COMPARATIVE STUDIES OF THE EFFECT OF CALCIUM OXIDE (CaO) AND ZEOLITE ZSM-5 CATALYST ON WASTE PLASTIC PYROLYSIS

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ABSTRACT

Increase in waste plastic disposal continues to pollute the environment and fuel oil production from waste plastic using pyrolysis have been suggested as a better option for mitigating these wastes. It was in view of this that the study compares the effect of CaO and ZSM-5 zeolite catalyst on waste plastic pyrolysis through the realization of objectives such as; characterization of CaO and ZSM-5 zeolite catalyst using XRF and XRD, catalytic pyrolysis of waste plastic using CaO and ZSM-5 zeolite catalyst, optimization of the parameters of pyrolysis using CaO and ZSM-5 zeolite catalyst, characterization of the pyrolysis oil product using GCMS and FTIR analysis as well as analysis of the properties of the catalyzed plastic pyrolysis oil. The XRD characterization was carried out and it shows that the crystalline structure of the CaO catalyst contains mainly CaO and small quantity of $Ca(OH)_2$at 2θ angle of 32.340°, 37.487°, 54.005°, 64.483° and 67.503° diffraction peak forportlandite (CaO) and 2θ angle of 28.881°, 34.417°and 64.203° for $Ca(OH)_2$ phase in the CaO catalyst while 98.848 wt.% CaO and <1% of other oxide were identified from XRF analysis, while ZSM-5 zeolite catalyst contains mainly silicate crystals with presence of a highly crystalline ZSM-5zeolitic structure and well-defined diffraction peaks at 2θ angle of 8.101°, 8.968°, 23.254°, 24.094°, 29.477°, 30.108°, 45.260° and 45.654°, of a high structural orderthat are indication of those of ZSM-5 zeolite, and a silica to alumina ratio of 50.03 from the XRF analysis were observed. The pyrolysis oil produced shows that zeolite catalyst gives much higher yield with better quality at lower temperature compared to CaO catalyst. The optimum temperature, heating rate and catalyst type observed for maximum plastic pyrolysis oil yield (58.385%) were 597 ^{o}C temperature, 29.909 ^{o}C/min and ZSM-5 zeolite catalyst type respectively while the optimum temperature and heating rate for CaO catalyst are 600 ^{o}C and 30 ^{o}C/min respectively for a maximum oil yield of 54.868% with temperature, heating rate and catalyst type as well as interaction between this parameters having predominant effect on the amount of liquid product yield. Furthermore, both the FTIR and GCMS analysis affirms that the zeolite catalyzed plastic pyrolysis oil comprises of better hydrocarbon mixture range of alkane, alkenes, cycloalkanes, aromatics and very minute organic acid compounds compared to CaO catalysed plastic pyrolysis oil. Additionally, the fuel properties of the zeolite catalyzed plastic pyrolysis oil compared favorably with diesel fuel oil, while CaO required upgrade to meet recommended diesel fuel standard, hence ZSM-5 zeolite catalyzed plastic pyrolysis oil show better fuel performance than CaO catalyzed plastic pyrolysis oil. Therefore, ZSM-5 zeolite catalyzed pyrolysis oil may be considered as a valuable component for use with automotive diesel fuels and may be directly used as fuels for industrial boilers, furnaces and power plants, as it shows better fuel quality than CaO catalyzed plastic pyrolysis oil.

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CHAPTER ONE

1.0 INTRODUCTION

1.1 Background to the Study

Over the years, there have been rise in environmental concern over plastic waste generation and disposal worldwide, resulting from the rise in population and industrialization. Plastics are materials that comprises of a wide range of synthetic and natural compound, and are malleable and can be molded into different shapes and sizes. Plastics have become an indispensable material used in several countries of the world, due to their durability, lightweight as well as flexibility and are utilized in a range of industrial and domestic areas (Khan, Sultana, Al-Mamun, and Hasan, 2016). In 2015, global plastics production was about 388 million tonnes and has reached over 407 million tonnes per annum in recent times and this figure is estimated to double in the next 20 years (Morten, Ryberg, and Michael, 2018). In the last decades, the utilization of plastic and its waste generation has continuously grown in several countries of the world and count for a reasonable part of solid waste generation. Nearly 8.3 billion metric tons of plastic have been produced since 1950, and 6.3 billion tons of plastic waste have been generated, of which 9% has been recycled, 12% incinerated, and 79% accumulated in landfills or abandoned in the environment (Meidl, 2018).

In Nigeria, cities and towns are currently facing serious environmental problem arising from solid waste generation. The rate of solid waste generation, particularly plastic waste in Nigeria has increased with rapid urbanization, due to their end-of-life management challenges and a larger fraction of waste plastic end up at dumpsites, landfills and even clogging of drainages (Babayemi, Ogundiran, Weber, and Osibanjo, 2018). A large proportion of plastics waste is being disposed of in landfills and dumpsites than ever before. Plastic waste generated in Nigeria are predominantly plastic bottles, bags and packages and remain a large proportion of municipal solid waste. According to the Nigeria Federal Ministry of Commerce and Industry, the production of the most common and cheapest source of drinking water, popularly known as “pure water” is one of the largest contributors to plastic waste generation in the country, and these waste account for about 20% of total waste generation (Akinola, Adeyemi and Adeyinka, 2014). This plastic waste generated are not biodegradable, but take about 100 years to degrade in the environment (World Environment Day, 2018). Added to the degradability challenges are risks of flooding by clogging of drains and degradation of air quality from open dumps, a serious concern of its management. This necessitate the need to source for an effective and sustainable plastic waste management system.

Over the years, different management methods have been developed to mitigate the threat posed by rising amounts of plastic waste generated by conversion to valuable and useful products that will significantly reduce the volume of waste generated. There have been focus on sustainable methods in the conversion of plastic waste to a valuable source of energy and chemical substances, as landfills and burning have resulted in serious environmental and health hazards (Dogan, Bahattin-Celik, and Ozdalyan, 2012). This makes energy recovery processes the most effective approach to reducing the volume of plastic waste significantly as they focus on potentially converting the plastic waste into other useful products such as fuel products through pyrolysis process (Baiden, 2018). Pyrolysis, as a method of waste conversion, is widely used in recent time for waste conversion to useful product. It simply implies the breaking down of chemically bonded material with the aid of thermal energy in the absence of air and can be carried out in the presence of catalyst to convert it into fuels and other valuable materials (Dogan *et al.*, 2012; Bursali, 2014).

Pyrolysis is an environmentally friendly means of plastic waste disposal with the production of valuable products when compared to other disposal methods. This method, in recent times, has become an alternative and sustainable method of waste-to-energy conversion to substitute fossil fuel while also mitigating the environmental degradation challenges caused by plastic waste disposal. Despite the environmental friendliness of the method, energy consumption of the process is high and a wide product distribution occurs for non-catalytic pyrolysis processes, hence, the use of catalyst to influence the product distribution and relatively reduce reaction temperature and time, as well as maximize product efficiency (Bursali, 2014; Osayi, Iyuke and Ogbeide, 2014). The use of catalyst during pyrolysis enhances the reaction by cracking down higher molecular weight hydrocarbon compounds to lighter hydrocarbon products. It has been reported by several authors that catalyst utilization in plastic waste pyrolysis process can greatly influence products yield, composition and quality (Williams, 2013; Osayi *et al.*, 2014; Strydom, 2017). This resulted in growing interest in the investigation of catalyst utilization in plastic wastes pyrolysis to enhance selectivity of products through appropriate selection of catalyst type.

1.2 Statement of the Research Problem

Increase in waste plastic disposal continues to pollute the environment and clog drainages which has been found to cause flooding during raining season in most part of the country coupled with its other environmental impact as a none biodegradable material, (Osayi *et al.*, 2014) hence the need for pyrolysis in order to recover valuable products. Pyrolysis have been suggested as a better option of mitigating the huge plastic wastes generation across the globe, however, plastic waste pyrolysis in the absence of catalyst require high energy due to high temperature involved, hence the use of catalyst to reduce cracking temperature and enhance selectivity. The use of catalysts in plastic wastes pyrolysis will enhance selectivity of the product yields and/or the upgrading of the pyrolytic oil to valuable chemicals while lowering the pyrolysis temperature and invariably the lower the energy requirement. The use of catalyst such as zeolite have shown good pyrolysis performance but expensive and as a result, will impact cost of pyrolysis, hence the need to source for a cheaper and readily available catalyst in Nigeria such as CaO obtainable from $CaCO_3$. This necessitate the need for the study

(Gandidi, *et al.*, 2018).

1.3 Aim and Objectives

The aim of this study is to compare the effect of CaO and zeolite ZSM-5 catalyst on waste plastic pyrolysis. The aim was achieved through the following objectives;

1. Characterization of CaO and zeolite ZSM-5 catalyst using XRF and XRD.
2. Waste plastic pyrolysis using CaO and zeolite ZSM-5 catalyst.
3. Optimization of the parameters of pyrolysis using CaO and zeolite ZSM-5 catalyst.
4. Characterization of oil product of pyrolysis using GCMS and FTIR.
5. Physiochemical characterization of the CaO and zeolite ZSM-5 catalyzed pyrolysis oil.

1.4 Scope of Study

The scope of the study is limited to catalytic pyrolysis of plastic wastes to produce oil that can serve as fuel oil.

1.5 Justification of the Study

Catalyst utilization in pyrolysis has become an important area of investigation in recent times and is considered a very promising field for the conversion of plastic wastes which has constitute environmental challenge to valuable products. Also, plastic waste pyrolysis will not only solve the disposal problems in our community, but will also enhance the production of products that are of economic value and can serves as alternative substitute to petroleum fuel, while promoting the conversion of waste to energy and wealth. Furthermore, the use of catalyst such as ZSM-5 zeolite catalyst during pyrolysis will increase the yield of aromatics, naphthalenes and alkylated naphthalenes.

Several studied have reported the use of zeolite catalyst for plastic waste pyrolysis (Williams, 2013; Osayi *et al.*, 2014; Ryan, 2015; Strydom, 2017). Zeolite catalyst is expensive and would impact cost of pyrolysis, thus the need to source for a cheap and readily available catalyst in Nigeria such as calcium oxide (CaO) obtainable from limestone ($CaCO_3$). This led to the investigation of the comparison between zeolite and kaolin catalytic pyrolysis by Gandidi, *et al.*, (2018). All these studies have deeply examined the effect of zeolite catalyst on pyrolysis oil from different perspectives, however, no studies have been reported to in current extant literatures on the comparative studies of the effect of a cheaply source catalyst like CaO from $CaCO_3$ which is readily available in large quantity in Nigeria with zeolite catalyst which is expensive, on waste plastic pyrolysis liquid. This therefore, necessitate the need for this study.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Introduction

There is rising environmental concern over plastic waste generation and disposal worldwide in recent times. Plastics have become an indispensable material used in several countries of the world, due to their durability, lightweight as well as flexibility and are utilized in a range of industrial and domestic areas. The utilization of plastic and its waste generation has continuously grown in several countries of the world, contributing part of solid waste generation globally (Khan *et al*., 2016). In Nigeria, plastic waste generated are predominantly plastic bottles, bags and packages and remain a large proportion of municipal solid waste. These plastics waste generated are not biodegradable and poses risks of flooding by clogging of drains and degradation of air quality from open dumps (Morten *et al.*, 2018). As a result, there have been concern for the need to source for an effective and sustainable plastic waste management system through conversion to valuable and useful products that will significantly reduce the volume of waste plastics generated. In lieu of this, there have been focus on conversion of plastic waste to a valuable source of energy and chemical substances through pyrolysis process.

This chapter therefore, review existing literature on plastic waste generation. It also, review literatures on used plastics, proximate and ultimate analysis of plastic wastes as well as plastic wastes disposal and its environmental impact. This chapter further reviews current methods for treating plastic wastes and their challenges. Likewise, literature review of pyrolysis of plastic wastes, types of pyrolysis process, plastic wastes pyrolysis products and application of plastic wastes pyrolized oil were carried out. Literature review of factors affecting pyrolysis of plastic wastes for fuel oil production and optimization of fuel oil yield were also carried out. Additionally, a review of literature on fuel properties were discussed.

2.2 Plastic

Plastics materials are made up of large, organic or carbon-containing molecules that can be formed into a variety of products. The molecules that compose plastics are long carbon chains that give plastics many of their useful properties. In general, materials that are made up of long, chainlike molecules are called polymers. The word plastic is derived from the words plasticus which is the Latin word for “capable of molding” and plastikos which is the Greek word for “to mold,” or “fit for molding” (Liu, 2007). Plastics can be made hard as stone, strong as steel, transparent as glass, light as wood, and elastic as rubber. Plastics are also lightweight, waterproof, chemical resistant, and produced in almost any color. More than 50 families of plastics have been produced, and new types are currently under development.

Like metals, plastics come in a variety of grades. For instance, nylons are plastics that are separated by different properties, costs, and the manufacturing processes used to produce them. Also, like metals, some plastics can be alloyed, or blended, to combine the advantages possessed by several different plastics. For example, some types of impact-resistant (shatterproof) plastics and heat-resistant plastics are made by blending different plastics together (Anthony, 2009). Plastics are moldable, synthetic (chemically-fabricated) materials derived mostly from fossil fuels, such as oil, coal, or natural gas. The raw forms of other materials, such as glass, metals, and clay, are also moldable. The key difference between these materials and plastics is that plastics consist of long molecules that give plastics many of their unique properties, while glass, metals, and clay consist of short molecules

Plastic plays a significant role in enhancing the lifestyles of human in numerous sectors such as automotive, construction, electronic, healthcare, packaging and many more. According to Runal, Hannan, Sachin, and Basavaraj (2015), plastic is a generic term for a wide range of polymers produced using highly refined fractions of crude oil, or chemicals derived from crude oil, known as monomers. Polymers are formed by the reaction of these monomers, which results in chain lengths of tens or hundreds of thousands of carbon atoms. Some polymers also contain oxygen (e.g. polyethylene terephthalate (PET)), whereas others contain chlorine (polyvinyl chloride (PVC)). It is worth noting that only a small proportion (< 5%) of the crude oil processed in the world is used to produce the monomers (e.g. ethane, propene etc.) used in the manufacture of polymers (e.g. polyethene, polypropylene, etc.). Plastic is widely used in industry, domestic, chemical engineering, construction and many other applications.

2.2.1 Global plastic production

The world's annual consumption of plastic which was five million tons in the 1950's has skyrocketed to a global production of 245 million tons in 2008 (Gao, 2010), and over 299 million tons of plastics produced in 2013, representing a 4 percent increase over 2012 (Anup and Vilas, 2014; Sharuddin, Abnisa, Daud and KAroua, 2017). As at 2016, the global annual production of plastics is put at 330 million metric tons (Plastics Europe, 2017). Including the resin used in spinning textile fibres, this figure was closer to 393 metric tons as at 2016, a value that interestingly matches the global human biomass (Lenzing Group, 2016). At the present rate of growth, plastics production is estimated to double within the next 20 years (Lebreton and Andrady, 2019). This impressive success of plastic is unparalleled by any competing materials used in packaging or construction which are the two major applications areas of plastics as shown in Figure 2.1.

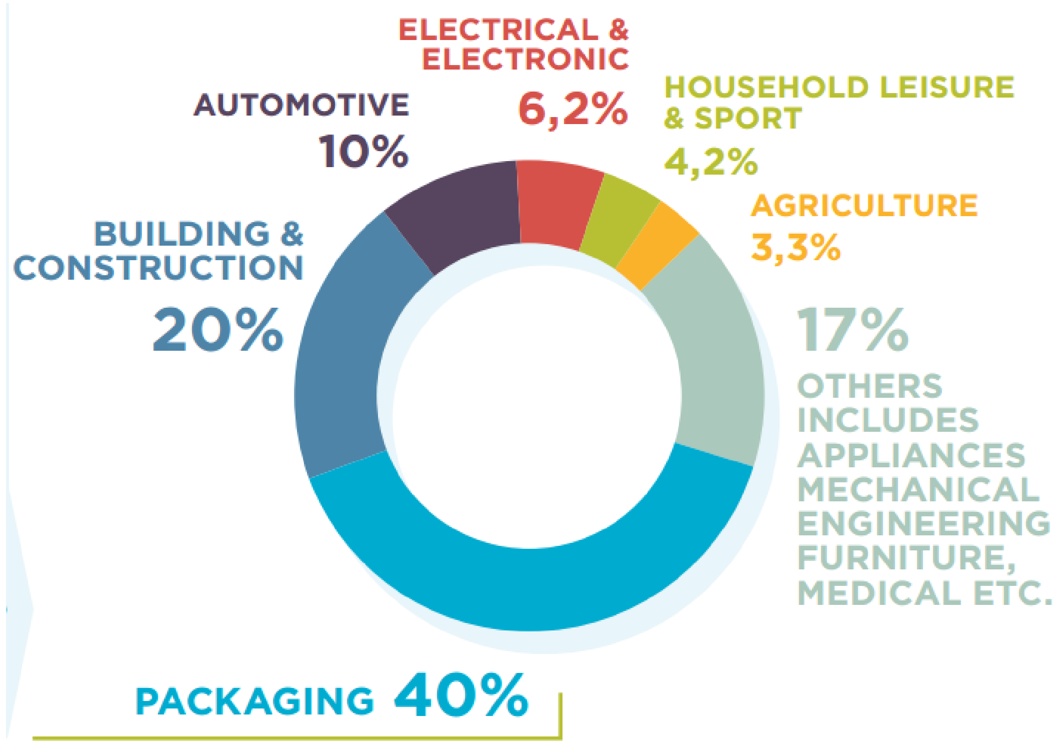

Figure 2.1: Worldwide plastic production in 2017 according to sector share (Plastics Europe, 2017)

It has been projected that global plastic production could triple by 2050 (Brussels, 2013), as its use has increased twentyfold in the past half-century and is expected to double again in the next 20 years. Over the years, plastic has increasingly replaced metals, glass, ceramics and wood in many products. Plastic packaging materials are now employed in the food, beverage and other fast moving consumer goods industries (Babayemi *et al.*, 2018). It is the considerable societal benefits of plastics that account for its popularity as a material as it represents a low-cost, easily formable, high-modulus, hydrophobic, bio-inert material that finds use in a bewildering range of consumer products. It is often the preferred and an indispensable choice in consumer packaging that accounts for 42% of the global annual resin production (Geyer *et al.*, 2017). Projected increase in future plastic use will result in a concomitant increase in post-consumer plastic waste as the end-of-life of plastics present solid waste management challenges. The challenge of plastic waste management, particularly recycling, is a global issue, especially in African countries where robust waste management systems are lacking.

