CATALYTIC PYROLYSIS OF PLASTIC WASTE TO LIQUID FUEL USING LOCAL CLAY CATALYST

BY

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DECLARATION

Declaration by Candidate

This thesis is my original work and has not been presented for a degree in any other University. No part of this thesis may be reproduced without the prior written permission of the author and/ or Moi University.

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DEDICATION

I dedicate this thesis to my family, my husband, Mr. Meshack Malakwen, and our children Ivy, Faith and Joy.

ABSTRACT

Plastics are non-biodegradable and safe disposal of this waste poses environmental challenge all over the world. One thermochemical disposal method is pyrolysis that produces clean liquid fuel. Catalytic pyrolysis is superior to thermal pyrolysis as it uses lower temperatures, hence, less energy. Imported conventional catalysts increase the production cost of the liquid fuel but local clay catalyst used in this research is a cheaper substitute. Therefore, the main objective in this study was to produce liquid fuel from plastic waste, using indigenous clay as a catalyst through catalytic pyrolysis. The liquid fuel can be used as an alternative source of energy in diesel engines as transport fuel, in turbines for electricity generation and as heating source in boilers and furnaces. The clay from Kisumu county was characterized through X-Ray Fluorescence spectrometer (XRFS) and X-Ray Diffractometer (XRD). Reaction setup consisted of a round bottom flask reactor through which plastic feed and catalyst were heated in a temperature controlled furnace. Vapour product was condensed using a liebig type water condenser to give pyrolysis liquid product. Solid char was recovered from flask at the end of reaction. Central composite design (CCD) and Response surface methodology (RSM) in Design expert software were used to study the effect of pyrolysis operating variables on the liquid fuel yield and also to identify conditions for optimal yield. Analysis of oil was done using Gas chromatography- Mass spectroscopy (GCMS). Results show that clay has composition of silica and alumina at 64.5wt% and 16.3wt% respectively indicating high acidity of the clay, being requirement for a good pyrolysis catalyst. For High density polyethylene and Polypropylene, the highest liquid yield of 87.23wt.% and 60.36wt.% respectively was at 300 ℃ and catalyst concentration of 10wt.%. GC-MS analysis showed that the oil from HDPE, PP and PS comprised of complex mixtures of organic compounds with aromatic, aliphatic and naphthenes as major components. The liquid fuel properties for HDPE, PP and PS were found to meet the ASTM D975 requirement for a liquid fuel. Indigenous clay was establised to be a suitable catalyst for catalytic pyrolysis of plastic waste, with a potential to replace imported catalysts, since high yields of liquid fuel were obtained at lower reaction temperatures of 300-450 ℃, as compared to 600 ℃ required for thermal pyrolysis. In conclusion waste plastics can be used to generate alternative fuel for industrial use. Further studies on modification of surface and structure of clay are suggested to enhance its catalytic perfomance in the pyrolysis process for a better fuel yield.

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NOMENCLATURE

AAS	Atomic Absorption Spectrometer
CCD	Central composite design
DOE	Design of experiments
GC-MS	Gas Chromatography- Mass spectroscopy
HDPE	High Density Polyethylene
HCL	Hydrogen chloride
HHV	High heating values
LCA	Life cycle assessment
LDPE	Low Density Polyethylene
MSW	Municipal solid waste
NEMA	National Environmental Management Authority
PE	Polyethylene
PP	Polypropylene
PS	Polystyrene
PSW	Plastic Solid waste
PVC	Polyvinyl Chloride
PET	Polyethylene Terephthalate
RSM	Response surface model
SPI	Society of Plastic Industry
XRD	X- ray Diffractometer
XRF	X-Ray Fluorescence spectrometer

ACRONYMS

m/z	mass to charge ratio
$	Dollar
α	denotes the distance from the center of the design space to a star point

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I also acknowledge my husband for his tremendous support, my children for being patient with me as I went through my studies. You are the source of my inspiration.

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Above all I give special thanks to God almighty for his favor and divine protection, his mercies and strength in this academic journey.

CHAPTER 1: INTRODUCTION

1.1 Background Information

Most modern plastics are derived from natural materials such as oil, coal, and natural gas. The starting point for the production process is distillation of the raw material in petrochemical refineries into fractions. The heavy fractions give lubrication oils and heavy oils used for heating fuels while the lighter fractions produce gas, petrol, paraffin, and naphtha. The chemical building blocks for making plastics is mainly from naphtha (Plastiquarian, 2015).

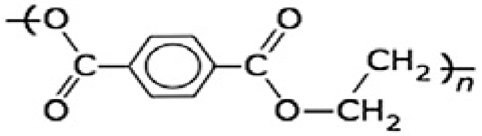
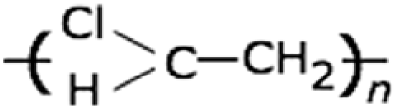
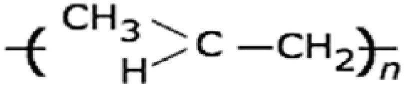
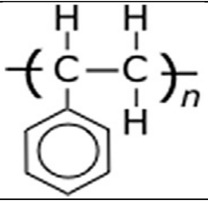
Naphtha undergoes a cracking process in which complex organic chemical compounds are separated into smaller molecules, dependent on their molecular weight. These smaller molecules include ethylene, propylene, butene and other hydrocarbons. The compounds produced through the cracking process are then further refined to produce the base plastic materials (Plastiquarian, 2015).

1.2 Different Types of Plastics

The Society of the Plastics Industry (SPI) established a classification system in 1988 to allow consumers and recyclers to identify different types of plastic (ryedale , 2014). Manufacturers place an **SPI** code, or number, on each plastic product, usually moulded into the bottom. This guide provides a basic outline of the different plastic types associated with each code number (Shafferina, 2016). Table 1.1 shows the SPI codes of different types of plastics and their names.

Many common household items such as carpet fiber, medicine jars, beverage bottles, mineral water bottles, fruit juice containers, clothing and rope are made of PET plastic. This PET plastics are preferred because they are lightweight, pressure-resistant and suitable for large-capacity (Cepeliogullar and Putun, 2013).

Table 1.1: SPI codes for different types of plastics and their names

SPI CODE	STRUCTURE	NAME
1 PET		Polyethylene Terephthalate
2 HDPE	$-\!\left(CH_2-CH_2\right)_n\!-$	High Density Polyethylene
3 V	 $-\!\left(\begin{matrix}Cl\\H\end{matrix}\!>C-CH_2\right)_n\!-$	Poly Vinyl Chloride
4 LDPE	$-\!\left(CH_2-CH_2\right)_n\!-$	Low Density Polyethylene
5 PP	 $-\!\left(\begin{matrix}CH_3\\H\end{matrix}\!>C-CH_2\right)_n\!-$	Polypropylene
6 PS		Polystyrene
7 OTHER		Miscellaneous types of plastics

HDPE is characterized by a long linear polymer chain with high degree of crystallinity and low branching which leads to high strength properties. HDPE is widely used in manufacturing of milk bottles, detergent bottles, oil containers, toys and more. The various applications contribute about 17.6% in plastic waste category which is the third largest plastic type found in municipal solid waste (MSW) (Michael, 2010).

Polyvinyl Chloride uses include wire and cable insulation, pipes, plumbing pipes, window frames, boots, medical devices, blood bags, automotive interiors, packaging, credit cards, synthetic leather etc. PVC is manufactured from the mixture of 57%

chlorine (derived from industrial grade salt) and 43% carbon (derived from hydrocarbon feedstock such as ethylene from oil or natural gas), hence making PVC harmful if ingested (British Plastics Federation, 2015).

LDPE has more branching that results in weaker intermolecular force, thus lower tensile strength, and hardness. However, LDPE has better ductility than HDPE since the side branching causes the structure to be less crystalline and easy to be molded. As a result of its high resistance to water, LDPE is used as wrapping foils for packaging, cling films, plastic bags, trash bags etc. LDPE items are widely used globally and its waste has accumulated to high and toxic levels. As a result, according to Michael, (2010) it is the second largest plastic waste in MSW after PP. It is durable and flexible.

Polypropylene being a saturated polymer has a linear hydrocarbon chain, it is strong and can usually withstand higher temperatures. PP contributes about 24.3% in plastic wastes category which are the largest number of plastics found in MSW (Michael, 2010). The diverse applications include flowerpot, lunch boxes, office folders, car bumpers, pails, carpets, furniture, storage boxes, margarine containers, yoghurt pots, syrup bottles, prescription bottles and plastic bottle caps.

Polystyrene is made of styrene monomers obtained from the liquid petrochemical. The structure consists of a long hydrocarbon chain with phenyl group attached to every other carbon atom. Naturally PS is colorless although it can be colored by colorants. It is heat resistant and it offers reasonable strength, durability and lightness making the polymer desirable to be used in variety of sectors such as in food packaging (disposable coffee cups, plastic cutlery, plastic food boxes), electronics, packaging foam, construction, toys and medical appliances. The wide range of applications signifies the large amount of waste from PS in MSW accumulated each year.

Miscellaneous types of plastic (Polycarbonate and Polylactide are included in this category). Code 7 is used to designate miscellaneous types of plastic not defined by the other six codes. Polycarbonate (PC) is used in baby bottles, compact discs and medical storage containers.

1.3 Plastic Waste and Disposal

The global production of plastics was reported to be 299 million tons in the year 2013 and an increase of 4% has been reported over the year 2014 reaching a production rate of 311 million tons (Wi, 2015). Plastics are vital in our daily lives. There is increased dependency on them that is justified by their light weight, versatility and low production cost relative to other classical materials such as concrete, wood and metal. Therefore, they are considered to be key material in numerous sectors including engineering applications, medical, construction, automotive, leisure, aerospace, packaging, electronics, food etc. The increased demand for plastic materials now and even in future has proved plastic revolution taking place in different sectors. Population explosion and economic growth have also led to increased demand on plastic materials and their feedstock chemicals used in their production. This on the other hand has made the demand for plastics grow more rapidly over the last two decades. Table 1.2 shows the global consumption of individual plastics.

As far as individual plastics are concerned, polyolefins account for 53% of the total consumption.

In Kenya’s capital city of Nairobi, an estimated 2,400 tons of solid waste is generated daily, 20% of which is in plastic form (The world bank, 2020).

Table 1.2: Global consumption of individual plastics

Type of plastic	**Consumption %**
Polythene (PE)	33.5
Polypropylene (PP)	19.5
Polyvinylchloride (PVC)	16.5
Polystyrene (PS)	8.5
Polyethylene terephthalate (PET) and polyurethane (PU)	5.5
Styrene copolymers (ABS, SAN, etc.)	3.5
Blends, alloys, high performance and specialty plastics, thermosetting plastics, and so forth	13

The increase in demand for plastics can only lead to the accumulation of plastic solid waste (PSW) which takes up a large share of the municipal solid waste (MSW) sector in developed and developing countries alike. The disposal and decomposition of plastics has been an issue which has caused a number of researches to be carried out in this regard. Currently the disposal methods employed are:

1. Land filling: scarcity of land, generation of explosive greenhouse gases (such as methane) and poor biodegradability of commonly used packaging polymers make landfilling an unattractive option for plastic waste disposal.
2. Mechanical recycling: This is reprocessing of the used plastics to form new similar products, where mechanical (physical) means of treatment are used to re-extrude process and convert PSW typically blended with virgin polymers aiming at reducing overall cost. It is not cost effective as it requires high energy for cleaning, sorting, transportation and processing to make a serviceable product.

3. Biological recycling: This is by enabling micro-organisms in the environment to metabolize the molecular structure of plastic films to produce an inert humus-like material that is less harmful to the environment. However, there are a number of difficulties over the use of degradable plastics. First, appropriate conditions are necessary for the degradation of such plastics, such as presence of light for the photodegradable plastics. Second, greenhouse gases such as methane is released when plastics degrade anaerobically (Panda *et al.,* 2010).
4. Thermal and chemical recycling: where a chemical alteration in the polymer structure is performed via chemical, thermo-chemical means, or where PSW is utilized as a monomer feedstock in industrial recycling loops.
5. Energy recovery: This entails recovery of steam, heat and electricity from waste through combustion.

The conversion of plastics to valuable energy is possible as they are derived from petrochemical source, essentially having high calorific value. Hence, pyrolysis is one of the routes to waste minimization that has been gaining interest recently.

1.4 Problem Statement

Due to increased littering in most parts of Kenya, a lot of concern has developed between scientists and philosophers about the plastic waste and currently it is an ongoing debate. Among the factors that have led to increase in amounts of waste in most parts of the world is rapid urbanization. This has posed a challenge in waste disposal particularly plastics because the time period for which the plastic remains in use is very small. The problem is more acute in developing countries such as Kenya. At present there is a large number of plastic wastes, particularly plastic bags, detergent containers, used yoghurt cups, packaging materials and plastic bottles, which are seen littered all over in Kenya. This has led to environmental degradation, especially in major cities and towns.

Despite the ban on plastic bags in Kenya in 2017, there are still other plastic waste from food packaging materials, drinking water bottles, disposable juice cups and disposable plates. The National Environment Management Authority (NEMA) of Kenya indicates that 50 million bottles are used in Kenya annually, creating monumental environmental challenge (Capital business, 2018).

Plastic is a major pollutant being composed of toxic chemicals and most importantly a non-biodegradable substance, plastic disposal leads to air and water pollution. It also mixes with food posing a negative impact on the environment, humans, and animals.

Thermal and catalytic pyrolysis has previously been of focus hence this research is an experimental analysis of a cheaper local clay catalyst to produce liquid fuel from waste plastics. Clays are hydrated silicates of Al, Fe, or Mg, both crystalline and amorphous composed mainly of silica, alumina and water (Murray, 2004). All clays are hydrous aluminosilicates with a phyllosilicate structure and with very small grain size of less than 4 μm. The minerals carry excess negative charge owing to internal substitution of Si^{+4} by lower valent cations and thereby increase internal chemical reactivity in ion exchange. Kenyan clay soil contain silica and alumina which makes it an appropriate catalyst in fast pyrolysis of plastic waste.

1.5 Justification

Plastics are not biodegradable and safe disposal of waste is an environmental challenge all over the world. One thermochemical disposal method of plastic waste is of pyrolysis which produces clean liquid fuel. Pyrolysis of plastic waste to liquid fuel is one way of creating job opportunity to the unemployed Kenyans. Catalytic pyrolysis is superior to thermal pyrolysis as it uses lower temperatures and hence less energy. The use of locally available clay reduces the overall cost of production.

Total global production of plastics has been on a steady rise over the last 10 years. Table 1.3 shows global production of plastics from 2010 to 2019 in million metric tons.

Table 1.3: Global production of plastics from 2010 to 2019 (in million metric tons) (Garside, 2020)

YEAR	Metric tons (million)
2019	368
2018	359
2017	348
2016	335
2015	322
2014	311
2013	299
2012	288
2011	279
2010	270

The liquid fuel can be used as an alternative source of energy in diesel engines as transport fuel, in turbines for electricity generation and as heating source in boilers and furnaces. This research is important in waste management and alternative energy generation.

1.6 Research Objectives

Main Objective

To produce liquid fuel for use in diesel engines, industrial furnaces and boilers from plastic waste through catalytic pyrolysis using local clay as a catalyst.

Specific Objectives

i. To characterize indigenous clay catalyst
ii. To determine the effect of pyrolysis operating variables (catalyst concentration and reaction temperature) on liquid fuel yield.
iii. To characterize the liquid product for hydrocarbon components.
iv. To determine the liquid oil for fuel characteristic properties.

CHAPTER 2: LITERATURE REVIEW

2.1 Introduction

Pyrolysis is a tertiary recycling technique in which organic polymers are converted into liquid oil, char and gases at high temperatures via thermal decomposition (Chen *et al*., 2014; Ouda *et al*., 2016; Anjum *et al*., 2016). It is the process of thermally degrading long chain polymer molecules into smaller, less complex molecules through heat and pressure. The process requires intense heat with shorter duration and in absence of oxygen. The three major products that are produced during pyrolysis are valuable for industries especially production and refineries. Pyrolysis has been chosen by many researchers since the process is able to produce high amount of liquid oil up to 80 wt.% at moderate temperature around 500 ℃. In addition, pyrolysis is also very flexible since the process parameters can be manipulated to optimize the product yield based on preferences. The liquid oil produced contain diesel oil, gasoline and light fuel oil. The pyrolysis of plastic wastes produces a whole spectrum of hydrocarbons including paraffins, olefins, iso-alkanes and aromatics.

Pyrolysis is a promising technology for converting plastic waste into liquid oil and other value-added products such as char and gases. It is mostly used compared to other thermal technologies such as plasma arc gasification and incineration with a lower annual capital cost (US $17–25 per ton) and net operational cost (US $2–3 per ton products) (Ouda *et al*., 2016).

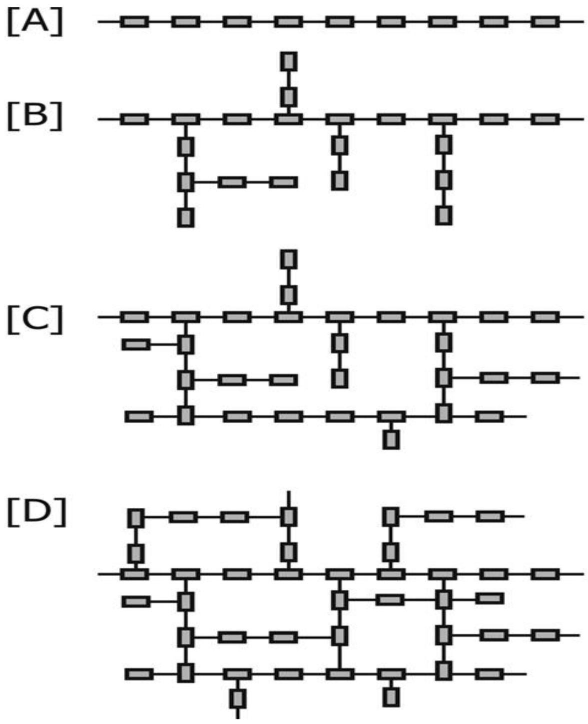
2.2 Classification of Plastics

Based on the chemical structure and the order of crosslinking between the macromolecules, plastics can be categorized as thermosets, elastomers and thermoplastics, (Frank and Biederbick, 1984) as shown in Figure 2.1.

Thermosetting polymers are converted into their final form by heat and once set cannot be softened by further heating. Examples of thermosetting plastics are melamine formaldehyde which is used in the manufacture of Formica and polyester resins which are used in kitchen work surfaces and glass reinforced plastics work respectively.

Through moderate heating, thermoplastics are softened and become fused (plastic). On cooling they harden again. This process can be repeated many times without radically altering the thermoplastic properties. Examples of thermoplastics are acrylic and styrene.

Elastomers are of soft elasticity and usually cannot be melted.



Thermoplastics (Linear or with branches macromolecule chains)

Elastomers (Far knit crosslinking)

Thermosets (Narrow knit crosslinking)

Figure 2.1: Principle structure of linear (A), with side chains (B) and crosslinked macromolecules (C and D). Chain structure (A) and (B) are thermoplastic types, structures with low crosslinking (C) elastomers and with strong crosslinking thermosets (D) (Frank & Biederbick, 1984).

Processing of plastics comprises a variety of operations involving flow and shaping of polymer melts into finished articles. For thermoplastic resins the most common processing operations are extrusion and molding. In extrusion, after melting solid plastic resin it is shaped in a continuous part of a defined cross-section. This is done through screw conveying. The melt is forced to flow through a die. Die forming is used in different activities such as pipe and tubing, wire, film, cable coating and in sheets. Non-continuous processes are involved in molding such as compression molding, injection molding, rotational molding and blow molding in which three-dimensional parts are made in a closed mold. Most of the molded products are solid, hollow, or surfed. Other thermoplastics operations include casting calendaring and thermoforming. In distinction to thermoplastics, thermosetting resins use low viscosity components which, through chemical reaction, produce the solid part in the mold. There are different processing methods for thermoset systems such as injection molding, transfer molding and compression molding. Pultrusion, open mold processing, reaction injection molding and resin transfer molding are some of the specialized techniques made for fiber reinforced thermosets.

2.3 Material Properties of plastics

2.3.1 Formation and structure

The basic structure of plastic polymers is given by macromolecular chains, formulated from monomer units by chemical reactions. Typical reactions for chain assembling are polyaddition (continuous or stepwise) and condensation polymerization (polycondensation) (Frank and Biederbick, 1984). Figure 2.2 shows the process for plastic generation.

1. **Polyaddition as chain reaction:** This is the process of chemical combination of a large number of monomer molecules, whereby the monomers are combined

to a chain either by orientation of the double bond or by ring splitting. No by products will be separated and no hydrogen atoms will be moved within the chain during the reaction. The process is started by energy consumption through heat or radiation or by use of catalysts.

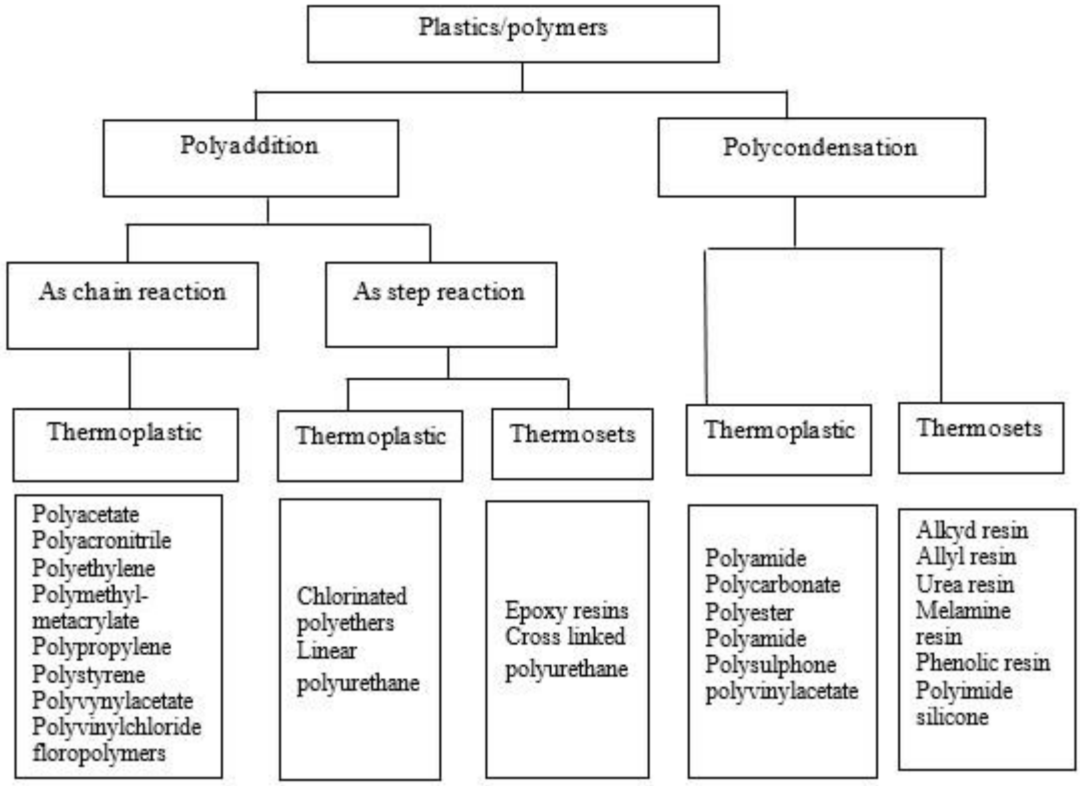
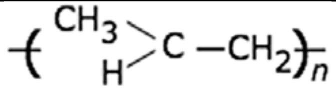
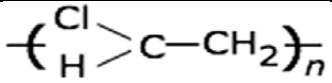


Figure 2.2: Process for plastic generation (Frank and Biederbick, 1984)

2. **Polyaddition as step reaction:** This is the process of combination of monomer units without a reaction of double bonds or separation of low molecular compounds. Hydrogen atoms can change position during the process.
3. **Polycondensation:** This is the generation of plastics by buildup of polyfunctional compounds. Typical small molecules like water or ammonia can be set free during the reaction. The reaction can occur as a step reaction.

The monomer units are organic carbon-based molecules. Carbon and hydrogen atoms are the main components while elements like oxygen, nitrogen, sulfur, fluorine or chlorine can be contained in the monomer unit. The type of elements, their proportion and placing in the monomer molecule gives the basis for generating different plastics as shown in Table 2.1.

