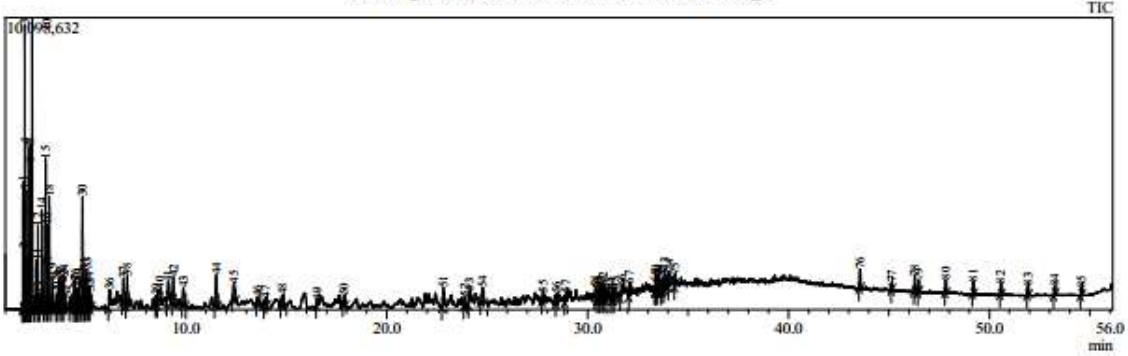

Peak Report TIC

Peak#	R.Time	Area%	Similarity	Base m/z	Name
1	1.881	2.07	97	41.05	Propene
2	1.924	0.99	97	43.05	Isobutane
3	1.969	4.83	98	41.05	1-Propene, 2-methyl-
4	1.997	2.67	98	41.05	2-Butene, (E)-
5	2.029	2.25	98	41.05	2-Butene, (Z)-
6	2.117	1.37	94	43.05	Butane, 2-methyl-
7	2.203	2.61	96	43.05	Pentane
8	2.233	3.23	95	55.00	2-Methyl-1-butene
9	2.272	2.88	97	55.00	2-Pentene, (Z)-
10	2.339	8.25	97	55.05	Cyclopropane, 1,2-dimethyl-, trans-
11	2.553	1.31	90	43.05	1-Pentene, 4-methyl-
12	2.627	2.07	98	41.05	2-Pentene, 4-methyl-
13	2.680	0.35	93	57.05	Pentane, 3-methyl-
14	2.834	2.52	96	56.05	1-Pentene, 2-methyl-
15	3.015	6.32	98	69.05	2-Pentene, 2-methyl-
16	3.065	2.10	98	41.05	2-Pentene, 3-methyl-
17	3.123	1.07	95	55.00	3-Hexene, (Z)-
18	3.193	3.30	98	41.05	2-Pentene, 3-methyl-
19	3.341	0.92	98	41.05	2-Butene, 2,3-dimethyl-
20	3.562	0.38	96	56.05	1-Pentene, 2,4-dimethyl-
21	3.644	1.13	95	83.05	2-Pentene, 4,4-dimethyl-, (E)-
22	3.742	1.58	89	41.05	3-Hexene, 2-methyl-, (E)-
23	3.858	1.01	95	69.05	4-Methyl-2-hexene,c&t
24	3.932	1.28	90	43.05	5-Methyl-2-hexene,c&t
25	4.236	0.42	93	56.05	5-Methyl-2-hexene,c&t
26	4.456	1.44	95	56.05	1-Hexene, 2-methyl-
27	4.530	0.83	87	70.05	2,3-Dimethyl-1-hexene
28	4.614	0.65	94	69.05	3-Methyl-3-hexene
29	4.676	1.02	96	41.05	3-Heptene
30	4.846	4.61	96	69.05	3-Methyl-3-hexene
31	4.910	1.20	87	56.05	2-Heptene
32	4.975	0.59	94	69.05	2-Pentene, 3-ethyl-
33	5.068	1.50	96	41.05	2-Hexene, 3-methyl-, (Z)-
34	5.184	0.83	93	83.05	2-Pentene, 4,4-dimethyl-, (E)-
35	5.235	0.59	81	56.05	Cyclopentane, methyl-
36	6.193	0.75	95	83.05	2-Hexene, 2,3-dimethyl-
37	6.888	1.22	89	43.05	Heptane, 4-methyl-
38	7.071	1.34	92	69.05	2-Methyl-2-heptene
39	8.519	0.33	96	56.05	1-Heptene, 2-methyl-
40	8.720	1.30	94	55.00	3-Heptene, 4-methyl-
41	9.114	0.90	93	55.00	3-Ethyl-2-hexene
42	9.379	1.46	94	69.05	2-Methyl-2-heptene
43	9.869	1.11	91	70.05	2-Heptene, 3-methyl-
44	11.508	1.93	90	83.05	Cyclohexane, propyl-
45	12.381	1.02	97	43.05	2,4-Dimethyl-1-heptene
46	13.570	0.49	91	55.00	4-Nonene
47	13.963	0.50	90	55.05	4-Decene, 8-methyl-, (E)-
48	14.790	0.71	89	69.05	1-Hexene, 3,3,5-trimethyl-
49	16.551	0.24	95	55.00	3-Heptene, 4-ethyl-
50	17.857	0.43	96	69.05	2-Methyl-2-octene
51	22.808	0.93	94	69.05	2-Octene, 2,6-dimethyl-
52	23.872	0.39	94	56.05	1-Octene, 2,6-dimethyl-
53	24.127	0.51	94	55.00	trans-4-Decene
54	24.779	0.91	92	70.05	2-Octene, 3,7-dimethyl-, (Z)-
55	27.772	0.31	93	55.00	Cyclopropane, 1-hexyl-2-propyl-, cis-