2.3 Plastic Waste Generation

Plastic waste, is a waste stream with recycling and recovery potential. However, the rate of recycling is not keeping up with the rate at which virgin plastics are being produced and a higher proportion of plastics is being disposed of in landfills and dumpsites than ever before. The predicted rise in global plastic production in the next 30 years could exacerbate those impacts or contribute to the rising rate of plastic waste generation. Since the beginning of the plastic production era, 8,300 million tonnes (Mt) of plastics have been produced and only 7% has been recycled (1950-2015) (Geyer *et al.*, 2017). According to Lebreton and Andrady (2019), projected increase in future plastic use will result in a concomitant increase in post-consumer plastic waste. Plastics Europe (2017) opined that, by 2025 the global urban population is estimated to generate over 6 million ton of solid waste daily which over 10% account for plastics in the solid waste stream. This amounts to over 200 million ton of waste plastics which was the entire global plastic resin production in 2002 (Plastics Europe, 2017).

A large chunk of this plastic waste generated are disposed indiscriminately. For instance, a large proportion, 4,600 Mt, has been discarded, entering landfill or leaking into the environment (Geyer *et al.*, 2017). This steady leakage of plastic into the ocean owing to lack of management is causing pressing environmental issues. This makes environmental concerns of plastic waste to become crucial nowadays. Scientists point out that we live in the Plasticene era (Bottero *et al.*, 2015), where geologists already find plastic conglomerates as deposits. Furthermore, the ocean biota are overwhelmed with plastic waste, both in water and biomass. Solutions for plastic waste are widely discussed and the first recommended solution is to substitute, the second is to recycle sorted waste or reuse waste for energy. However, in Africa, the lack of appropriate solid waste management is a major problem in Africa and other developing countries and a major reason for plastic pollution.

2.3.1 Environmental impact of waste plastic disposal

Plastics are easy and cheap to make and last a long time, which sharpened its usefulness and underpin the huge environmental impact and pollution problem associated with their disposal. According to Forbid, Ghogomu, Busch, and Frey (2011), plastics are readily discarded due to low cost and low density yet their persistence in the environment causes land pollution and blockages in drainage lines causing floods in some cities. According to statistic, about 38% of the plastic waste still went to the landfill, 26% were recycled while 36% were utilized for energy recovery with the waste discarded still on the rise (Association of Plastic Manufacturers Europe, 2015). This signifies that the percentage of plastic waste dumped in the landfill is high and it occupied a large space. Moreover, the degradation of these waste plastics may take up thousands of years which makes its continuous disposal in the landfill to have continuous and negative environmental impact. Studies have suggested that plastic bags and containers contaminate the soil and water, and poses significant ingestion, choking and entanglement hazards to wildlife on land and in the ocean. Due to their light weight and balloon-shaped design, plastic bags are easily blown in the air, eventually ending up on land and in the ocean. According to Jambeck (2015), plastics in the environment pose significant hazards to wildlife both on land and in the ocean. High concentrations of plastic materials, particularly plastic bags, have been found blocking the breathing passages and stomachs of hundreds of different species. Plastic bags in the ocean resemble jellyfish and are often ingested by turtles and dolphins who mistake them for food. There is emerging evidence that the toxic chemicals added during the manufacturing process transfer from the ingested plastic into the animals' tissues, eventually entering the food chain for humans as well.

When plastic breaks down into microplastic particles, it becomes even more difficult to detect and remove from the open oceans. Plastic waste and microplastics, if ingested by fish or other marine life, can enter our food chain. Microplastics have already been found in common table salt and in both tap and bottled water (Yang, Shi, Li, Li, Jabeen and Kolandhasamy, 2015; Kosuth, Wattenberg, Mason, Tyree, and Morrison, 2017). Although in recent years' research on the effects of microplastics has been growing, still little is known about the exact impacts on human health. Other impacts of plastic waste pollution include:

a) Plastic components eaten by animals, birds and fishes causing intestinal blockages, digestive and starvation crisis resulting in death
b) Oceans" pollution is on the rise with over 90% of articles and waste at sea beaches containing post-consumer plastics
c) Plastic waste causes aesthetic nuisance in cities, presents risk to biodiversity destruction resulting from direct entanglement and trapping of plant roots.
d) The potential environmental impacts from plastics are categorised under global warming, acidification, eutrophication and photochemical ozone creation (Yang *et al.*, 2015). Limitations to plastic recycling includes: recycled plastics have lower quality compared to virgin materials and possess a low economic profile due to high recycling cost. Although, the application of the substitution factor (SF) has improved the cost effectiveness of plastic recycling to about 10%, this is still below expected economic incentive level. Thermal recycling of non-recyclable waste plastics offers the most attractive and cost-effective option (Kosuth *et al.*, 2017).

2.4 Degradation of Polymeric Materials

With an increase in the use of various types of plastics, the release of their waste into the environment also increased and the growing amount of the plastic wastes is becoming dangerous (Jan, Shah and Gulab, 2010). Polymer wastes are regarded as a potential cheap source for energy need & chemical industry. In Europe, the plastic consumption (growing annually by 4-8 %) was 45 Mt while the amount of waste from plastics was nearly 30 Mt in 2000. The amount of plastic consumption is increasing continually. So, it can be said that the plastic waste amount is also increasing day by day (Bursali, 2014). The plastics wastes are estimated about 10 % (by weight) of total municipal solid wastes. The percentage is nearly 20 % in volume. Plastics cause a serious environmental problem because of their low biodegradability. Therefore, new radical solutions which are based on source reduction, recycling, and re-using are being searched nowadays.

One-way to dispose the plastic wastes is landfilling which is not recommended because of economic and environmental reasons. Besides, the landfilling areas have become inadequate lately. One of the other treatment options for plastic wastes is incineration which is hazardous to the environment because of the toxic gases and soot particles which are released during the incineration process. There is the Kyoto Protocol which considers of reducing CO_2 emission by 20% and apart from these, another alternative for treating industrial and municipal polymer wastes is recycling (Bursali, 2014). This method is considered as promising solution to the problem of increasing plastic waste amount in the world. The recycling can be done both mechanical and chemical. Mechanical recycling is the conversion of used polymeric materials into new, utilizable products. This method is a popular recovery path for manufacturers. The recycling process takes place on single-polymer waste streams which is considered as a market for recycled products. But the quality of the products might not be close to the original ones. Moreover, these products are often higher priced than the virgin ones.

The other recycling method is chemical recycling. The aim of this method is to convert polymer wastes into basic petrochemicals which can be used as hydrocarbon feedstock or fuel oil for a variety of downstream processes (Singhal, Singhal and Upadhyayula, 2010). There are three main approaches in chemical recycling, they are partial oxidation, depolymerisation and cracking. Cracking process is the breaking down of the polymer chains. At the end of this reaction, useful lower molecular weight compounds are obtained. Cracking of polymeric materials includes mainly, non-catalytic thermal degradation, catalytic thermal degradation and hydrocracking degradation

Hydrocracking of polymers is the reaction of polymers using H_2 over a catalyst in an autoclave at moderate pressures & temperatures. The most important purpose of this method is to produce a high-quality gasoline using a wide range of feeds. Polyolefins, PET, PS, PVC and mixed polymers can be regarded as the typical feeds for hydrocracking while the non-catalytic thermal degradation is the process which produces a broad product range. However, it requires high operating temperature and long reaction time (Bursali, 2014). The non-catalytic thermal decomposition of polymers refers to the case where polymers at elevated temperatures start to undergo chemical changes without the involvement of another compound. The thermal degradation reaction is carried out at an inert atmosphere. The catalytic thermal decomposition of plastic waste offers considerable advantages such as lower temperatures and upgraded product quality when compared to the noncatalytic thermal decomposition.

2.4.1 Catalytic thermal degradation of polymeric material

Catalytic degradation takes place at considerably lower temperatures & reaction times. Hydrocarbons which can be used as motor engine fuel are produced by this method, eliminating the necessity of further processes (Singhal *et al.*, 2010). The advantages of catalytic thermal degradation are as follows:

a) In the presence of catalyst, the polymer molecules start breaking down at lower temperatures compared to the non-catalytic thermal degradation. A notable catalytic conversion of polyolefins into volatile end products has been detected at low temperatures even at 200 °C. On the other hand, in the non-catalytic thermal degradation of polyethylene and polypropylene, to observe the formation of gases, the reaction temperature should be high, more than 400 °C.
b) In the same reaction temperature, the catalytic thermal degradation of polymers is faster than the non-catalytic thermal degradation. At the temperature of about 400 °C, the first volatile products are observed just after a few minutes of contact of polymer with the catalyst.
c) The end products of catalytic degradation of polymers have higher quality than that of the products of thermal degradation. Produced oils have similar properties to commercial gasolines with the presence of high proportion of branched, cyclic and aromatic structures.

2.4.2 Catalysts used for catalytic degradation

A wide variety of catalyst such as, acidic and basic solids, Friedel-Crafts catalysts, bifunctional solids has been studied in the degradation reaction. They were effective in promoting the decomposition of plastic materials. The mostly used catalysts in plastic degradation reactions are acidic solids which are mainly, zeolites, amorphous silica-alumina and alumina because they show high catalytic activities. These types of materials are usually used in petroleum processing and petrochemical industries. Their catalytic activity and product selectivity depend on their textural and acid properties. Because the performance of the catalyst in the degradation reaction is mainly related to the type of the acid sites in the material, the acidity of the catalyst is an important factor. The acid sites are closely related to the Lewis and Bronsted acid sites. Also, the presence of acid sites in the catalysts accounts for their capability to produce carbocations on their surface, which facilitate degradation of the polymeric materials (Bursali, 2014).

Zeolites are microporous crystalline silicoaluminates. They have a perfectly defined crystalline structure based on the linkage between SiO_4 and AlO_4^- tetrahedra through oxygen bridges. The pore sizes which are below 1 nm allow different molecules to enter, diffuse and react within them. Zeolites are classified according to their pore size (small, medium and large), the number of channel systems, and aluminum content (Singhal *et al.,* 2010). Alumina and amorphous silica-alumina are usually mesoporous materials. The pore size, pore volume, and surface area of alumina and amorphous silica-alumina depend mainly on the synthesis method. Also, their textural properties can be controlled to a certain extent by changing the synthesis conditions. These parameters are also highly relevant in determining the catalytic properties of these materials (Bursali, 2014).

2.5 Pyrolysis

Pyrolysis processes have been used by chemists since the 16th century with landmark discoveries such as Valentine's discovery of sulfuric acid and Brandt's discovery of phosphorous (Lovett, 1997). Pyrolysis of organic compounds was a common technique for the investigation of structural and chemical behavior until about the end of the nineteenth century. In 1929 Hurd’s, “The Pyrolysis of Carbon Compounds,” provided an extensive review of pyrolytic processes at the time and have been a valuable source of factual information and an influence on organic chemical research for over 50 years.

Pyrolysis is generally defined as the controlled heating of a material in the absence of oxygen. In plastics pyrolysis, the macromolecular structures of polymers are broken down into smaller molecules and sometimes monomer units and further degradation of these subsequent molecules depends on a number of different conditions including (and not limited to) temperature, residence time, presence of catalysts and other process conditions (Mantesh and Basavarajappa, 2017). The pyrolysis reaction can be carried out with or without the presence of catalyst. Accordingly, the reaction will be thermal and catalytic pyrolysis. Plastic waste is continuously treated in a cylindrical chamber. The plastic is pyrolised at 300 ^{0}C – 500 ^{0}C.

Gaurh and Pramanik (2013), stated that, the Pyrolysis process consists of the thermal degradation of the wastes in the absence of oxygen/air. In pyrolysis process, the polymeric materials are heated to high temperatures, so their macro-molecular structures are broken down into smaller molecules and a wide range of hydrocarbons are formed. These pyrolytic products can be divided into; a gas fraction, liquid fraction (paraffin’s, olefins, napthenes and aromatics), solid residues and can either be by thermal cracking or catalytic cracking. Pyrolysis process is basically a cracking process usually applied to long chain heavy hydrocarbons to break them down to light hydrocarbons, a process known in many books and researches as depolymerization (Bright, 2018).

Extensive studies on pyrolysis as a way to convert waste such as tires, plastic, biomass etc. into useful products have been carried out for decades (Sermin, 2012). According to Altayeb (2015), pyrolysis of involves the thermal degradation of the materials such as plastic or rubber at temperature in the range of 300 – 900 °C in an inert atmosphere. The pyrolysis, have received increasing attention since the process conditions may be optimized to produce high energy oil, gas and residual char. In the pyrolysis process, the organic volatile matter of the feed materials is decomposed to low molecular weight products, liquid or gases. The inorganic components and the non-volatile carbon black remain as a solid residue which is relatively unaltered, and therefore can be recycled in worthwhile applications.

2.5.1 Types of pyrolysis process

Pyrolysis process can be performed under different operating conditions (Table 2.1) and are classified base on these conditions. Pyrolysis can have a variety of types such as Torrefaction, slow pyrolysis, vacuum pyrolysis, and flash pyrolysis. Although all of these and other additional ones were thoroughly reviewed for the present study. According to Osayi *et al.* (2014), pyrolysis process is differentiated by residence time of the pyrolysed material in the reactor, process temperature, feed particle size and heating rate. The various types of pyrolysis include slow pyrolysis, fast pyrolysis, flash pyrolysis and catalytic pyrolysis as shown in Table 2.1.

Table 2.1: Pyrolysis: Technologies (Osayi *et al.*, 2014)

Technology	Residence time	Heating rate	Temp (°C)	Major products
Slow pyrolysis	Hours – days	Very low	300 - 500	Charcoal
Conventional pyrolysis	5 – 30 min	Medium	400 - 600	Char, liquids, syngas
	5 – 30 min	Medium	700 - 900	Char, syngas
Fast pyrolysis	0.1 – 2 sec	High	400 - 650	Liquids
	< 1 sec	High	650 - 900	Liquids, syngas
	< 1 sec	Very high	1000 - 3000	Syngas

2.5.1.1. *Flash Pyrolysis*

According to Antoniou and Zabaniotou (2013), flash pyrolysis is characterized by high heating rates, temperatures between 450 °C to 600 ℃ and short residence times of less than one second which make these conditions perfect to prevent cracking of the gases into non-condensable gases while maximizing the liquid product yield. It is a process characterized by residence time of less than 0.5 sec, high heating rate of more than 200 ℃, particle size of less than 0.2 mm, and high reaction temperature of up to 1000 ℃ and above (Osayi *et al.*, 2014). However, the major technological challenge of the flash pyrolysis process is poor thermal stability, solids in the oil, and production of pyrolytic water.

In order to have a successful flash pyrolysis system, a large amount of heat must be fast and continuously transferred to the material to sustain the pyrolysis reactions. The process is characterized by rapid devolatilization in an inert atmosphere, high heating rate of the particles, high reaction temperatures between 450 ℃ and 1000 ℃ and very short gas residence time of less than a second (Osayi *et al.*, 2014). This process has some technological limitations such as; solids in the oil, increase of the viscosity over time by catalytic action of char, poor thermal stability and corrosiveness of the oil, alkali concentrated in the char dissolves in the oil and production of pyrolytic water.

2.5.1.2 *Fast Pyrolysis*

Fast pyrolysis as the name implies indicates a rapid thermal decomposition that is characterized by higher heating rates and usually requires a feedstock with small particle sizes and the reactor is specially designed to allow quick removal of the vapors released. Fast pyrolysis is recognized as an effective conversion route for the production of liquid fuels, chemicals and derived products with higher yield usually in the range of 50 – 60 wt.% (Martinez *et al.*, 2013). Altayeb (2015) stated that fast pyrolysis involves the rapid heating of the feed material to a high temperature in the absence of oxygen with a short residence time of the condensable vapour in the reactor.

Osayi *et al.*, (2014) reported the operating parameters for fast pyrolysis as; solid residence time of 0.5 – 10 sec, heating rate of 10 – 200 ℃/sec, feed particle size less than 5 mm, and reaction temperature of 550 –1200 ℃ and usually requires a feedstock with small particle sizes and specially-designed devices to allow quick removal of the vapors released. This type of pyrolysis has received much popularity in producing liquid fuels and a range of specialty and commodity chemicals. On weight basis, fast pyrolysis typically yields 60 – 75% and 50 – 60% oil with 15 – 25% higher yield compared to other processes (Osayi *et al.*, 2014; Altayeb, 2015). Fast pyrolysis has been reported to have low investment costs and high energy efficiencies particularly on a small scale compared to other type of pyrolysis.

2.5.1.3 *Slow Pyrolysis*

Slow pyrolysis, as the name suggests, is a slow thermal decomposition at low temperatures and is characterized by low heating rates, relatively long solid and vapor residence times, and sometimes by low temperature (Altayeb, 2015). For instance, it is necessary to heat materials in slower rates in order to analyze the degradation of the materials and the products. Longer residence times result in leading secondary conversion of primary products, yielding more coke, tar, as well as thermally-stable products. According to Martinez *et al.* (2013), slow pyrolysis is sometimes referred to as carbonization and unlike fast pyrolysis, the objective of slow pyrolysis is the char production, although tar and gases are also obtained but not necessarily recovered.

In slow pyrolysis, vapor remains in the reactor between 10 – 60 min and it is mostly used for char production and the range of heating rate is between 0.1 and 1 ℃/sec. Osayi *et al.*, (2014) stated that, the solid residence time in the slow pyrolysis reactor is in the range of 450 – 550, heating rate is 0.1 – 1 ℃, and feed particle size of 5–50 mm with temperature of 550 – 950 ℃ used to pyrolized used tyres as a slow rate. This process enhances char production and is unlikely to be unsuitable for high quality bio-oil production. Also, due to high residence time, secondary reaction is favourable as cracking of primary product occurs which could adversely affect bio-oil yield and quality. Altayeb (2015) reported that, the longer residence times result in leading secondary conversion of primary products, yielding more coke, tar, as well as thermally- stable products and this is why slow pyrolysis is sometimes referred to as carbonization.

2.5.1.4 ***Vacuum Pyrolysis***

Vacuum pyrolysis was investigated, developed, and several studies have been conducted. As a result, a pilot plant with scrap tire feed material of 15 – 20 t/hr. has been established. Vacuum pyrolysis have some advantages compared with pyrolysis operated at atmospheric pressure which includes shorter residence time in the reactor which result in reduced undesirable reactions, higher pyrolysis oil yield and higher aromatic chemical concentration in the pyrolysis oil which enhanced the octane value (Altayeb, 2015). Conversely, naphtha content of low boiling point fractions in the pyrolysis oil is low, due to the evacuation of volatile vapors from the pyrolysis reactor by a vacuum pump, which prevents secondary cracking of volatile vapors, hence, the condensed pyrolysis oil composed mainly, of compounds with a high boiling point while the content of naphtha in pyrolytic oil was low (Jasmin *et al.*, 2008).