Table 2.1: Examples of common plastics and their monomers

Monomer		**Polymer**	
Ethylene	$CH_2 = CH_2$	Polyethylene (PE)	$-\!\left(CH_2-CH_2\right)_n$
Propylene	$CH(CH_3) = CH_2$	Polypropylene (PP)	 $-\!\left(\begin{smallmatrix}CH_3\\H\end{smallmatrix}\!>C-CH_2\right)_n$
Vinyl chloride	CH_2-CH(Cl)	Polyvinylchloride (PVC)	 $-\!\left(\begin{smallmatrix}Cl\\H\end{smallmatrix}\!>C-CH_2\right)_n$
Tetraflorethylene	$CF_2 = CF_2$	Polytetraflorethylene (PTFE)	**- $(CF_2 = CF_2)_n$-**

The coupling between the atoms of a macromolecular chain happens by primary valence bonding (Kauffman, 1988). The main chain comprises of carbon atoms joined together by either single or double bond. The electron configuration of carbon atoms gives the link between the carbon atoms which occur at a certain angle, for example, for single bonding at an angle of 109.5 ℃. Atoms like hydrogen which are linked to the carbon atoms, hinder the free rotation of the carbon atoms around the linking axis. The ‘cis’- link of carbon atoms have the highest bonding energy while the ‘trans’-link has the lowest (Jarecki, 1979). Figure 2.3 shows the potential energy for rotation of ethylene molecules around the carbon-linking axis.

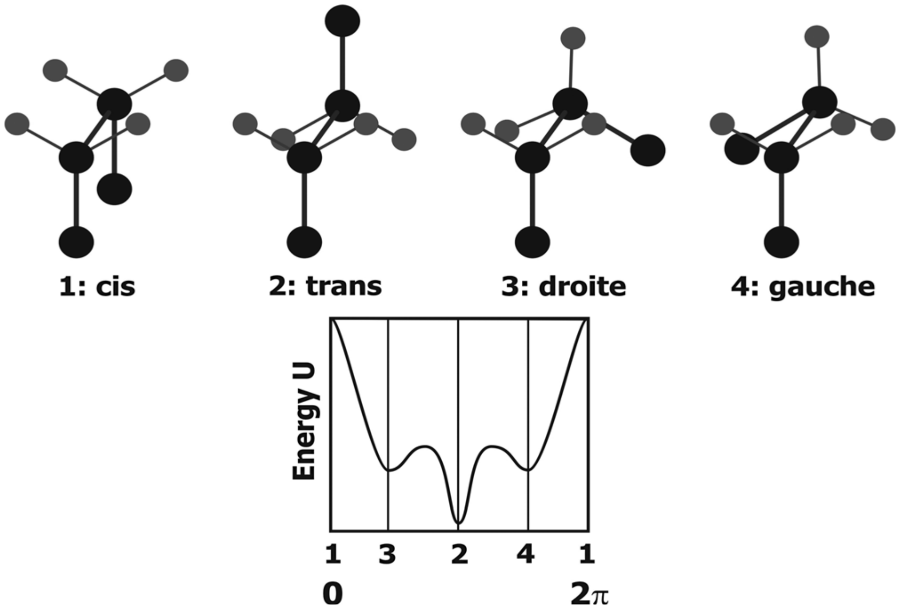
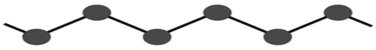


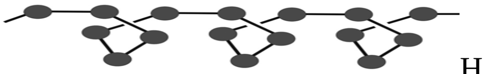
Figure 2.3: Potential energy for rotation of ethylene molecules around the carbon-linking axis (Jarecki, 1979).

Different chain conformations are possible depending on the kind of bonding partners such as zig-zag conformation (e.g., PE or PVC) or helix conformation (e.g., PP or PTFE) as shown in Figure 2.4.

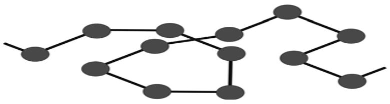
Linear conformation



Zig-zag conformation



Helix conformation



Ball-shaped conformation

Figure 2.4: Conformation types of macromolecules (Jarecki, 1979).

2.3.2 Thermal Properties of plastics

Thermal properties of thermoplastics strongly depend on the molecular structure. Orientation and length of macromolecular chains, number and distribution of side chains, crystalline structure or level of molecular links influence the thermal properties (Jarecki, 1979). The phase transitions of thermoplastic resins are glass transition, crystallites melting and thermal degradation of macromolecular chains. Physical properties like specific volume, heat capacity, heat conduction or thermal conduction, characterize the material behaviour regarding thermal energy absorption and transport, this therefore show a distinctive dependence of the material temperature and vary particularly in the ranges of phase transitions. Depending on the physical and chemical structure of thermoplastic resin, the following phase transitions will occur on increasing material temperature (Jarecki, 1979).

1. Glass transition (Tg)

Below the glass temperature (Tg) the mobility of the molecules (Browns macro-mobility) is strongly curbed by intermolecular interaction. There are no position change processes, only restricted thermal induced movements of chain segments or side chains. At the glass temperature Browns micro-mobility of chain segments and side chains starts to occur and the plastic becomes softer but is still mechanically stable. Before the molecules reach the glass temperature second order relaxation processes are possible. The single-molecule segments obtain a restricted mobility.

2. Flow temperature (Tf)

When the temperature is increased the hindering influence of intermolecular interaction decreases. On attaining the flow temperature (Tf) complete macromolecular chains can slip against each other (Browns macro-mobility). The amorphous structures of the plastic become softer and begins to melt. There is no chemical degradation of the macromolecules of the plastic at this state.

3. Crystallite melting temperature (Tm)

The semi crystallite thermoplastics on reaching the crystallite melting temperature, the forces responsible for crystallite forming will break and the crystallites begin to melt. The entire thermoplastic is plasticized because the temperature range of crystallite melting exceeds the flow temperature of the amorphous state. The resin can be solidified by cooling as long as there is no thermal degradation in the molten phase. Depending on duration and speed of cooling crystallite phases will be generated. The size and distribution of the crystallites can differ from the original status.

4. Thermal decomposition (Td)

When the decomposition temperature is exceeded in the molten phase of thermoplastics and thermoplastic elastomers, the macromolecules start to decompose caused by intensive thermal oscillations. Separation of monomer units, oxidation or chemical conversion into reaction products are possible reactions. The resin will be irreversibly chemically modified. The decomposition products will be separated as gaseous phase or will remain as components in the residual material. The start of decomposition is dependent on the intensity of the thermal input. Table 2.2 gives a summary of phase transition temperatures of typical thermoplastic resins.

Table 2.2: Phase transition temperatures for thermoplastic resins (Jarecki, 1979)

Resin	**Glass temp T_g (℃)**	**Flow temp T_f (℃)**	**Crystallite melt temp T_m (℃)**	**Decomposition temp T_d (℃)**
HDPE	-95	210-270	130 – 146	360 – 390
PS	97	160	180 – 200	318 – 348
PP	-18	230	160 – 208	336 – 366

2.3.3 Thermal decomposition of plastics

Phase-transition temperature are dependent on the molecular structure of the plastic. Limited mobility of the molecule chains, for example, by loop forming, long side chains or high molecular weight cause an increased phase-transition temperature.

2.3.4 TGA Analysis of plastic wastes

TGA analysis of the plastic has been carried out to determine optimum conditions for thermal decomposition under controlled conditions. The thermal degradation of PP starts at the lowest temperature of around 240 ℃ and shows a single step decomposition with maximum decomposition at around 425 ℃. PP half carbon chain consists of tertiary carbons which favor carbocation process during the thermal degradation which may lead to its degradation at a lower temperature (Jung *et al.*, 2010).

PS also shows single stage decomposition that starts at 330 ℃ and attains maximum decomposition at around 470 ℃. PS degradation follows both end-chain and random chain scission mechanisms which enhance its degradation process (Lee *et al.*, 2012).

PE showed two-stage degradation, the first stage started at around 270 ℃ and the second thermal degradation started at temperature of around 400 ℃. PE plastics requires high temperature to degrade as compared to PVC and PS (Wu *et al.,* 2014). PE consists of long chain and follows the random chain scission mechanism during its thermal degradation, which requires relatively higher temperature (Lee *et al.*, 2012).

2.4 Pyrolysis

In the present study the characteristics of pyrolysis liquid oil was analyzed and compared with conventional diesel and gasoline. Table 2.3 shows the characteristics of conventional diesel oil. The fuel properties such as viscosity, density, pour point, freezing point, flash point and HHV are important for analyzing the quality of fuel. The kinematic viscosity of fuel dictates the spray pattern and atomization of injected fuel in a combustion chamber. The higher viscosities of fuel results in poor atomization, leading to poor engine start-up and performance. Furthermore, highly viscous fuels have reduced flow ability, especially during winters, which adversely affects the fuel injector function and causes problems in engine start up and running (Miandad *et al*., 2016). HHV is an important characteristic of any petroleum product, especially when considered for energy production. High HHV means high energy contents that result in achieving the required target energy with less amount of fuel.

Table 2.3: Characteristics of conventional diesel oil

Parameters	**Units**	**Conventional Diesel**	**Reference**
Dynamic Viscosity	mm^2/s	2.0-5.0	Syamsiro et al. (2014)
Kinematic Viscosity	cSt	2.0-5.0	Syamsiro et al., 2014
Density @ 15 ℃	g/cm^3	0.815-0.870	Syamsiro et al., 2014
Pour Point	℃	6	Ahmad et al. (2015)
Flash Point	℃	52	Syamsiro et al., 2014
HHV	MJ/Kg	43.06	Syamsiro et al., 2014

The liquid oil produced can be used in multiple applications such as furnaces, boilers, turbines and diesel engines without the needs of upgrading or treatment. The gaseous pyrolysis by product has substantial calorific value and can be reused to provide the energy requirement for the pyrolysis plant. Pyrolysis process is much easier and flexible than recycling method since it does not need an intense sorting process, thus less labor intensive.

In gasoline production aromatics, naphthene and isoalkanes are highly desirable, whereas olefins and n-paraffins are less desired. Accordingly, it is desirable that the pyrolytic conversion of plastic wastes produces more aromatics, naphthene and iso-alkanes with carbon number in the range C_5–C_8.

2.4.1 Pyrolysis operating parameters

It should be noted that the product yield and quality heavily depend on a number of operating parameters. The main parameters include temperature, residence time, feedstock composition, choice of catalyst, particle size, type of reactors, pressure, heating rate and type of fluidizing gas with its flow rate. The optimum operating conditions are obtained after the study because they affect the quality of pyrolytic oil.

1. Temperature

Temperature is the most important factor affecting the quality and quantity of pyrolysis products. Temperature affects the cracking reactions that alter the yield of gases and liquid oil. There is little effect on the amount of produced char (Lopez *et al.*, 2011c). At low temperature long chain hydrocarbons are produced, while an increase in temperature results in short carbon chain compounds due to the cracking of C-C bonds. Aromatic compounds are produced at higher temperatures due to triggering of secondary process reactions.

2. Retention time and feedstock composition

Retention time has shown little effect on the quality of pyrolysis, the same yield of liquid oil has been observed at 30 min and 120 min retention times (Lopez *et al.*, 2011). The aromatic compounds present in liquid oil were similar at different retention time with the same temperature (Lee and Shin, 2007). The feedstock composition affects the yield of pyrolysis products, PE and PP types of plastics require higher temperatures for their complete degradation as compared to PS plastic, due to their complex structure (Miskolczi *et al.*, 2009).

3. Use of catalyst

Catalysts improve the quality of pyrolysis products and also reduce the process temperature and retention time. Fe_2O_3 (Sarker and Rashid, 2013), $Ca(OH)_2$ (Sarker *et al.*, 2011a,b), FCC (Lee, 2009), natural zeolite (Syamsiro *et al.*, 2014) and synthetic zeolite (Lopez *et al.*, 2011) are different catalysts used in the process of catalytic pyrolysis. A range of other catalysts have been utilized, including Red Mud (Lopez *et al.*, 2011a), ZSM-5 (Lopez *et al.*, 2011a), HZSM-5 (Hernandez *et al.*, 2007), Y-zeolite (Lee, 2012), in catalytic pyrolysis to improve the quality of liquid oil (Wang and Wang, 2011). Catalysts increase the rate of cracking reactions that lead to increase in the yield of gases and reduction in the yield of liquid oil (Syamsiro *et al.*, 2014). The catalysts improve the quality of liquid oil, some of the larger carbon chain compounds are adsorbed into the catalysts or broken down further into small carbon chain compounds. The catalysts increase the lighter fractions in the liquid oil such as gasoline (Lerici *et al.*, 2015), and decrease the overall process energy-inputs (Lopez *et al.*, 2011a). For instance, the use of ZSM-5 catalyst decreased the impurities such as solid residue, sulphur, nitrogen, and phosphorous in the produced liquid oil (Miskolczi *et al.*, 2009). The catalysts characteristics that affect the catalytic activity of the catalysts are BET surface area, pore size, pore volume and acidity. It is also reported that the use of catalysts with a high BET surface area allows more contact between reactants and the catalyst surface, resulting in an increased rate of cracking reaction to produce more gases than liquid oil (Syamsiro *et al.*, 2014).

2.4.2 Products of pyrolysis process

1. Liquid oil and its applications

Liquid oil from pyrolysis of plastics can be used as an alternative source of energy (Rehan *et al*., 2016b). Lopez *et al*. (2011) and Williams, (2006) reported that the pyrolysis process can convert 78–84% plastic by weight into liquid oil. Table 2.4 shows the product distribution in plastic pyrolysis.

Table 2.4: Product distribution in plastic pyrolysis (% wt of feed) (Kaminsky, 1992)

Feed	Pyrolysis temperature (℃)	Gas	Oil	Residue	Other
PE	760	55.8	42.4	1.8	-
PP	740	49.6	48.8	1.6	-
PS	581	9.9	24.6	0.6	64.9(styrene)
PE/PP/PS	750	52.0	46.6	1.4	-

In thermal pyrolysis, temperatures above 700 ℃ are required for polymer cracking whereas in catalytic pyrolysis the temperature can be lowered to 300- 400 ℃.

2. Char and its applications

Char is a by-product of the pyrolysis process. It is the unburnt plastic left over in the reactor. The remaining char has fixed carbon, volatile matter, moisture content and a small amount of ash. Production of char is very low in quantity (1–1.3 g from 1 kg plastic) in comparison to other process products such as liquid oil and gases (Lopez *et al*., 2009; Williams, 2006). Jindaporn and Lertsatitthanakorn (2014) prepared a briquette after crushing the HDPE char into powder. The produced briquette (1 kg) was used to heat 1 litre of water (from room temperature to boiling temperature) within 13 min. The char has the potential to be used in various environmental and energy applications such as heavy metal adsorption from the municipal and industrial wastewater and toxic gases (Heras *et al*., 2014). Bernando, (2011) upgraded the char from co-pyrolysis of PE, PS and PP waste with biomass and waste tires. The activated char was used for the adsorption of methylene blue dye that showed a significant adsorption of dye (3.59–22.2 mg/g). Moreover, char can be used as a feedstock for activated carbon or source of energy for boilers (Fernandez *et al*., 2011).

3. **Gases and its potential applications**

The main gases produced from pyrolysis are methane, hydrogen, propane, propene, ethane, ethene and butane (Williams and Williams, 1998). However, PET produced additional gas components of carbon dioxide and carbon monoxide while hydrogen chloride was also produced by PVC. The gas produced in pyrolysis process also has significant calorific value. Pyrolysis of Poly-vinyl chloride produces Chlorine gas (Chen *et al*., 2014) which is hazardous, this is the reason PVC plastic is not commonly used in pyrolysis. Miskolczi *et al,*. (2009) reported that gases produced from pyrolysis of agriculture plastic waste have 45.9 and 46.6 MJ/kg HHV. In addition, gases produced from PP and PE pyrolysis have HHV of 50 and 42 MJ/kg respectively (Jung *et al*., 2010). The gases produced from pyrolysis can be used for heating in boilers or in gas turbine for generation of electricity without any flue gas treatment (Fernandez *et al*., 2011). On the basis of their composition, 1-butene and isoprene can be recovered through condensation and can be used in tires production (Frigo *et al*., 2014). While, propene and ethane after separation from other gases, can be used as chemical feedstocks to produce polyolefins (Sharuddin *et al*., 2016).

2.4.3 Thermal pyrolysis

A comprehensive study of the mechanism of plastic pyrolysis has been presented (Cullis and Hirschler, 1981). Mechanisms of plastic pyrolysis:

(a) End-chain scission or depolymerization- the polymer is broken up from the end groups yielding the corresponding monomer.

(b) Random chain scission- the polymer is broken up randomly into fragments of uneven length.

(c) Chain stripping- elimination of reactive substitutes or side groups on the polymer chain, leading to the evolution of a cracking product and a charring polymer.

(d) Cross linking- formation of a chain network, this often occurs for thermosetting polymers when heated.

2.4.4 Catalytic Pyrolysis

Catalyst speeds up chemical reaction but remains unchanged towards the end of the process. When catalyst is used, the activation energy of the process is lowered down, thus speeds up the rate of reaction. Therefore, catalyst reduces the optimum temperature required and this is very crucial since the pyrolysis process requires high energy (highly endothermic) that hinders its commercial application (Miandad *et al.*, 2016). The usage of catalyst may help in saving energy as heat is one of the most expensive costs in industry. Besides that, catalyst has been used by many researchers for product upgrading to improve the hydrocarbon distribution in order to obtain pyrolysis liquid that has similar properties to the conventional fuel such as gasoline and diesel. Figure 2.5 shows comparison between thermal and catalytic pyrolysis.

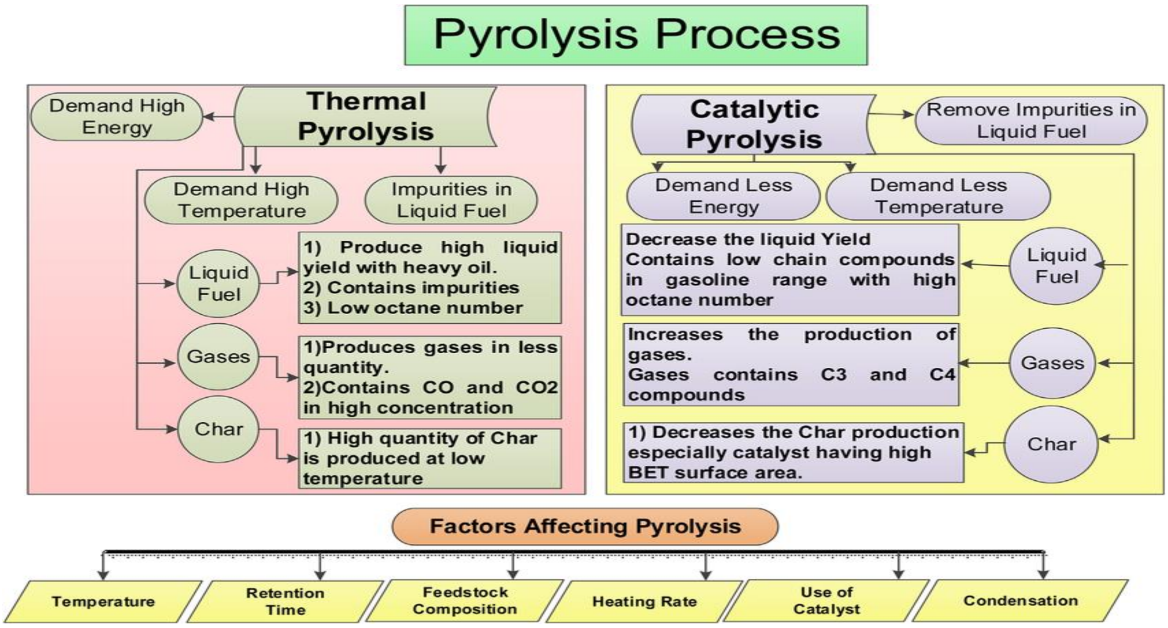


Figure 2.5 Comparison of thermal and catalytic pyrolysis (Miandad, 2016)

The initial stage of catalytic pyrolysis, thermal cracking occurs on the external surface of a catalyst. The internal porous structure of the catalyst act as channels for selective movement and breakdown of larger compounds into smaller ones (Lee, 2009). Because of the small pores of the catalyst gases are mainly produced inside the pores and wax production is due to external cracking on the external site of the catalyst (Liu, 2000; Mastral *et al.*, 2006). Degradation of high olefin molecules occur in the outer surface of the catalyst, further degradation and product selectivity take place in the internal pores of the catalyst.

2.5 Reaction Mechanism for Plastic pyrolysis

2.5.1 Catalytic mechanism of Polyethylene

The mechanism of the process which involves the formation of carbenium ion (isomerization, random chain scission and β cleavage, hydrogen transfer, oligomerization/alkylation, aromatization) is influenced by the strength, density and distribution of the acid sites of the catalyst. These determines the products obtained in the pyrolysis reactions (Serrano, 2005).

The catalytic decomposition of the HDPE occurs following the carbonium ion mechanism. The initial step occurs either by abstraction of the hydride ion (for Lewis acid sites) or by addition of a proton (the Bronsted acid sites) in the C-C bonds of polyethylene molecules or by thermal decomposition of polyolefins. Successive scission of the main chain occurs to produce fragments having lower molecular weights than that of polyethylene, the resulting fragments are cracked in subsequent steps (Park, 1999). The acid sites on the catalyst surface are responsible for the initiation of the carbocation mechanism, which induces the degradation of HDPE. The acid sites originate from the load imbalance AlO_4^- incorporated in the structure of the clay catalyst. The content of AlO_4^- determines the number of acid sites in the catalyst while topological factors related to its crystalline or amorphous structure influence the strength of these acidic sites (Aguado, 2007).

The catalytic effects of catalysts in oil cracking are due to their acidic properties and is explained by carbonium ion theory (Gates *et al*., 1979). The catalytic mechanism involves the following**:**

Initiation- Initiation may occur on some defect sites of the polymer chains. For instance, an olefinic linkage could be converted into an on-chain carbonium ion by proton addition:

$$–CH_2CH_2CH\_CHCH_2CH_2– + HX \longrightarrow –CH_2CH_2 + CH{=}CHCH_2CH_2 + X^- \tag{2.1}$$

Then the polymer chain may be broken up through ß-scission:

$$–CH_2CH_2C^+HCH_2–CH_2CH_2{=} \longrightarrow –CH_2CH_2CH{=}CH_2 + C^+\ H_2CH_2– \tag{2.2}$$

Initiation may also take place through random hydride ion abstraction by low molecular weight carbonium ions (R^+)

$$-CH_2CH_2CH_2CH_2CH_2CH_2- + R^+ \longrightarrow -CH_2CH_2{}^+CHCH_2CH_2CH_2- + RH \tag{2.3}$$

The newly formed on- chain carbonium ion then undergoes ß-scission as in equation 2.2

Depropagation- The molecular weight of the main polymer chains is reduced through successive attacks by acidic sites or other carbonium ions and chain cleavage, yielding an oligomer fraction (approximately C_{30}-C_{80}). Further cleavage of the oligomer fraction by direct ß-scission of chain end carbonium ion leads to gas formation and a liquid fraction (approximately C_{10}-C_{25}).

Isomerization -The carbonium ion undergoes rearrangement by hydrogen- or carbon-atom shifts leading to a double bond isomerization of an olefin:

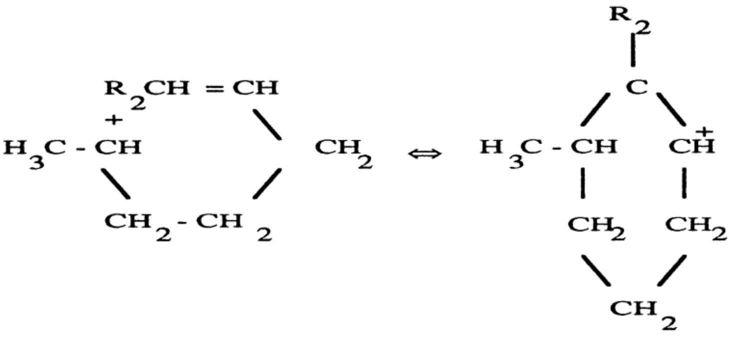
$$CH_2{=}CH{-}CH_2{-}CH_2{-}CH_3\ \mathbf{H^+} \longrightarrow CH_3{=}CH{-}CH_2{-}CH_2{-}CH_3\ \mathbf{-H^+} \longrightarrow CH_3{-}CH{=}CH{-}CH_2{-}CH_3 \qquad (2.4)$$

Other important isomerization reactions are methyl-group shift and isomerization of saturated hydrocarbons.

Aromatization- Some carbonium ion intermediates undergo cyclization reactions. The hydride ion abstraction first takes place on an olefin at a position several carbons removed from the double bond, the result is the formation of an olefinic carbonium ion:

$$R_1^+ + R_2CH \longrightarrow -CH{-}CH_2CH_2CH_2CH_2CH_3 \longleftrightarrow R_1H + R_2CH \longrightarrow -CHCH_2CH_2CH_2C^+HCH_3 \qquad (2.5)$$

This carbonium ion undergoes intramolecular attack on the double bond:

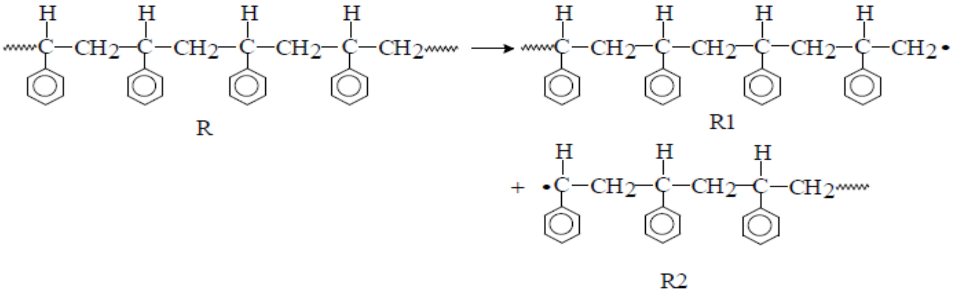


(2.6)

These reactions provide a route to cyclization and formation of aromatics.