Peak#	R.Time	Area%	Similarity	Base m/z	Name
56	28.442	0.45	91	69.05	Cyclohexane, 1,1-dimethyl-2-propyl-
57	28.919	0.43	93	55.05	5-Undecene
58	30.378	0.37	92	69.05	3-Dodecene, (E)-
59	30.485	0.46	92	55.00	5-Dodecene, (E)-
60	30.595	0.35	87	69.05	Cyclopropane, 1,2-dimethyl-1-pentyl-
61	30.655	0.79	88	57.05	3-Trifluoroacetoxy-6-ethyldecane
62	30.785	1.04	90	83.05	1-Dodecanol, 3,7,11-trimethyl-
63	31.017	1.00	91	69.05	3-Undecene, 2-methyl-, (Z)-
64	31.231	0.47	85	70.05	4-Undecene, 9-methyl-, (Z)-
65	31.355	0.43	90	69.05	4-Undecene, 9-methyl-, (Z)-
66	31.716	0.46	91	69.05	Cyclohexane, 2-butyl-1,1,3-trimethyl-
67	32.091	0.40	92	70.05	2-Undecene, 2,5-dimethyl-
68	33.360	0.34	83	69.05	5-Nonanol, trifluoroacetate
69	33.405	0.35	87	83.05	3-Hexene, 2,5-dimethyl-3,4-bis(1-methylethyl)
70	33.533	0.58	91	69.05	Cyclopentane, 1-pentyl-2-propyl-
71	33.669	0.25	86	69.05	3-Decene, 2,2-dimethyl-, (E)-
72	33.736	0.59	90	70.05	5-Tetradecene, (E)-
73	33.854	0.63	87	83.05	2-Octene, 2,3,7-trimethyl-
74	34.046	0.38	88	69.05	2-Isopropyl-5-methyl-1-heptanol
75	34.338	0.20	89	43.05	2-Isopropyl-5-methyl-1-heptanol
76	43.555	0.47	94	43.05	Heptadecanenitrile
77	45.143	0.17	95	57.05	Tetracosane
78	46.279	0.42	96	43.00	Octadecanenitrile
79	46.471	0.31	96	57.05	Tricosane
80	47.823	0.33	96	57.05	Tetracosane
81	49.195	0.34	96	57.05	Tetracosane
82	50.556	0.32	96	57.05	Tetracosane
83	51.913	0.26	96	57.05	Hexatriacontane
84	53.256	0.24	96	57.05	Tetracosane
85	54.577	0.25	95	57.05	Tetracosane
		100.00			