At low pyrolysis temperature, the oil was mainly composed of small molecule compounds with low boiling points. As a result, the content of naphtha in pyrolytic oil was higher, but the yield of pyrolysis oil was very low and thus the total yield of naphtha would be rather low, a factor which should be considered (Altayeb, 2015). In general, the content of naphtha in the pyrolysis oil obtained under vacuum conditions is often lower than that obtained under atmospheric pressure and the percentage of limonene in naphtha is the highest which has high economic value and extensive applications, so market demand for limonene has increased rapidly. Hence, when the

2.5.1.5 *Catalytic Pyrolysis*

Catalytic Pyrolysis is considered as an advanced conversion technology in which an organic waste degradation reaction at high temperature is reached with total or partial absence of oxygen to obtain liquids, solids, and gas products (Claudinho and Oscar, 2017). Catalytic pyrolysis is becoming an important area of investigation and is considered a very promising field. The influence of the catalyst is to reduce the yield of oil with a consequent increase in the gas yield. Hence, the catalyst causes an increase in the cracking of hydrocarbons into shorter chain lengths, which decreases oil yield while increasing the amount of gases evolved (Altayeb, 2015). As pyrolysis processes are endothermic unlike the combustion process the supply of heat is essential to the system. According to Osayi *et al.,* (2014), catalytic pyrolysis is a pyrolysis process that includes the use of a catalyst in enhancing the pyrolysis reaction kinetics by cracking down higher molecular weight hydrocarbon compounds to lighter hydrocarbon products. Catalytic pyrolysis has been used to enhance the concentration of higher value chemicals (limonene, benzene, toluene) in the oil and produce oil which can be used as a chemical feedstock rather than fuel (Alkhatib, 2015).

Heterogeneous catalysts are the most commonly applied catalyst for plastic pyrolysis. Zeolites and mesoporous materials are the most important heterogenous catalysts due to their porous structure and acid properties. The most used catalysts are Y-type zeolite, ZSM-5, and Al_2O_3. In addition, single ring aromatic hydrocarbons, benzene, toluene and xylenes present in the oils, can noticeably increase in the presence of the catalyst. Naphthalene and alkylated naphthalene show a similar increase in concentration when a catalyst is present. According to Islam *et al*. (2010), NaOH, $CaCO_3$, MgO, Zeolite are the most famous used catalysts while NaOH, for example, can promote the rapid cracking of organic compounds in feed materials into small molecular compounds, even at low temperatures.

Williams (2013) reported that the use of catalyst in pyrolysis systems can greatly influence the composition, quality, and yield of products. The major catalysts used in pyrolysis are; Aluminium-based catalyst, $CaCO_3$, CaC_2, $Cu(NO_3)_2$, Na_2CO_3, NaOH, MgO, perlite, zeolite-based catalyst among others (Williams, 2013; Osayi *et al.*, 2014), and operating conditions can determine different product distribution for different catalysts. Also, Ni-Mg-Al catalyst was reported by Alkhatib (2015), to increase the yield of gas product from 22% without catalyst into 43% with catalyst, and the H_2 concentration, as well, in the gas product was changed from 26% into 67% in respect. Pyrolysis catalyst can be categorized based on their method of application. The first category is when the catalyst is added to the feedstock before being fed into the reactor while the second category is when catalyst is added after the feed is already heated up in the reactor allowing it to have immediate contact with vapours, solid, and char, however, the third categorized is when the catalyst is placed in another reactor located downstream from the pyrolysis reactor (Osayi *et al.*, 2014).

2.5.2 Plastic pyrolysis process

Pyrolysis process is basically a cracking process usually applied to long chain heavy hydrocarbons to break them down to light hydrocarbons, a process known as depolymerization. Plastic pyrolysis has been found to produce an average liquid yield of 50 wt% (Wong *et al*., 2015). Over the past decades, several researchers studied plastic waste pyrolysis with focus on understanding the process to optimize it and also, the impact of different type's of plastics on the process has also been studied by several authors. Researchers including Kaminsky, Scheirs and their associates investigated the effects of reaction conditions on the products and identified temperature as the most influential condition (Kaminsky, Schlesselmann and Simoon, 1995). Other conditions included plastic waste substrate or chemical composition of feedstock, reaction time, catalyst, heating rate, pressure, and other chemical interference like the presence of air, and H_2. The effect of chemical interference is not a concern as the process used in this study did not incorporate any chemical for the pyrolysis process (Bright, 2018).

Others including Williams have studied the pyrolysis of different plastic types, and mixed plastic wastes and found out that different plastic types produce different product yield and product composition. They also identified that the percentage of liquid oil yield produced using mixed plastic waste is significantly lower than the yield for individual plastic types with high liquid oil (Williams, 2013). Also, Mantesh and Basavarajappa (2017), examine plastic waste into fuel using pyrolysis process (without oxygen and in high temperature of about 300 °C) using low density polyethylene plastic wastes to get fuel oil that has the same physical properties as the fuels like petrol, diesel etc. they found that, converting waste plastics into fuel hold great promise for both the environmental and economic scenarios, hence, the process of converting plastics to fuel has now turned the problems into an opportunity to make wealth from waste. All of these studies were centered on the effects of operating temperature, heating rate, and catalyst on product yield (Bright, 2018). Laboratory scale process including batch or semi-batch systems were used in these studies.

According to Bright (2018), most of these studies however were focused on the plastic waste types commonly known to the public such as High-density polyethylene (HDPE), Low density polyethylene (LDPE), Polypropylene (PP), Polyethylene Terephthalate (PET), and Polystyrene (PS) among the seven main categories of plastics which are usually identified in domestic waste streams. There are several plastic types categorized as others, an example being thermoplastic polyurethane (TPU). Some of these plastic types are mostly produced for special purposes including the manufacturing of medical equipment and TPU is one of them. TPU find use in a number of medical applications including catheter and general-purpose tubing, hospital bedding, surgical drapes, wound dressings, as well as in a variety of injection molded devices and also as a short-term implant all as a result of it good biocompatibility, flexibility, high resistance to abrasions and strength, and versatility (American Chemistry Council, 2018). This study was therefore focused on low density plastic waste (LDPE).

2.6 Factors Affecting Plastic Waste Pyrolysis

Several factors have been reported to affect pyrolysis of materials. Pyrolysis is the use of heat to break down materials without the presence of oxygen. The yield and products obtainable from plastic waste are influenced by several factors or operating conditions which have direct or indirect effect on the pyrolysis process. The factors that influences pyrolysis of plastics are, chemical composition of the feedstock, cracking temperature and heating rate, type of reactor, residence time, use of catalyst, pressure, and other chemical interference like the presence of air, and H_2 (Gao, 2010; Alsaleh and Sattler, 2014; Alkhatib, 2015; Rowhani and Rainey, 2016; Mulaudzi, 2017). The pyrolysis process provides various operational, environmental, and economical advantages. Under pressure and heat, the long chain polymers of hydrogen, oxygen, and carbon decompose into short-chain petroleum hydrocarbons with a ceiling length of around 18 carbons. Hence, the factors that affect the yield and product obtainable from plastic waste pyrolysis are mainly, pressure, temperature, residence time, particle size, heating rate, and presence and type of catalyst. These factors are discussed subsequently.

2.6.1 Composition of feedstock

Plastic materials are polymers made up of a combination of monomers using chemical reaction technologies. Hence, this implies that plastic material is made up of long chain of monomers. When plastics are subjected to a cracking process, the chains linking this monomer together is broken returning the polymer material into its initial monomer state. This implies that the constituent of the product obtained by pyrolysis of plastic is dependent on the monomer composition of the plastic waste materials. Ahmad *et al.,* (2014), stated that polyethylene plastic pyrolyzed is likely to yield a product with an ethylene constituent. Some of the most commonly used polymeric hydrocarbons include HDPE, LDPE, PP, PS, PET, PVC, TPU and others. The plastic wastes generated in most part of the country are made up of all these plastic types and a few under those categorized as others and a few of these types (HDPE, LDPE and PP) were selected for this study as the materials to be investigated because of their dominant presence as plastic waste in most part of the country.

For more specific classification of plastics is based on the shape of the polymer structure, polymerization mechanism and whether the structure of the polymer is linear, branched, or cross linked. Both structure and side chain functional group affect the product of pyrolysis. For instance, according to Gao (2010), the dominant component in the polystyrene pyrolysis product is styrene molecules and there are also possible reformation reactions taking place due to the composition of feedstock as it is evident that other component is identified in the product of pyrolysis of some plastic materials. Kumar and Singh (2013) work on the pyrolysis of HDPE showed that the dominant components are; n-Octadecane, n-Heptadecane, 1-Pentadecene, Octadecane, Pentadecane, and 1-Nonadecene resulting from reformation. This shows that the type of plastic materials being utilized for pyrolysis therefore had significant effect on the process and products obtainable from plastic pyrolysis.

Zhang *et al*. (2008) examine the characterization of the product obtained from pyrolysis of Thermoplastic Polyurethane (TPU) extensively, using temperatures ranging from 250 – 750 °C and found that the product composition distribution was dependent on the pyrolysis temperature. Also, pyrolysis of semi-rigid polyether-polyurethane have been reported to give weight yields of methane (16%), ethylene (4.8%) and benzene (4.6%) at 700 °C and 800 °C, with TPU pyrolysis at temperature greater than 450 ^{o}C reported to typically gives 5 – 25 %wt. char, 10 – 45 %wt. liquids and >40 %wt. gases (Baiden, 2018). It can be inferred from literature that possible fuel or fuel additives can be obtained from TPU pyrolysis.

Another commonly found plastic type across most state in Nigeria is the HDPE which are long chain polymers with high strength due to their linearization. Ahmad *et al.*, (2014), examine micro steel reactor pyrolysis of HDPE using a temperature range of 300 – 400 °C at a heating rate of 5 to 10 °C/min. It produces a liquid product yield of 80.88 wt%. Also, Kumar and Singh (2013) also reported liquid oil yield of 79.08 wt% using a pyrolysis temperature range of 400 – 500 °C in a semi-batch reactor and found from the

GCMS characterization of fuel the presence of functional groups such as alkanes, alkenes, alcohols, ethers, carboxylic acids, esters, and phenyl ring substitution bands with the main constituents as n-Octadecane, n-Heptadecane, 1 Pentadecene, Octadecane, Pentadecane, and 1-Nonadecene. Ahmad *et al.* (2014) also, conducted a study on PP pyrolysis and reported a liquid product yield of 69.82 wt% at a temperature of 300 ºC with a total conversion of 98.86%.

Similarly, Baiden (2018) also reported a liquid product yield of 80.1 wt% at a temperature of 380 ºC from PP and that the highest liquid product yield of about 82.12 wt% at a temperature of 500 ºC with further increase in temperature reducing the liquid product yield from PP pyrolysis. GC-MS characterization of liquid product from PP pyrolysis found to contain mainly, 2-methyl-4-octene; 2-methyl-2-octene; 2,6-dimethyl-2,4-heptadiene; 2,4-dimethyl-1-heptene; 2-methyl-1-octene (Baiden, 2018). The reports by these studies indicates different liquid yield produced for different plastic types which goes to confirm the influence of the raw material composition on product yield. Table 2.2 shows a comparison of products of the thermal and catalytic cracking of various plastic materials.

Table 2.2: Comparison of products of the thermal and catalytic cracking of plastic waste Baiden (2018)

	Property	HDPE	LDPE	LP	PP	PS	Average
Thermal cracking	Liquid yield (%) State of liquid	91.30 Milk white	91.71 Milk white	93.80 Milk white	91.05 Yellow	99.02 Rufous	93.38
	Product at normal temperature	Wax	Wax	Wax	Solid & liquid mixture	Liquid	
	Gas yield (wt %)	7.61	7.42	5.60	7.60	-	7.06
	Coke yield (%)	0.14	0.15	0.14	0.14	0.15	0.14
	Total yield (%)	99.05	99.28	99.54	98.79	99.17	99.17
	Lost (%)	0.95	0.72	0.46	0.21	0.83	0.63
Catalytic cracking	Liquid yield (%)	76.81	77.40	85.20	87.20	86.20	82.57
	State of liquid	Solid +	Solid +	Light yellow	Light yellow	Rufous	
	Product at normal temperature	Liquid mixture	Liquid mixture	Liquid	Liquid	Liquid	
	Gas yield (wt %)	14.08	14.08	8.15	9.34	0.34	9.20
	Coke yield (%)	8.04	8.04	6.52	3.35	13.02	7.80
	Total yield (%)	99.79	99.79	99.87	99.89	99.56	99.78
	Lost (%)	0.21	0.21	0.13	0.11	0.44	0.22
Other properties	Temperature range (°C)	400-450	420		450-640		400-640
	Conversion rate (%)	95% oil products			50-80% in catalyst & water		
	Characteristic products	Oil: C_{10}-C_{30} (94.5%); Gas: H_2, C_1- C_5 (5.5%)	Olefins (65%); Terminal olefin (35%); Non terminal olefin (5%)		Qualified gasoline for use		

2.6.2 Reaction temperature

Pyrolysis is basically a cracking process in which temperature is the most dominant thermodynamic parameter to consider and is responsible for the change in the physical properties of the plastic at different level before reaching the decomposition temperature. Pyrolysis reaction temperature resulted in the carbon chain been broken into shorter chains over the course of the processing temperature. During pyrolysis, thermoplastics materials gains sufficient energy as temperature rises to allow it chains to move freely during the glass transition state thereby obtaining a rubber-like form and the temperature at this point is known as the glass transition temperature (T_g) (Gao, 2010). The melting state is the state where a liquid-like form is obtained and the temperature at this point is the melting temperature (T_m) while, beyond this state is where decomposition starts and the temperature at this state is the decomposition temperature (T_d). During pyrolysis, plastic material goes through different stages and an understanding of the temperature profile during this stage transitions is vital to determining the optimum operating temperature for the pyrolysis process. For instance, Figure 2.2 shows the various transition as applied to Polyethylene Terephthalate (PET) with it corresponding temperature profile showing the plastic going through glass transition, cold crystallization, melting before decomposition (Baiden, 2018).

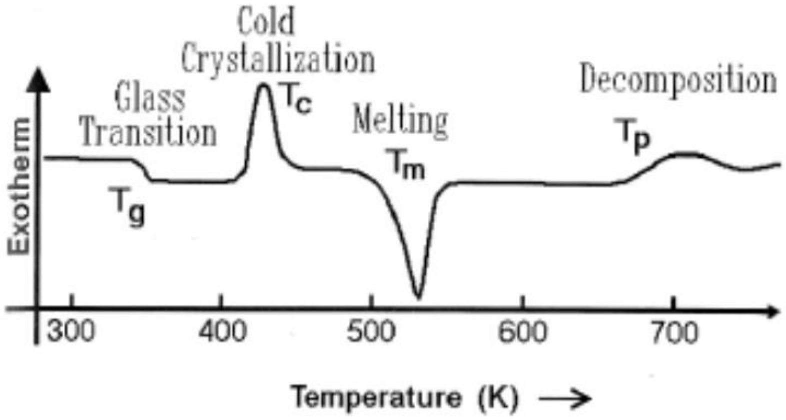

Figure 2.2: The transitions phase of PET with temperature variation (Baiden, 2018)

Several studies have been reported on effect of temperature on plastic waste pyrolysis and indicates that the thermal cracking temperature range differ according to the composition or type of plastic waste materials utilized. Cepeliogullar and Putun (2013) and Shafferina *et al*., (2016) reported that only a small change in weight occur during PET pyrolysis between 200 – 400 ºC with the major degradation occurring above 400 ºC. Cepeliogullar and Putun (2013) in their study on the utilization of two different types of plastic wastes from daily and industrial life, observe that maximum degradation of PET occurred at 427.7 ºC whereas no further degradation occurred beyond 470 ºC and they therefore concluded that degradation of PET material occurred within the temperature range of 350 ºC to 520 ºC. In a similar study, Chin, Yusup, Ahmed and Shaharin (2014) examine the kinetic studies of co-pyrolysis of rubber seed shell with high density polyethylene and found that thermal degradation of HDPE started at 378 – 404 ºC and almost completed at 517 – 539 ºC using thermogravimetric analysis with different heating rate. They also found that higher heating rate increases the rate of the reaction. Also, Baiden (2018) reported that the maximum degradation rate of HDPE occurred at 467 ºC and as such, temperature needs to be considered when running the pyrolysis experiment to ensure the most optimum liquid yield.

The investigation of the effect of temperature on HDPE and PP pyrolysis in a fluidized bed reactor shows that the decomposition of HDPE and PP happened within the range of 400 – 500 ºC based on derivative thermogravimetry analysis (DTG) curves (Shafferina *et al.*, 2016). They however, observed that the weight loss of PP fraction started to occur at lower temperature below 400 ºC in comparison to the HDPE fraction. Theoretically, PP degraded faster than HDPE since half of the carbon in PP chain is tertiary carbon, consequently ease the formation of tertiary carbocation during the degradation. Likewise, Shafferina *et al.*, 2016) investigated the pyrolysis of PS in a batch reactor and found that no reaction seems to take place at 300 ºC. However, they found that PS degraded completely into highly viscous dark-colored oil at lower temperature of 350 ºC. Hence it implies that the thermal degradation temperature of PS would be in the range of 350 – 500 ºC approximately (Shafferina *et al.,* 2016).

Aylon *et al*. (2010) reported that temperature increases from 425 °C – 600 °C promotes the formation and percentage increase from 13.1 – 22.9 wt% of C_{10} aromatic compounds from olefin due to Diels-alder reaction. In contrast, the percentage of non-aromatic C_5 – C_{10} decreases, due to thermal cracking and secondary reactions at high temperature. López *et al*., (2017) reported that higher temperatures favours aromatic formation reactions like the Diels-Alder reaction, recombination of aliphatics and aromatics free radicals, and the cyclisation of aromatic chains. An increase in temperature results in a decrease in limonene yield with a noticeable increase in aromatic compounds like benzene, toluene and xylene (BTX). Limonene is unstable at temperatures of above 500 °C and decomposes to form aromatics such as benzene, xylene, toluene, trimethylbenzene, m-cymene and indane (Danon *et al.*, 2015). An increase in temperature also generally results in an increase of the yield of unsaturated hydrocarbon gases at the expense of saturated hydrocarbon, as consequence of thermal cracking of the saturated hydrocarbons (Rowhani and Rainey, 2016). The change in gas composition has an effect on the calorific value of the gas fraction. The calorific value of the gas would increase with temperature due to the subsequent increase in composition of lighter hydrocarbons and hydrogen (Rodriguez *et al.*, 2001). Reactor temperature also has an effect on the composition of the oil product and the valuable chemicals in the oil. An increase in temperature results in an increase of the aromatic fraction whereas the aliphatic fraction decreases.

Osayi *et al.,* (2014) reported that, thermogravimetry analysis confirms that the pyrolysis of scrap tyre at atmospheric pressure commences at 250 °C and completes at 550 °C. The three primary products obtained from used tyre pyrolysis are 36 wt.% solid residues, 55wt.% liquid fraction and 9wt.% gas fraction. Also, thermogravimetry studies shows that initial devolatilisation of the different materials in the fedstock occurs in the temperature range of 150 °C – 350 °C and a final weight loss is observed at temperatures of around 450 °C – 500 °C (Mulaudzi, 2017). Rodriguez *et al.* (2001) reported that pyrolysis starts 300 °C, and concluded that pyrolysis had not been completed in the temperature range of 300 °C – 400 °C. Alsaleh and Sattler (2014), from several studies reported a temperatures range of 425 °C – 720 °C for oil production. Rowhani and Rainey (2016) reported a temperature range of 300 – 750 °C for tyre pyrolysis from several studies investigated. Aslo, Alkhatib (2015) reported a temperature range of 400 – 600 °C for tyre pyrolysis from several studies investigated. Furthermore, Strydom (2017) reported 400 – 600 °C from several studies investigated.