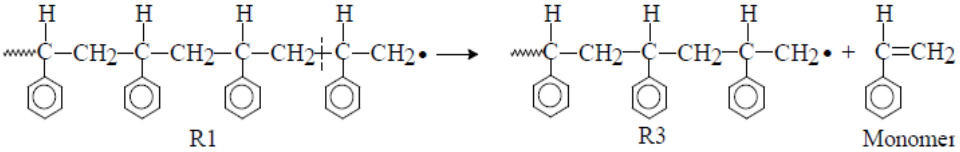
2.5.2 Thermal decomposition of polystyrene

Polystyrene decomposes to produce free radicals R1 and R2 by random chain-breaking (equation 2.7).

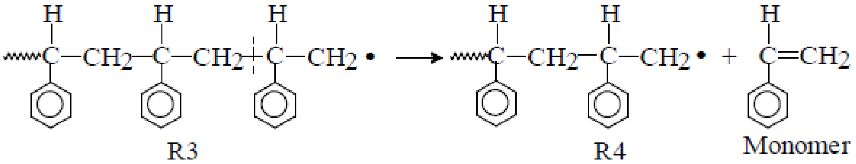


(2.7)

The large free radicals continue to decompose to form styrene monomer and other radical R3 and R4 which have shorter carbon chain (equations 2.8 and 2.9).

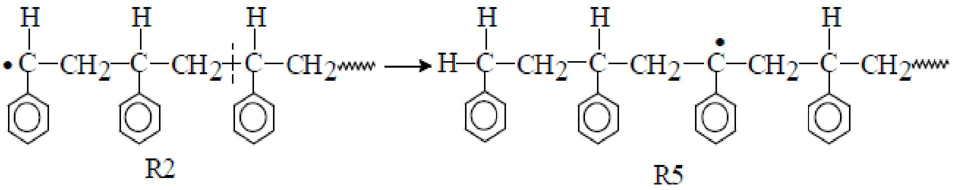


(2.8)



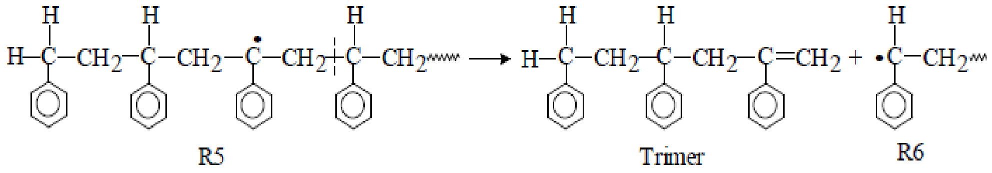
(2.9)

1,5- hydrogen transfer reaction occurs in the free radical R2. The hydrogen radical produced by the breaking of main chain C-H bond combines with 1 carbon radical to form R5 (equation 2.10).



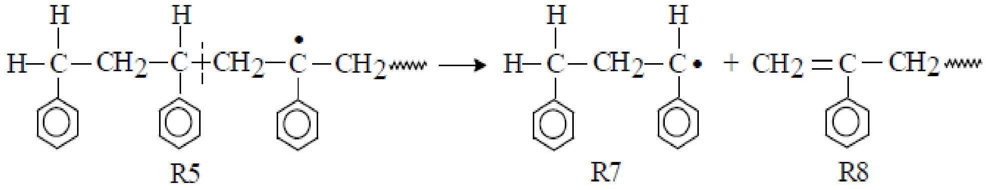
(2.10)

R5 decompose to generate the styrene trimer and radical R6 (equation 2.11).



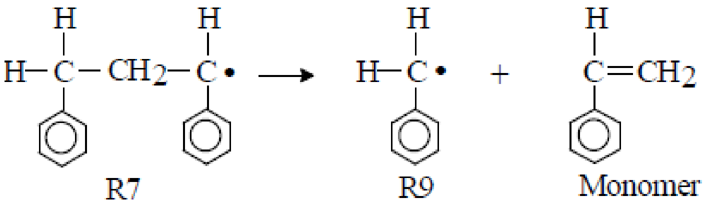
(2.11)

R5 produces the styrene dimer through the scission, combination and dehydrogenation process (reactions 2.12 to 2.15). R5 decomposes to form radical R7 and polymer R8 which contain the terminal double bond (equation 2.12).



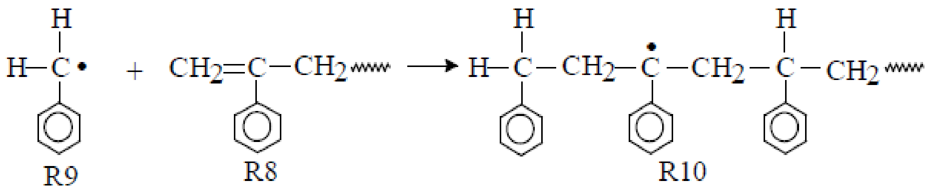
(2.12)

R7 undergoes scission and subsequent 1,3- hydrogen transfer reaction to obtain benzyl R9 and styrene monomer (equation 2.13)

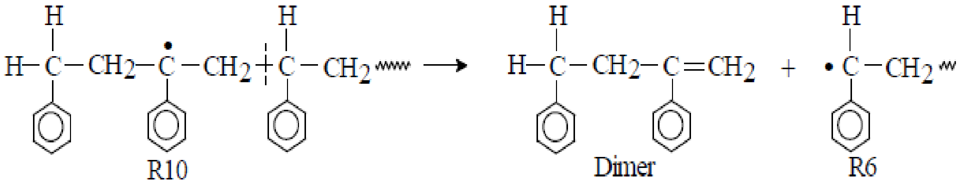


(2.13)

The addition reaction between benzyl R9 and polymer R8 form radical R10 (equation 2.14), which generates the styrene dimer by the scission and dehydrogenation reaction (equation 2.15).

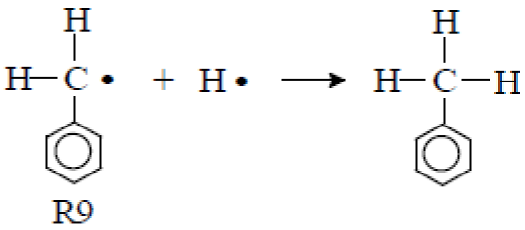


(2.14)



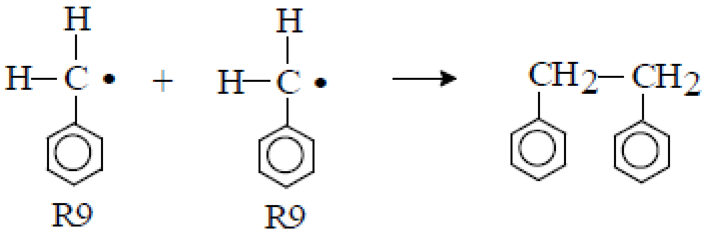
(2.15)

There are some small molecular species with low content such as toluene, diphenyl methane, 1-2-diphenyl propane and allyl benzene which are formed beside the main products during the decomposition process. These products are generated by the reaction among benzyl, hydrogen radical and other free radicals.



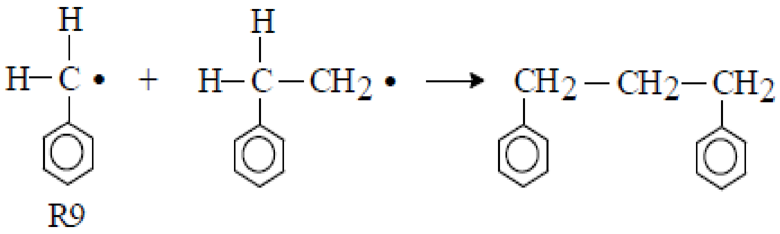
(2.16)

The reaction between benzyl R9 and hydrogen radical gives toluene (equation 2.16).



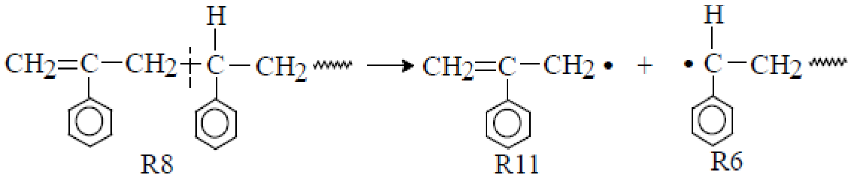
(2.17)

Combination of two benzyl R9 radicals generate diphenyl ethane (equation 2.17). The reaction between benzyl and the radical formed by chain scission gives diphenyl propane (equation 2.18).

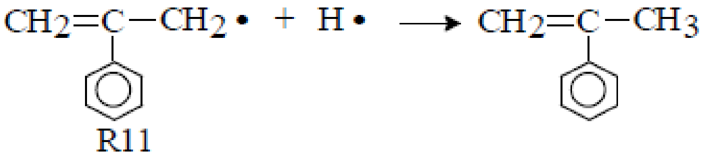


(2.18)

The radical R11 formed by the scission of polymer R8 react with hydrogen radical to produce allyl benzene (equations 2.19 and 2.20).



(2.19)



(2.20)

2.6 Thermal and Catalytic Pyrolysis of Plastic Waste

Miandad *et al.,* (2016) evaluated the factors affecting pyrolysis process such as the temperature, retention time, feedstock composition and the use of catalyst in detail. Pyrolysis can be carried out via thermal or catalytic routes. However, there are certain limitations with the conventional thermal pyrolysis, where the whole process is temperature-dependent (Sadaf *et al.*, 2015; Tahir *et al.*, 2015). The liquid oil from thermal pyrolysis may contain impurities and residues (Borsodi *et al.*, 2011). The thermal pyrolysis of different types of plastic has been carried out extensively in the past, including PE (Murata *et al.*, 2004; Cha *et al.*, 2002), PP (Dolezal *et al.*, 2001; Kim and Kim, 2004) and PS plastics (Faravelli *et al.*, 2001; Cha *et al.*, 2002). Moreover, only few studies have focused on PVC, PET, polymethyl methacrylate and polyurethane pyrolysis (Kaminsky *et al.*, 2004a; Miskolczi *et al.*, 2004). Thermal pyrolysis of PS was easily carried out in comparison to HDPE, LDPE and PP pyrolysis (Uddin *et al.*, 1997), as the PE (HDPE and LDPE) and PP require higher temperatures for degradation (Miskolczi *et al.*, 2009). PE is converted into wax instead of liquid oil. This applies in absence of a catalyst (Lee, 2012). The liquid oil produced by thermal pyrolysis is composed of large carbon link compounds (Lopez *et al.*, 2011c) and has low quality due to low octane number, presence of high solid residues (Kim and Kim, 2004; Seth and Sarker, 2004) and impurities such as nitrogen, phosphorous sulphur and chlorine (Miskolczi *et al.*, 2009). Thermal pyrolysis of PE type plastics such as HDPE and LDPE along with PP are difficult to conduct due to their crossed chain hydrocarbon structures (Achilias *et al.*, 2007).

A range of catalysts have been utilized, including Red Mud (Lopez *et al.*, 2011a), FCC (Lee, 2009), ZSM-5 (Lopez *et al.*, 2011a), HZSM-5 (Hernandez *et al.*, 2007), Y-zeolite (Lee, 2012), Fe_2O_3 (Sarker and Rashid, 2013), Al_2O_3, $Ca(OH)_2$ (Sarker *et al.*, 2011a,b) and natural zeolite (Syamsiro *et al.*, 2014), in catalytic pyrolysis to improve the quality of liquid oil (Wang and Wang, 2011). The catalysts increase the lighter fractions in the liquid oil such as gasoline (Lerici *et al.*, 2015), and decrease the overall process energy-inputs (Lopez *et al.*, 2011a). For instance, the use of ZSM-5 catalyst decreased the impurities such as solid residue, sulphur, nitrogen and phosphorous in the produced liquid oil (Miskolczi *et al.*, 2009). It is also reported that the use of catalysts with a high BET surface area allows more contact between reactants and the catalyst surface, resulting in an increased rate of cracking reaction to produce more gases than liquid oil (Syamsiro *et al.*, 2014). The conversion rate was increased at low temperature in catalytic conditions in comparison to thermal pyrolysis (Ding *et al.*, 1997; Park *et al.*, 1999; Lee, 2001). Catalytic pyrolysis has the potential to convert 70-80% of plastic waste into liquid oil that has similar characteristics to conventional diesel fuel; such as the high heating value (HHV) of 38–45.86 MJ/kg, a density of 0.77–0.84 g/cm^3, a viscosity of 1.74 –2.5 mm^2/s, a kinematic viscosity of 1.1–2.27 cSt, a pour point of (−9) to (−67) ℃, a boiling point of 68–352 ℃, and a flash point of 26.1–48 ℃. Thus, the liquid oil obtained from catalytic pyrolysis being of higher quality is useful in different energy-related applications including transport fuel, electricity generation and heating source. By-products obtained from the process like char is used as an adsorbent material in removal of heavy metals, polluted air, pollutants and odour from waste water. Gases produced are used as energy carriers.

Although catalytic pyrolysis is more advantageous, still it has some limitations such as catalyst costs, increased parasitic energy demand and less reuse of catalyst. Scientists have recommended a number of solutions to avert these problems including catalyst regeneration, exploration of cheaper catalysts, overall process optimization etc. This research solves the limitation of catalyst cost by exploring a cheaper clay catalyst.

2.7 Catalytic Pyrolysis Using Natural and Synthetic Zeolite Catalysts

Catalytic pyrolysis of various plastic wastes in the presence of natural and synthetic zeolite catalysts was examined using a small pilot scale reactor. The catalytic pyrolysis of polyethylene (PE), polypropylene (PP), polystyrene (PS) and their mixtures in different ratios was commissioned (Miandad *et al*., 2017). The prepared sample of feedstock was put into the heating reactor/chamber for pyrolysis. In each experiment, the feedstock was heated to 450 ℃ with the heating rate of 10 ℃ per min and retention time of 75 min. The catalytic pyrolysis of mixed plastic wastes in different ratios was conducted with both natural and synthetic zeolite catalysts separately. At the end of each experiment, the obtained yield was calculated by measuring the fractions of liquid, gases and char on a weight basis. The obtained liquid oil was further characterized to determine the effect of feedstock composition in the presence of natural and synthetic zeolite catalysts. PS plastic waste resulted in the highest liquid oil yield of 54% using natural zeolite and 50% using synthetic zeolite catalysts. Mixing of PS with other plastic wastes showed reduced liquid oil yields as compared to single PS feedstock in all the cases, except for slightly higher oil yields obtained in PS/PE/PP and PS/PE/PP/PET samples with synthetic zeolite catalyst. The mixtures of PE and PP yielded higher liquid oil as compared to single PE or PP feedstocks. In mixed plastic wastes, the highest liquid oil yield of 60% was obtained from PS/PE/PP with the ratios of 50/25/25% sample with synthetic zeolite, and the lowest yield of 18% was from PP/PE (50/50%) sample with natural zeolite catalysts. The highest gases (69.2%) and char (25.5%) yields were from PP/PE (50/50%) and PS/PE (50/50%) with natural zeolite catalyst.

The GC–MS analysis revealed that the pyrolysis liquid oils from all samples mainly consisted of aromatic hydrocarbons with a few aliphatic hydrocarbon compounds. The types and amounts of different compounds present in liquid oils vary with some common compounds such as styrene, ethylbenzene, benzene, azulene, naphthalene, and toluene. The FT-IR data also confirmed that liquid oil contained mostly aromatic compounds with some alkanes, alkenes and small amounts of phenol group. The produced liquid oils have high heating values (HHV) of 40.2–45 MJ/kg, which are similar to conventional diesel. The liquid oil has potential to be used as an alternative source of energy or fuel production.

Considering the economic optimization of the process, natural zeolite was used as a cheaper catalyst due to its availability along rivers for various plastic waste catalytic pyrolysis in this study. The natural zeolite catalyst's low BET surface area, microporous structure and low acidity affect its catalytic activities. According to Miandad *et al.,* (2016) modification of the surface and structure of natural zeolite is needed to enhance its catalytic activities in the pyrolysis process. The modification of natural zeolite could be carried out by acid leaching, thermal treatment and wet impregnation, as the next step via physical or chemical treatments in order to increase its catalytic performance. For instance, Sriningsih *et al*., (2014) carried out doping of Ni, Ni-Mo, Co and Co-Mo metals on natural zeolite and observed that doping increased the catalytic properties of natural zeolite. Life cycle assessments (LCA) studies (Rathore *et al*., 2016) of different plastic waste types, catalytic process and products are vital for understanding the economic, technical and environmental aspects of catalytic pyrolysis and its upscaling and commercialization. For example, Wang *et al*,. (2015) investigated the LCA of pyrolysis process and concluded that pyrolysis is one of the optimum practices for plastic waste management among the waste disposal techniques. The study showed the potential of Saudi Arabian natural zeolite as an alternative promising cheap catalyst in pyrolysis technology. The Saudi Arabian zeolite had low acidity and microporous structure which enhanced its catalytic properties, this is also determined in this research for Kisumu county clay

2.8 Pyrolysis of different types of Plastics

Different types of plastics have different compositions that are normally reported in terms of their proximate analysis. Proximate analysis is a measure of the chemical properties of the plastic compound based on four particular elements which are moisture content, fixed carbon, volatile matter and ash content (Kreith, 1998). Volatile matter and ash content are the major factors that influence the liquid oil yield in pyrolysis process. High volatile matter favours the liquid oil production while high ash content decreases the amount of liquid oil, consequently increase the gaseous yield and char formation (Abnisa and Wan, 2014).

Cepeliogullar and Putun, (2013) have explored the potential of PET in pyrolysis process to produce liquid oil using fixed-bed reactor at 500 ℃. The heating rate was 10 ℃/min and nitrogen gas was used as the sweeping gas in this experiment. It was observed that the liquid oil yield was lesser than the gaseous product. The liquid oil obtained was 23.1 wt.% while the gaseous product was 76.9 wt. % with no solid residue left. The low liquid yield could be explained by the relatively low volatile content of PET around 86.83% in comparison with other plastics in which the volatile contents were all above 90%. Half of the oil composition contained benzoic acid which was around 49.93% based on the gas chromatography– mass spectroscopy (GC–MS) analysis. The acidic characteristic in pyrolysis oil was unfavourable due to its corrosiveness that deteriorated the fuel quality (Cepeliogullar and Putun, 2013). Besides that, benzoic acid was a general sublime that could clog piping and heat exchanger, thus need a serious attention if running in industrial scale (Wan, 2015 and Shioya *et al*., 2005).

Fakhrhoseini and Dastanian, (2013) reported liquid yield of 39.89 wt.%, gaseous was 52.13 wt.% and solid residue was 8.98 wt.% on PET pyrolysis. Therefore, it can be concluded that the liquid oil production from the PET pyrolysis obtained in the ranges of 23–40 wt.% while gaseous yield in the ranges of 52–77 wt.%. Based on these results, PET might be the most suitable plastic to be used in pyrolysis if gaseous product became a preference, for instance to provide energy supply to heat up the reactor at the desired temperature.

Ahmad *et al*., (2014) explored the catalytic pyrolysis study of HDPE using micro steel reactor. The pyrolysis temperatures were within 300– 400 ℃ at heating rate of 5–10 ℃/min. Nitrogen gas was used as the fluidizing medium. From the experiment, they found that the highest total conversion happened to be at 350 ℃ with liquid oil being the dominant product yield (80.88 wt.%). The solid residue was very high at 300 ℃ (33.05 wt.%) but the amount was reducing to 0.54 wt.% at the highest temperature of 400 ℃.

Kumar and Singh, (2011) did the thermal pyrolysis study of HDPE using semi-batch reactor at higher temperature range of 400–550 ℃. It was observed that the highest liquid yield (79.08 wt.%) and gaseous product (24.75 wt.%) obtained at temperature of 550 ℃ while wax started to dominate in product fraction at higher temperature of 500–550 ℃. The dark brownish oil obtained from the pyrolysis had no visible residue and the boiling point was from 82 ℃ to 352 ℃. This suggested the mixture of different oil component such as gasoline, kerosene and diesel in the oil that matched the properties of conventional fuel as shown in Table 2.5. Besides, the sulphur content in the HDPE pyrolytic oil was very low (0.019%) that made it cleaner to the environment.

Table 2.5: Comparison of HDPE pyrolytic oil and conventional fuel properties (Shafferina, 2016)

Type of oil	**Boiling point ℃**	**CV (MJ/kg)**
Gasoline	40–200	43.4–46.5
Kerosene	150–300	43.0–46.2
Diesel	150–390	42.8–45.8
HDPE pyrolytic oil	82- 352	42.9

Marcilla *et al*., (2009) have also studied the HDPE pyrolysis at 550 ℃ using batch reactor. The liquid oil yield was 84.7 wt.% and gaseous product around 16.3 wt.%. The above results showed higher liquid oil was obtained at high temperature. Further increase in temperature decreased the production of liquid oil and increased the gaseous products. This was because the process already surpasses the maximum thermal degradation threshold. According to Mastral *et al*., (2007) while investigating HDPE pyrolysis in a fluidized bed reactor at 650 ℃, he observed gaseous production was about 31.5 wt.% and liquid oil production was about 68.5 wt.%. This shows that the liquid was cracked to gaseous when further heated up at temperature above 550 ℃.

Miranda *et al*., (1998) conducted the pyrolysis of PVC in a batch reactor at temperature range of 225–520 ℃ and heating rate of 10 ℃/min. The experiment was done under vacuum and total pressure of 2 kPa was applied. Liquid oil obtained varied from 0.45 wt.% to 12.79 wt.% as the temperature increased. Tar accumulation was even higher than the liquid oil obtained and the amount kept increasing up to 19.6 wt.%. Toxic and corrosive Hydrogen chloride (HCl) was found to be the main product obtained from the experiment with the highest yield of 58.2 wt.%.

PVC was not preferable for pyrolysis as the production of liquid oil was minimal. Also, the reaction is very toxic to the environment as it releases harmful products (e.g., HCl and chlorinated compounds such as chlorobenzene in the pyrolysis liquid). In order to reduce chlorine amount in liquid oil, dichlorination process of PVC was done. This process could be achieved through several methods such as stepwise pyrolysis, catalytic pyrolysis and pyrolysis with adsorbents added to the PVC sample (Lopez et al., 2011). Hence, the pyrolysis of PVC required an additional cost when an extra dichlorination step was needed which was one of the disadvantages to the industry.

In a study conducted by Ahmad *et al.*, (2014) on PP pyrolysis within 250–400 °C using micro steel reactor, they summarized that the highest liquid oil was achieved at temperature of 300 °C around 69.82 wt.% with total conversion of 98.66%. The increase in temperature to 400 °C only reduced the total product conversion to 94.3% and increased solid residue from 1.34 to 5.7 wt.%. This indicates that coke formation started to dominate at higher temperature.

However, Sakata *et al.*, (1999) have explored the PP pyrolysis at higher temperature of 380 °C. They found higher liquid yield of 80.1 wt.%, 6.6 wt.% gaseous and 13.3 wt.% solid residue left. On the other hand, Fakhrhoseini and Dastanian, (2013) obtained higher liquid yield about 82.12 wt.% when performed PP pyrolysis at 500 °C. Nevertheless, further increase in temperature more than 500 °C only reduced the liquid yield collected. This was proven by Demirbas, (2004) who carried out the PP pyrolysis at extreme temperature of 740 °C in a batch reactor which resulted in 48.8 wt.% liquid yield, 49.6 wt.% gaseous and 1.6 wt.% char.

Onwudili *et al.*, (2009) investigated the pyrolysis of PS in a batch pressurized autoclave reactor at 300–500 °C for one-hour duration. The heating rate used was 10 °C/min and the experimental pressure given was 0.31 MPa up to 1.6 MPa. From the experiment, they found that the PS pyrolysis produced a very high liquid oil yield around 97.0 wt.% at optimum temperature of 430 ℃. The maximum amount of gas produced was only 2.5 wt.%.

Liu *et al.*, (1999) reported high yield of liquid oil (98.7 wt.% at 600 ℃) product in the pyrolysis of PS using fluidized bed reactor at temperature range of 450–700 ℃. Nevertheless, the amount of liquid oil produced was also considered high at lower temperature of 450 ℃ which was around 97.6 wt.% and it differed by only 1.1 wt.%. In the case when energy saving was the priority, lower temperature was preferable as it could reduce the energy cost incurred. Based on the study done by Demirbas, (2004), the liquid oil reduced to 89.5 wt.% when the PS pyrolysis was running at 581 ℃ in a batch reactor. Therefore, the PS pyrolysis was not recommended to run at temperature more than 500 ℃ to optimize the liquid oil production. It can be concluded from the various researches that, for thermal pyrolysis the temperature requirement is higher for optimum liquid oil production.