Therefore, from the literatures reviewed, it can be seen that temperature had significant impact on reaction rate and desired product yield. The different temperature values reported in literature are due to the different materials utilized during pyrolysis (PP, PS, PE, etc.) at different reaction temperatures. It was found that higher reaction temperature favors the gas production and production of heavy molecular weight products in the liquid. This was significant to this study as the effect of reaction temperature, on the product yield and composition was to be investigated for plastic waste. This study also involves optimization of the pyrolysis operating parameters in enhancing the recovery of fuel oil from plastic waste pyrolysis, and as such, pyrolysis temperatures that generally result in high yields, on the basis of the plastic waste needs to be considered. From the reviewed literature, the various authors have suggested varied pyrolysis temperature range in their studies and have shown a maximum oil yield to be in pyrolysis temperature range of 300 °C – 600 °C (Aylon *et al.*, 2010; Lopez *et al.*, 2010; Cepeliogullar and Putun, 2013; Chin *et al.* 2014; Osayi *et al.*, 2014; Danon *et al.*, 2015; Shafferina *et al.* 2016; Mulaudzi, 2017; Baiden, 2018). This study therefore, adopted a temperature range of 400 – 600 °C for the optimization study of plastic waste pyrolysis.

2.6.3 Heating rate

The other thermal dynamic parameter that affected pyrolysis is heating rate which implies the increase of temperature per unit time. The influence of the heating rate on the plastic waste pyrolysis process and product distribution varies in different studies due to the differences in the pyrolysis reactor, operation conditions (temperature and pressure), and temperature measurement location. Typically, in fast or flash pyrolysis, heating rate refers to the temperature change of the plastic from when it was dropped on the hot surface till decomposed and vaporized. Heating rate is a major factor that affect pyrolysis and a vital parameter that has to be maintained in order to ensure a constant supply of the heat required to effect degradation of plastic waste into various products (Martinez *et al.*, 2013).

According to Alsaleh and Sattler (2014), an increase in heating rate generally increases the temperature at which maximum cracking of volatile constituent from the plastic occurs, which increases the degradation rate. Higher heating rates lead to higher temperatures, which can result in formation of more secondary reactions vis-à-vis production of more gas-phase products and the nature of the secondary reactions can impact the composition of the gas as well as the liquid. Williams and Slaney (2007) found that heating rate usually varied from10 to 100 °C/minute in previous slow pyrolysis researches. Gao, (2010) reported the influence of heating rate on the reaction process of

Coca Cola drink PET bottles pyrolysis using TGA and found that higher heating rate promotes the rate of pyrolysis reactions.

Osayi *et al.,* (2014) reported that a heating rate of 20 °C/min, resulting in a pyrolysis product yield of 36 wt.% solid residues, 55wt.% liquid fraction and 9 wt.% gas fraction. Rowhani and Rainey (2016) reported the heating rate of a fast pyrolysis of 1200 °C/min, showed a direct dependency between pyrolysis temperature and product yields. Also, Martinez *et al.,* (2013) reported that the shifting of thermal decomposition during pyrolysis to higher temperatures with an increase in heating rate can be attributed to the combined effects of heat transfer and changes in the kinetics of devolatilisation which result in delayed decomposition. According to Alsaleh and Sattler (2014), operating at higher heating rates results in higher pyrolysis temperatures, which can result in an increase in the gas yield at the expense of the oil yield due to the occurrence of secondary reaction. Hence, an increase in heating rate increases the yield of primary devolatilisation products at the expense of secondary devolatilisation as maximum devolatilisation is moved to higher temperatures as heating rate has an effect on the characteristics of primary vapour products. Therefore, to obtain higher oil yield, a relatively low heating rate is required to prevent the formation of more secondary reactions which results in the production of more gas-phase products. Hence, a heating range of 15 – 50 ^{o}C/min is considered for investigation in the optimization study of plastic waste pyrolysis.

2.6.4 Pyrolysis pressure

Operating pressure in the pyrolysis reactor is another factor that have significant effect on both the pyrolysis process and the products. The boiling points of the pyrolysis products are increased under higher pressure, therefore, under pressurised environment heavy hydrocarbons are further pyrolyzed instead of vaporized at given operation temperature (Gao, 2010). The effect of pressure on hydrocarbon number and their fractions in the pyrolysis products of PE have been reported and found that under pressurized pyrolysis, more energy is required for further hydrocarbon cracking (Murata *et al.*, 2004).

High pressure has been reported to increases the yield of non-condensable gases and decreases the yield of liquid products because under pressurized pyrolysis, more energy is required for further hydrocarbon cracking. The average molecular weight of gas product also decreases with the increase of pressure (Murata *et al.*, 2004), and that the influence of pressure on the concentration of double bond, C=C, of the liquid product was not significant. Hence, pressure has major effects on the pyrolysis reaction and the distribution of PE pyrolysis products, but has minor effect on the double bond components.

2.6.5 Catalyst type

In order to optimize plastic pyrolysis reactions and alter the distribution of pyrolysis products, catalysts are widely used. Catalysts can be used to improve the rate of pyrolysis, oil yield and quality, and enhance selectivity of compounds such as aromatics for chemical production (Alsaleh and Sattler, 2014). The use of catalyst in plastic pyrolysis is to enhance the concentration of high value products and also to produce oil which can be used as a chemical feedstock such as limonene, benzene, toluene, etc., rather than fuel. Osayi *et al.*, (2014) reported that catalyst enhanced the pyrolysis reaction kinetics by cracking down higher molecular weight hydrocarbon compounds to lighter hydrocarbon products and has been reported that the use of catalyst in pyrolysis systems can greatly influence the composition, quality, and yield of products. The main, advantages of catalytic utilization during pyrolysis is to lower the activation energy required for cracking, thereby, lowering cracking temperature, increased reaction rate, increased production of isoalkanes, branched and cyclic molecules and aromatics as well as increased efficiency, and improved selectivity and quality of the product (Punkkinen *et al.*, 2017).

Osayi *et al.* (2014) reported the use of aluminium-based catalyst, perlite, CaC_2, $Cu(NO_3)_2$, zeolite-based catalyst while Alkhatib (2015) reported that $CaCO_3$, MgO, NaOH, Na_2CO_3 and Zeolite are the most famous used catalysts in addition to the above listed catalyst. Also, Ni-Mg-Al catalyst has been reported by Williams *et al.* (2010), that it increases the yield of gas product from 22% without catalyst into 43% with catalyst, and the H_2 concentration, as well, in the gas product was changed from 26% into 67% in respect. However, Shah, Jan and Mabood (2008) reported the use of calcium carbide (CaC_2) catalyst in tyre pyrolysis and observed about 60% increase in the oil yield comparing to non-catalytic pyrolysis. They found that the presence of a catalyst resulted in the increase of oil yield from 22.8 wt.% (non-catalytic) to 38.4 wt.% while the gas product decreased from 37 wt.% (non-catalytic) to 29.6 wt.%. Rowhani and Rainey (2016) however, reported that CaC_2 enhanced the diesel production but adding either of the catalysts reduced the amount of fuel oil and heavy oil.

Williams and Brindle (2003), examined three types of different zeolite catalysts, particularly, ZSM-5, Y-Zeolite (CBV-400), and Y-Zeolite (CBV-800), and observed higher yield of tyre pyrolyzed oil products compared to USY. Using these catalyst increases the yield of gas products by up to 20 wt %. When no catalyst was used, the maximum oil yield was 55.8 wt % and the minimum gas of 6.1 wt % was obtained. The use of three catalysts led to an oil reduction among which the ZSM-5 yielded the maximum oil yield of 35.8wt% in comparison to Y-zeolite (CBV-400) and Y-zeolite

(CBV-780). The different oil yields are due to the difference in catalysts pore size and the ratio of silica/alumina which influenced the number of catalytically active sites on the catalyst surface. Table 2.3 shows the effect of catalyst on plastic pyrolysis processes.

Table 2.3: Effect of catalyst in plastic pyrolysis processes (Punkkinen *et al.*,2017) **Note: NR** = Not Reported

CATALYST USED	CATALYST QUANTITY	FEEDSTOCK	EFFECT ON YIELD			CATALYST EFFECT
			Liquid	Gases	Char	
HZSM-5	20	HDPE	NR	NR	NR	• Increased the yield of volatile compounds • Increased the cracking process and the overall yield of pyrolysis
FCC	50	LDPE, HDPE, PP	72.1 44.2 64.7	19.4 52.5 20.0	8.5 3.3 15.3	• Thermal cracking of HDPE was most difficult, followed by LDPE and PP • Thermal cracking of PE produced wax Thermal cracking increased the demand of energy; however, the use of catalyst increased the cracking process. Hence reduced the demand of energy.
Na_2CO_3	2, 5, 10	Tires	NR	NR	NR	• Decreased the reaction temperature • Increased the conversion with increase in liquid yield
ZSM-5	5	HDPE, PP	NR	NR	NR	• Increased the process of cracking • Increased the overall yield of each fraction i.e. gases, gasoline and light oil • Yield of lighter fraction (gasoline) increased Promoted the production of i-butane in gases
HZSM-5, Zeolite Y and Mordenite	30	PE wax	47.18 66.98 82.59	51.04 28.95 15.11	1.78 4.08 2.3	• Overall increase the aromatic compounds in the oil • Catalyst dimension played a vital role in the conversion of wax into light hydrocarbon Catalyst with more than one dimension (HZSM-5 and zeolite Y) showed higher conversion of wax into light hydrocarbon than one dimension (mordenite) catalyst
ZSM-5	10	Industrial packaging waste	41.5	8.6	49.9	• Decreased the temperature of pyrolysis process from 500 ˚C to 440 ˚C • Liquid oil produced from catalytic pyrolysis contained high fraction of aromatic, while gases contained high amount of C3-C4

ZSM-5	10	PE, PP, PS, PET, PVC	56.9	40.4	3.2	• Dechlorination step was carried out at low temperature. It reduced the chlorination but also had a negative affect on the catalyst performance. • Increased the yield of gases that decrease in liquid yield. Moreover, a very slight increase in solid fraction • 80 % of the liquid yield contained C5-C9 compounds due to presence of catalyst However, dechlorination step with catalyst decreased the C5-C9 fraction, meaning that it affected on the catalytic activity of ZSM-5 • Dechlorination step increased the yield of C13 compounds in liquid yield • Catalytic pyrolysis produced liquid with 95 % aromatic compounds
Natural Zeolite (Ni/Z, NiMo/Z, Co/Z, CoMo/Z)	5	LDPE	23.88 12.20 23.92 14.91	75.18 86.30 76.00 83.71	0.94 1.51 0.92 1.39	• Natural zeolite modification was carried out by metal (Ni, Ni-Mo, Co and Co-Mo) impregnation on natural zeolite to increase the catalyst activity and its selectivity for hydrocracking process • Impregnation of catalyst did not affect the crystallinity of the natural zeolite • Ni/Z composite produced high liquid yield. However, maximum gasoline (71.49 %) was produced from Co-Mo/Z at 350 ˚C due to its high acidic nature. • Liquid oil produced contained compounds between C6 and C19, showing that it contained paraffins, napthenes and olefins.
H-Y Zeolite	50	PE, PP, PS	42 44 71	46 52 24	8 10 5	• Polyolefin (PE and PP) showed high yield of gaseous hydrocarbons while PS showed high yield of liquid hydrocarbons due to its stable benzene ring structure • Polyolefin produced wax while PS did not • Liquid oil produced from PS mainly consisted of styrene (81 %)
MgO, CaCO3	1 – 20	Tyre mixture	40	38	22	• $CaCO_3$ yields less liquid, but more gas than MgO. • Oil from MgO contains 40% gasoline fraction and 60% diesel, CaCO3 yields 10% and 90% respectively.

Different type of catalysts, natural and synthetic, can be used for conversion of organic wastes into valuable fuels. Miteva *et al.*, (2016) investigated the conversion of waste polyolefin mixture and production of liquid fuel using mixture of Al_2O_3 and SiO_2 as a catalyst with the pyrolysis conducted at temperature range of 400 – 550 ^oC and obtained products were liquid fuel, gas and minor solid residue. Under the optimized reaction conditions, the condensed liquid fraction is much larger than the gaseous fraction. They reported that the obtained results show that the retention time and the percent of SiO_2 in the catalyst mixture have predominant effect on the amount of liquid product and that decrease in the quantity of SiO_2 in the catalyst mixture increased the yield of liquid product. According to Gao (2010), catalysts are found to be mainly applied to PE pyrolysis because the primary product from other plastics, such as PP and PS, are mainly light hydrocarbons, with similar carbon chain length to the range of commercial fuels while the products from non-catalytic PE pyrolysis contain high proportion of 1-alkenes and dialkenes. Some catalysts are applied specifically to reduce the unsaturated hydrocarbons and promote the yield of aromatics and naphthenes and as a result, significantly increase the stability and cetane number of the oil products. Blazso (2006) reported that activation energies (Ea) measured in the PE pyrolysis with catalysts such as HZSM-5, HY, and MCM-41 were much lower than those when no catalyst was added.

Despite the potential advantages of the catalytic pyrolysis plastic waste, some limitations such as high parasitic energy demand, catalyst costs and less reuse of catalyst are remaining, hence, there is the need explore cheaper catalytic materials, catalyst regeneration and overall process optimization (Miandad *et al.*, 2016). All the reviewed literatures have critically examined different aspect of plastic pyrolysis. From, the review of literature, this study therefore adopted the use of CaO and zeolite catalyst for the optimization study of plastic waste pyrolysis since the focus of this study is to investigate the comparative studies of the effect of CaO and zeolite catalyst on plastic waste pyrolysis.

2.6.6 Other factor that affect plastic pyrolysis

There are a number of other factors that affect the yield of pyroysis products to a certain extent. For instance, reactive additives such as air, oxygen, or hydrogen are sometimes present in the reaction for different purposes, have been found to interfere with pyrolysis reactions and affect the quality of the products (Gao, 2010). Another factor is the particle size of the feedstock. In terms of the particle size, the smaller the particles size, the more the gas-phase product, but reduced char and increased oil yield.

Further pyrolysis of the primary product occurs in most processes. Secondary cracking reactions were found in many reports which are enhanced by high refluxes (Gao, 2010). Although many researchers observed the impact of secondary cracking, few have investigated the influence of secondary cracking process on the yield and the quality of the products. Most secondary cracking occurred during the pyrolysis of PE and very limited cracking was found in PS pyrolysis. This is possibly due to the difference in their primary products. The primary products produced from PE pyrolysis contain large proportion of heavy hydrocarbons with carbon chain number up to 80. The average molecular weight of the primary products from PE is much higher than that of other plastics, PS, PP, PVC and PET. The secondary cracking is mainly effective for heavy hydrocarbons, hence, has less effect on the pyrolysis of PS, PVC, PET and other plastics.

2.7 Catalyst

Catalyst usage for pyrolysis reactions is vital in order to alter the distribution of pyrolysis products and to improve the rate of pyrolysis, oil yield and quality, and enhance selectivity of compounds such as aromatics for chemical production (Alsaleh and Sattler, 2014). Hence, the use of catalyst in plastic pyrolysis is to enhance the concentration of high value products and also to produce oil which can be used as a chemical feedstock such as limonene, benzene, toluene, etc., rather than fuel. The key advantages of catalytic utilization during pyrolysis is to lower the activation energy required for cracking, thereby, lowering cracking temperature, increased reaction rate, increased production of isoalkanes, branched and cyclic molecules and aromatics as well as increased efficiency, and improved selectivity and quality of the product (Punkkinen *et al.*, 2017). Catalyst such as zeolite are expensive and cost intensive, though often gives quality products yield. Hence the need for comparison with cheaper catalyst sources in order to save cost and ensure economic feasible of pyrolysis process. One option is by developing catalyst from natural resources such as bone, waste and natural rock like limestone which can be found as a raw material for cement production. Hence the need comparative study of zeolite and CaO as catalyst for plastic pyrolysis.

2.7.1 Zeolite

Zeolites are crystalline aluminosilicates with composition expressed chemically by the formula $M_{x/n}(AlO_2)_x(SiO_2)_y.zH_2O$ (M stands for the compensating cation with valence n, z is the water contained in the zeolite, x and y represents number of tetrahedrons SiO_4 and AlO_4^- and y/x is the atomic ratio Si/Al, which can change from the minimum value of 1 to infinite (Agnieszka, 2014). Zeolites as a porous material is an important material for catalytic processing in the cracking of crude oil distillate or distillates conversion to gasoline. Zeolites can be described as materials made up of micro aluminosilicate crystals which are used as ion exchangers in the detergent industry, in radioactive waste storage, in the treatment of liquid waste, as separators in purification, environmental treatment, in the catalytic cracking of petroleum and in refining petrochemical, coal and fine chemical industries (Mgbemere *et al.*, 2017). The structure of zeolite is an extensive three-dimensional framework where oxygen atoms links the tetrahedral sites resulting in a microporous structure, with a big probability of channels and cavities being formed and as a consequence, each type of zeolite has a different structure. The main individual structural element of zeolite is a tetrahedral silicon or aluminium atom, connected with four oxygen atoms (SiO_4 and AlO_4^-) shown in Figure 2.3.

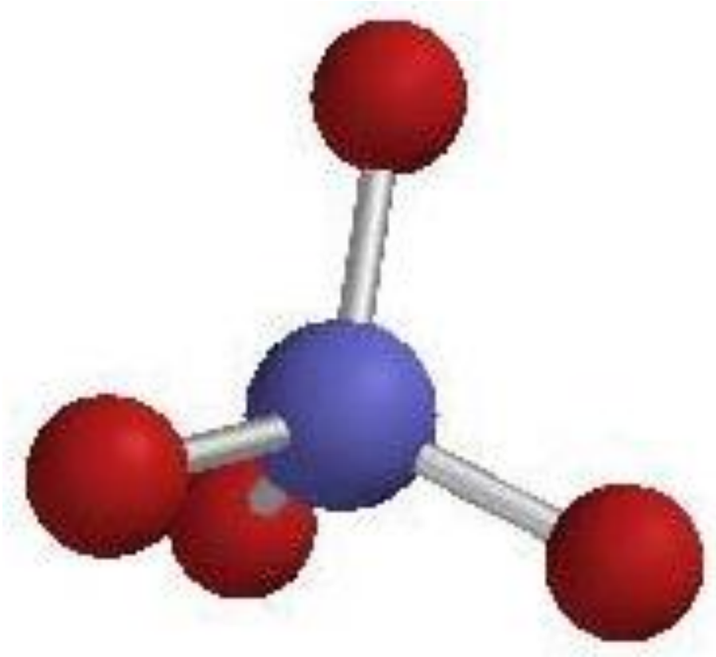

Figure 2.3: Primary building unit of zeolite [a tetrahedral T-site - T-atom (blue) connected to four oxygen atoms (red)] (Mgbemere *et al.*, 2017)

Zeolite frameworks are usually anionic, due to the existence of trivalent aluminium atoms in an essentially siliceous structure; this negative charge is neutralized with cations which are located within the framework, to obtain electrical neutrality (Kovo, 2011; Holmes *et al.*, 2012; Mgbemere *et al.*, 2017). These cations are usually exchangeable, under appropriate conditions and if the counter cation present in the structure is a proton, then the zeolite will have acid characteristics. This makes zeolites a highly potent catalyst material that is widely use. The properties which enables zeolite to perform in wider functions in several industrial applications are their uniform pore size and shape, the mobility of their cations to act as catalysts and their hydrophilic and/or hydrophobic nature to some solutes. Typical zeolite pore sizes include,

1 Small pore zeolites with 8-ring pores, free diameters of 0.30 - 0.45nm (example, zeolite A)
2 Medium pore zeolites with 10-ring pores, free diameter of 0.45 - 0.60nm (example, ZSM-5).
3 Large pore zeolites with 12-ring pores of 0.60 - 0.80nm (example, zeolites X, Y).
4 Extra-large pore zeolites with 14-ring pores (example, UTD-1) (Mgbemere *et al.*, 2017).

Zeolites can operate both as ion-exchange materials and also reversible adsorption systems for water or small organic molecules, with a potential capacity of more than 25% of the framework weight, however, the two most significant properties for zeolites are acidity and porosity. The acidity of a zeolite is usually responsible for the catalytic activity of catalysts, whilst the porosity is responsible for the catalytic selectivity during the reactions. These catalytic properties can be modified to provide enhanced flexibility across a range of applications.

Several studies have reported the use of zeolite in pyrolysis processes (Table 2.3). Williams and Brindle (2003), reported the use of three different zeolite catalysts, particularly, ZSM-5, Y-Zeolite (CBV-400), and Y-Zeolite (CBV-800) for tyre pyrolysis and observed higher yield of pyrolysis oil products compared to USY. Using these catalyst increases the yield of gas products by up to 20 wt % with the three catalysts resulting in an oil reduction among which the ZSM-5 yielded the maximum oil yield of 35.8wt% compared to Y-zeolite (CBV-400) and Y-zeolite (CBV-780). A wide variety of catalyst has been applied in the pyrolysis of waste plastics with the most common catalyst being zeolites. According to López *et al.* (2017), HZSM-5 proved to be suitable for the production of valuable light olefins compared to other catalyst. However, Quesada *et al.* (2020) state that other larger pore size zeolites such as HY, HUSY or spent FCC catalysts are a better alternative for the production of liquid hydrocarbons from plastic pyrolysis while MCM-41, or the less acidic mesoporous SiO_2-Al_2O_3 are also interesting options to produce liquid fuels.

2.7.2 Calcium oxide

Calcium oxide (CaO), also known as quicklime is one of the promising metal oxides with many potential applications in areas such as catalyst, used as dopant to modify the electric and dielectric properties, toxic waste remediation agent, in CO_2 capture and flue gas desulfurization as well as used as emission control agent in pollution among other (Balaganesh *et al.*, 2018). Calcium oxide is a high-volume chemical which finds applications many industries and is plenty in nature, inexpensive and easy to produce. Quicklime is a solid material that is produced from thermal decomposition of limestone from which carbon dioxide gas (CO_2) is evolved and upon hydration, forms white powder and releases large amount of heat to form hydrated lime. Calcium oxide is obtained from the calcination of limestone, shell, or equivalent, and consists of CaO in natural association with a lesser amount of magnesium oxide. However, a major source of CaO is from the calcination of limestone ($CaCO_3$).

Limestone in Nigeria is majorly deposited in Cross River, Ebonyi, Kogi and Ogun states but are still found available in commercial deposit in Abia, Akwa Ibom, Anambra, Bauchi, Bayelsa, Benue, Borno, Edo, Enugu, Imo, Ondo and Sokoto, making Nigeria the most richly deposited West African country when it comes to Limestone (Akande *et al.*, 2014; RMRDC, 2016; National Bureau of Statistics, 2017). $CaCO_3$ is found in all the geo-political zones of the country with different degrees of concentration.

If lumps of limestone are heated to a temperature in excess of about 800 ^{o}C, CO_2 is driven off and what remains is CaO (Harraz, 2017). Limestone decomposes into CaO and CO_2 as shown in equation 2.1 through a process called ‘calcination’. If calcination is carried out correctly the lumps of CaO are approximately the same size as the original lumps of $CaCO_3$ but much less dense, because of the weight loss arising from the removal of CO_2 (Akande *et al.*, 2014). The reactivity of CaO produced is a measure of the rate at which the quicklime reacts in the presence of water (Harraz, 2017).

$$CaCO_3 + \text{Heat} \rightarrow CaO + CO_2 \qquad (2.1)$$

The reactivity of CaO depends on different parameters related to the raw material and the process. These parameters include; burning temperature and time, crystalline structure of the limestone, impurities and even kiln type and fuel. The classification of CaO is often seen in terms of its reactivity, such as: dead burned, hard, medium, and soft as shown in Figure 2.4.

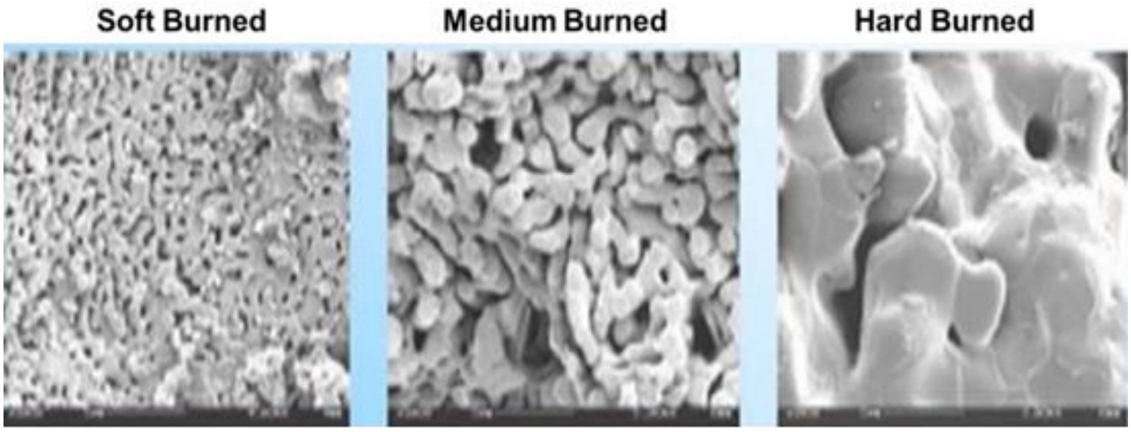

Figure 2.4: Classifications of quicklime in terms of reactivity (Harraz, 2017)

There are several references in literature concerning factors that may affect the quality of CaO. Balaganesh *et al.,* (2018) reported these factors as characteristics of the raw limestone material, calcination temperature, pressure acquired in kilns, rate of calcination, and fuel quality. The effect of calcination parameters on CaO produced from various limestone deposits have been reported by several authors (Akande *et a.l*, 2014; Balaganesh *et al.*, 2018). The material such as CaO has been used as catalyst in areas such as heterogeneous biodiesel production process and is one of the most studied heterogeneous catalyst for biodiesel production due to high activity, availability and its low cost. However, there is scarce use of CaO as catalyst in pyrolysis process, considering availability of raw materials (limestone, $CaCO_3$).

Linggawati *et al.,* (2016) reported the characterization of CaO catalyst using X-ray diffraction (XRD), thermogravimetric analysis (TGA), X-ray fluorescence spectrometry (XRF), and Fourier transform infrared spectroscopy (FTIR) and found that the XRD patterns of calcined catalyst showed intense peaks of CaO of 32.24^o, 37.38^o and 64.16^o at 2θ angle with the XRF indicating >99% of CaO which indicated that calcium was the major element present in the catalyst.

Also, Ding *et al.*, (2018), have reported the use of a CaO and HZSM-5 dual catalyst bed to convert acid in xylan pyrolysis products into hydrocarbons while Chen *et al*. (2017) applied CaO to the pyrolysis of a cotton stover to promote the formation of ketone, reduce the amount of acid, increase the concentrations of H_2 and CH_4, and decrease the concentration of CO_2, Wu *et al*., (2018), using chemical-looping gasification of biomass, introduces steam and CaO into a fixed bed to produce syngas and observed that the addition of steam can promote the reforming and the water-gas shift reactions.

Generally, CaO has several advantages as catalytic for pyrolysis process, including nontoxicity and low cost, as such, is widely used in catalytic cracking of biomass pyrolysis and can increase the calorific value of pyrolysis gas and the production of H_2, CH_4, and other gases, improve the quality of gas, catalyze the cracking of bio-oil as well as reduce the production of bio-oil (Qing *et al.*, 2020). Calcium oxide as catalyst also has the capacity to neutralize acidic substances, and promote the formation of hydrocarbons in char which makes CaO an important catalyst for biomass pyrolysis.

2.8 Optimization

Optimization is the act of achieving the best result under circumstances. In design, construction, maintenance, etc., engineers have to take decisions. The goal of all such decision is either to minimize effort or to maximize benefit. The effort or the benefit can be usually expressed as a function of certain design variables. Hence, optimization is the process of finding the condition that give the maximum or the minimum value of a function (Jia *et al*., 2018). It is obvious that if a point X corresponds to the minimum value of a function f(x), the same point corresponds to the maximum value of the function -f(x). Thus, optimization can be taken to be minimization. There is no single method available for solving all optimization problems efficiently. Hence, a number of methods have been developed for solving different type of problems. Optimum seeking methods are also known as mathematical programming techniques, which are a branch of operations research. Operation research is coarsely composed of the following areas.

Mathematical programming methods: these are useful in finding the minimum of function of several variables under a prescribed set of constraints.

Stochastic process techniques: These are used to analyze problems which are described by a set of random variables of known distribution.

Statistical method: These are used in the analysis experimental data and in the construction of empirical models (Jia *et al.*, 2018).

Pyrolysis has received more attention in the area of research because the process conditions can be optimized to produce high energy density liquids, char, and gas. Also, the condensable fraction or the bio-crude can be stored and easily transported to where it can be most proficiently utilized. The conversion of used plastics or tyre to fuel oil are govern by several factors such as temperature, heating rate and presence of catalyst among others (Alsaleh and Sattler, 2014). The optimization of factors that affects pyrolysis resulting in maximizing the desired product quality and quantity is an important subject that requires attention in order to minimizing costs and environmental concerns. Several techniques have been utilized to optimize production operating conditions using approach that is based on the technique of design of experiments (DOE) to identify the most significant variables which affect the product quality and quantity. The parametric optimization using response surface and factorial method have been found to be useful in optimization of at least 2 or more factors of a process. The significance of optimization in this study is to obtain the highest amount of fuel oil from pyrolysis of plastic waste and the use of an appropriate experimental design approach becomes paramount. Response surface methodology and factorial method have been found to be a useful tool to study the interactions of two or more factors (Abnisa *et al.*, 2010). Response surface methodology (RSM) and factorial method is a collection of statistical and mathematical techniques that has been successfully used to determine the effects of several variables and optimize processes. However, this study adopted the use of factorial method for the optimization study.

2.8.1 Factorial design of experiment

Factorial designs are used primarily for understanding if factors are important to the process. This can take the form of screening for few important factors out of many possibilities, or utilized for characterizing how known factors interact and individually, effect the process. These designs are often used as a starting point for more complex response surface modeling. Though, factorial designs are commonly used for screening significant factors, but can also be used sequentially to model and refine a process. A full factorial experiment is an experiment whose design consists of Designed experiments with full factorial design (left), response surface with second-degree polynomial (right) two or more factors, each with discrete possible values or “levels”, and whose experimental units take on all possible combinations of these levels across all such factors. A full factorial design may also be called a fully crossed design. Such an experiment allows the investigator to study the effect of each factor on the response variable, as well as the effects of interactions between factors on the response variable (Montgomery, 2013).

For the vast majority of factorial experiments, each factor has only two levels. For example, with two factors each taking two levels, a factorial experiment would have four treatment combinations in total, and is usually called a 2×2 factorial design. If the number of combinations in a full factorial design is too high to be logistically feasible, a fractional factorial design may be done, in which some of the possible combinations (usually at least half) are omitted

2.8.1.1 Advantages of factorial experiments

Compared to such one-factor-at-a-time (OFAT) experiments, where the effect of only a single factor or variable is being investigated, factorial experiments offer several advantages as follows;

a. Factorial designs are more efficient than OFAT experiments. They provide more information at similar or lower cost. They can find optimal conditions faster than OFAT experiments.
b. Factorial designs allow additional factors to be examined at no additional cost.
c. When the effect of one factor is different for different levels of another factor, it cannot be detected by an OFAT experiment design. Factorial designs are required to detect such interactions. Use of OFAT when interactions are present can lead to serious misunderstanding of how the response changes with the factors.
d. Factorial designs allow the effects of a factor to be estimated at several levels of the other factors, yielding conclusions that are valid over a range of experimental conditions (Montgomery, 2013).

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Introduction

The materials and major equipment that were used in the course of the research are shown in Table 3.1 and Table 3.2 respectively. Also, the experimental procedure carried out in the course of the research are discuss in detail in this section.

3.2 Equipments, Materials and Chemical

Table 3.1: List of Materials/Chemicals

S/N	Materials	Source
1	Waste Plastics	Communities within Kaduna Metropolis, Kaduna
2	ZSM-5 Zeolite	Chemical Engineering, FUT. Minna
3	Limestone	NARICT, Zaria, Kaduna
4	Distilled water	Chemical Engineering Laboratory, ABU, Zaria

Table 3.2: List of Major Equipment

S/No	Equipment	Model	Manufacturer
1	Weighing balance	Melrose Pack,	Illinois, US
2	Furnace/ Reactor	Carbolite furnace, CWF 12/13	Philip Harris, UK
3	Heating mantle	Brain Weighs	Brain England
4	Digital Thermometer	Not Available	Zeal, England
5	Beaker and measuring cylinder	Pyrex,	Pyrex, England
6	Stirrer	Pyrex	Pyrex, England
7	Funnels and filter paper	Pyrex Glass	Pyrex, England
8	GCMS	GC/MS-QP2010-Ultra	Panalytical, UK
	XRD	XPERT-PRO	Panalytical, UK
	FTIR	X-MET8000	SHIMADZU, UK
9	Viscometer	Not Available	Not Available

3.3 Methodology

The methodology and experimental procedures that were used in achieving the goal of the comparative studies of the effect of CaO and ZSM-5 zeolite catalyst on waste plastic pyrolysis liquid are presented in Figure 3.1.

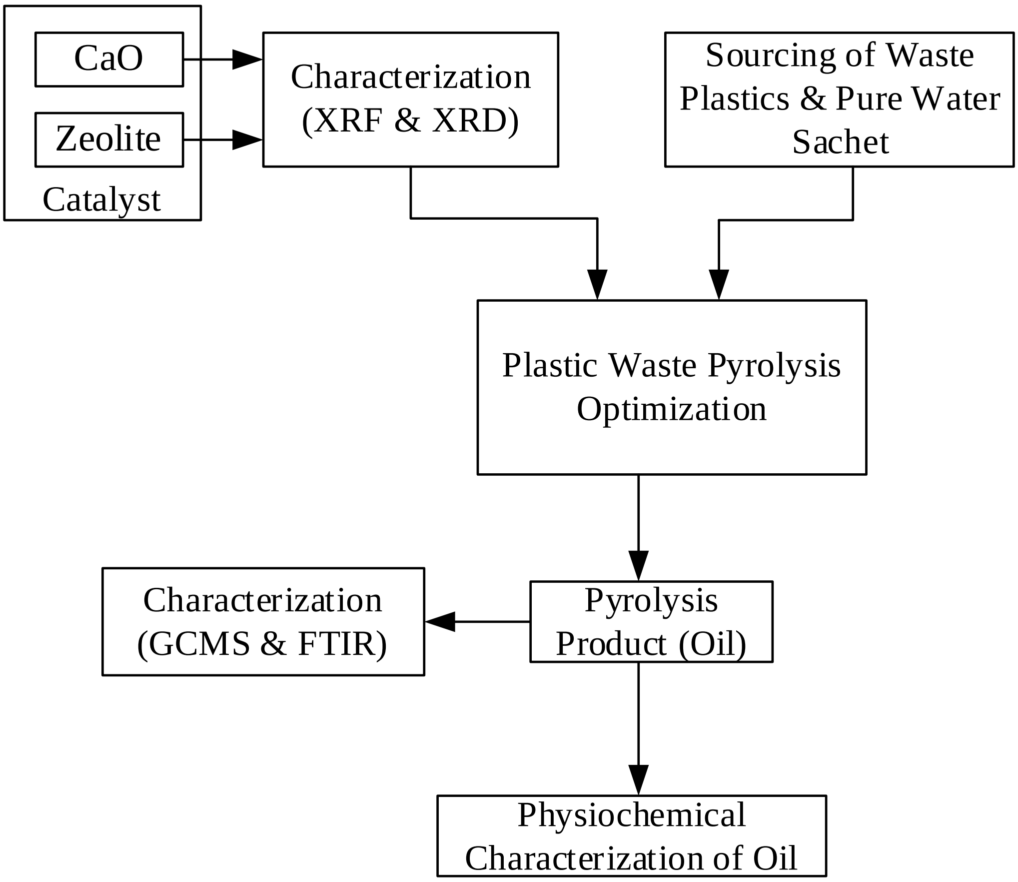

Figure 3.1: Experimental procedure for catalytic pyrolysis of waste plastic

3.3.1 Sample preparation

Waste plastic materials are collected from communities within Kaduna Metropolis in Kaduna state. The collected waste plastics were washed clean with detergent and water to remove all stains and dirt, and afterward dried in the sun. The cleaned waste plastics were reduced in size to 2 – 5 mm to enhance the rate of pyrolysis. The cleaned and size reduced plastic waste were stored for subsequent use. Also, the zeolite used in this study was sourced from Chemical Engineering Department, Gidan Kwano, Minna, Niger State while the CaO was obtained from the calcination of $CaCO_3$ gotten from NARICT Zaria to obtained CaO which was used as catalyst in comparison with zeolite for waste plastic pyrolysis. Detail of the catalyst preparation are discussed subsequently.

3.3.2 Limestone calcination to calcium oxide

A laboratory muffle furnace was used to calcine the limestone obtained from NARICT Zaria into CaO. Carbolite furnace model CWF 12/13, manufactured by Philip Harris UK with a maximum operating temperature of 1200 ^{o}C was used for the calcination. The furnace is electrically heated with temperature regulator thermostatically controlled. The temperatures used in the study was set and a measured quantity (100 g) of limestone (310 µm) was placed in a very clean nickel crucibles and placed in the furnace for calcination at a set temperature of 950 ^{o}C for 45 min (Akande *et al.*, 2016). The weight of the samples were monitored over the periods of calcination using an electronic balance to ~0.01, by withdrawing the sample from the furnace at intervals and taking the weight in order to monitor the mass loss overtime. The measurement was done very fast to ensure that the sample readily assumes the temperature of the furnace and to ensures the sweeping of air through the furnace to keep the composition of the gas phase around the sample fairly constant during each run. The experiment was stopped when no further mass loss was recorded indicating calcination has been achieved.