2.9 Definition of Clay and Clay Minerals

Clay is defined differently by people in different disciplines and workers based on its use, the nature of operations involved in its use and the purpose of the definition (Grimshaw, 1971). Some definitions on such bases are; “Clay is plastic when wet” (Grim, 1962), “Clay is any fine-grained natural earthy argillaceous material” (Grim, 1968). “Clay is any material whose particles are finer than 4μ” (Moore, 1989). Clay implies an earthy, fine-grained material which develops plasticity when mixed with limited amount of water (Mason, 1968). A concise definition by the American Ceramic Society is, “Clay is a fine-grained rock which, when suitably crushed and pulverized, becomes plastic when wet, leather-hard when dried and on firing is converted to a permanent rock-like mass (Lawrence, 1982). Clay is composed mainly of silica, alumina and water, frequently with appreciable quantities of iron, alkalis and alkaline earths (Ralph, 1968). Clay mineral is defined as a stony or earthy mineral aggregate consisting essentially of hydrous silicates of alumina, plastic when sufficiently pulverized and wetted, rigid when dry, and vitreous when fired at a sufficiently high temperature (Murray, 2004). They are essentially hydrous aluminous sheet silicates that are fine-grained with variable composition and water content (Hans and Andrei, 2004). They are crystalline in nature with layer silicates formed by condensation of sheets of linked Si $(OH)_4$ tetrahedra with those of linked M2-3$(OH)_6$ octahedra, as the basic structure (M is either a divalent or trivalent cation) (Theng, 1974). The grains are plate-shaped and slide over each other's surface thereby contributing to the smooth feel. They contain impurities that contribute to plasticity, melt and color (Zakin, 2001).

2.10 Occurrence of the Clay Minerals

Clay minerals may be formed from weathering process, diagenesis, metamorphism or hydrothermal process (Grimshaw, 1972; Weaver and Pollard, 1973). The nature of the formation process significantly affects the crystallinity and purity of clay and its associated minerals. Clays that are deposited and found at the site of formation are called primary clays while those formed and eroded to a different site after formation are called secondary clays (Theng, 1979). Clay mineral deposits occur either as a relatively pure concentration of the mineral or a mixture of clay minerals. The four major mineral groups with different chemical and mineral composition, physical structures, and crystal orientations include kaolin, smectites (or montmorillonites), illites, and palygorskite-sepiolite groups which occur in relatively pure concentrations (Hans and Andrei, 2004). Other mineral groups are chlorites and vermiculites which occur as mixtures with non-clay minerals such as shales (Murray, 2004).

Kaolin is one of the widely used clay materials for a large number of applications such as in ceramics, paper coating, paper filling, paint extender, rubber filler, cracking catalyst for cements, oil refinery and water treatment (Belver *et al.*, 2002; Caulcante *et al.*, 2005; Vaga, 2007; Salawudeen, 2007), cracking catalyst in the petroleum industry, use in water and oil-based paints, pencil heads, carrier of fertilizers, desiccants, and insecticides, among others (Murray, 2004). The percentage uses of kaolin in some of the technological industries are: paper filling and coating 45%; refractories and ceramic 31%, fiberglass 6%; cement 6%, rubber and plastic 5%, paint 3%, others 4% (Murray, 2002).

Kaolinite is the major mineral component of kaolin, which may usually contain quartz and mica and also less frequently feldspar, illite, montmorillonite, anastase, haematite, bauxite, zircon, rutile, kyanite, silliminate, graphite, attapulgite and halloysites. Kaolinite is a clay mineral with chemical composition $Al_2Si_2O_5(OH)_4$ (Belver *et al.*, 2002; Vaga, 2007). It is a layered silicate mineral comprising of one tetrahedral sheet linked through oxygen atoms to one octahedral sheet of alumina (Deer *et al.*, 1992). Kaolin is used as raw material to make zeolites and Al silicates for use as catalysts in refining of petroleum (Murray, 1994). Halloysites are used for manufacture of petroleum cracking catalyst (Murray, 2004).

2.11 Structure and Composition of Clay Mineral

The basic phyllosilicate structure is the presence of SiO_4 tetrahedral linked by sharing of three of the four oxygens to form sheets of pseudohexagonal network (Mason, 1968). Clay minerals are sheet structures basically composed of fine grains of silica-tetrahedral layers and alumina octahedron layers. Figure 2.6 and 2.7 show silica tetrahedral layers and alumina octahedral layers.

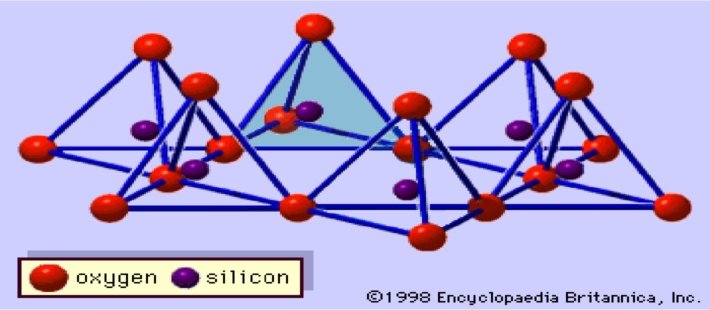


Figure 2.6: Silica tetrahedral layers (Encyclopaedia Britannica, 1998)

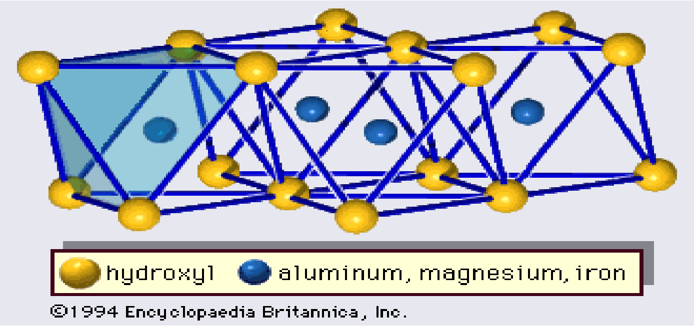


Figure 2.7: Alumina-octahedron layer (Encyclopedia Britannica, 1994)

The grains are plate-shaped and slide over each other's surface hence cause the slippery property of clays (Zakin, 2001). The silica-tetrahedron and alumina-octahedron layers are combined differently in each clay mineral and this forms the basis of their identification and differentiation by x-ray diffraction. Each tetrahedron consists of a cation, T, coordinated to four oxygen atoms, and linked to adjacent tetrahedra by sharing three corners (the basal oxygen atoms, Ob) to form an infinite two-dimensional 'hexagonal' mesh pattern along the **a**, **b** crystallographic directions common tetrahedral cations are Si^{4+}, Al^{3+}, and Fe^{3+}.

In the octahedral sheet, connections between each octahedron, M, to neighbouring octahedra is made by sharing edges. The edge-shared octahedra form sheets of hexagonal or pseudo-hexagonal symmetry. Octahedral cations are usually Al^{3+}, Fe^{3+}, Mg^{2+}, and Fe^{2+}, but other cations, such as Li^{+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, V^{3+}, Cr^{3+}, and Ti^{4+} are identified. Octahedra show two different topologies related to (OH) position, i.e., the cis- and the trans-orientation

2.12 Clay as a Catalyst

Clays have very fine particles that yield very large-specific surface areas that are physically adsorptive and chemically surface-active. Many clay minerals carry excess negative electric charge owing to internal substitution of Si^{+4} by lower valent cations and thereby increase internal chemical reactivity in chemical combination and ion exchange. These characteristics contribute to the properties of clays which are of technical applications (Murray, 2004).

Clays are in general constituted essentially by minerals that are hydrous silicates of aluminum and/or magnesium, with significant amounts of iron, nickel, chromium and other cations in the crystalline structure as an isomorphic substitution (Murray, 2007). The peculiar crystalline structure of some clay minerals generates a capacity of reversible exchange with organic or inorganic cations and metal-organic (Murray, 2007). The exchange of specific cations can generate active centers in the clay minerals, making them catalysts, which can then be used for a large number of chemical reactions in industries.

The properties of clays, that make them useful as catalysts are

(a) The crystalline structure.
(b) The modification of the original crystalline structure in a controlled way.
(c) The anisometric morphology and small sizes of the particles quite adapted for use in catalysis.
(d) the change of its basal spacing by acid treatment and subsequent modification.

The classes of clay minerals include smectites (montmorillonite, saponite), mica (illite), kaolinite, serpentine, pylophyllite (talc), vermiculite and sepiolite (Shichi and Takagi, 2000). Clays have adsorption capabilities which result from a net negative charge on the structure of minerals and sorption properties attributed to their high surface area and high porosity (Alkan *et al*., 2004).

Atomic lattices of most clay minerals consist of two basic structural units, one consisting of closely packed oxygens and hydroxyls in which aluminium, iron and magnesium atoms are embedded in an octahedral combination so that they are equidistant from six oxygens or hydroxyls. The second unit is built of silica tetrahedrons arranged to form a hexagonal network that is repeated indefinitely to form a sheet of composition, $Si_4O_6(OH)_4$ hydrated aluminium silicates with very fine particle size, usually <2mm (Ralph, 1968). A layered structure is formed by the tetrahedral sheet(s) linked to octahedral sheet through sharing of apical oxygens. The tetrahedra contain mainly Si (IV) as the central atom, while the octahedral sites are occupied mostly by Al (III), Fe (III) or Mg (II).

Clay minerals are sheet structures basically composed of fine grains of silica-tetrahedral layers and alumina octahedron layers. The basic phyllosilicate structure is the presence of SiO_4 tetrahedral linked by sharing of three of the four oxygens to form sheets of pseudo-hexagonal network (Mason, 1968).

The grains are plate-shaped and slide over each other's surface hence cause the slippery property of clays (Zakin, 2001). The alumina tetrahedron has a negative charge of -1, the aluminium has a valence of +3, which is less than the valence of +4 silicon. This charge is balanced by cations of alkali metals or alkaline earth metals (Na^+, K^+, Ca^{+2} or Mg^{+2}) present inside the porous clay structure by means of cation exchange. When these cations are exchanged for protons, clay acid sites are formed. This exchange allows modification of original properties of the clay. The acidity of the clay can be the

Bronsted acid type, proton donors or Lewis acid type, pair of electron acceptor (Manos G. , 2006).

2.13 Chemical Analysis of Kano Plains Clay

In this research, clay from Kano plains was used as a catalyst. According to Oswago, (2016) the major elements present in clays of Kano Plains, expressed in oxide form, are silica (SiO_2), Alumina (Al_2O_3), Iron (iii) oxide (Fe_2O_3) and water, H_2O. The other elements present in appreciable levels are potassium oxide, K_2O, sodium oxide, Na_2O titanium oxide, TiO_2 and calcium oxide, CaO, while those present in trace amounts are magnesium oxide, MgO and Manganese oxide, MnO. The clay was found to have appreciable amount of silica (50-56%) and alumina (12-17%) being requirements for a good pyrolysis catalyst.

Deductions from literature survey

According to the literature survey studied above the following gaps were identified in both thermal and catalytic pyrolysis of plastic waste:

- High cost of conventional catalysts
- Less reuse of catalyst after the pyrolysis process
- High energy demand for pyrolysis process
- Chemical and physical treatments of natural zeolite to increase catalytic activity.
- Oil from PET plastics contained corrosive benzoic acid
- HDPE oil had wax content
- Liquid Oil from PVC contained toxic and corrosive HCl

CHAPTER 3: METHODOLOGY

3.1 Materials/ Equipment

Specifications of apparatus and instruments include: Pulverizer (Retsch model No. Rs 200, at 1200rpm), Electronic weighing balance (Kernpu), Atomic Absorption Spectrophotometer (Shimadzu model No. AA 7000), X-ray diffractometer (Rigaku Miniflex 11) and X-ray fluorescence (Rigaku model No. ZSX primus 11). The current and voltage settings for analysis of the elements are done automatically by the ZSX software upon selection of the sample. Other equipment's are the Pelleting machine, Bomb calorimeter (Coshwania), Gas Chromatography - Mass spectrometer (GCMS QP 2010 SE) and Centrifuge (Hettich zentrifugen, at 2000 rpm). Round bottomed flasks, Liebig condenser, Oil collection flasks, Electric brick furnace with Thermocouple for temperature control, Rubber Tubing, Stands, Rubber corks, Density bottle, Thermometer and Viscometer.

Waste plastics: The plastics were collected locally from Nandi Hills town dumpsite as used detergent bottles (High density Polyethylene), used yoghurt cups (Polypropylene) and used packaging materials (Polystyrene). Manufacturers place an SPI code, or number, on each plastic product, usually moulded into the bottom. This guide provided the basic outline for the different types of plastic associated with each code number.

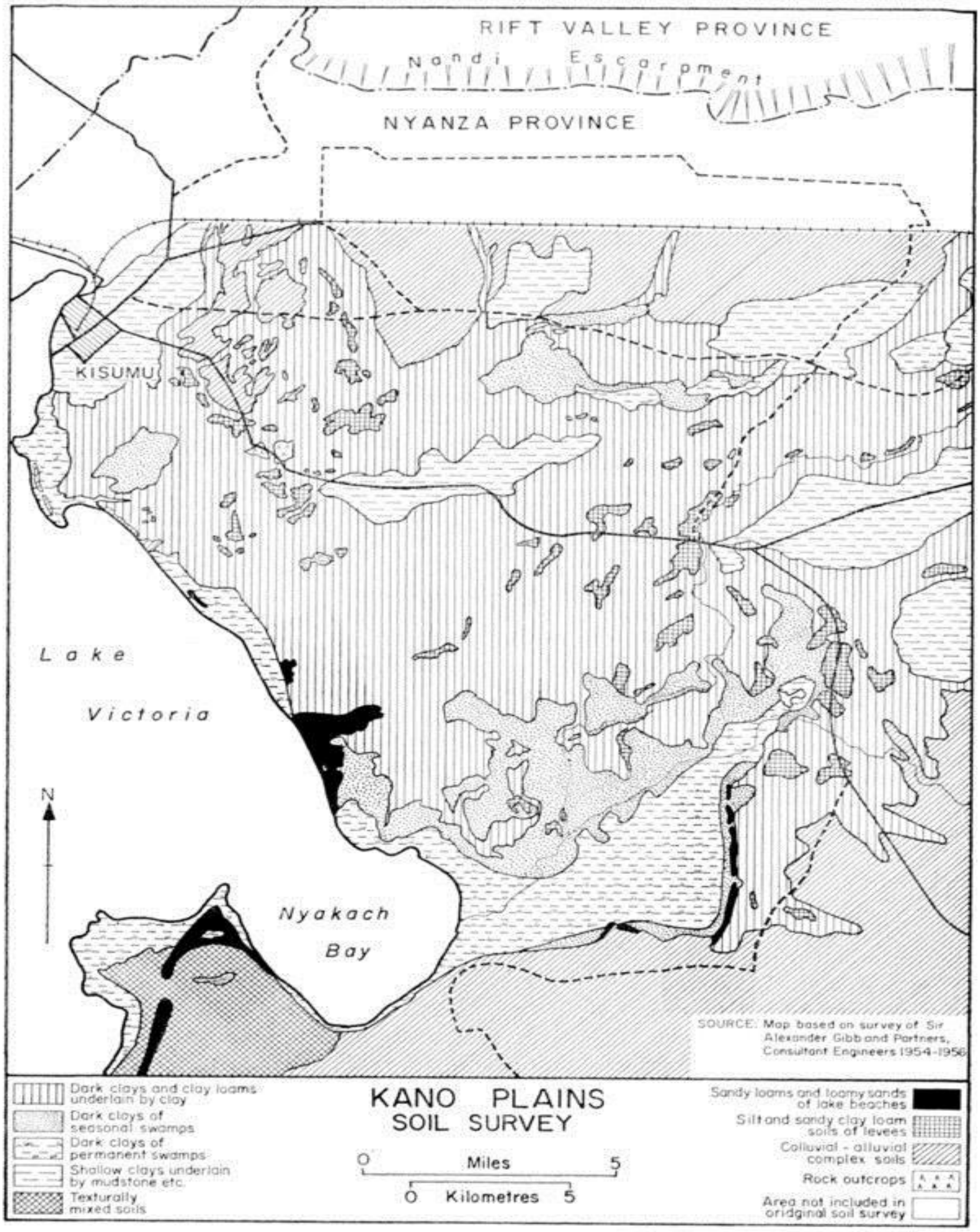
Catalyst: The clay soil from Kisumu county was used to pyrolyze the plastic wastes. The clay soil occur naturally along River Oren near Awasi town.

3.2 Catalyst Characterization

Characterization of the clay catalyst involved study of chemical composition, concentration of specific metal elements and crystallographic structure of the clay.

3.2.1 Collection of clay sample

Awasi town is located in Kano plains of Kisumu county at the junction between Kisumu-Kericho road. Figure 3.1 shows the soil map of Kano plains.



SOURCE: Map based on survey of Sir Alexander Gibb and Partners, Consultant Engineers 1954-1956

FIGURE 2

Figure 3.1: Soil survey maps for Kano plains, Kenya (Oswago, 2016)

The map reveal that the soils are majorly clay of different depths mixed sparingly with loams and a few areas with sandy soils. This is supported by the physical clay characteristics such as poor drainage which lead to flooding due to inability to absorb water leading to surface run-off, hardening and cracking of the soils during dry seasons and plasticity when wet. The clay soil was collected from the river banks of River Oren near Oren market in Awasi. The ground was cleared of vegetation and any organic matter. The soil was dug to approximately 60 cm to eliminate much of the organic matter and obtain the clay soil. About 5 Kg of clay soil was collected and kept in a clean container. The sample was dried in the sun for 7 days and then mixed thoroughly.

3.2.2 Clay sample Preparation

The collected clay soil was transferred into clean glass beakers, dried in the oven at 120 ℃ for 3 hours and then cooled in a desiccator. Dried clay sample was fed into a container and put inside the pulverizer for 2 minutes for grinding. Clay was ground into fine powder of size 400 µm suitable for use in XRD and XRF laboratory analysis (Norton, 1974, Richerson, 1992).

3.2.3 X-Ray Fluorescence Spectrophotometer (XRFS) Analysis

XRF analysis was used to determine the percentage composition of the elements in oxide form. Oven dried clay powder was accurately weighed in an electronic weighing balance and transferred into a clean dry porcelain crucible. Starch powder weighing 2g was added to the sample. The mixture was then ground and uniformly mixed into a fine powder using the pulverizer and then transferred into the pellet binder. Clay-starch mixture was placed into a compressor and compressed 175 KN to form clay pellets which were labelled and analyzed for mineral composition.

Clay pellets were fed into the sample holders in the XRF spectrometer and “EZ analysis” mode was selected from default program in the ZSX software, the element of choice was also selected. ZSX software had default calibrations for a given element to be analyzed and the analysis proceeded automatically upon the press of a button. The percentage composition of the element in oxide form was displayed on the screen. This procedure was repeated for the other elements on test and the results recorded.

3.2.4 X-Ray Diffraction (XRD) Analysis

XRD analysis was performed to determine the crystalline structure of the clay samples. Dried clay powder was fed into the cavity of the glass-walled sample holder of the spectrometer. Each sample holder had a capacity that held about 0.35 g of powdered sample after which the sample surface was flattened and compressed. Any extra sample remaining on the glass plate portion of the glass sample plate was wiped off using a clean paper soaked with alcohol.

The door on the front side of the XRD was opened and the glass sample plate mounted onto the designated position of the standard sample holder. After closing the door, the door knob was turned in clockwise direction to lock the door. X-ray diffractometer is then set to rotate the sample holder through angle θ while the detector rotates through 2 θ. X-rays of Cu αk wavelength 1.54056×10^{-10} m will be selected and used to scan the samples. Scans are taken between 2 θ of 10^{o} and 2 θ of 45^{o}. X-ray diffractometer produces signals on a screen and the names and formulae of the minerals are printed.

3.3 Design of catalytic pyrolysis experiment

In an experiment, one or more process variables (or factors) are changed in order to observe the effect the changes have on one or more response variables. The statistical design of experiments (*DOE*) is an efficient procedure for planning experiments so that the data obtained can be analysed to yield sound, valid, reliable and objective conclusions.

In this experiment Response surface design was applied, this is important in optimization of the experiments. Central composite design (CCD) contains an imbedded factorial or fractional factorial design with centre points that is augmented with a group of `star points’ or ‘axial points' that allow estimation of curvature. If the distance from the centre of the design space to a factorial point is ±1 unit for each factor, the distance from the centre of the design space to a star point is $\pm\alpha$ with $| \alpha | > 1$. The precise value depends on certain properties desired for the design and on the number of factors involved. A central composite design always contains twice as many star points as there are factors in the design. The star points represent new extreme values (low and high) for each factor in the design. To maintain rotatability, the value of α depends on the number of experimental runs in the factorial portion of the central composite design:

$\alpha = [\text{number of factorial runs}]^{1/4}$. For full factorial $\alpha = [2^k]^{1/4}$

where k – number of variables

In this experiment Design Expert software was used as it offers comparative tests, screening, characterization, optimization, robust parameter design, mixture designs and combined designs. The software determines the main effects of each factor as well as the interactions between factors by varying the values of all factors in parallel. A response surface model (RSM) was used to map out a design space using a relatively small number of experiments. RSM provides an estimate for the value of responses for every possible combination of the factors by varying the values of all factors in parallel making it possible to comprehend a multi-dimensional surface with non-linear shapes. The optimization feature was used to calculate the optimum operating parameters for the process (Robert, 2010). Factors affecting the liquid oil yield are temperature, catalyst amount and time of residence. Retention time has shown little effect on the quality of pyrolysis, the same yield of liquid oil has been observed at 30 min and 120 min retention times (Lopez *et al.*, 2011). The aromatic compounds present in liquid oil were similar at different retention time with the same temperature (Lee and Shin, 2007). Based on the above the independent variables chosen in this study were temperature and catalyst amount. The temperature range chosen was 158.58 ℃ – 441.42 ℃ and catalyst amount range was 2.93 wt.% - 17.07 wt.%, this was determined from literature review. Table 3.1 shows the independent variables and their levels in CCD.

Table 3.1: Independent variables and their levels in CCD.

Independent variables	**Codes**	**Variable levels**				
		-α =1.41421	-1	0	1	+α =1.41421
Temperature (^{0}C)	A	158.58	200	300	400	441.42
Catalyst amount (wt.%)	B	2.93	5	10	15	17.07

A total of 13 experiments, including 5 replications at the center point were conducted. Replicates at the center point give pure error. Experimental runs from design expert software are shown in Table 3.2.

Table 3.2: Experimental runs from Design Expert software

Std	**Run**	**Factor 1 A: Temp ℃**	**Factor 2 B: catalyst wt.%**	**response 1 Yield (mass %)**
11	1	300	10	
5	2	158.58	10	
13	3	300	10	
3	4	200	15	
2	5	400	5	
1	6	200	5	
8	7	300	17.07	
10	8	300	10	
12	9	300	10	
9	10	300	10	
4	11	400	15	
7	12	300	2.93	
6	13	441.42	10	

3.4 Experimental Setup

3.4.1 Waste plastic Sample Preparation

Waste Plastics were washed using tap water to remove dirt that was on the surface of the plastics. They were then sun dried to remove moisture that could interfere with pyrolysis process. The plastics were then chopped by a knife to the required particle size range of 5-8 mm, this is the average size for higher production of liquid oil. Smaller particle size results in higher gas yield. The feedstock was then ready for pyrolysis.

3.4.2 Preparation of catalyst

Clay soil was dried in an oven at 105 ℃ for 1 hour. The dried clay catalyst was crushed using a pulverizer. Powdered clay was sieved using 400 μm sieve to get a homogeneous fine powder.

3.4.3 Experimental procedure

The pyrolysis set up consisted of electric coil furnace, electric sensor connected to temperature control box, a round bottomed glass flask with arm, Liebig condenser, water and sample collection flask. Chopped plastics were mixed with the catalyst and put into the round bottomed flask for catalytic pyrolysis. In each experiment, 50 g of the HDPE feedstock was mixed with varying concentration of catalysts (2.93wt% - 17.07wt%) and heated by electric coil furnace in a reaction flask to a specific temperature (range of 158.58 ℃ - 441.42 ℃). Pyrolysis products were separated through condensation whereby the Liebig condenser was used to cool and condense the gases from the glass reactor, the vapors coming out after melting of the waste were passed through Liebig condenser and the liquid oil obtained was collected in a sample collection flask. The condensable gases produced liquid oil upon cooling while uncondensed gases produced during the experiment were left to escape to the atmosphere. At the end of each experiment, the mass of gas (non-condensable) was obtained by subtracting the mass of liquid oil and char from the total mass.

$m_g = m_t - m_l - m_c$ ……………………………………………………Equation 3.1

m_g – mass of gas, g

m_t– total mass of plastic feedstock and catalyst, g

m_l– mass of liquid oil, g

m_c– mass of char, g

The procedure was repeated for the other plastic types PP and PS at different temperature levels (158.58 ℃ – 441.42 ℃) and amount of catalyst (2.93wt% - 17.07wt%) as shown in table 3.2. Figure 3.2 show the experimental set up of the experiment. Batch reactor was used in the pyrolysis process because the reactor is better for producing small amounts of products while still in testing phase.