3.3.3 Zeolite ZSM-5 activation

Prior to usage, the ZSM-5 zeolite catalyst was activated with ammonium nitrate and the mixture placed in an oven at a temperature of 80 ^{o}C for 12 h. The ammonium nitrate treated ZSM-5 zeolite was transformed to acidic by calcination in a furnace at 550 ^{o}C for 2 hrs. After the time elapse, the activated ZSM-5 zeolite was removed, cooled and place in a container for further experimental usage.

3.4 Catalyst Characterization

The ZSM-5 zeolite and CaO catalyst prepared from previous sections were characterized using XRD and XRF analysis. The procedures are discussed subsequently.

3.4.1 X-ray fluorescence (XRF)

The elemental compositions of the ZSM-5 zeolite and CaO catalyst materials were determined using X-Ray Fluorescence (XRF) technique machine, SHIMADZU X-MET8000 Analyzer model. Sample of the ZSM-5 zeolite was analysis and result of elemental compositions obtained. The same procedure was repeated with CaO catalyst.

3.4.2 X-ray diffraction (XRD)

X-ray diffraction (XRD) analysis was performed on the prepared ZSM-5 zeolite and CaO catalyst powder. The ZSM-5 zeolite and CaO catalyst were grounded into fine powder prior to XRD measurements. The scans were performed for each sample and the values reported for the basal spacing. The x-ray diffraction patterns were obtained using a XPERT-PRO x-ray diffractomer with CuKα radiation (λ=1.54 Å). The experiment was run at room temperature with an angle range (2θ) and step size of 0.02˚ with the machine operating at 40 kV and 40 mA.

3.5 Experimental Design

Three factors; pyrolysis temperature, heating rate and catalyst type were considered for the optimization of oil yield from plastic pyrolysis at two levels. Full factorial design of experiment method was used for the optimization to determine the effect of pyrolysis temperature, heating rate and catalyst type on the liquid product yield. The effect of the selected factors were studied using full factorial design. The levels of the factors were selected based on preliminary study. The uncoded levels of the factors are presented in Table 3.3.

Table 3.3: Code and uncoded level of the independent variables

Factors	**Type**	**Level**	
Pyrolysis Temperature (^{o}C)	Numeric	300	650
Heating Rate (^{o}C/min)	Numeric	10	40
Catalyst Type	Text	CaO	ZSM-5 Zeolite

The relationship between the responses product yield and selected factors were defined using full factorial method. Design Expert 12. software package was used for the implementation of the method. Experimental design for the studied factors are presented in Table 3.4.

Table 3.4: Design of Experimental of the factors in uncoded values

Run	Factors			Response
	Pyrolysis Temp. (^{o}C)	Catalyst Type	Heating Rate (^{o}C/min)	Yield (%)
1	600	ZSM-5 Zeolite	30	
2	400	CaO	30	
3	400	ZSM-5 Zeolite	15	
4	400	ZSM-5 Zeolite	30	
5	500	CaO	22.5	
6	500	CaO	22.5	
7	600	CaO	30	
8	500	ZSM-5 Zeolite	22.5	
9	400	CaO	15	
10	600	CaO	15	
11	500	ZSM-5 Zeolite	22.5	
12	600	ZSM-5 Zeolite	15	

3.5.1 Waste plastic pyrolysis

An improvised pyrolysis reactor in Chemical Engineering Department, ABU Zaria was used for the pyrolysis experiment. The schematic setup of the reactor is as shown in Figure 3.2. The setup is an improvised reactor system where the temperature was constant and the desired heating rate set. The condenser attached to the reactor is to condense the vapourized products from the reactor by cooling with water passing through the shell side of the condenser. The waste plastic pyrolysis was carried out using 50g of the cleaned and size reduced waste plastic material with 5g (10%) catalyst according to the conditions of the first run presented in Table 3.4. That is, the temperature was set to 600^{o}C using 5g of zeolite (10%) at a heating rate of 30^{o}C/min. Subsequent runs were carried out according to the set conditions in Table 3.4 using the same procedure.

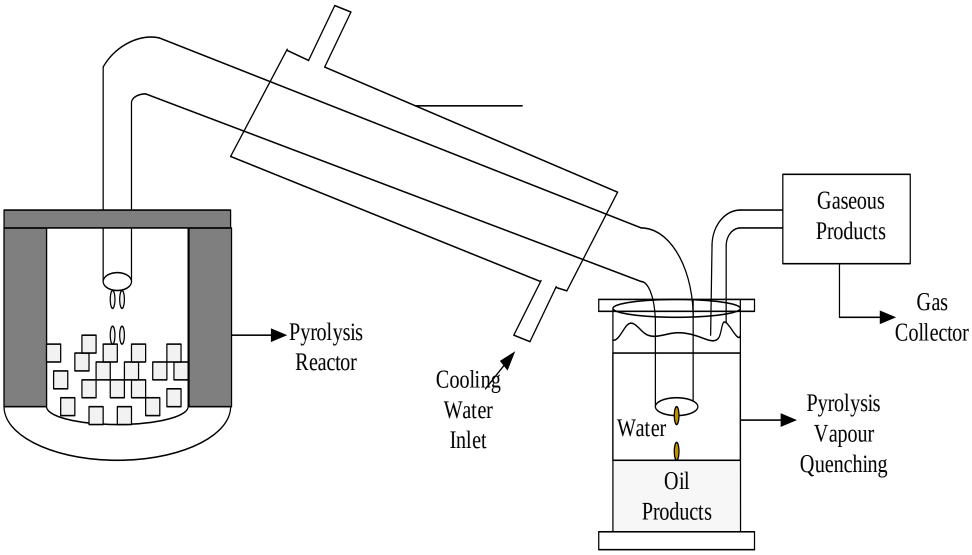

Figure 3.2: Pyrolysis reactor setup

3.6 Product Characterization

The product (oil) that were produced from the waste plastic pyrolysis in this study were characterized using GCMS and FTIR for the produced oil.

3.6.1 Gas chromatography and mass spectrometry (GCMS) analysis

The composition of produced plastic pyrolysis oil at the optimum condition was analyzed using gas chromatography and mass spectrometry (GCMS) instruments (GC/MS-QP2010-Ultra), equipped with flame ionization and mass spectrometry detection. A capillary column coated with a 0.25 um film of DB-5 with length of 30 m and diameter 0.25 mm was used. The gas spectrum is equipped with a split injector at 200^{o}C and have a split ratio of 1:10. Helium gas of 99.95% purity was used as carrier gas at flow rate of 1.51 ml/min. The mass spectrometer was operated at an interface temperature of 240^{o}C with ion source temperature of 200^{o}C of range 40 – 1000 m/z. All the compounds were identified by means of the NIST library.

3.6.2 Fourier transform infrared spectroscopy (FTIR) analysis

Fourier Transform Infrared Spectroscopy (FTIR) was performed on a SHIMADZU FTIR-8400S, UK to characterize the produced pyrolysis oil at the optimum condition into the various organic functional groups present in the oil. The FTIR spectra were collected using KBr pellet technique in the wavelength range of 400 – 4000 cm^{-1} at a resolution of 4.0 cm^{-1}.

3.7 Analysis of pyrolysis oil

The produced pyrolysis oil at the optimum condition was evaluated to determined its performance and suitability for use in combustion engine. The combustion engine performance properties that were evaluated are cetane number, flash point, specific gravity, kinematic viscosity and heating value for the produced pyrolysis oil at optimum condition.

3.7.1 Kinematic viscosity

Kinematic viscosity test was carried out using the NDJ-5S Digital Rotary viscometer and the DBK MiniMag Stirrer/Heater. The produced pyrolysis oil was placed in beakers and the beaker placed on the heater with the piston of the viscometer placed inside the beaker. As the viscometer piston rotate in the beaker and the oil get heated. A thermometer was placed at the side of the beaker to monitor temperature and readings were taken from the viscometer at temperatures of 40 °C and 100 °C.

3.7.2 Density and specific gravity

About 10 cm^3 of the produced waste plastic pyrolysis oil was measured in a pre-weighed measuring cylinder. The weight of the cylinder and the oil were measured. The weight of the pyrolysis oil was obtained by subtracting the weight of the cylinder from the combine weight of the oil and cylinder. The specific gravity of the waste plastic pyrolysis oil was obtained using equations by Warra *et al.,* (2011).

$$\rho_{water} = \frac{W_1 - W_0}{V_0} \tag{3.1}$$

where

W_1 = weight of empty measuring cylinder + oil
W_0 = weight of measuring cylinder
V_0 = volume of oil

$$\rho_{pyrolysis\ oil} = \frac{W_1 - W_0}{V_0} \tag{3.2}$$

where

W_1 = weight of empty measuring cylinder + oil
W_0 = weight of measuring cylinder
V_0 = volume of oil

$$Specific\ gravity = \frac{\rho_{pyrolysis\ oil}}{\rho_{water}} \tag{3.3}$$

3.7.3 Flash point

Flash point analyser was used for the test. The waste plastic pyrolysis oil was poured into the analyser copper container up to the prescribed mark and the cover fitted to its position. Heating was carried out using Bunsen burner, at the same time stirring of the sample follows. The injector burner was lighted and injected into the sample container at about 30 sec intervals and the temperature at which a clean flash occurred was recorded as the flash point.

3.7.4 Heating value

Heating value of the waste plastic pyrolysis oil was obtained from complete combustion of a unit quantity (mass or mole) of the oil in an oxygen-bomb calorimeter under carefully defined conditions according to ASTM standard method (Sivaramakrishnan and Ravikumar, 2012). The experimental correlation as a function of viscosity, density, flash point by empirical linear equation obtained by Sivaramakrishnan and Ravikumar (2012) for fuel oil will be adopted for the estimation of Heating value (HHV).

$$\text{HHV (MJ/kg)} = 40.3667 + 0.04527\mu - 0.0008\rho - 0.0003\text{FP} \quad (3.4)$$

where

HHV = (MJ/kg), μ = viscosity (mm^2/sec)

ρ = density (g/L), FP = flash point (K)

3.7.5 Cetane Number

Cetane Number (CN), which is a measure of the performance quality of fuel oil was also measured using the correlation given by Sivaramakrishnan and Ravikumar, (2012), and shown by equation 3.5.

$$Cetane\ Number\ (CN) = -109.94\rho + 0.0254FP - 2.556HHV + 0.0165\mu + 246.4344 \quad (3.5)$$

where

HHV = (MJ/kg), μ = viscosity (mm^2/sec)
ρ = density (g/L), FP = flash point (K)

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 Introduction

This chapter present the result obtained from the comparative studies of the effect of CaO and zeolite catalyst on waste plastic pyrolysis. It also presents the discussion of the obtained results.

4.2 Characterization of Catalyst

The CaO and zeolite catalyst used for this study was characterized using XRD and XRF analysis to determine the crystal structure and composition of the catalyst respectively.

4.2.1 XRD analysis of catalyst

The crystal structure of the CaO and zeolite catalyst was characterized by XRD. Figure 4.1 and 4.2 presents the XRD pattern of the CaO and zeolite catalyst respectively. From Figure 4.1, the diffraction peak at 2θ angle of 32.340°, 37.487°, 54.005°, 64.483° and 67.503° was the typical diffraction peak of lime and shows that the CaO catalyst comprises mainly of lime with the main peak appearing at 2θ angle of 37.487°. These peaks correspond to (111), (200), (220), (311) and (222) planes assigned to CaO phase respectively. The XRD result of the CaO catalyst is consistent with those reported for CaO/g-C_3N_4 composites and synthesis of Nano-Calcium Oxide (Ramacharyulu *et al.*, 2017; Habte *et al.*, 2019). However, the diffraction peak at 2θ angle of 18.054°, 28.952°, 34.309°, 47.229°, 51.011°, and 64.483° was the typical diffraction peak of portlandite and shows that the CaO catalyst contains small quantity of $Ca(OH)_2$. The XRD analysis shows that the CaO catalyst contains mainly CaO and small quantity of $Ca(OH)_2$ as shown in Figure 4.1.

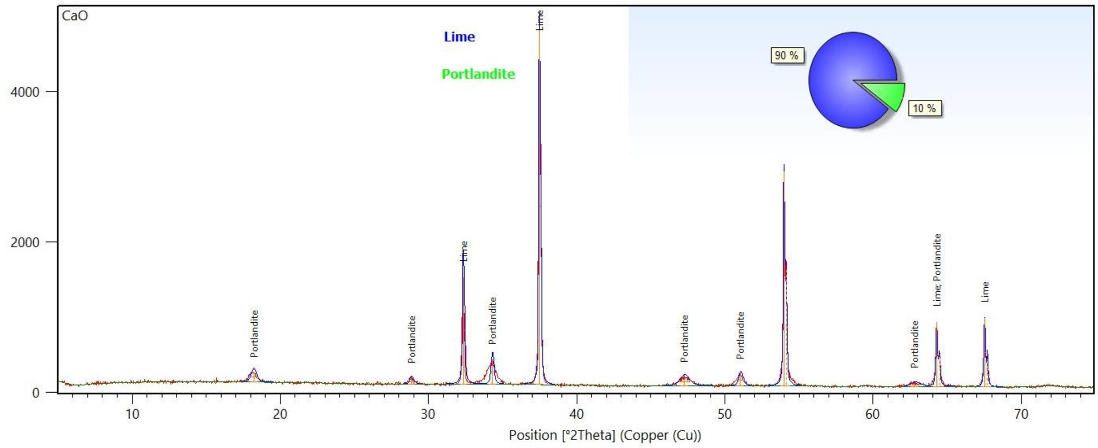

Figure 4.1: XRD analysis of CaO catalyst

From the XRD analysis ZSM-5 zeolite catalyst was also analysed. From Figure 4.2, the diffraction peak at 2θ angle of 8.101°, 8.968°, 23.254°, 24.094°, 29.477°, 30.108°, 45.260° and 45.654° was similar to the diffraction peak of zeolite ZSM-5 reported in literatures. These peaks are similar to those reported by Heman *et al*. (2019). It also shows that the crystalline structure of the zeolite catalyst contains mainly silicate crystals. All the peaks show the presence of a highly crystalline zeolitic structure with well-defined diffraction peaks of a high structural order that are comparable to XRD pattern of ZSM-5 from JCPDS card No. 44-0002 (Phan *et al.*, 2017). The presence of other non-zeolitic phases was not detected, which indicated the purity of the ZSM-5 zeolite catalyst used for pyrolysis.

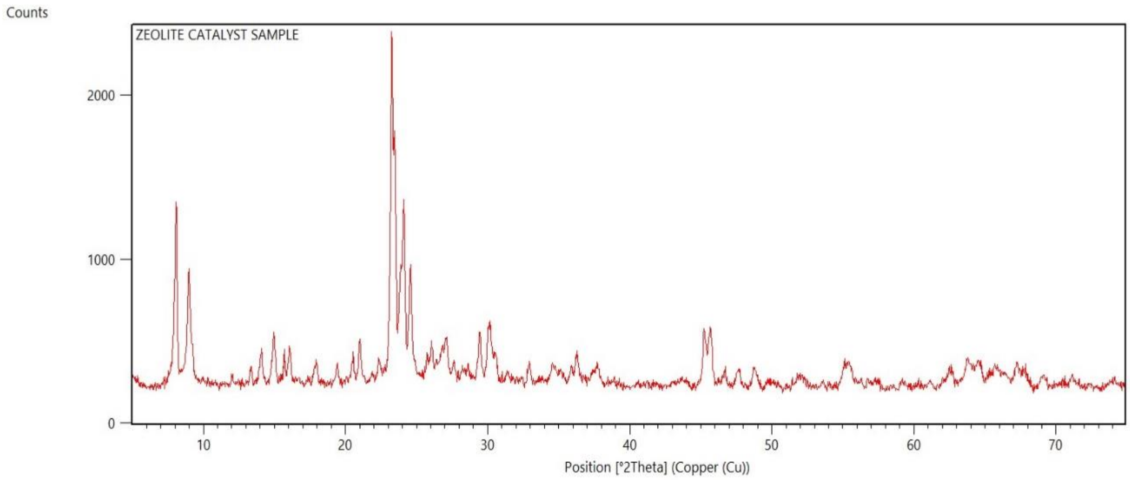

Figure 4.2: XRD analysis of ZSM-5 zeolite catalyst

4.2.2 XRF analysis of catalyst

The CaO and ZSM-5 zeolite catalyst used were characterized for their elemental compositions using XRF. Table 4.1 shows the chemical composition of the catalyst samples. From Table 4.1, the zeolite catalyst contains 3.133% Al_2O_3 and 92.356% SiO_2, to give a silica to alumina ratio of 29.48:1. This also confirms the high silicate presence from the XRD analysis. The dominating oxides in the zeolite catalyst are; SiO_2 and Al_2O_3, while other oxides present in the zeolite catalyst samples were less than 1%. Also, the CaO catalyst contains mainly, 98.848% CaO and all other oxide were less than 2%. This further confirms the high presence of CaO observed in the XRD analysis of CaO catalyst. Table 4.1 shows that the silica to alumina ratio of the ZSM-5 zeolite catalyst is high (50 on molar basis), portending high crystallinity of the ZSM-5 zeolite catalyst. This indicated that the zeolite framework contains relatively minimal amount of aluminum atom, which contribute towards the acidity of ZSM-5 zeolite catalyst. This further corroborate the XRD analysis which shows that the crystalline structure of the zeolite catalyst contains mainly silicate crystals.

Table 4.1: Chemical Compositions of Catalyst

Metal Oxide	Zeolite	CaO
Fe_2O_3	0.049	0.026
Al_2O_3	3.217	0.000
CaO	0.022	98.054
Cl	0.051	0.068
Cr_2O_3	0.005	0.000
CuO	0.001	0.000
K_2O	0.000	0.001
MgO	0.976	0.625
MnO	0.001	0.003
Na_2O	0.000	0.051
Nb_2O_5	0.002	0.002
NiO	0.350	0.000
P_2O_5	0.235	0.004
PbO	0.004	0.000
S	0.000	0.102
SiO_2	94.840	0.501
SrO	0.000	0.558
SO_3	0.229	0.000
Ta_2O_5	0.000	0.001
TiO_2	0.010	0.001
WO_3	0.003	0.000
Y_2O_3	0.000	0.002
ZnO	0.005	0.001

4.3 Optimization of Plastic Pyrolysis Oil Yield

The result of the production and optimization of plastic pyrolysis oil parameter for maximum oil yield are presented in Table 4.2. Design Expert 12 software package was used for the implementation of the 3 factor 2-level full factorial experimental design. The optimization study was executed using Full Factorial experimental design approach. The results of the plastic pyrolysis oil yield for each experimental run of the input parameters (temperature, catalyst type and heating rate) are presented in Table 4.2. The experimental values for the response parameter (pyrolysis oil yield) and the three factors in actual form are also presented in Table 4.2.