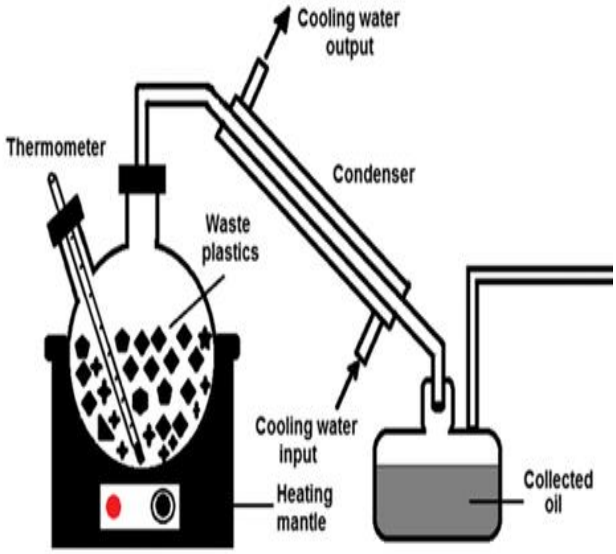


Figure 3.2: Plastic waste pyrolysis set-up

3.5 Analysis of Plastic Waste Liquid Oil

Liquid oil produced by the catalytic pyrolysis of various plastic wastes was characterized by using Gas chromatography coupled with mass spectrophotometry (GC–MS) following the standard ASTM methods (Apha, 1998). Gas chromatography-mass spectrometry (GC-MS) of the produced liquid oil sample was carried out to find out its chemical composition.

3.5.1 GC-MS analysis for Liquid oil composition

The GC-MS (QP 2010 SE) used had the column specification as BPX5, 30m; 0.25 mm ID; 0.25 μm and the oven program was set at 50 ℃ for 1 minute; heating rate of 10 ^{0}C/minute to 250 ℃ for 25 minutes this is important to optimize the separation of the analyte. Helium was used as the carrier gas with a flow rate of 1 ml/minute, injection temperature of 200 ℃ and the injection mode was split, ratio 1:10. The split injection was applied at 250 ℃. The ion source and transfer line temperatures were 200 ℃ and 250 ℃, respectively. Interface temperature was 250 ℃, solvent cut-time of 2.5 minutes and a scan range between 50 – 600 m/z. The NIST 2014 library of standards was used to identify the molecules in the samples.

3.6 Determination of Fuel properties

The liquid fuel from plastic waste must meet certain quality specifications for it to be used as a fuel. In the United States, the fuel must meet the American Society for Testing and Materials (ASTM) requirements for petrol-diesel fuel standards ASTM D 975 and the standard in Europe is EN 590. Liquid oil was subjected to tests to ascertain the following fuel properties: calorific value, density, viscosity, flash point and freezing point.

1. Calorific value

Calorific value of fuel was determined using a Bomb Calorimeter. Bomb Calorimeter was used to assess the high heating value (HHV) of produced liquid oils by following the ASTM D 240 methods (Miandad *et al*., 2016b). The crucible of the calorimeter was filled with the 100ml of fuel and then ignited. This heats the surrounding water, and the initial and final temperatures were recorded using a thermometer. The calorific value was then determined using the heat balance. Heat given by the fuel is equal to the heat gained by the water.

$m_f x\ C_v = m_w\ x\ C\ x\ \Delta T$ .... Equation 3.2

where:

m_f - Mass of fuel, g

C_v - Calorific value, KJ/kg

m_w - Mass of water, g

C - Specific heat of water, j/kg K

ΔT - Change in temperature, ℃

2. Density

Density and specific gravity of liquid oil samples was determined using density bottle.

3. Viscosity

Viscosity is very crucial in petroleum industry since it determines how easy the oil can flow from the reservoir to the well during extraction process and also plays a crucial role in fuel injection process (Ahmad *et al*., 2014). Kinematic viscosity was measured by noting the time it takes oil to travel through the orifice of a capillary under the force of gravity using capillary U-tube viscometer.

4. Flash point

This is the lowest temperature that the vapors of a material will ignite when exposed to an ignition source. Flash point was determined experimentally by Flash point apparatus (Pensky Marten) which works by heating the liquid in a container and then introducing a small flame just above the liquid surface. 150 ml of the oil was placed in the Flash point apparatus, the sample was heated and gently stirred. The flame was introduced after every 2 ℃ rise, upto a temperature at which there is a flash or ignition is recorded as the flash point.

5. Freezing point

This is the lowest temperature at which the fuel remains free of solid hydrocarbon crystals that can restrict the flow of fuel through filters in the fuel system of an engine. The freezing point was determined using the freezing point apparatus. 50 ml of oil was put in a slightly slanted ice bag and placed in an orbital shaker, the temperature at which the oil solidified was recorded as the freezing point.

CHAPTER 4: RESULTS AND DISCUSSIONS

4.1 Introduction

The experimental results and discussions are outlined in this chapter. It is divided into four sections as per the research objectives. The first section is the results of elemental characterization of the River Oren clay catalyst. The second section is the results of laboratory experiments to study the effect of pyrolysis operating variables. The third section presents analysis of the pyrolysis fuel using GC-MS and the last section are the results for testing the pyrolysis oil for fuel characteristic properties.

4.2 Material characterization

XRF was used to determine the mineral composition of the clay and the results presented in oxide percentage. XRD was used to determine the mineral analysis, name, formula and crystallographic structure of the clay while AAS determined the concentration of specific metal elements in the clay.

4.2.1 XRF characterization

Clays from Kisumu County, Oren river was observed to have Silica (64.5%), alumina (16.3%) and Iron II oxide (9.3%) as the major elements. Other elements present are: Potassium oxide, Sodium Oxide, Titanium Oxide, Calcium Oxide, Magnesium Oxide and Manganese Oxide. Comparison is attributed to analysis of clay from Kano plains done by Oswago, 2016 (Silica 65.92% and alumina 19.55%). From the results, it was established that the clay has high composition of silica and alumina 64.5wt% and 16.3wt%, respectively and a SiO_2/Al_2O_3 ratio of 3.96, being requirements for a good pyrolysis catalyst. Table 4.1 gives the percentage composition of elements from XRF analysis.

Table 4.1: X-Ray Fluorescence Analysis Result

Component	**Result (mass %)**
Na_2O	1.9592
MgO	0.5597
Al_2O_3	16.3294
SiO_2	64.4654
P_2O_5	0.0721
SO_3	0.1052
Cl	0.0775
K_2O	4.3336
CaO	1.1729
TiO_2	0.7714
MnO	0.4677
Fe_2O_3	9.2879
ZnO	0.0304
Ga_2O_3	0.0068
As_2O_3	0.0023
Rb_2O	0.0205
SrO	0.0167
Y_2O_3	0.0123
ZrO_2	0.1526
Nb_2O_5	0.0508
BaO	0.0674
CeO_2	0.0382

Silica-alumina catalysts are amorphous catalysts having Lewis-acid sites as electron acceptors and Bronsted acid sites with ionizable hydrogen atoms. The acidity of the catalysts is determined by using mole ratio of SiO_2/Al_2O_3. Acidity of the catalysts affects the clay's reactivity, production yield and composition of liquid oil from pyrolysis of plastics Uddin, (1997). Artetxe *et al.*, (2013) proved that the ratio SiO_2/Al_2O_3 of zeolite catalyst highly affected the product fraction yield in pyrolysis process. Low ratio of SiO_2/Al_2O_3 indicated the high acidity of the catalyst. Miandad *et al.*, (2017) reported a SiO_2/Al_2O_3 ratio of 5.1 for Saudi Arabian natural zeolite and 9.2 for synthetic zeolite and the liquid oil production was 54% and 50% respectively. Sakata et al., (1996) also carried out the pyrolysis of HDPE by using three different types of silica alumina catalysts SA-1, SA-2, and ZSM-5. The obtained results indicated that SA-2 catalyst with lower acidity produced maximum quantity of liquid oil (74.3 wt.%), while ZSM-5 with higher acidity produced lower quantity of liquid oil (49.8 wt.%).

4.2.2 XRD characterization

The XRD analysis was performed on clay catalyst samples and results are presented in Figure 4.1(a), (b), (c) and (d). The major minerals are Anorthoclase $KAlSi_3O_8$, Albite $Na(AlSi_3O_8)$, Quartz SiO_2 and Mordenite $(Ca,Na_2,K_2)Al_2Si_{10}O_{24}.7H_2O$. The XRD pattern of the clay shows crystalline peaks at D(ang) = 3.758, 3.343 and 3.251 which revealed the presence of Anorthoclase. The crystalline peaks corresponding to position D(ang) = 3.696 and 3.207 showed that Albite mineral is available in the sample. The crystalline peak of quartz at D(ang) = 3.308 and 2.267. The crystalline peak at position D(ang) = 3.174 showed the presence of mordenite. The results agree with those reported on clay from Oren river showing crystalline structure (Nizami, 2016b). The results establish that the clay mineral is composed of tetrahedra of silica and alumina as structural components and are linked through oxygen atoms. Each oxygen atom is shared by two silicon or aluminium atoms, thus giving rise to a three-dimensional microporous structure (Manos G. , 2006). The crystalline microporous structure favor hydrogen transfer reactions and thereby make the catalyst suitable for high conversions at relatively low temperatures between 300 to 400 ℃ (Park, 1999). The silica-tetrahedron and alumina-octahedron layers are combined differently in each clay mineral and this forms the basis of their identification and differentiation by X-ray diffraction. Figure 4.1 (a), (b), (c) and (d) shows XRD analysis of clay. Table 4.2 (a) and (b) shows the crystalline peak list.

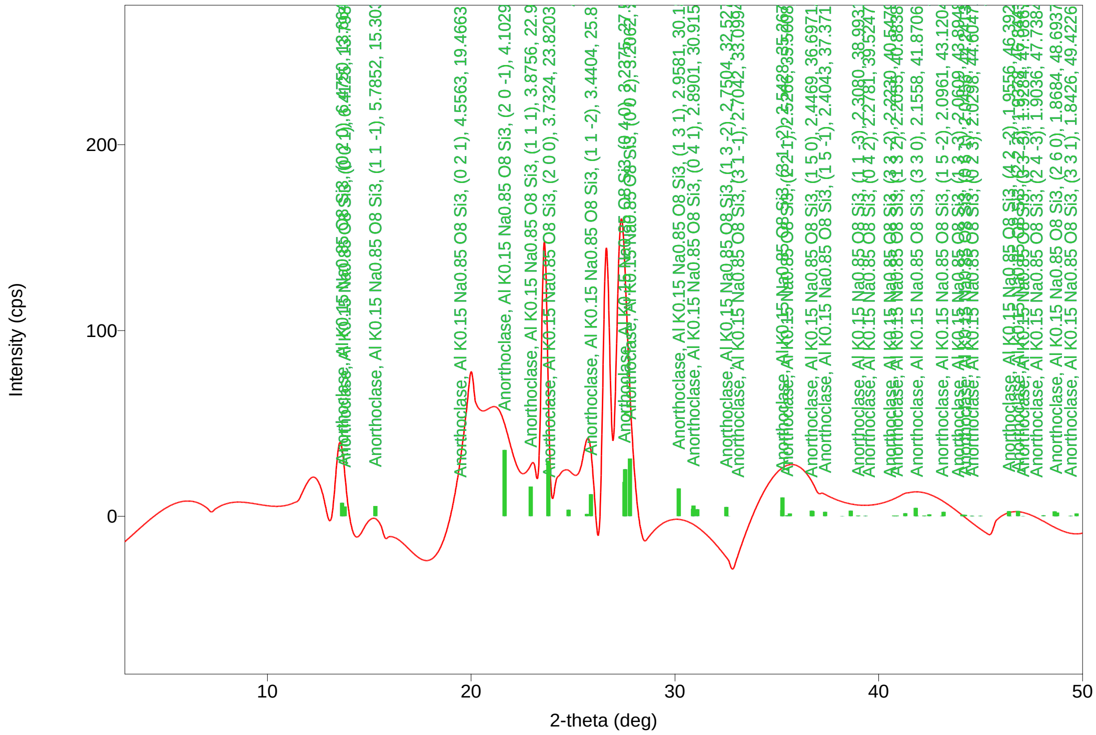


Figure 4.1(a): XRD analysis of clay

Table 4.2(a): Peak list

No.	2-theta (deg)	D (ang.)	Height (cps)	FWHM (deg)	Int. I (cps deg)	Int. W (deg)	Asym. Factor
1	13.6253	6.49353	18.634	0.709403	26.807	1.438610	1.28816
2	23.66(5)	3.758(8)	53(9)	1.5(3)	165(14)	3.1(8)	5(5)
3	26.6436	3.34295	40.8965	0.709403	58.8341	1.438610	1.28816
4	27.41(2)	3.251(3)	111(14)	0.71(7)	130(9)	1.2(2)	1.2(4)
5	34.92(7)	2.567(5)	47(9)	0.60(10)	43(7)	0.9(3)	1.3(6)

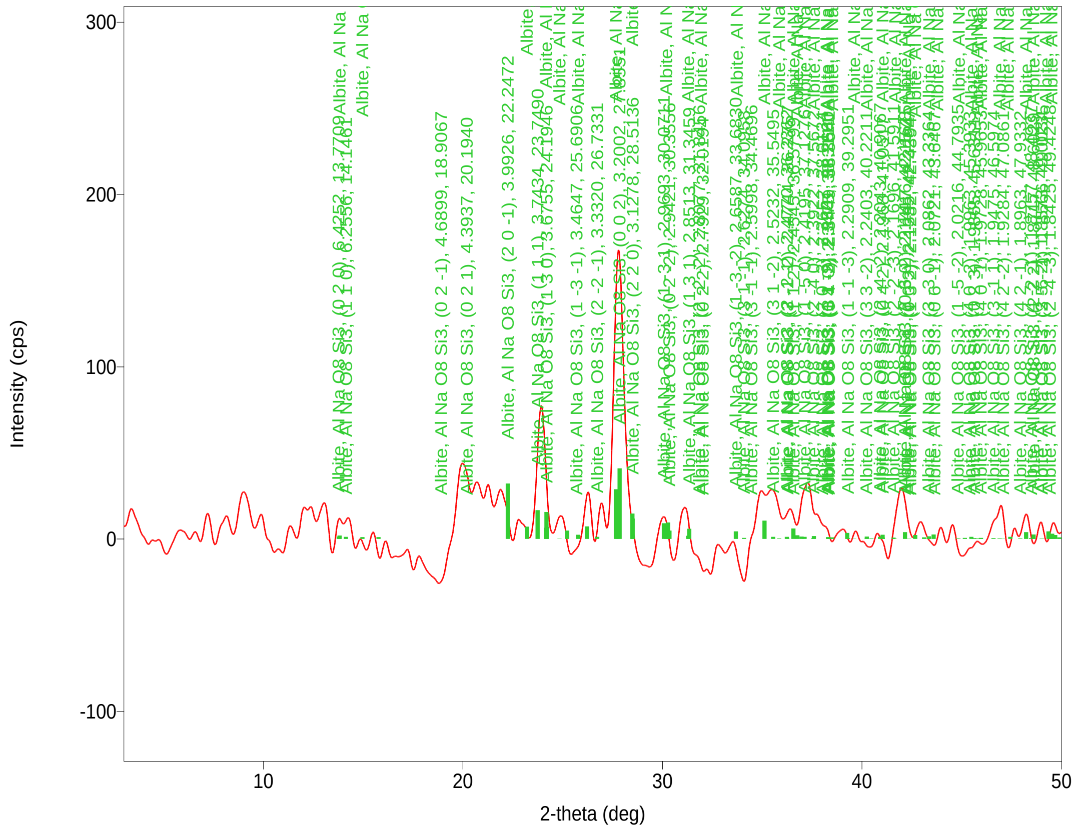


Figure 4.1(b): XRD analysis of clay

Table 4.2(b): Peak list

No.	2-theta (deg)	d(ang.)	Height (cps)	FWHM (deg)	Int. I (cps deg)	Int. W (deg)	Asym. Factor
1	8.9348	9.8890	17.230	0.1	4.05162	0.235148	1
2	20.134	4.4065	30.857	0.1	7.25615	0.235148	1
3	24.059	3.6958	54.354	0.1	12.7815	0.235148	1
4	27.792	3.2073	132.65	0.1	31.1929	0.235148	1
5	37.460	2.3988	25.531	0.1	6.00372	0.235148	1
6	42.055	2.1467	22.454	0.1	5.28002	0.235148	1
7	47.032	1.9304	13.236	0.1	3.11245	0.235148	1

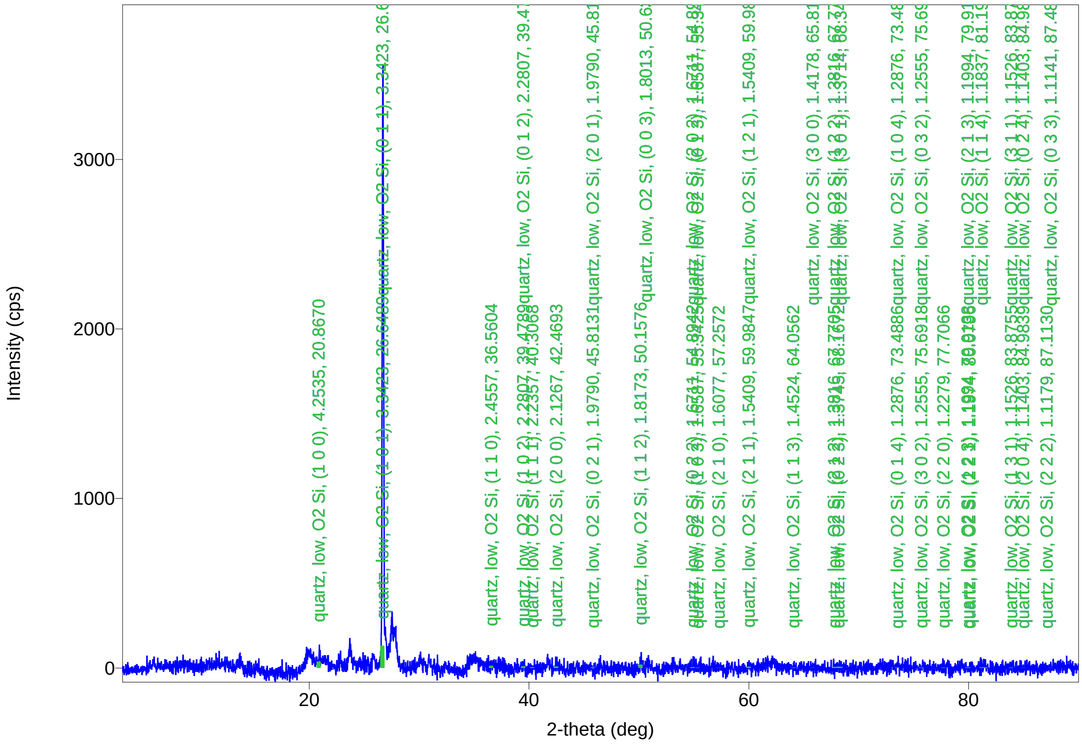


Figure 4.1(c): XRD analysis of clay

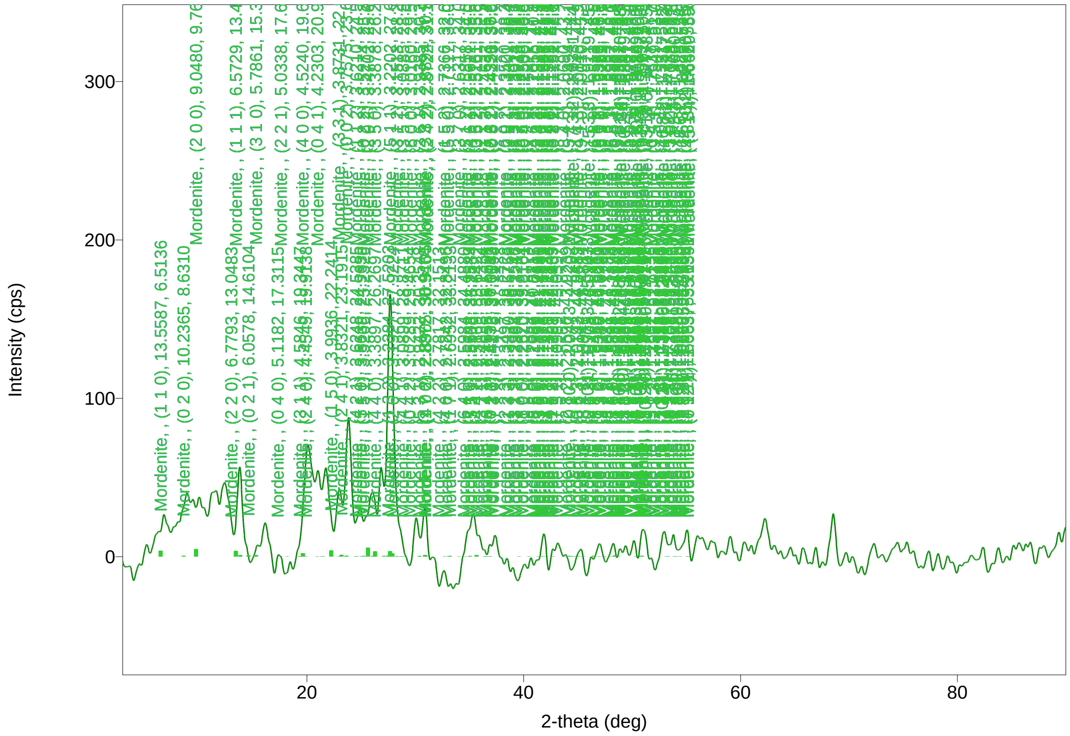


Figure 4.1(d): XRD analysis of clay

4.3 Optimization Studies

The second objective was to study the pyrolysis operating variables that is the catalyst concentration and reaction temperature on liquid oil yield. Optimization studies involved analyzing the process variables for maximum yield. Experimental data were fitted into the correlation, which was then plotted in surface and contour plots that depict the optimum conditions. The waste plastics identified for this research were High density polyethylene, polypropylene and polystyrene. The temperature requirement for thermal pyrolysis is higher for optimum liquid oil production. Table 4.4 is a summary of thermal pyrolysis done by researchers.

Table 4.4: Thermal pyrolysis of different types of plastic waste

Type of Plastic	**Temperature,** ℃	**Liquid yield, (mass%)**	**Researcher**
HDPE	550 ℃	79.08	Marcilla et al., 2009
HDPE	650 ℃	68.5	Mastral et al., 2007
PP	500 ℃	82.12	Fakhrhoseini, 2013
PP	740 ℃	48.8	Dermibas, 2004
PS	600 ℃	98.7	Liu et al, 1999
PS	581 ℃	89.5	Dermibas, 2004

4.3.1 Experimental design for HDPE

The pyrolysis temperatures varied from 158.6 ℃ to 441.2℃; and catalyst amount ranged from 2.93 wt.% to 17.07 wt.%. HDPE consists of long chain and follows the random chain scission mechanism during its thermal degradation, this requires relatively higher temperature it is for this reason that at temperatures below 200 ℃, there is no degradation of the waste plastic. From the experiment it was found that the highest total conversion happened at 300 ℃ and 10% catalyst concentration with liquid oil being the dominant product yield (87.23wt.%). The gaseous product was high at temperatures above 400 ℃ and the liquid oil yield decreased, this was mainly because the process had passed the maximum thermal degradation point. The increase in amount of catalyst does not give a direct proportionality in terms of its effectiveness in plastic pyrolysis. Increase in catalyst amount increases the conversion upto a particular limit, but a further increase in the catalyst percentage does not give any appreciable increase in the conversion rate.This effect of polymer to catalyst has also been studied by Akpanudoh *et al.* 2005 and observed the same.

During the catalytic pyrolysis, the polymer melts and is dispersed around the catalyst. The molten polymer is drawn into the spaces between the particles and the active sites on the external surface of the catalyst. The reaction rate is governed by the nature and strength of the acid sites involved in catalysis.

According to Marcilla *et al*., (2009) thermal pyrolysis of HDPE produced liquid oil yield of 84.7 wt.% at 550 ℃. Mastral *et al*., (2001) found that the liquid oil production from HDPE thermal pyrolysis at 650 ℃ was around 68.5 wt.%. This shows that the liquid was cracked to gas when further heated up at a very high temperature above 550 ℃.

It can be concluded that the main effect of catalyst addition in plastic pyrolysis is that the pyrolysis temperature for achieving the conversion is drastically reduced. Under non catalytic conditions a temperature above 550 ℃ is usually required; on the other hand, under catalytic conditions the pyrolysis temperature is lowered to 300 – 400 ℃

as observed in this study. Table 4.5 gives the details of 13 experiments in terms of actual levels as per CCD, and experimental and predicted liquid oil yields.

Table 4.5: CCD matrix with Liquid oil yield for HDPE waste plastics

Runs	Temp (℃)	Catalyst amount (wt%)	Liquid Yield (mass%)	Predicted Yield	Char (mass %)	Gas (mass%)
1	300	2.93	47.56	47.73	16.55	35.89
2	200	5	19.23	19.19	61.20	19.57
3	300	17.07	50.12	50.14	10.23	39.65
4	441.42	10	21.48	21.73	8.84	69.68
5	300	10	87.01	87.13	11.28	1.71
6	300	10	87.27	87.13	11.27	1.45
7	400	5	38.06	37.81	9.37	52.57
8	300	10	87.09	87.13	11.30	1.61
9	200	15	22.54	22.61	55.45	22.01
10	158.58	10	0	-2.18	98.54	1.46
11	400	15	37.96	37.81	10.02	52.02
12	300	10	87.27	87.13	11.26	1.47
13	300	10	87.02	87.13	11.40	1.58

Data in Table 4.5 were tested for fit for a linear, two-factor interaction, quadratic and cubic polynomials.

Yield = $87.13 + 8.45\,A + 0.8538\,B - 0.8525\,AB - 39.68\,A^2 - 19.10\,B^2$ ....Equation 4.1

Table 4.6 shows sequential model sum of squares.

Table 4.6: Sequential model sum of squares

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Mean vs Total	34581.30	1	34581.30			
Linear vs Mean	577.48	2	288.74	0.2445	0.7876	
2FI vs Linear	2.91	1	2.91	0.0022	0.9635	
Quadratic vs 2FI	**11805.28**	**2**	**5902.64**	**1.625E+05**	**< 0.0001**	**Suggested**
Cubic vs Quadratic	0.1167	2	0.0583	2.12	0.2154	Aliased
Residual	0.1376	5	0.0275			
Total	46967.22	13	3612.86			

Based on the F-value (1.625E +05) and p-value (0.0001), Quadratic model was suggested. Cubic was aliased.

Table 4.7 gives the Analysis of Variance (ANOVA)

Table 4.7: ANOVA for Quadratic model

Source	Sum of Squares	Df	Mean Square	F-value	p-value	
Model	12385.67	5	2477.13	68199.92	< 0.0001	Significant
A-Temperature	571.65	1	571.65	15738.55	< 0.0001	
B-Catalyst amount	5.83	1	5.83	160.56	< 0.0001	
AB	2.91	1	2.91	80.04	< 0.0001	
A^2	10407.48	1	10407.48	2.865E+05	< 0.0001	
B^2	2537.58	1	2537.58	69864.01	< 0.0001	
Residual	0.2543	7	0.0363			
Lack of Fit	0.1870	3	0.0623	3.71	0.1191	not significant
Pure Error	0.0673	4	0.0168			
Cor Total	12385.92	12				

Std. Dev.	0.1906	**R^2**	1.0000
Mean	51.58	**Adjusted R^2**	1.0000
C.V. %	0.3695	**Predicted R^2**	0.9999
		Adequate Precision	689.8064

The **Model F-value** of 68199.92 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise.

P-values less than 0.0500 indicate model terms are significant. In this case A, B, AB, A^2, B^2 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant.

The **Lack of Fit F-value** of 3.71 implies the Lack of Fit is not significant relative to the pure error. There is a 11.91% chance that a Lack of Fit F-value this large could occur due to noise. The lack of Fit was insignificant hence the model did fit.

The Predicted R^2 of 0.9999 was in reasonable agreement with the Adjusted R^2 of 1.0000; i.e. the difference is less than 0.2. Adequate Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 689.806 indicates an adequate signal. This model can be used to predict Yield as a function of variables A and B. Table 4.8 gives the values of coefficients for the model.

Table 4.8: Coefficients for the quadratic model

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	87.13	1	0.0852	86.93	87.33	
A-Temperature	8.45	1	0.0674	8.29	8.61	1.0000
B-Catalyst amount	0.8538	1	0.0674	0.6945	1.01	1.0000
AB	-0.8525	1	0.0953	-1.08	-0.6272	1.0000
A^2	-38.68	1	0.0723	-38.85	-38.51	1.02
B^2	-19.10	1	0.0723	-19.27	-18.93	1.02

All the terms were significant hence the model was:

$Yield\ = 87.13 + 8.45A + 0.8538B - 0.8525AB - 39.68A^2 - 19.10B^2$.........Equation 4.2

Predicted Liquid oil yields obtained from equation 4.1 is given in Table 4.5. Equation 4.2 can also be used for response surface plots.

4.3.2 Experimental design for Polypropylene waste plastics

The pyrolysis temperatures varied from 158.6 ℃ to 441.2 ℃ ; and catalyst mass % ranged from 2.93 wt.% to 17.07 wt.%. From this study, it was found that the highest total conversion happened at 300 ℃ with liquid oil being the dominant product yield (60.36 wt.%). The thermal degradation of Polypropylene waste plastics starts at around 240 ℃. The increase in temperature to 400 ℃ reduced the product conversion and increased the gaseous product. Demirbas, (2004) carried out the PP thermal pyrolysis at extreme temperature of 740 ℃ in a batch reactor which resulted in 48.8 wt.% liquid yield. Ahmad *et al*., (2014) on PP catalytic pyrolysis summarized that the highest liquid oil was achieved at temperature of 300 ℃ around 69.82 wt.% which is comparable to this study. Kim *et al.*, (2002) explained that natural zeolite with low BET surface area, microporous structure and low acidity support the initial degradation of PP that may increase gas production as observed. Table 4.9 shows the experimental liquid oil yield and predicted yield of Polypropylene plastics.

Table 4.9: CCD matrix with experimental liquid oil yield from PP waste plastics

Runs	Temp (℃)	Catalyst amount (wt%)	Liquid Yield (mass%)	Predicted Yield	Char (mass %)	Gas (mass%)
1	300	10	60.40	60.36	14.68	24.92
2	200	15	9.36	9.53	69.30	21.34
3	300	10	60.14	60.36	15.20	24.66
4	300	10	60.18	60.36	15.25	24.57
5	300	10	60.36	60.36	14.91	24.73
6	400	5	40.10	39.75	7.27	52.63
7	158.58	10	0	-5.05	98.72	1.28
8	300	10	60.72	60.36	14.34	24.94
9	300	2.93	43.82	43.99	6.18	50.00
10	441.42	10	38.01	38.38	10.18	51.81
11	200	5	20.71	20.77	55.75	23.54
12	300	17.07	44.68	44.69	16.36	38.96
13	400	15	52.20	51.97	18.55	29.25

Data in Table 4.9 were tested for fit for linear, two-factor interaction, quadratic and cubic polynomials.

$Yield, Y = 60.36 + 15.36A + 0.2458B + 5.86AB - 21.85A^2 - 8.01B^2$...Equation 4.3

Table 4.10 shows the result.

Table 4.10: Sequential model sum of squares

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Mean vs Total	22917.72	1	22917.72			
Linear vs Mean	1886.79	2	943.39	2.59	0.1243	
2FI vs Linear	137.48	1	137.48	0.3526	0.5673	
Quadratic vs 2FI	**3508.38**	**2**	**1754.19**	**19523.84**	**< 0.0001**	**Suggested**
Cubic vs Quadratic	0.3539	2	0.1770	3.22	0.1264	Aliased
Residual	0.2750	5	0.0550			
Total	28451.00	13	2188.54			

Based on the F-value (19523.84) and p-value (0.0001), quadratic model was suggested, and Cubic was aliased. Table 4.11 gives Analysis of Variance (ANOVA).

Table 4.11: ANOVA for Response Surface Quadratic model

Source	Sum of Squares	Df	Mean Square	F-value	p-value	
Model	5532.65	5	1106.53	12315.48	< 0.0001	Significant
A-Temperature	1886.31	1	1886.31	20994.25	< 0.0001	
B-Catalyst amount	0.4833	1	0.4833	5.38	0.0535	
AB	137.48	1	137.48	1530.08	< 0.0001	
A^2	3319.87	1	3319.87	36949.55	< 0.0001	
B^2	446.40	1	446.40	4968.36	< 0.0001	
Residual	0.6289	7	0.0898			
Lack of Fit	0.4169	3	0.1390	2.62	0.1873	not significant
Pure Error	0.2120	4	0.0530			
Cor Total	5533.28	12				

Std. Dev.	0.2997	**R^2**	0.9999
Mean	41.99	**Adjusted R^2**	0.9998
C.V. %	0.7139	**Predicted R^2**	0.9994
		Adeq Precision	321.1920

The Model F-value of 12315.48 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise.

P-values less than 0.0500 indicate model terms are significant. In this case A, AB, A^2, B^2 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. The Lack of Fit F-value of 2.62 implies the Lack of Fit is not significant relative to the pure error. There is a 18.73% chance that a Lack of Fit F-value this large could occur due to noise. Non-significant lack of fit is good.

The Predicted R^2 of 0.9994 is in reasonable agreement with the Adjusted R^2 of 0.9998; i.e. the difference is less than 0.2. Adequate Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 321.192 indicates an adequate signal. This model can be used to predict Yield as a function of the variables A and B. Table 4.12 gives the values of coefficients for the model.

Table 4.12: Coefficients for the full quadratic model

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	60.36	1	0.1341	60.04	60.68	
A-Temperature	15.36	1	0.1060	15.10	15.61	1.0000
B-Catalyst amount	0.2458	1	0.1060	-0.0048	0.4964	1.0000
AB	5.86	1	0.1499	5.51	6.22	1.0000
A^2	-21.85	1	0.1136	-22.11	-21.58	1.02
B^2	-8.01	1	0.1136	-8.28	-7.74	1.02

All the terms were significant hence the model was:

$$Yield, Y = 60.36 + 15.36A + 0.2458B + 5.86AB - 21.85A^2 - 8.01B^2 \text{......... Equation 4.4}$$

The predicted liquid oil yields obtained from Eqn 4.4 is given in Table 4.9. Eqn 4.4 can also be used for response surface plots.

4.3.3 Experimental design for Polystyrene waste plastics

The pyrolysis temperature varied from 350 – 550 °C; and catalyst mass ranged from 2.93 wt% to 17.07 wt%. From the experiment it was found that the highest total conversion happened at 450 °C with liquid oil being the dominant product yield (93.20 wt.%). Increasing the temperature further reduced the production of liquid oil and increased the gaseous product. PS plastic waste produced the highest amounts of liquid oil as compared to all other types of plastic waste in this study. Polystyrene degradation follows both end-chain and random chain scission mechanisms which enhance its degradation process.

Optimum temperature obtained is comparable to Onwudili *et al*, (2009) who investigated the pyrolysis of PS and found that very high liquid oil yield around 97.0 wt.% was reached at optimum temperature of 430 ℃. The high yield of liquid oil product was also supported by Liu *et al*., (1999) the amount of liquid oil produced was around 97.6 wt.% at a temperature of 450 ℃. Lee *et al.,* (2001) reported higher liquid oil yield from the catalytic pyrolysis of PS with natural zeolite, correlating it with low BET surface area, acidity, and microporous structure of natural zeolite. Based on the study done by Demirbas, (2004) the liquid oil reduced to 89.5 wt.% when the PS pyrolysis was running at 581℃ in a batch reactor, therefore, the PS pyrolysis was not recommended to run at temperature more than 500 ℃ to optimize the liquid oil production. Table 4.13 shows the experimental data of polystyrene waste plastics.

Table 4.13: CCD matrix with experimental liquid oil yield from PS waste plastics

Std	**Run**	**Temp** ℃	**Catalyst amount (wt.%)**	**Liquid Yield (mass%)**	**Predicted Yield**	**Char (mass%)**	**Gas (mass%)**
11	1	450	17.07	77.47	78.05	16.23	6.30
5	2	308.58	10	64.02	64.68	28.18	7.80
13	3	450	10	93.86	93.30	3.60	2.54
3	4	350	5	77.14	77.01	12.38	10.48
2	5	350	15	71.79	70.95	14.78	13.43
1	6	550	5	67.01	67.71	7.62	25.37
8	7	450	10	93.45	93.30	4.55	2.00
10	8	450	10	92.73	93.30	2.73	4.54
12	9	450	10	93.27	93.30	3.64	3.09
9	10	591.42	10	54.55	54.04	11.34	34.11
4	11	450	10	93.18	93.30	4.55	2.27
7	12	550	15	65.22	65.20	14.78	20.00
6	13	450	2.93	84.54	84.11	11.67	3.79

Data in table 4.13 were tested for fit for a linear, two-factor interaction, quadratic and cubic polynomials,

$Yield, Y = 93.30 - 3.76A - 2.14B + 0.89AB - 16.97A^2 - 6.11B^2$..........Equation 4.5

Table 4.14 gives the result.

Table 4.14: Sequential model sum of squares

Source	Sum of Squares	Df	Mean Square	F-value	p-value	
Mean vs Total	81327.46	1	81327.46			
Linear vs Mean	149.91	2	74.96	0.3540	0.7103	
2FI vs Linear	3.17	1	3.17	0.0135	0.9101	
Quadratic vs 2FI	**2110.86**	**2**	**1055.43**	**2377.82**	**< 0.0001**	**Suggested**
Cubic vs Quadratic	2.39	2	1.19	8.31	0.0257	Aliased
Residual	0.7183	5	0.1437			
Total	83594.51	13	6430.35			

Based on the F-value (2377.82) and p-value (0.0001), Quadratic model was suggested and Cubic was aliased. Table 4.15 gives Analysis of Variance (ANOVA).

Table 4.15: ANOVA for Quadratic model

Source	Sum of Squares	Df	Mean Square	F-value	p-value	
Model	2263.94	5	452.79	1020.10	< 0.0001	Significant
A-Temperature	113.20	1	113.20	255.02	< 0.0001	
B-Catalyst amount	36.72	1	36.72	82.72	< 0.0001	
AB	3.17	1	3.17	7.14	0.0319	
A^2	2003.40	1	2003.40	4513.54	< 0.0001	
B^2	259.72	1	259.72	585.14	< 0.0001	
Residual	3.11	7	0.4439			
Lack of Fit	2.43	3	0.8103	4.79	0.0821	not significant
Pure Error	0.6763	4	0.1691			
Cor Total	2267.05	12				

Std. Dev.	0.6662	**R^2**	0.9986
Mean	79.09	**Adjusted R^2**	0.9977
C.V. %	0.8423	**Predicted R^2**	0.9919
		Adequate Precision	86.7406

The Model F-value of 1020.10 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. P-values less than 0.0500 indicate model terms are significant. In this case A, B, AB, A^2, B^2 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. The Lack of Fit F-value of 4.79 implies there is a 8.21% chance that a Lack of Fit F-value this large could occur due to noise. The Predicted R^2 of 0.9919 is in reasonable agreement with the Adjusted R^2 of 0.9977; i.e. the difference is less than 0.2. Adequate Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 86.741 indicates an adequate signal. This model can be used to predict Yield as a function of variables A and B. Table 4.16 gives the values of coefficients for the model.

Table 4.16: Coefficients for the model

Factor	Coefficient Estimate	Df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	93.30	1	0.2979	92.59	94.00	
A-Temperature	-3.76	1	0.2355	-4.32	-3.20	1.0000
B-Catalyst amount	-2.14	1	0.2355	-2.70	-1.59	1.0000
AB	0.8900	1	0.3331	0.1023	1.68	1.0000
A^2	-16.97	1	0.2526	-17.57	-16.37	1.02
B^2	-6.11	1	0.2526	-6.71	-5.51	1.02

All the terms were significant, hence the model was:

$Yield, Y = 93.30 - 3.76A - 2.14B + 0.89AB - 16.97A^2 - 6.11B^2$..........Equation 4.6

Predicted liquid oil yields obtained from Eqn 4.6 is given in Table 4.13. Equation 4.6 can be used for response surface plots.

4.4 Optimization using Response Surface Methodology

Design expert software was used to determine the optimum conditions for HDPE, PP and PS waste plastics.

4.4.1 High density Polyethylene

Figure 4.2 gives a plot for Yield as a function of Temperature and Catalyst amount. The optima lies close to a temperature of 300 ℃ and Catalyst concentration of 10 wt.%. The observations made in RSM plots (Figure 4.2, 4.3 and 4.4) confirm that the experimental values were in agreement with the predicted values (Tables 4.5, 4.9 and 4.13).

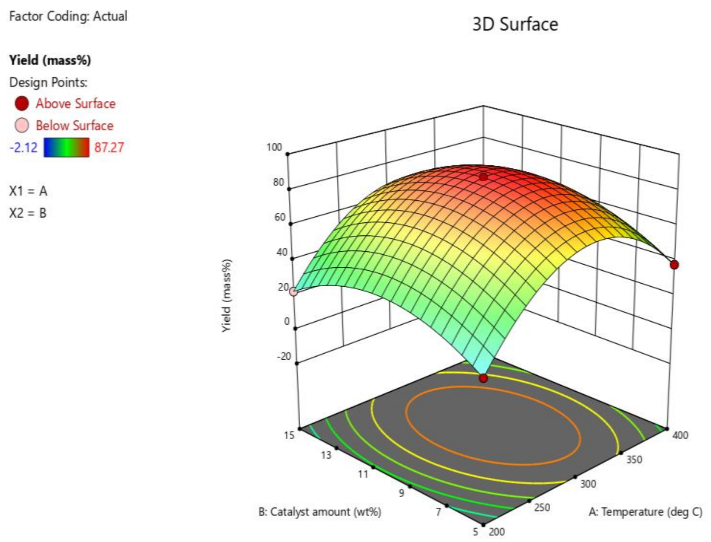


Figure 4.2: RSM plot for effect of catalyst concentration and Temperature on Yield for HDPE liquid oil

4.4.2 Polypropylene waste plastics

Figure 4.3 gives a plot for Yield as a function of Temperature and Catalyst concentration. The optima lies close to a temperature of 300 ℃ and catalyst concentration of 10 wt.

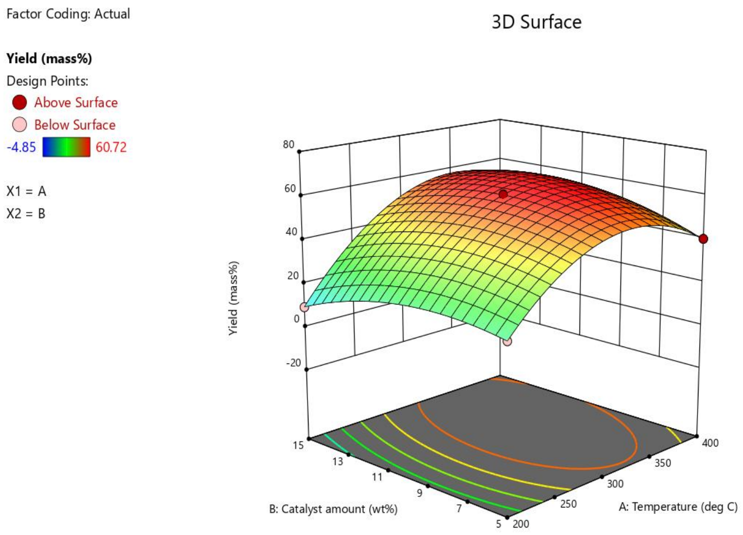


Figure 4.3: RSM plot for effect of catalyst concentration and Temperature on Yield for PP liquid oil

4.4.3 Polystyrene waste plastics

Figure 4.4 gives a plot for Yield as a function of Temperature and Catalyst amount. The optima lies close to a temperature of 450 ℃ and Catalyst concentration of 10 wt.%. The observations made in RSM plots confirm that the experimental values were in agreement with the predicted values.

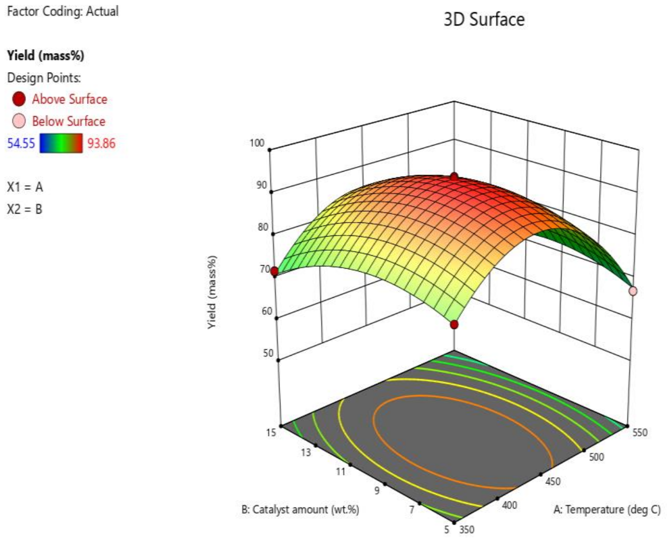


Figure 4.4: RSM plot for effect of catalyst concentration and Temperature on Yield for PS liquid oil

4.5 Analysis of the hydrocarbon composition in liquid fuel

4.5.1 Composition of liquid oils derived from the pyrolysis of waste plastics

The produced liquid oil by catalytic pyrolysis of different plastic wastes in the presence of natural clay catalyst showed different compounds as shown in Figures 4.5, 4.6 and 4.7. The GC-MS analysis revealed that the pyrolysis liquid oils from all plastic types mainly consisted of aromatic hydrocarbons, phenol group and aliphatic hydrocarbon compounds. The types and amounts of different compounds present in the liquid fuel varied with common compounds like toluene, benzene, styrene, ethylbenzene and naphthalene.

In gasoline production aromatics, naphthene and isoalkanes are highly desirable, whereas olefins and n-paraffins are less desired. Accordingly, it is desirable that the pyrolytic conversion of plastic wastes produces more aromatics, naphthene and iso-alkanes with carbon number in the range C_5–C_8.

4.5.2 Hydrocarbon composition for High density polyethylene pyrolytic oil

The study found that molecular composition of HDPE derived liquid oil showed high composition of n-Pentadecanol, 1-Tetradecene and 2,4-Dimethyl-1-heptene. This shows the presence of alcohols, alkenes and alkyl halides in the pyrolytic oil. During the catalytic pyrolysis there are two possible mechanisms for the degradation of HDPE; carbenium ion mechanism due to the attack of the proton or hybrid ion abstraction through Lewis acid sites (Rizzarelli *et al.*, 2016). According to De Stefanis *et al.*, (2013) the catalytic degradation of HDPE involves the carbenium ion mechanism by proton addition (Bronsted acid sites) to C-C bonds or hybrid ion abstraction by Lewis acid sites to the HDPE molecules. When the degradation has started, it further proceeds step by step into light hydrocarbon molecules. The higher molecules are degraded on the external surface of the catalyst, while microporous catalyst hinders their entrance that results in the formation of high carbon chain compounds and char deposition (Lopez *et al.*, 2011). Figure 4.5 shows the qualitative test report from GC-MS for HDPE liquid oil. Table 4.17 shows the molecular composition of the liquid oil.

Qualitative Analysis Report

Sample Information

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Analyzed : 26-Feb-20 7:57:16 AM
Sample Type : Unknown
Level # : 1
Sample Name : 26-02-2020_PE_29_1
Sample ID : UNK-0002
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Sample Amount : 1
Dilution Factor : 1
Vial # : 2
Injection Volume : 1.00
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Method File : C:\GCMSsolution\Data\Project1\Martin\Volatiles_fames.qgm
Org Method File : C:\GCMSsolution\Data\Project1\Martin\Volatiles_fames.qgm
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Modified : 26-Feb-20 4:32:44 PM

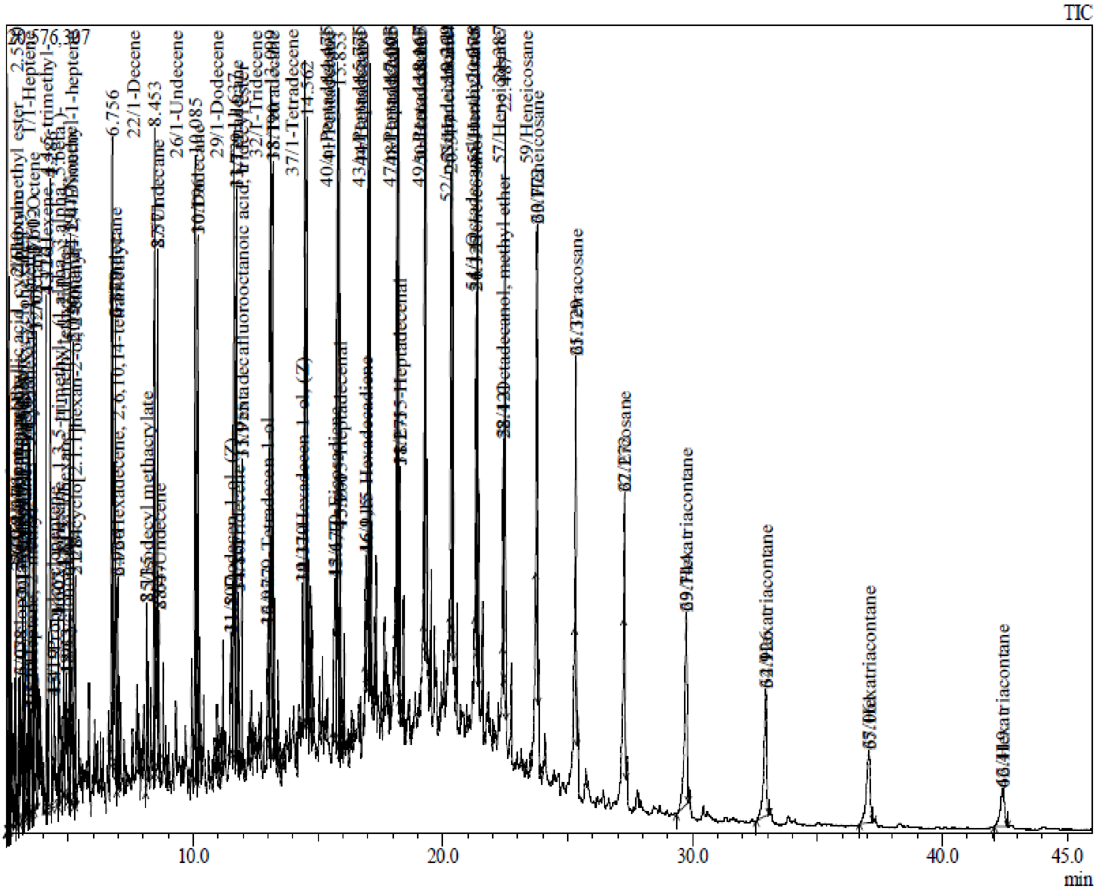


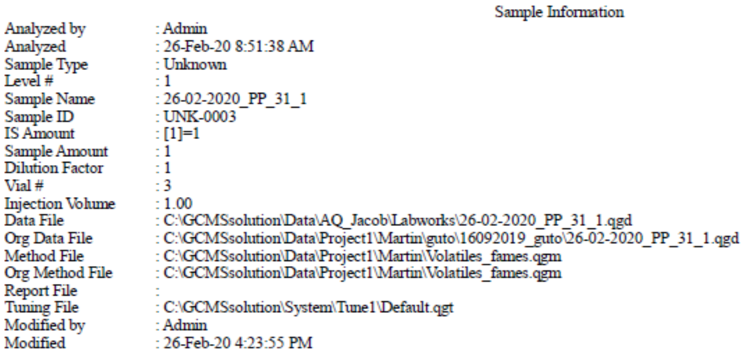
Figure 4.5: Qualitative analysis report of HDPE liquid oil from GC-MS

Table 4.17: A summary of information obtained from GC-MS showing retention time, retention index, Area %, molecular weights, chemical formula and names based on compared NIST entries for HDPE pyrolytic oil.