Table 4.2: Experimental design and response factor of full factorial analysis of oil yield

	Factors			Response (Oil Yield)		
Run	Temperature °C	Catalyst Type	Heating Rate °C/min	Actual %	Predicted %	Deviations
1	600	ZSM-5 Zeolite	30	58.34	58.77	-0.4317
2	400	CaO	30	25.16	26.54	-1.38
3	400	ZSM-5 Zeolite	15	45.24	45.67	-0.4317
4	400	ZSM-5 Zeolite	30	40.56	39.18	1.38
5	500	CaO	22.5	43.54	43.42	0.1167
6	500	CaO	22.5	45.2	43.42	1.78
7	600	CaO	30	55.3	54.87	0.4317
8	500	ZSM-5 Zeolite	22.5	57.78	58.46	-0.6767
9	400	CaO	15	19.94	19.51	0.4317
10	600	CaO	15	19.9	21.28	-1.38
11	500	ZSM-5 Zeolite	22.5	57.24	58.46	-1.22
12	600	ZSM-5 Zeolite	15	40.08	38.70	1.38

From the production and optimization of plastic pyrolysis oil yield, the t-distribution, coefficients and p-values for the experimental results were obtained. The sum of squares and the F-distribution were also determined. The 95% confidence level was used for the statistical calculations. The regression equation coefficients were also established from the fit of the pyrolysis oil yield. The statistical significance of a particular result based on the sample means were determined using F- and t- distributions. Values for the t- and F-distributions were compared to tabulated values based on the number of degrees of freedom 1 and 95% confidence interval. Also, the p-value was also used to established the statistical significance of the model and the parameters. The p-value is the smallest level of significance that would lead to the rejection of the null hypothesis and the conclusion that data is statistically significant (Montgomery, 2004). If the p-value is <0.05, then the factor is statistically significant at the 95% confidence level.

4.3.1 Analysis of variance (ANOVA)

Statistical analysis of the model was performed to evaluate the ANOVA and check the adequacy of the empirical model. The results of ANOVA for fitting the quadratic response model by a mean square method are summarized in Table 4.3. The coefficients of the full factorial method model in actual factor were also evaluated. The significance of each of the coefficients were checked from p-values, which also indicate the interaction strength of each parameter.

Table 4.3: ANOVA for factor of full factorial analysis of oil yield

Source	Sum of Squares	df	Mean Square	F-value	p-value	Remark
Model	1755.64	6	292.61	87.00	0.0003	Significant
A-Temperature	228.12	1	228.12	67.83	0.0012	Significant
B-Catalyst Type	678.00	1	678.00	201.59	0.0001	Significant
C-Heating Rate	367.20	1	367.20	109.18	0.0005	Significant
AB	38.19	1	38.19	11.36	0.0280	Significant
AC	352.72	1	352.72	104.87	0.0005	Significant
BC	91.40	1	91.40	27.17	0.0065	Significant
Residual	13.45	4	3.36			
Lack of Fit	11.93	2	5.96	7.83	0.1133	not significant
Pure Error	1.52	2	0.7618			
Cor Total	2211.13	11				

The p-value which is an index measuring the discrepancy of the fit of a model or the strength of evidence against the null hypothesis (the hypothesis that there is no association between the factors and response variable) was examined for the response factor (pyrolysis oil yield) (Gelman, 2013; Maqsood and Ibrahim, 2015). To quantify the strength of evidence against null hypothesis, $p < 0.05$ (5% significance) is used as a standard level for concluding that there is evidence against the hypothesis tested. The significance of the regression coefficients was tested using F-value and the p-values, and was also used to test the significance of the effect of each variable in the model. From Table 4.3, the model p-value is 0.0003 ($p<0.05$), which implies that the oil yield model is significant (Gelman, 2013; Sedgwick, 2014; Maqsood and Ibrahim, 2015). Also, the p-value for all model term are significant ($p<0.05$).

However, model p-value of 0.0003 demonstrating high significance of the model in predicting the response values of the oil yield and the suitability of the model (Montgomery, 2004, Maqsood and Ibrahim, 2015). Furthermore, from Table 4.3, the model F-value is 87.00, which also implies that the model is significant and that there is only a 0.03% chance that an F-value this large could occur due to noise in the experiments (Adepoju and Olawale, 2015; Maqsood and Ibrahim, 2015). The model F-value with low probability value 0.0003 ($p<0.05$) indicated the high significance of the fitted model (Scheffe, 2005). Additionally, the Lack of Fit is also an important index to evaluate the reliability of model. From Table 4.3, the Lack of Fit F-value of 7.83 implies the Lack of Fit is not significant relative to the pure error and that there is a 11.33% chance that a Lack of Fit F-value this large could occur due to noise (Jia *et al.*, 2018). Non-significant lack of fit is good well fitted model.

4.3.2 Factorial method modelling of pyrolysis oil yield

The relationships of the response (pyrolysis oil yield) with the input factor (independent variables) were explored by using the regression model. The regression model was evaluated with a 2-way linear interaction of the factors. The regression model in terms of coded factors that correlates the pyrolysis oil yield to the various input factors are presented in Table 4.4.

Table 4.4: Model coefficient in terms of coded factor for pyrolysis oil yield

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	38.07	1	0.6484	36.26	39.87	
A-Temperature	5.34	1	0.6484	3.54	7.14	1.0000
B-Catalyst Type	-7.52	1	0.5294	-8.99	-6.05	1.0000
C-Heating Rate	6.77	1	0.6484	4.97	8.58	1.0000
AB	2.19	1	0.6484	0.3848	3.99	1.0000
AC	6.64	1	0.6484	4.84	8.44	1.0000
BC	3.38	1	0.6484	1.58	5.18	1.0000
R^2	0.9924					
Adjusted R^2	0.9810					
Predicted R^2	0.8237					

The regression modeled in term of coded factors as shown in Table 4.4 is therefore expressed as Equation 4.1.

$$\mathrm{Yield} = 38.07 + 5.34\mathrm{A} - 7.52\mathrm{B} + 6.77\mathrm{C} + 2.19\mathrm{AB} + 6.64\mathrm{AC} + 3.38\mathrm{BC} \qquad \text{Equation (4.1)}$$

The coefficient estimated in Table 4.4 represents the expected change in response per unit change in factor value when all remaining factors are held constant. The intercept in an orthogonal design is the overall average response of all the runs. The coefficients are adjustments around that average based on the factor settings. When the factors are orthogonal the VIFs are 1 while VIFs greater than 1 indicate multi-collinearity. The higher the VIF the more severe the correlation of factors as such VIFs less than 10 are tolerable and acceptable. Also, the regression model in terms of coded factors (Eq4.1) can be used to make predictions about the response for given levels of each factor which by default, the high levels of the factors are coded as +1 and the low levels of the factors are coded as –1. The coded equation is useful for identifying the relative impact of the factors by comparing the factor coefficients. Conversely, this equation is not suitable for making predictions about the response in actual term. The regression model in terms of actual factor for pyrolysis oil yield is therefore, expressed as Equation 4.2 and 4.3 for CaO and zeolite catalyst respectively.

$$\text{Oil Yield (CaO Catalyst)} = 62.05833 - 0.12395 * \text{Temperature} - 3.07267 * \text{Heating Rate} + 0.008853 * \text{Temperature} * \text{Heating Rate} \quad \text{Equation} \qquad (4.2)$$

$$\text{Oil Yield (Zeolite Catalyst)} = 119.22167 - 0.16765 * \text{Temperature} - 3.974 * \text{Heating Rate} + 0.008853 * \text{Temperature} * \text{Heating Rate} \quad \text{Equation} \qquad (4.3)$$

The model equation in terms of actual factors are presented in Eq. 4.2 and 4.3 for catalyst type of CaO and zeolite respectively. The equation in terms of actual factors is suitable for making predictions about the response for a given levels of each factor in its actual term. A such, the levels are specified in the original units for each factor. However, this equation is not suitable in determining the relative impact of each factor because the coefficients are scaled to accommodate the units of each factor and the intercept is not at the center of the design space.

The model's equations were also evaluated based on the regression coefficients, R^2, Adjusted R^2 and Predicted R^2 of the model. R^2 value is a measure of the goodness of fit of a model. R^2 value lies between 0 and 1, and the closer the R^2 value is to 1, the better the model prediction (Jia *et al.*, 2018). This is because as R^2 value approaches 1, the model gets fitted at almost all points. The Adjusted R^2 plateaus when insignificant terms are added to the model, and the Predicted R^2 will decrease when there are too many insignificant terms, therefore, a rule of thumb is that the difference between Adjusted and Predicted R^2 values should be within 0.2 of each other (Montgomery, 2004).

The goodness of fit of the model was checked using the regression coefficient of determination. The R^2, Adjusted R^2 and Predicted R^2 for pyrolysis oil yield model are 0.9924, 0.9810 and 0.8237 respectively (Table 4.4) which implies that 99.24% of the experimental data are explainable by the model and the high value of R^2 (0.9924) further indicates high significance of the model in predicting the response variable (Akossou and Palm, 2013). From Table 4.4, the difference between the Adjusted R^2 value and Predicted R^2 value are less than 0.2, which further implies that there is good agreement between the experimental data and predicted data for pyrolysis oil yield (Adepoju and Olawale, 2015; Jia *et al.*, 2018). This confirms that the accuracy and general ability of the model was good, and analysis of the associated response trends was reasonable.

Further more, the validity of the model was checked using the plot of actual against predicted. Figure 4.3 presents the plot of the actual or experimental responses against the predicted responses. From Figure 4.3, the waste plastic pyrolysis oil yield both experimental and predicted results are very close with R^2 of 0.9924. This further suggest that the model's equation generated can be used to predict waste plastic pyrolysis oil yield and indicate that the models adequately represent the experimental data (Akossou and

Palm, 2013; Adepoju and Olawale, 2015). Therefore, the developed models provide good predictions for average outcomes.

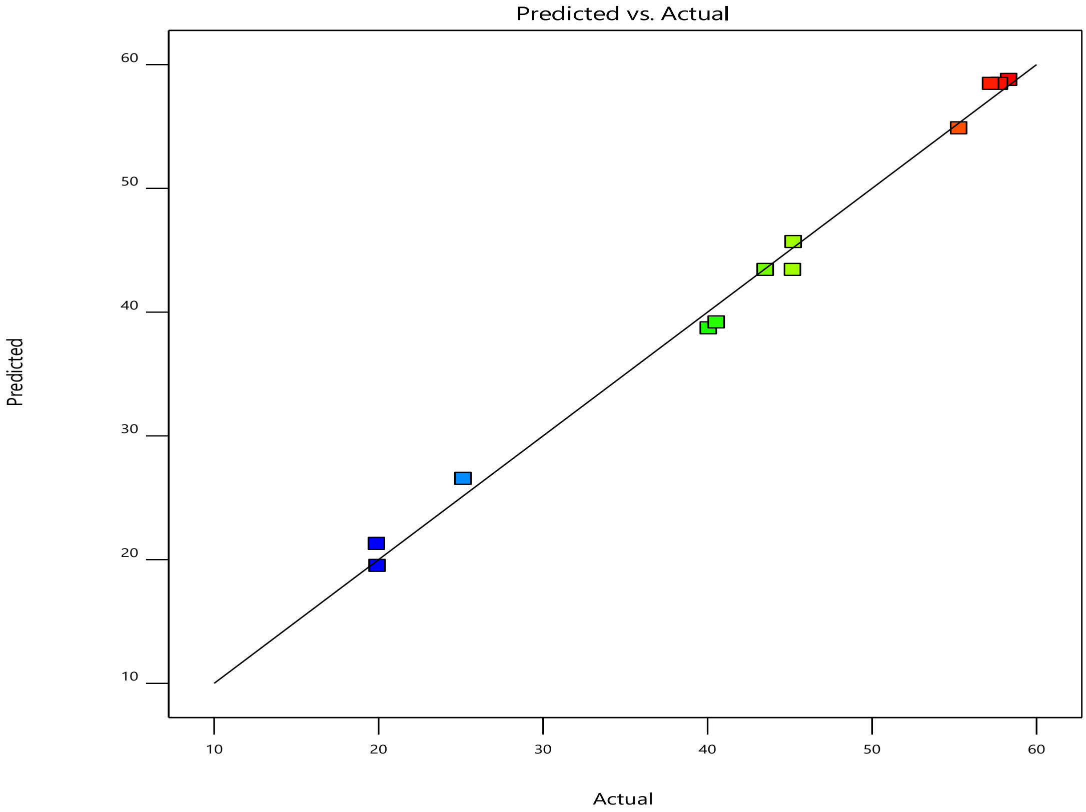

Figure 4.3: Plot of Actual against Predicted pyrolysis oil yield.

4.3.3 Factorial optimization of waste plastic pyrolysis oil yield

The result of the factors that will maximize the pyrolysis oil yield was also evaluated using surface plot. Surface plot was use to explore the relationship between three variables and to view the combinations of x and y factors that produce desirable response values (Saleem and Somá, 2015; Gul, 2016). A typically 3D surface plot consists of an x-axis and y-axis representing values of a continuous predictor variable. The surface plots are useful in regression analysis for viewing the relationship among a dependent and two independent variable or factors. The surface plot shown in Figures 4.4 and 4.5 was used to describe the interaction of different variables on plastic waste pyrolysis oil yield.

Figure 4.4 presents the effect of the temperature, heating rate and CaO catalyst type on waste plastic pyrolysis oil yield at the center level of the parameters. It can be seen that oil yield increases with the increase in the temperature and heating rate. Moreover, waste plastic pyrolysis oil yield is more sensitive to both temperature and heating rate. Hence, high oil yield is obtained at high temperature and heating rate, and decrease as temperature and heating rate decreases for CaO catalyst. This is attributed to the fact that increasing pyrolysis temperature and heating rate tends to accelerate chemical degradation of hydrocarbon molecule into oil. Also, the high yield at relatively low temperature could be attributed to fact that CaO could enhance the rate of degradation of the plastics (Zhang *et al.*, 2008). This corroborate with the fact that plastic waste pyrolysis depends upon sets of parameters such as catalyst type, temperature (Alfa, Zubairu and Alhassan, 2019).

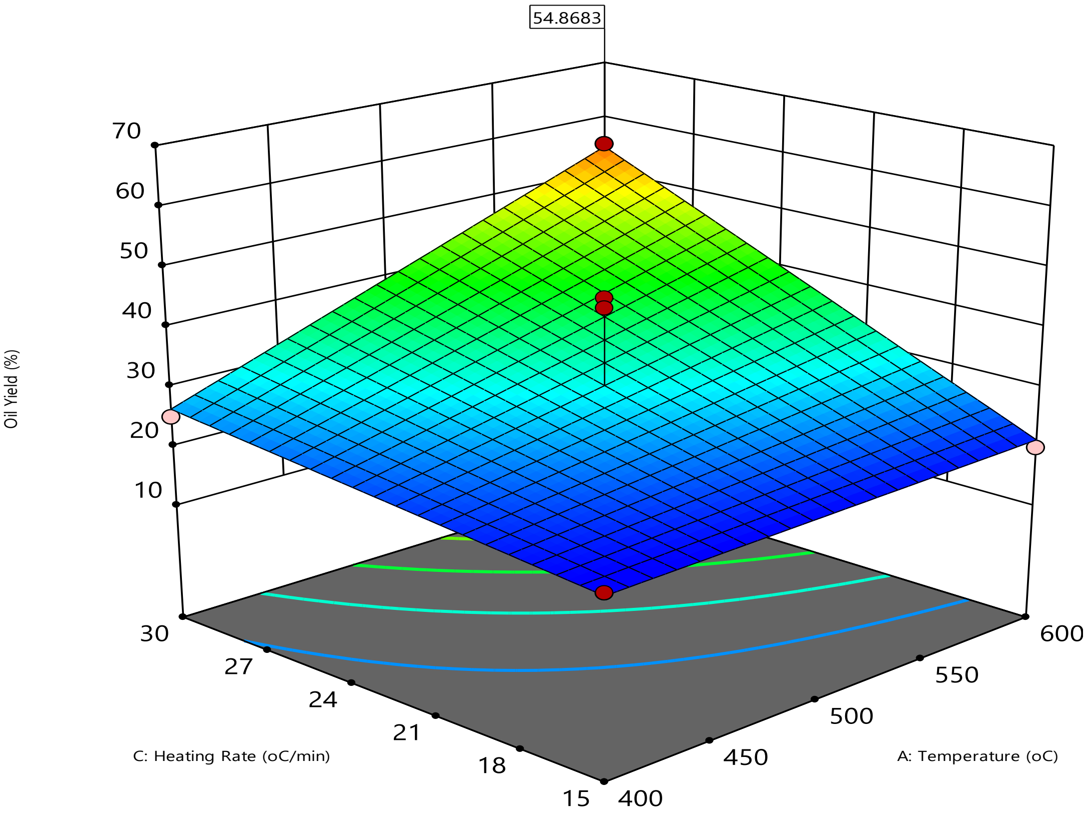

Figure 4.4: 3D surface plot effect of temperature and heating value on oil yield using CaO catalyst

Figure 4.5 presents the effect of the temperature, heating rate and ZSM-5 zeolite catalyst type on waste plastic pyrolysis oil yield at the center level of the parameters. The oil yield increases with the increase in the temperature and heating rate using ZSM-5 zeolite catalyst. This also confirms that waste plastic pyrolysis oil yield is also sensitive to both temperature, heating rate and catalyst type. Hence, high oil yield is obtained at high temperature and heating rate, and decrease as temperature and heating rate decreases for ZSM-5 zeolite catalyst. This corroborate with the fact that plastic waste pyrolysis depends upon sets of parameters such as catalyst type, temperature (Alfa *et al.*, 2019).