Peak number	Retention time	Retention index	Area %	Molecular weight	Chemical formula	Structure	Name
43	15.775	1755	3.02	228	$C_{15}H_{32}O$		n-Pentadecanol
37	13.099	1403	2.89	196	$C_{14}H_{28}$		1-Tetradecene
14	4.286	819	2.74	126	C_9H_{18}		2,4-Dimethyl-1-heptene
32	11.637	1304	2.73	182	$C_{13}H_{26}$		1-Tridecene
33	11.739	1413	2.67	198	$C_{14}H_{30}$		Tetradecane
29	10.085	1204	2.63	168	$C_{12}H_{24}$		1-Dodecene
44	15.853	1711	2.55	240	$C_{17}H_{36}$		Heptadecane
59	22.487	2109	2.54	296	$C_{21}H_{44}$		Heneicosane
26	8.453	1105	2.51	154	$C_{11}H_{22}$		1-Undecene
22	6.756	1005	2.41	140	$C_{10}H_{20}$		1-Decene
01	2.55	707	2.25	98	C_7H_{14}		1-Heptene
41	14.562	1512	2.24	212	$C_{15}H_{32}$		Pentadecane
52	19.269	2153	2.13	284	$C_{19}H_{40}O$		n-Nonadecanol-1

4.5.3 Hydrocarbon composition for Polypropylene pyrolytic oil

PP plastic waste liquid oil showed high composition of 1,3,5,7-Cyclooctatetraene, Benzene, 1,3-dimethyl-, alpha-Methyl styrene and Toluene. Abbas-Abadi *et al*,. (2014) carried out catalytic pyrolysis of PP and reported the production of aliphatic, paraffin, aromatic and naphthenes compounds which were comparable to the present study . The use of acid catalyst increased the production of poly-aromatic compounds that may be produced through aromatization, oligomerization and deoxygenation occuring on the active acidic sites of the catalyst. Ramli *et al.,* (2011) reported that the use of catalysts with Brownsted acid sites increased the cracking process of polymers which leads to the production of shorter chains hydrocarbons. Figure 4.6 shows the qualitative test analysis report for PP pyrolytic oil from GC-MS. Table 4.18 shows the laboratory Test report of Molecular composition for PP pyrolytic oil



Sample Information

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Sample Amount : 1
Dilution Factor : 1
Vial # : 3
Injection Volume : 1.00
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Method File : C:\GCMSsolution\Data\Project1\Martin\Volatiles_fames.qgm
Org Method File : C:\GCMSsolution\Data\Project1\Martin\Volatiles_fames.qgm
Report File :
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Modified by : Admin
Modified : 26-Feb-20 4:23:55 PM

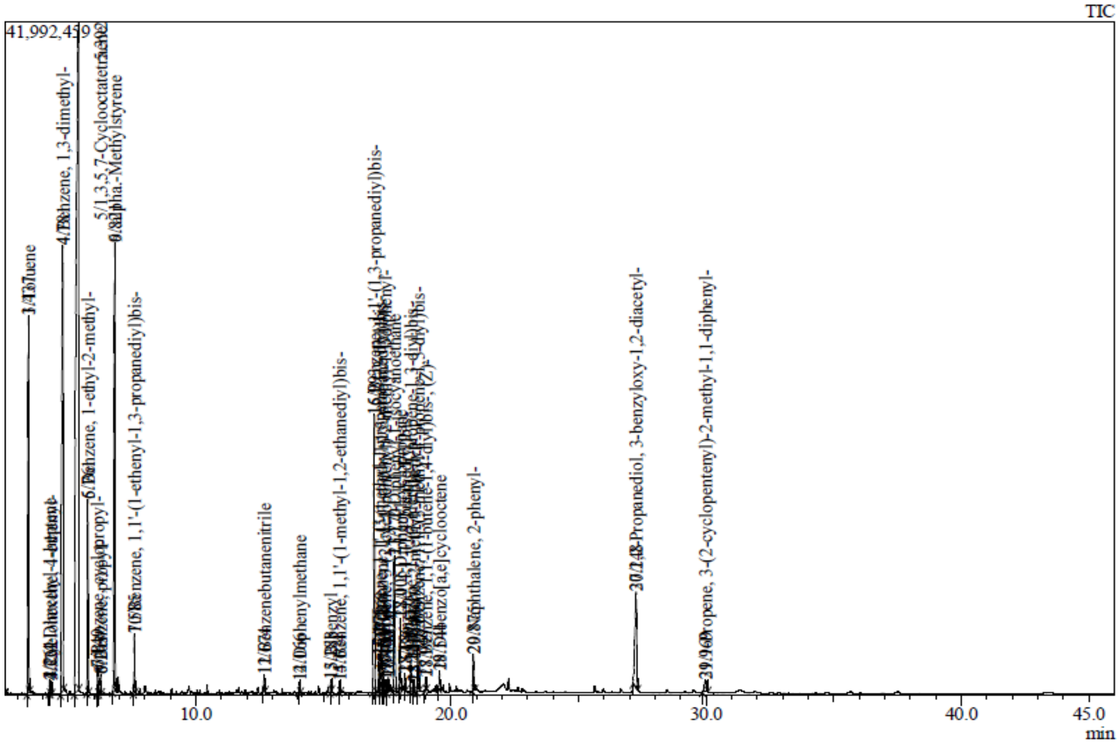
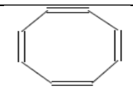
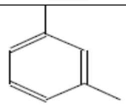
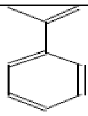
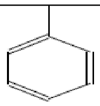
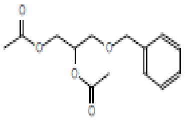
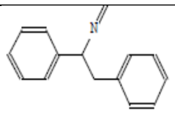
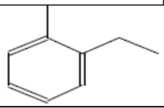
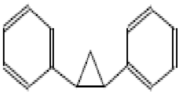
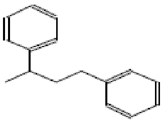
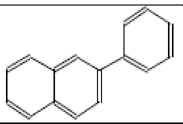
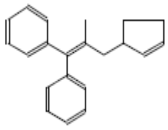


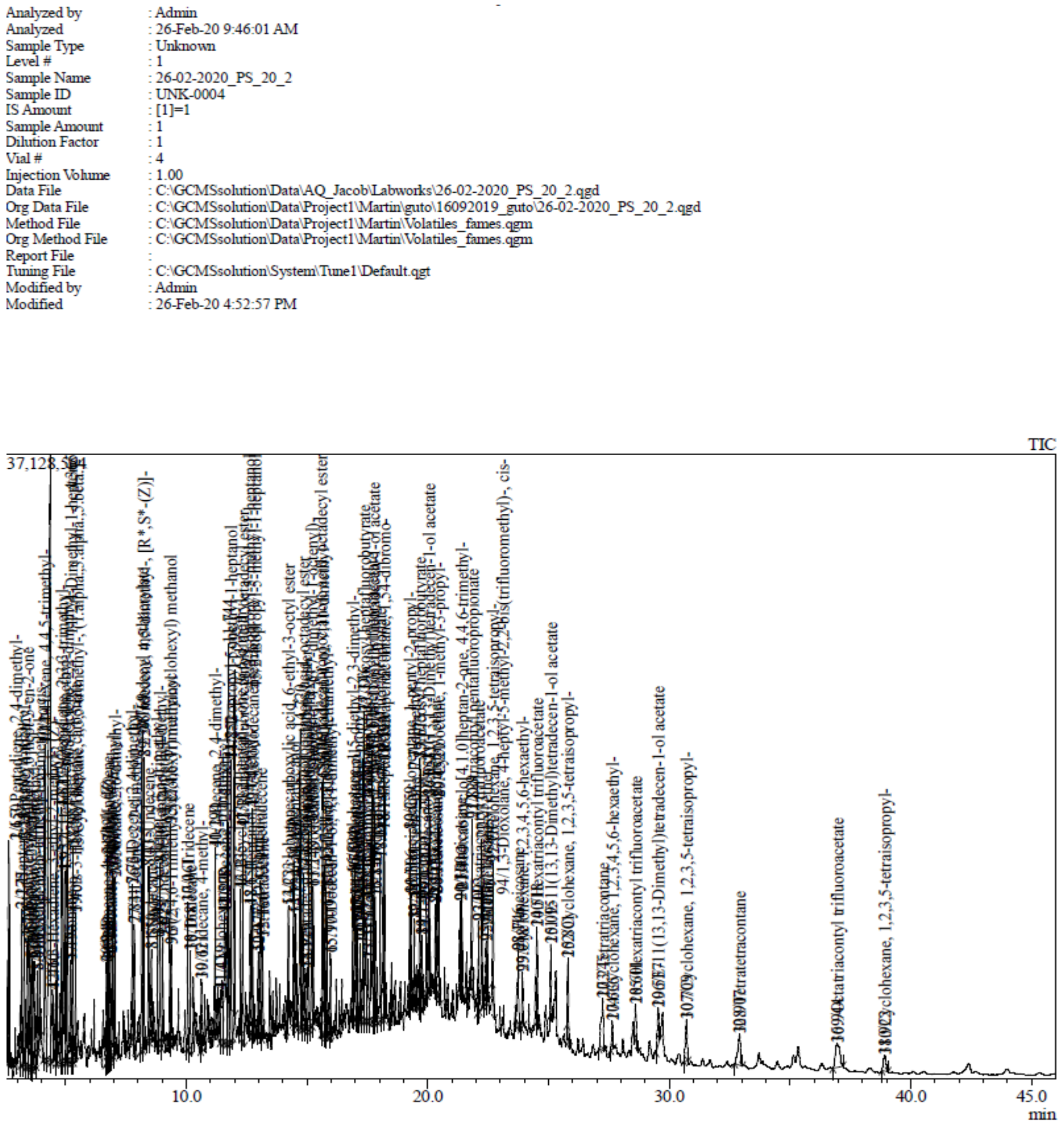
Figure 4.6: Qualitative analysis report for Polypropylene from GC-MS

Table 4.18: A summary of information obtained from GC-MS showing retention time, retention index, Area %, molecular weights, chemical formula and names based on compared NIST entries for PP pyrolytic oil.

Peak number	Retention time	Retention index	Area %	Molecular weight	Chemical formula	Structure	Name
5	5.392	888	38.69	104	C_8H_8		1,3,5,7-Cyclooctatetraene
4	4.781	907	13.59	106	C_8H_{10}		Benzene, 1,3-dimethyl-
9	6.821	960	11.56	118	C_9H_{10}		.alpha.-Methylstyrene
1	3.437	794	7.7	92	C_7H_8		Toluene
15	16.993	1665	6.78	196	$C_{15}H_{16}$		Benzene, 1,1'-(1,3-propanediyl)bis-
30	27.248	1836	4.13	266	$C_{14}H_{18}O_5$		1,2-Propanediol, 3-benzyloxy-1,2-diacetyl-
21	17.77	1799	3.71	207	$C_{15}H_{13}N$		1,2-Diphenyl-1-isocyanoethane
6	5.761	1006	2.71	120	C_9H_{12}		Benzene, 1-ethyl-2-methyl-
22	18.005	1629	1.5	194	$C_{15}H_{14}$		1,2-Diphenylcyclopropane
17	17.268	1701	1.2	210	$C_{16}H_{18}$		Benzene, 1,1'-(1-methyl-1,3-propanediyl)bis-
29	20.875	1918	0.8	204	$C_{16}H_{12}$		Naphthalene, 2-phenyl-
31	29.969	2249	0.58	274	$C_{21}H_{22}$		1-Propene, 3-(2-cyclopentenyl)-2-methyl-1,1-diphenyl-

4.5.4 Hydrocarbon composition for Polystyrene pyrolytic oil

PS plastic waste showed high composition of 2,4-Dimethyl-1-heptene, 2-Isopropyl-5-methyl-1-heptanol and 2-Hexene, 4,4,5-trimethyl-. Ukei *et al*,. (2000) and Shah and Jan (2014) reported that high temperature might lead to hydrogenation of styrene due to the secondary reactions that may decrease styrene and increase its derivative compounds. Figure 4.7 shows qualitative analysis report of polystyrene plastics from GC-MS. Table 4.19 shows laboratory Test Report of Molecular composition from GC-MS for Polystyrene waste plastics (PS).



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Sample Amount : 1
Dilution Factor : 1
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Injection Volume : 1.00
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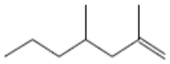
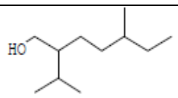
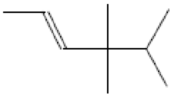
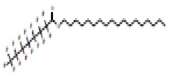
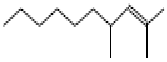
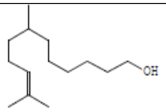
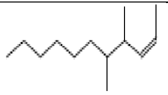
Modified by : Admin
Modified : 26-Feb-20 4:52:57 PM

Figure 4.7: Qualitative analysis report of Polystyrene plastics from GC-MS

Table 4.19: A summary of information obtained from GC-MS showing retention time, retention index, Area %, molecular weights, chemical formula and names based on compared NIST entries for PS pyrolytic oil.

Peak number	**Retention time**	**Retention index**	**Area %**	**Molecular weight**	**Chemical fromula**	**Structure**	**Name**
11	4.365	819	7.69	126	C_9H_{18}		2,4-Dimethyl-1-heptene
43	11.744	1165	3.53	172	$C_{11}H_{24}O$		2-Isopropyl-5-methyl-1-heptanol
10	4.140	775	2.99	126	C_9H_{18}		2-Hexene, 4,4,5-trimethyl-
28	8.169	1483	2.14	226	$C_{14}H_{26}O_2$		Isodecyl methacrylate
71	17.346	2330	2.13	522	$C_{26}H_{45}F_7O_2$		Docosyl heptafluorobutyrate
74	17.678	2309	1.94	408	$C_{23}H_{43}F_3O_2$		Heneicosyl trifluoroacetate
16	5.081	939	1.88	140	$C_{10}H_{20}$		3-Octene, 2,2-dimethyl-
56	14.720	0	1.85	666	$C_{26}H_{37}F_{15}O_2$		Pentadecafluorooctanoic acid, octadecyl ester
83	19.673	2131	1.64	494	$C_{24}H_{41}F_7O_2$		Eicosyl heptafluorobutyrate
42	11.578	1135	1.61	168	$C_{12}H_{24}$		2-Decene, 2,4-dimethyl-
62	15.646	1577	1.59	212	$C_{14}H_{28}O$		10-Dodecen-1-ol, 7,11-dimethyl-
29	8.239	1193	1.54	182	$C_{13}H_{26}$		2-Undecene, 4,5-dimethyl-, [R*,S*-(Z)]-

From the study it can be concluded that HDPE pyrolytic oil contained phenols (n-pentadecanol and n-nonadecanol) and aliphatic compounds. The aliphatic compounds are saturated (tetradecane and heptadecane), unsaturated (1-tetradecene and 1-dodecene) and cyclic (2,4-dimethyl-1-heptene). Similar results were reported by Jung *et al*., (2010), HDPE pyrolysis liquid oil contained primarily high concentrations of aliphatic and monoaromatic compounds, this is also observed in this study. This indicates the complexity of the HDPE structure to degrade during thermal degradation process. Manos *et al.,* (2000) reported that catalytic degradation of PE with Y-zeolite produced more gasoline range compounds, mainly the isoparaffins with high octane numbers. Catalytic degradation of HDPE and LDPE with the FCC catalyst produced gasoline range hydrocarbons (C_7-C_{15}) with the main components of iso-alkenes or iso-alkanes (Achilias *et al.,* 2007)

PP plastic waste liquid oil showed high composition of 1,3,5,7-Cyclooctatetraene, Benzene, 1,3-dimethyl-, alpha-Methyl styrene, Toluene, Benzene, 1,1'-(1,3-propanediyl)bis-,and 1,2-Propanediol, 3-benzyloxy-1,2-diacetyl-. The most abundant compound was 1,3,5,7-Cyclooctatetraene which is an unsaturated cyclic compound, other molecules comprised of aromatic hydrocarbons (benzene and Toluene). Single aromatic ring compounds like benzene,1,3-dimethyl and alpha methylstyrene found in the PP pyrolytic oil was also observed by Kaminsky, 1992. Abbas-Abadi *et al.* (2014) carried out catalytic pyrolysis of PP and reported the production of aliphatic, paraffin, aromatic and naphthene compounds which were comparable to the present study. The use of acid catalyst increased the production of poly-aromatic compounds that may be produced through aromatization, oligomerization and deoxygenation occuring on the active acidic sites of the catalyst. Mastral *et al.,* (2006) reported the formation of branched hydrocarbons with aromatics from PP pyrolytic oil. The high catalytic activity enables the degradation of heavy hydrocarbons into lower hydrocarbons. Ramli *et al.,* (2011) reported that the use of catalysts with Brownsted acid sites increased the cracking process of polymers which leads to the production of shorter chains hydrocarbons. PP pyrolytic oil also contained paraffins which are known to release extra energy for combustion than other hydrocarbon groups such as olefins and naphthenes (Shafferina, 2016).

Catalytic pyrolysis of PS plastic waste produced complex liquid oil composition as confirmed by GC-MS analysis. PS plastic waste showed high composition of 2,4-Dimethyl-1-heptene, 2-Isopropyl-5-methyl-1-heptanol and 2-Hexene, 4,4,5-trimethyl-. The pyrolytic oil from PS contained cyclic aliphatic and phenols as the major hydrocarbon compounds. Aguado, (2003) and Artetxe, (2015) carried out pyrolytic pyrolysis of PP with various types of catalysts and reported that aromatic hydrocarbons and cyclic aliphatics are the primary compounds found in the produced liquid oil, which is in agreement with the current study. Siddiqui and Redhwi (2009) and Sarker and Rashid (2013) also reported presence of aromatic compounds in the liquid oil produced by PS plastic waste. Ukei *et al.* (2000) and Shah and Jan (2014) reported that high temperature lead to hydrogenation of styrene due to the secondary reactions that decrease styrene and increase its derivative compounds. Table 4.20 shows the main oil composition from the pyrolysis of waste plastics.

Table 4.20: Liquid oil composition from the pyrolysis of waste plastics

HDPE	PP	PS
n-Pentadecanol	1,3,5,7-Cyclooctatetraene	2,4-Dimethyl-1-heptene
1-Tetradecene	Benzene, 1,3-dimethyl-	2-Isopropyl-5-methyl-1-heptanol
2,4-Dimethyl-1-heptene	. alpha. -Methylstyrene	2-Hexene, 4,4,5-trimethyl-
1-Tridecene	Toluene	Isodecyl methacrylate
Tetradecane	Benzene, 1,1'-(1,3-propanediyl)bis-	Docosyl heptafluorobutyrate
1-Dodecene	1,2-Propanediol, 3-benzyloxy-1,2-diacetyl-	Heneicosyl trifluoroacetate
Heptadecane	1,2-Diphenyl-1-isocyanoethane	3-Octene, 2,2-dimethyl-
Heneicosane	Benzene, 1-ethyl-2-methyl-	Pentadecafluorooctanoic acid, octadecyl ester
1-Undecene	1,2-Diphenylcyclopropane	Eicosyl heptafluorobutyrate
1-Decene	Benzene, 1,1'-(1-methyl-1,3-propanediyl) bis-	2-Decene, 2,4-dimethyl-
1-Heptene	Benzene, 1,1'-(3-methyl-1-propene-1,3-diyl) bis-	10-Dodecen-1-ol, 7,11-dimethyl-
Pentadecane	Benzene, 1,1'-(1-ethenyl-1,3-propanediyl) bis-	2-Undecene, 4,5-dimethyl-, [R*,S*-(Z)]-
n-Nonadecanol-1	Naphthalene, 2-phenyl-	Cyclohexane, 1,3,5-trimethyl-, (1.alpha.,3. alpha.,5.beta.)-
Dodecane	1-Propene, 3-(2-cyclopentenyl)-2-methyl-1,1-diphenyl-	2,4-Heptadiene, 2,6-dimethyl-
Undecane	Benzene, cyclopropyl-	1-Heptadecene
1-Nonene	Dibenzo[a,e]cyclooctene	E-11(13,13-Dimethyl)tetradecen-1-ol acetate
Hexatriacontane	Benzene, 1,1'-(1,4-butanediyl)bis-	1,7-Octadiene, 2,3,3-trimethyl-
Octane	Benzene, propyl-	Styrene

4.6 Pyrolytic Liquid Fuel Properties

The liquid fuel from waste plastics was tested for fuel characteristic properties, namely; density, kinematic viscosity, calorific value, flash point and freezing point these are important for analyzing the quality of fuel by following the ASTM D 240 methods. Table 4.21 shows the experimental results of the fuel properties for different waste plastics and petroleum diesel.

Table 4.21: Properties of liquid fuel produced from different types of waste plastics and petroleum diesel.

Fuel property	HDPE	PP	PS	DIESEL
Density at 20 ℃ (kg/m^3)	753.2	748.7	887.9	815-870
Kinematic viscosity at 25 ℃ (cSt)	12.68	11.19	9.56	2.0-5.0
Calorific value (MJ/kg)	33.150	33.338	30.769	46.67
Flash point (℃)	Above 24.0	Above 24.0	Above 24.0	52
Freezing point (℃)	-20	-19	-15	-9.5

The HHV found for pyrolysis liquid oil was 30.769- 33.338 MJ/Kg which is slightly lower than HHV of 43.06 MJ/Kg for petroleum diesel (Kamal, 2015). The density is another important characteristic of any fuel. The density of pyrolysis liquid oils were found to be in the range of 753.2- 887.9 Kg/m^3 which is comparable to 815- 870 Kg/m^3 for diesel (Syamsiro, 2014). The kinematic viscosity of fuel is very important characteristic as it dictates the spray pattern and atomization of injected fuel in a combustion chamber. The higher viscosities of fuel results in poor atomization, leading to poor engine start-up and performance. Furthermore, highly viscous fuels have reduced flow ability, especially during winters, which adversely affects the fuel injector function and causes problems in engine start up and running (Miandad *et al.*, 2016). The kinematic viscosities of pyrolysis liquid oil found in this study were in the range of 9.56 – 12.68 cSt at 25 ℃ which is higher than the standard range of 2.0– 5.0 cSt at 40 ℃ for conventional diesel (Syamsiro, 2014). Kinematic viscosity increases with decrease in temperature, this explains the high viscosity obtained for the pyrolytic fuel at 25 ℃. The flash point of pyrolysis oils were found to be above 24 ℃ which is lower than 52 ℃ for diesel, the pyrolysis oil is volatile. This is probably due to high aromatic contents and volatility of pyrolysis liquid oils. The quality of the fuel is also determined by its cold flow properties which dictate the lowest temperature at which the fuel injected system works on its full potential. The freezing points for the pyrolysis liquid oils were found to range from -15 ℃ - -20 ℃. This is beneficial for operation in areas where very low temperatures occur during winter.

CHAPTER 5: CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

A petroleum-based fuel was produced using three types of waste plastics through catalytic pyrolysis, namely: High density Polyethylene, Polypropylene and Polystyrene.

Indigenous clay was found to have potential to be used for pyrolysis of plastic wastes, since high yields of liquid fuel were obtained at lower reaction temperatures of 300-450 ℃, as compared to 600 ℃ required for thermal pyrolysis. In addition, the clay has high composition of silica and alumina at 64.5 wt% and 16.3 wt% respectively and SiO_2/Al_2O_3 ratio of 3.96, being requirements for a good pyrolysis catalyst. This will reduce the energy requirement considerably, overall process optimization and improve the fuel quality by having more aromatics, naphthene and isoalkanes. The optimum conditions for the plastic waste were found, based on the liquid oil yield. The chemical composition and properties of the liquid oil have been analyzed. The liquid oil produced by all types of plastic wastes using clay catalyst, mainly consisted of aromatic hydrocarbons such as styrene, benzene, naphthalene and toluene with a few aliphatic hydrocarbon compounds and phenol group as confirmed by GC-MS analysis. Liquid oils produced from all plastic wastes using clay catalysts had HHV ranging from 30.769- 33.338 MJ/Kg which is comparable to conventional diesel. The liquid oil may be used in multiple applications such as in diesel engines, in turbines to generate electricity or for combustion in furnaces and boilers. The liquid oil from catalytic pyrolysis is of higher quality and can be used in several energy-related applications such as electricity generation, transport fuel and heating source. The gaseous products can be used to reheat the raw material to reduce the cost of production.

5.2 Recommendations

Based on the findings, this study recommends;

1. Further characterization of clay (BET surface area and porosity)
2. Modification of surface and structure of clay to enhance its catalytic activities in the pyrolysis process. Modification can be done by doping of other elements, acid leaching, thermal treatment and wet impregnation.
3. Further studies using mixed plastics for any synergetic effect on oil production.
4. Post treatment of liquid oil through distillation and refining or blending with conventional diesel is required so as to use the oil as a transport fuel due to the presence of high aromatic compounds.

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APPENDICES

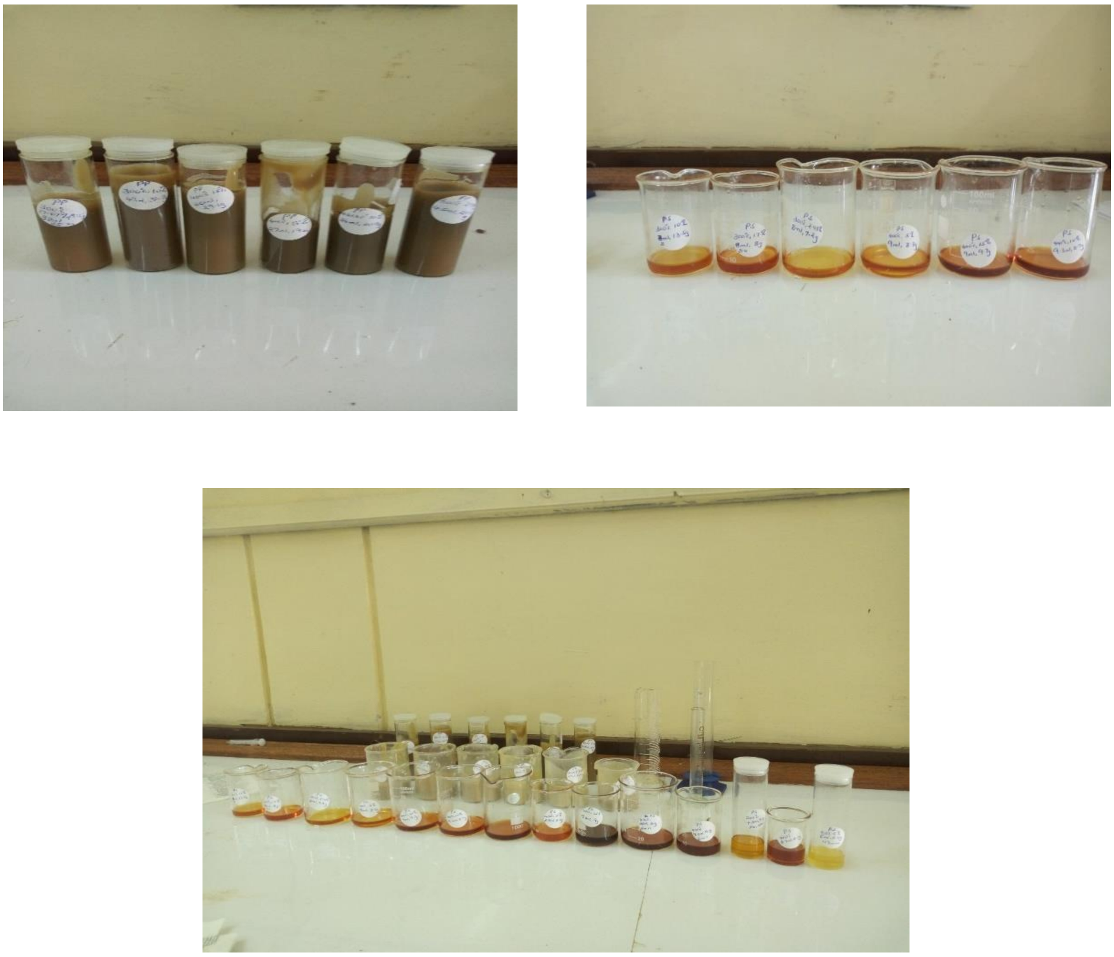
Appendix 1: Photographs of raw materials used and experimental layout

Appendix 1a: Waste plastics (PP, HDPE and PS)

Appendix 1b: Preparation of raw materials (PS, and clay soil)

Appendix 1c: Chemical Engineering Lab

Appendix 1d: Experimental setup for pyrolysis process



Appendix 1e: Pyrolytic oil for HDPE, PP and PS

Appendix 1f: Char (By product of pyrolysis process)

Appendix 2: GC-MS data

Appendix 2a: Molecular composition of pyrolytic oil from HDPE waste plastics

Retention time	Area	Area %	Height	Height %	Name
15.775	50929783	3.02	17375024	2.63	n-Pentadecanol
13.099	48729182	2.89	16872775	2.56	1-Tetradecene
14.475	48194192	2.86	16907915	2.56	n-Pentadecanol
4.286	46124192	2.74	16031127	2.43	2,4-Dimethyl-1-heptene
11.637	45943988	2.73	15939598	2.41	1-Tridecene
11.739	44927479	2.67	14546320	2.2	Tetradecane
10.085	44260017	2.63	15925613	2.41	1-Dodecene
15.853	43032034	2.55	16864842	2.55	Heptadecane
22.487	42774964	2.54	14987539	2.27	Heneicosane
8.453	42307839	2.51	16436592	2.49	1-Undecene
17.003	42161158	2.5	16283191	2.47	n-Pentadecanol
18.235	42159846	2.5	16333143	2.47	Heneicosane
21.387	41908739	2.49	15926929	2.41	Heneicosane
18.167	41046193	2.44	15776831	2.39	n-Pentadecanol
20.378	41071520	2.44	15937047	2.41	Heneicosane
19.334	40818695	2.42	15763380	2.39	Heneicosane
6.756	40572567	2.41	15758073	2.39	1-Decene
17.075	39967919	2.37	16029588	2.43	Heptadecane
2.55	37836475	2.25	19315396	2.93	1-Heptene
14.562	37792115	2.24	15461539	2.34	Pentadecane
13.19	37491218	2.22	15222122	2.31	Tetradecane
19.269	35957089	2.13	14566185	2.21	n-Nonadecanol-1
10.196	34679739	2.06	13946060	2.11	Dodecane
8.571	33465959	1.99	13238162	2.01	Undecane
5.077	33332599	1.98	14436453	2.19	1-Nonene
29.744	32574701	1.93	4898060	0.74	Hexatriacontane
3.703	30411067	1.8	12183432	1.85	Octane
5.199	29900598	1.77	11780896	1.78	Nonane
23.772	29412483	1.75	10884972	1.65	Heneicosane
6.879	27081607	1.61	11669556	1.77	Undecane
20.317	27090300	1.61	11648731	1.76	1-Octadecanol, methyl ether
3.602	26978901	1.6	14170014	2.15	1-Octene
25.329	24677266	1.46	8585749	1.3	Tetracosane
32.926	24421292	1.45	3237982	0.49	Hexatriacontane
4.116	22981161	1.36	13080934	1.98	2-Hexene, 4,4,5-trimethyl-
2.61	21826179	1.3	14087006	2.13	Heptane
21.325	21292756	1.26	8849150	1.34	1-Heneicosanol
37.061	17673403	1.05	1823482	0.28	Hexatriacontane
4.933	15863455	0.94	3112257	0.47	Cyclononene
15.677	15503279	0.92	4023080	0.61	1,19-Eicosadiene

4.419	15345850	0.91	2803400	0.42	1-Propylcyclopentene
22.421	14721724	0.87	5762809	0.87	1-Octadecanol, methyl ether
3.425	14043841	0.83	9450906	1.43	Cyclohexene, 1-methyl-
11.955	13324899	0.79	7852781	1.19	Pentadecafluorooctanoic acid, tridecyl ester
3.078	12984204	0.77	3697565	0.56	Cyclopentanepropanol, 2-methylene-
27.272	12386673	0.74	4904247	0.74	Eicosane
11.807	12288492	0.73	4319826	0.65	1-Tridecene
11.507	12052237	0.72	2986366	0.45	8-Dodecen-1-ol, (Z)-
6.966	11926911	0.71	5414597	0.82	2-Hexadecene, 2,6,10,14-tetramethyl-
3.277	11517271	0.68	6717264	1.02	Heptane, 4-methyl-
4.819	11224138	0.67	5715710	0.87	Cyclohexane, (1-methylethylidene)-
2.646	11062051	0.66	6586770	1	Cyclopropanecarboxylic acid, cyclohexylmethyl ester
3.172	10946908	0.65	5630479	0.85	1-Methyl-2-trifluoroacetoxycyclohexane
42.419	10994953	0.65	961130	0.15	Hexatriacontane
5.284	10619355	0.63	5848842	0.89	Bicyclo[2.1.1]hexan-2-ol, 2-ethenyl-
2.918	10124875	0.6	6645176	1.01	Cyclohexane, methyl-
4.607	9580187	0.57	4779752	0.72	Cyclohexane, 1,3,5-trimethyl-, (1.alpha.,3.alpha.,5.beta.)-
3.529	9465128	0.56	2656247	0.4	1-Heptene, 2-methyl-
15.9	9497032	0.56	5727857	0.87	E-15-Heptadecenal
18.275	9298397	0.55	6137072	0.93	E-15-Heptadecenal
12.977	8850737	0.53	2832536	0.43	cis-9-Tetradecen-1-ol
2.676	8338122	0.49	7734296	1.17	2-Heptene, (E)-
16.915	8064169	0.48	2962915	0.45	1,15-Hexadecadiene
14.37	7987496	0.47	3571747	0.54	11-Hexadecen-1-ol, (Z)-
8.135	7461939	0.44	4664541	0.71	Isodecyl methacrylate
8.647	5854951	0.35	3873027	0.59	5-Undecene

Appendix 2b: Molecular composition of pyrolytic oil from PP waste plastics

Retention time	Area	Area %	Height	Height %	Name
5.392	275146072	38.69	41656725	20.82	1,3,5,7-Cyclooctatetraene
4.781	96716539	13.59	27763054	13.87	Benzene, 1,3-dimethyl-
6.821	82248064	11.56	27999951	13.99	.alpha.-Methylstyrene
3.437	54765495	7.7	23520565	11.75	Toluene
16.993	48268310	6.78	17318614	8.65	Benzene, 1,1'-(1,3-propanediyl)bis-
27.248	29371647	4.13	5989311	2.99	1,2-Propanediol, 3-benzyloxy-1,2-diacetyl-
17.77	26410977	3.71	8431773	4.21	1,2-Diphenyl-1-isocyanoethane
5.761	19270827	2.71	12088015	6.04	Benzene, 1-ethyl-2-methyl-
18.005	10648178	1.5	4526749	2.26	1,2-Diphenylcyclopropane
17.268	8564822	1.2	3320438	1.66	Benzene, 1,1'-(1-methyl-1,3-propanediyl)bis-
18.699	6689835	0.94	2781013	1.39	Benzene, 1,1'-(3-methyl-1-propene-1,3-diyl)bis-
18.421	6323162	0.89	1829142	0.91	Benzene, 1,1'-(3-methyl-1-propene-1,3-diyl)bis-
7.585	6230135	0.88	3691622	1.84	Benzene, 1,1'-(1-ethenyl-1,3-propanediyl)bis-
20.875	5704901	0.8	2255445	1.13	Naphthalene, 2-phenyl-
17.175	5461335	0.77	2270116	1.13	Benzene, 1,1'-(3-methyl-1-propene-1,3-diyl)bis-
29.969	4148410	0.58	749644	0.37	1-Propene, 3-(2-cyclopentenyl)-2-methyl-1,1-diphenyl-
17.333	2847364	0.4	1317694	0.66	EMDP
6.149	2557143	0.36	1575976	0.79	Benzene, cyclopropyl-
19.544	2453572	0.34	1148584	0.57	Dibenzo[a,e]cyclooctene
17.541	1936619	0.27	947219	0.47	EMDP
18.186	1756249	0.25	956210	0.48	Benzene, 1,1'-(1,4-butanediyl)bis-
6.263	1731572	0.24	1196346	0.6	Benzene, propyl-
12.674	1723758	0.24	978651	0.49	Benzenebutanenitrile
18.999	1549307	0.22	784642	0.39	Benzene, 1,1'-(1-butene-1,4-diyl)bis-, (Z)-
17.406	1522209	0.21	769509	0.38	1-Propene, 3-(2-cyclopentenyl)-2-methyl-1,1-diphenyl-
15.288	1410078	0.2	768325	0.38	Bibenzyl
18.547	1449659	0.2	627294	0.31	1H-Indene, 2-methyl-3-phenyl-
14.066	1192963	0.17	664315	0.33	Diphenylmethane

4.322	1139689	0.16	805995	0.4	Cyclohexene, 4-ethenyl-
15.634	1148901	0.16	624101	0.31	Benzene, 1,1'-(1-methyl-1,2-ethanediyl)bis-
4.261	1084282	0.15	854979	0.43	2,4-Dimethyl-1-heptene

Appendix 2c: Molecular composition of pyrolytic oil from PS waste plastics

Retention time	Area	Area %	Height	Height %	Name
4.365	195380364	7.69	36105115	3.65	2,4-Dimethyl-1-heptene
11.744	89979551	3.53	23816548	2.42	2-Isopropyl-5-methyl-1-heptanol
4.14	76302956	2.99	18774714	1.91	2-Hexene, 4,4,5-trimethyl-
11.995	65443721	2.57	20882733	2.12	2-Isopropyl-5-methyl-1-heptanol
8.169	54662161	2.14	18990330	1.93	Isodecyl methacrylate
17.346	54354018	2.13	18426035	1.87	Docosyl heptafluorobutyrate
17.678	49558886	1.94	16165352	1.64	Heneicosyl trifluoroacetate
5.081	47997787	1.88	17573828	1.78	3-Octene, 2,2-dimethyl-
11.852	47856128	1.88	16922875	1.72	2-Isopropyl-5-methyl-1-heptanol
14.72	47196179	1.85	17801453	1.81	Pentadecafluorooctanoic acid, octadecyl ester
19.673	41910483	1.64	14896237	1.51	Eicosyl heptafluorobutyrate
11.578	41153543	1.61	7737596	0.79	2-Decene, 2,4-dimethyl-
15.646	40463888	1.59	15189900	1.54	10-Dodecen-1-ol, 7,11-dimethyl-
8.239	39166285	1.54	17363441	1.76	2-Undecene, 4,5-dimethyl-, [R*,S*-(Z)]-
18.193	33769453	1.32	15369351	1.56	Tetrapentacontane, 1,54-dibromo-
4.632	32614212	1.28	16747569	1.7	Cyclohexane, 1,3,5-trimethyl-, (1.alpha.,3.alpha.,5.beta.)-
4.957	31739070	1.24	11314802	1.15	2,4-Heptadiene, 2,6-dimethyl-
18.157	31497869	1.24	11251472	1.14	1-Heptadecene
17.765	31424016	1.23	13458082	1.37	E-11(13,13-Dimethyl)tetradecen-1-ol acetate
4.837	30872438	1.21	15141849	1.54	1,7-Octadiene, 2,3,3-trimethyl-
5.293	30386898	1.19	12848367	1.3	Styrene
20.452	30295146	1.19	12055263	1.22	Cyclooctane, 1-methyl-3-propyl-
3.286	27956698	1.1	13472898	1.37	Heptane, 4-methyl-
9.337	27997621	1.1	13074106	1.33	(2,4,6-Trimethylcyclohexyl) methanol
15.188	27945075	1.1	12206679	1.24	Cyclopropanol, 1-(3,7-dimethyl-1-octenyl)-
12.332	27871846	1.09	12699407	1.29	Pentadecafluorooctanoic acid, octadecyl ester
21.829	27510007	1.08	10054363	1.02	Dotriacontyl pentafluoropropionate
12.743	26407124	1.04	13794490	1.4	Cyclododecanemethanol
19.259	26536101	1.04	10499032	1.07	Cyclopentane, 1-pentyl-2-propyl-

6.743	26289706	1.03	12355031	1.25	1-Undecene
15.067	26386048	1.03	11845224	1.2	1-Dodecanol, 2-hexyl-
22.233	25833234	1.01	10054324	1.02	1,3-Dioxolane, 4-heptyl-5-methyl-2,2-bis(trifluoromethyl)-, cis-
6.964	25297383	0.99	11047524	1.12	Decane, 4-methyl-
20.052	25325550	0.99	11798050	1.2	E-11(13,13-Dimethyl)tetradecen-1-ol acetate
14.45	24634933	0.97	9727430	0.99	n-Pentadecanol
2.65	24409310	0.96	13306721	1.35	1,3-Pentadiene, 2,4-dimethyl-
18.029	23441248	0.92	9676941	0.98	Dotriacontyl pentafluoropropionate
3.693	22969279	0.9	6446420	0.65	Cyclohexanol, 2,4-dimethyl-
15.751	22339618	0.88	10345480	1.05	n-Heptadecanol-1
8.916	22196754	0.87	10641868	1.08	1-Heptanol, 2,4-diethyl-
11.419	22033592	0.86	3113985	0.32	Cyclohexanone, 3,3,5-trimethyl-
11.194	21213465	0.83	10898965	1.11	2-Decene, 2,4-dimethyl-
16.98	21198379	0.83	8885455	0.9	n-Pentadecanol
8.435	20937117	0.82	10429918	1.06	1-Undecene
3.175	19849513	0.78	9292769	0.94	2-Heptene, 4-methyl-, (E)-
14.835	19549782	0.77	9266373	0.94	Pentadecafluorooctanoic acid, octadecyl ester
16.894	19169769	0.75	8538901	0.87	Cyclohexane, 1,5-diethyl-2,3-dimethyl-
27.245	19054044	0.75	3081645	0.31	Tetratriacontane
7.761	18980786	0.74	9114729	0.93	2-Decene, 2,4-dimethyl-
7.036	18329990	0.72	10603876	1.08	Nonane, 2,6-dimethyl-
23.746	18450631	0.72	4542026	0.46	Heneicosane
17.439	18118137	0.71	6106280	0.62	Hexatriacontyl trifluoroacetate
36.944	18174601	0.71	1471083	0.15	Octatriacontyl trifluoroacetate
13.074	17671656	0.69	9203881	0.93	1-Tetradecene
3.53	16996438	0.67	7322283	0.74	1-Heptene, 2-methyl-
10.061	17175560	0.67	8777325	0.89	1-Tridecene
22.703	16929851	0.66	7980988	0.81	Cyclohexane, 1,2,3,5-tetraisopropyl-
5.409	15937815	0.63	8847447	0.9	cis-3-Hexenyl heptine carbonate
15.821	15950048	0.63	7729602	0.78	Heptadecane, 2,6,10,15-tetramethyl-
24.518	15955258	0.63	5825005	0.59	Hexatriacontyl trifluoroacetate
3.426	15919532	0.62	7740000	0.79	7-Methylenebicyclo[3.2.0]hept-3-en-2-one
5.195	15801847	0.62	6023376	0.61	Nonane
7.841	15930278	0.62	7435355	0.75	3-Decene, 2,2-dimethyl-, (E)-

12.654	15839412	0.62	7525499	0.76	1-Heptanol, 2,4-diethyl-
4.46	15642952	0.61	4351949	0.44	1,3-Hexadiene, 3-ethyl-2-methyl-, (Z)-
10.168	15436957	0.61	6134881	0.62	Dodecane
15.248	14980222	0.59	8237905	0.84	1-Dodecanol, 2-hexyl-
12.235	14805430	0.58	8541483	0.87	Bicyclo[3.1.1]heptan-2-one, 6,6-dimethyl-
32.907	14230288	0.56	1841473	0.19	Tetratetracontane
14.534	13912223	0.55	6685568	0.68	Pentadecane
25.801	13544098	0.53	4571658	0.46	Cyclohexane, 1,2,3,5-tetraisopropyl-
17.047	13082273	0.51	6332051	0.64	Heptadecane
22.092	12985786	0.51	5398049	0.55	Hexatriacontyl trifluoroacetate
6.694	12801986	0.5	5974049	0.61	2-Decene, 4-methyl-, (Z)-
17.816	12850400	0.5	7457686	0.76	1-Dodecanol, 2-hexyl-
6.789	12392354	0.49	6075937	0.62	2-Decene, 4-methyl-, (Z)-
9.025	12544789	0.49	6394985	0.65	2-Undecanethiol, 2-methyl-
10.621	12127556	0.48	4290275	0.44	Tridecane, 4-methyl-
19.306	12363268	0.48	6796708	0.69	Heneicosane
30.709	12202309	0.48	2514027	0.26	Cyclohexane, 1,2,3,5-tetraisopropyl-
14.223	11974942	0.47	6813490	0.69	Cyclobutanecarboxylic acid, 6-ethyl-3-octyl ester
22.417	12040698	0.47	3701675	0.38	Methyl tetracosyl ether
19.944	11851521	0.46	5717897	0.58	1-Dodecanol, 2-octyl-
8.55	11530681	0.45	5488880	0.56	Undecane
25.095	11535957	0.45	4461766	0.45	E-11(13,13-Dimethyl)tetradecen-1-ol acetate
3.595	11136942	0.44	6542898	0.66	1-Octene
3.817	10993172	0.43	5280292	0.54	1-Hexene, 3,3,5-trimethyl-
6.859	11074888	0.43	6352781	0.64	Octane, 3,5-dimethyl-
13.16	10985765	0.43	6014289	0.61	Tetradecane
21.414	11079924	0.43	6224904	0.63	7-Oxabicyclo[4.1.0]heptan-2-one, 4,4,6-trimethyl-
20.359	10693961	0.42	5796980	0.59	Heneicosane
8.809	10384592	0.41	6370324	0.65	1,7-Octadiene, 2,3,3-trimethyl-
17.095	10507522	0.41	5405954	0.55	Cyclohexane, 1-ethyl-2-propyl-
9.375	10274834	0.4	5955286	0.6	(2,4,6-Trimethylcyclohexyl) methanol
17.535	9937778	0.39	3745103	0.38	Triacontyl heptafluorobutyrate
12.977	9574773	0.38	4973301	0.5	1,22-Docosanediol
20.307	9564803	0.38	4861711	0.49	1-Octadecanol, methyl ether
21.36	9358810	0.37	5306131	0.54	Heneicosane
17.189	9185012	0.36	4546400	0.46	2-Cyclohexylnonadecane

22.466	9136988	0.36	4502340	0.46	Heneicosane
29.537	9192370	0.36	2245990	0.23	E-11(13,13-Dimethyl)tetradecen-1-ol acetate
3.923	8862408	0.35	5275354	0.54	Cyclopentane, 1,1,3,4-tetramethyl-, cis-
15.97	8953793	0.35	5109184	0.52	10-Dodecen-1-ol, 7,11-dimethyl-
14.929	8745898	0.34	3654674	0.37	Pentadecafluorooctanoic acid, octadecyl ester
19.447	8644885	0.34	4969104	0.5	11-Dodecen-2-one, 7,7-dimethyl-
19.75	8508857	0.33	4502647	0.46	1-Dodecanol, 2-octyl-
23.918	7807929	0.31	3270111	0.33	Cyclohexane, 1,2,3,4,5,6-hexaethyl-
28.601	7476879	0.29	2146080	0.22	Hexatriacontyl trifluoroacetate
38.922	6976320	0.27	939741	0.1	Cyclohexane, 1,2,3,5-tetraisopropyl-
27.636	5598454	0.22	1678222	0.17	Cyclohexane, 1,2,3,4,5,6-hexaethyl-