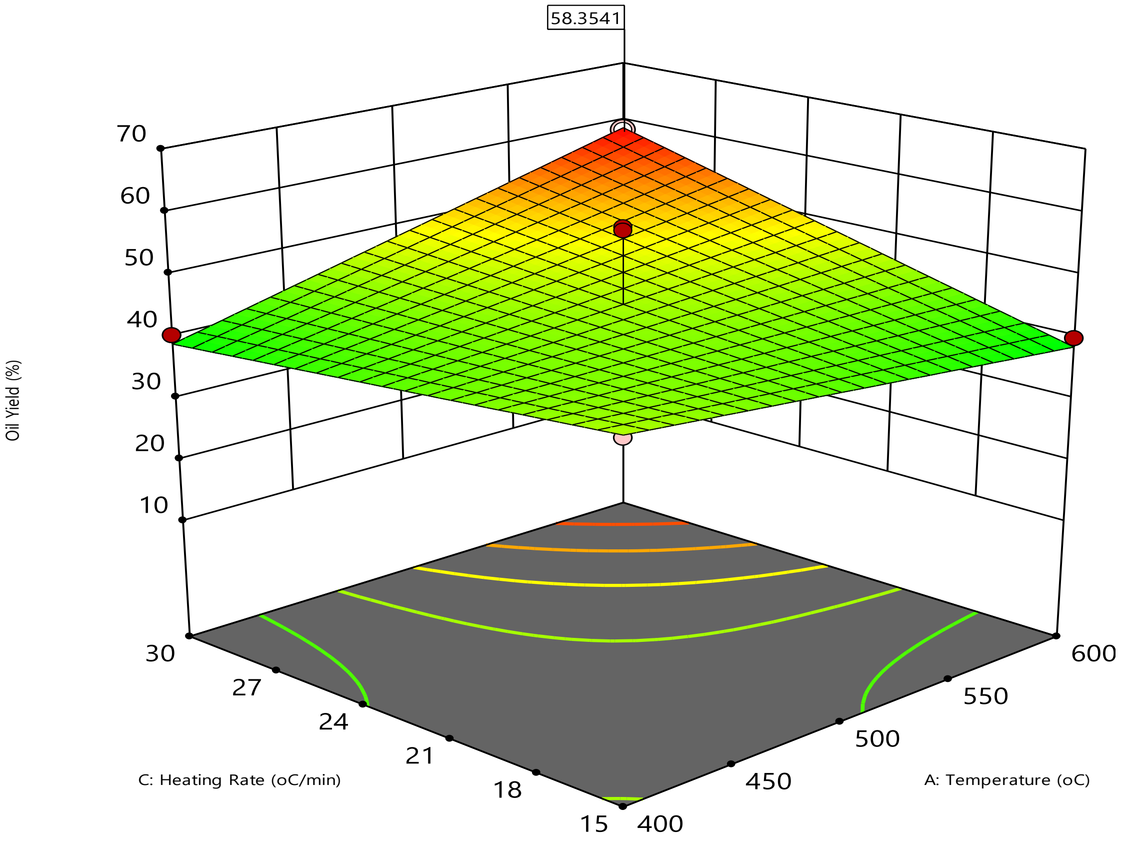

Figure 4.5: 3D surface plot effect of temperature and heating value on oil yield using zeolite catalyst

Comparatively, it was observed that waste plastic pyrolysis oil yield using ZSM-5 zeolite catalyst was slightly higher than that from when CaO catalyst was used. This could be attributed to the fact that high Si/Al ratio in the ZSM-5 zeolite portends acid site which decreases with increase in Si/Al ratio and affect product distribution while higher Si/Al ratio increases crystallinity. The Si/Al ratio in the ZSM-5 zeolite used as catalyst has 29.50:1 Si/Al ratio on molar basis, which can be attributed to the high oil yield obtained with ZSM-5 zeolite.

Table 4.5 presents the yield of oil obtained from waste plastic pyrolysis in the absence of catalyst. It can be seen that, though the oil yield increases from 12.18 – 31.24% as the temperature increases from 400 – 600 °C, however, the yield was very low when compared to those with catalyst (Table 4.2). The performance of pyrolysis process can be improved by using catalyst because it will enhance the rate of plastic molecule degradation (Kolsoom *et al.*, 2017; Alfa *et al.*, 2019). Hence, shows the influence of the presence of catalyst on pyrolysis is significant.

Table 4.5: Plastic pyrolysis oil yield without catalyst

No.	Temperature (°C)	Yield (%)
1	400	12.18
2	500	21.42
3	600	31.24

4.3.4 Optimum waste plastic pyrolysis parameter

The primary objective of optimization in this study was to find the conditions which gave the maximum waste plastic pyrolysis oil yield. Table 4.6 present the optimization result of the parameters that maximum waste plastic pyrolysis oil yield using optimum desirability function with the setup constraint for temperature, heating rate and catalyst type to be in range between the lower and upper limit while the constraint for the response (waste plastic pyrolysis oil yield) was set at maximum. Desirability is an optimization function that is used to determine the optimum result (region) that satisfied the set criteria or optimization goal. It reflects the desirable ranges for each response. The desirable ranges are from zero to one (least to most desirable, respectively). The simultaneous objective function is a geometric mean of all transformed responses. The optimum factors and corresponding response generated for optimization study are presented in Table 4.6.

Table 4.6: Factorial Optimization Result for Pyrolysis oil yield

Number	Temperature	Catalyst Type	Heating Rate	Oil Yield	Desirability	
1	597.269	ZSM-5 Zeolite	29.909	58.385	1.000	Selected
2	600.000	ZSM-5 Zeolite	30.000	58.772	1.000	
3	598.171	ZSM-5 Zeolite	29.820	58.354	1.000	
4	599.467	ZSM-5 Zeolite	29.857	58.529	1.000	
5	598.389	ZSM-5 Zeolite	29.975	58.581	1.000	
6	596.915	ZSM-5 Zeolite	29.992	58.459	1.000	
7	596.164	ZSM-5 Zeolite	29.979	58.369	1.000	
8	598.387	ZSM-5 Zeolite	29.902	58.484	1.000	
9	599.198	ZSM-5 Zeolite	29.735	58.341	1.000	
10	599.888	ZSM-5 Zeolite	29.789	58.478	1.000	
11	599.949	ZSM-5 Zeolite	29.718	58.390	1.000	
12	599.101	ZSM-5 Zeolite	29.796	58.412	1.000	
13	599.494	ZSM-5 Zeolite	29.937	58.638	1.000	
14	594.010	ZSM-5 Zeolite	30.000	58.185	0.996	
15	581.715	ZSM-5 Zeolite	30.000	56.981	0.965	
16	600.000	CaO	30.000	54.868	0.910	
17	598.995	CaO	30.000	54.726	0.906	
18	600.000	CaO	29.718	54.237	0.893	
19	587.057	CaO	30.000	53.035	0.862	
20	563.695	CaO	30.000	49.726	0.776	

From Table 4.6, the established optimum values for maximum waste plastic pyrolysis oil yield are 597 ^{o}C temperature, ZSM-5 zeolite catalyst type and 29.909 ^{o}C/min heating rate to give a maximum waste plastic pyrolysis oil yield of 58.385% at a desirability of 1. However, 600 ^{o}C, CaO catalyst type and 30 ^{o}C/min to obtained a yield of 54.868% at

0.9097 desirability function. Figure 4.6 shows the optimization plot of the established optimum from Table 4.6.

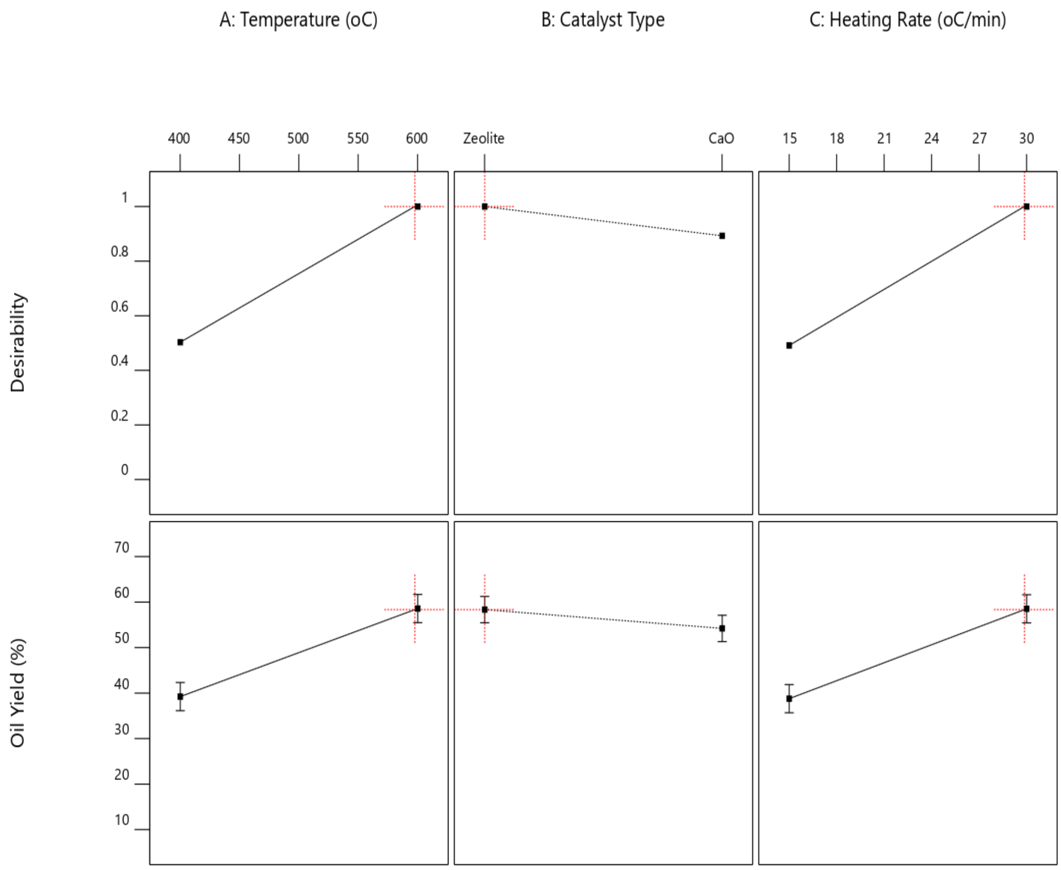

Figure 4.6: Factorial Optimization plot

4.3.5 Validation of optimum parameter

A validation experiment was conducted to determine the reliability of the optimum factors for the waste plastic pyrolysis oil yield. Waste plastic pyrolysis was carried out using ZSM-5 zeolite catalyst type at 597 ^{o}C temperature and 29.909 ^{o}C/min heating rate according to the procedure highlighted in the methodology. To establish the validity of the optimum conditions, 3 experiments were conducted. The obtained waste plastic pyrolysis oil yield for the 3-validation experiment conducted are 58.60%, 57.94% and 58.56% with an average oil yield of 58.367%. The waste plastic pyrolysis oil yield obtained from the validation experiment was found to be very close to the predicted maximum of 58.385% using ZSM-5 zeolite. The results clearly indicated that no much significant difference was observed between the predicted optimum and validate value. This therefore, indicated that the optimization achieved in the present study was reliable.

4.4 Characterization of Plastic Pyrolysis Fuel Oil

The oil products from plastic pyrolysis in the presence of CaO and ZSM-5 zeolite catalyst was characterized using FTIR analysis to evaluate the functional group in the produced pyrolysis oils and GCMS analysis used to determine the constituent of the produced pyrolysis oils.

4.4.1 Gas chromatography and mass spectrometry of plastic pyrolysis oil

The GCMS analysis of the produced catalyzed plastic pyrolysis fuel oil was carried to determine the constituent of the pyrolysis oil. The GCMS instrument was used to separate the produced plastic pyrolysis oil into individual components and to identify the various components from their mass spectra. Table 4.7 presents the compounds identified and their percentage area of chromatogram for CaO catalyzed plastic pyrolysis oil obtained at optimum condition.

Table 4.7: Chromatographic analysis of CaO catalyzed plastic pyrolysis oil

S/N	Retention Time	Area (%)	Compound Identified	Molecular Formula	Mol. Weight
1	5.4834	0.3758	Cyclododecane	$C_{12}H_{24}$	168.3
2	5.6934	0.7257	Vinyl lauryl ether	$C_{14}H_{28}O$	212.4
3	6.0139	20.4739	Heptadecane	$C_{17}H_{36}$	240.5
4	6.6704	1.0817	Hexadecane, 1,1'-oxybis-	$C_{32}H_{66}O$	466.9
5	6.9728	17.3915	Octadecane	$C_{18}H_{38}$	254.5
6	7.1265	0.9583	1-Octadecene	$C_{18}H_{36}$	252.5
7	7.6064	0.5994	Cyclohexadecane	$C_{16}H_{32}$	224.4
8	7.9257	12.7195	Nonadecane	$C_{19}H_{40}$	268.5
9	8.6251	0.4197	5-Eicosene, (E)-	$C_{20}H_{40}$	280.5
10	8.8983	13.1728	Eicosane	$C_{20}H_{42}$	282.5
11	9.2381	0.4345	Cyclohexane, 1,4-dimethyl-	C_8H_{16}	112.2
12	9.5711	0.4541	Tetrapentacontane, 1,54-dibromo-	$C_{54}H_{108}Br_2$	917.2
13	9.8484	8.4515	Heneicosane	$C_{21}H_{44}$	296.6
14	10.7804	6.3616	Docosane	$C_{22}H_{46}$	310.6
15	10.9335	0.5313	1-Docosene	$C_{22}H_{44}$	308.6
16	11.6529	11.1074	Tricosane	$C_{23}H_{48}$	324.6
17	12.496	4.1787	Tetracosane	$C_{24}H_{50}$	338.7
18	13.3237	0.5626	Pentacos-1-ene	$C_{25}H_{50}$	350.7

From Table 4.7, CaO catalyzed plastic pyrolysis oil consists of 18 prominent hydrocarbons compound. The compounds identified from the CaO catalyzed plastic pyrolysis oil vary from C8 – C54 with C8 accounting for 0.4345%, 1.0817% for C32 and 0.4541% for C54 while C12 – C25 accounted for 98.0297% showing clear similarities to diesel. Also, the GCMS characterization of the CaO catalyzed plastic pyrolysis oil comprising of 93.86% Alkane compounds, 1.41% cycloalkanes and other compounds make up 4.73%. The CaO catalytic pyrolysis of polyethylene and polypropylene in the plastic proceed via a random scission reaction resulting in the formation of a large number of hydrocarbon species (Achyut, 2018).

The viscous pyrolysis oil product obtained from the CaO catalyzed plastic pyrolysis oil could be attributed to the presence of C54 (Tetrapentacontane, 1,54-dibromo-) and C32 (Hexadecane, 1,1'-oxybis-) compounds. The presence of Vinyl lauryl ether (C14H28O) from the GCMS characterization further confirmed the FTIR results obtained which indicates the presence of functional groups of Vinyl C–H and Carbonyl group of ethers (Table 4.7) and also, the presence of Tetrapentacontane, 1,54-dibromo- (C54H108Br2) further confirms Aliphatic bromo compounds functional group identified from the FTIR characterisation (Table 4.7). The GCMS characterization of the oil compared favourably with that reported by (Claudinho and Oscar, 2017). Therefore, both the FTIR and GCMS analysis affirms that the CaO catalyzed plastic pyrolysis oil contained complex mixture of compound of mainly paraffins with small amount of naphthenes, olefins, and ether compound.

Similarly, the GCMS characterization of the ZSM-5 zeolite catalyzed plastic pyrolysis oil was carried to determine the constituent of the oil. Table 4.8 presents the compounds identified and their percentage area of chromatogram for ZSM-5 zeolite catalyzed plastic pyrolysis oil obtained at optimum condition.

Table 4.8: Chromatographic analysis of zeolite catalyzed plastic pyrolysis oil

S/N	Retention Time	Area Pct (%)	Compound	Molecular Formula	Mol. Weight
1	6.011	2.5962	Heptadecane	$C_{17}H_{36}$	240.5
2	6.4253	0.2072	E-15-Heptadecenal	$C_{17}H_{32}O$	252.4
3	6.9012	2.6833	1-Octadecene	$C_{18}H_{36}$	252.5
4	7.1384	0.427	Octacosyl trifluoroacetate	$C_{30}H_{57}F_3O_2$	506.8
5	7.6606	0.178	3-Eicosene, (E)-	$C_{20}H_{40}$	280.5
6	7.9252	2.1798	Nonadecane	$C_{19}H_{40}$	268.5
7	8.354	0.7899	Decanoic acid, dodecyl ester	$C_{20}H_{40}O_2$	312.5
8	8.5657	0.3306	3-Octadecene, (E)-	$C_{18}H_{36}$	252.5
9	8.96	8.31	3-methylbut-2-enylbenzene	$C_{11}H_{14}$	146.23
10	9.8473	1.8384	Heneicosane	$C_{21}H_{44}$	296.6
11	10.4927	5.4536	Cyclotetradecane	$C_{14}H_{28}$	196.37
12	10.7801	1.6837	Docosane	$C_{22}H_{46}$	310.6
13	11.6591	1.8458	Tricosane	$C_{23}H_{48}$	324.6
14	12.4986	2.0657	Tetracosane	$C_{24}H_{50}$	338.7
15	12.9453	13.0904	1-Nonadecene	$C_{19}H_{38}$	266.5
16	13.1762	12.0205	1-Docosene	$C_{22}H_{44}$	308.6
17	13.5679	3.2556	9-Tricosene, (Z)-	$C_{23}H_{46}$	322.6
18	14.1926	3.4232	Nonacos-1-ene	$C_{29}H_{58}$	406.8
19	14.5397	10.18	Eicosane	$C_{20}H_{42}$	282.5
20	15.5487	1.286	Octadec-9-enoic acid	$C_{18}H_{34}O_2$	282.5
21	16.18	5.95	2-Methyl-naphthalene	$C_{11}H_{10}$	142.2
22	20.515	4.39	2,7-Dimethyl naphthalene	$C_{12}H_{12}$	156.22
23	20.5731	3.2798	Hexadecane, 1-(ethenyloxy)-	$C_{18}H_{36}O$	268.5
24	22.7121	1.7176	Oleic Acid	$C_{18}H_{34}O_2$	282.5
25	24.1223	0.6595	9-Octadecenoic acid, (E)-	$C_{18}H_{34}O_2$	282.5
26	26.9052	8.7105	Cyclotetracosane	$C_{24}H_{48}$	336.6
27	27.479	0.7308	1H-Indole, 5-methyl-2-phenyl-	$C_{15}H_{13}N$	207.27
28	29.7447	0.2266	Octasiloxane, 1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15-hexadecamethyl-	$C_{16}H_{48}O_7Si_8$	577.2
29	29.9372	0.4351	Hexahydropyridine, 1-methyl-4-[4,5-dihydroxyphenyl]-	$C_{12}H_{17}NO_2$	207.3
30	31.1019	0.0552	1-methyl-4-phenyl-5-thioxo-1,2,4-triazolidin-3-one	$C_9H_9N_3OS$	207.25

From Table 4.8, 30 compounds were identified in the ZSM-5 zeolite catalyzed plastic pyrolysis oil. The compounds identified for the ZSM-5 zeolite catalyzed plastic pyrolysis oil vary from C9 – C30 with C8 accounting for 0.0552%, 3.4232% for C29 and 0.427 % for C30 while C11 – C24 accounted for 96.0946% indicating clear similarities to diesel. Also, the GCMS characterization of the zeolite catalyzed plastic pyrolysis oil comprising of 22.39% Alkane, 14.16% cycloalkanes, 18.65% aromatics, 34.98% Alkenes, 0.79% ester, 3.66% organic acid and other compounds make up 5.36%. The ZSM-5 zeolite catalytic pyrolysis of the plastic proceeds via a random scission reaction resulting in the formation of a large number of hydrocarbon species. The formation of relative high number of alkenes compounds in the zeolite pyrolysis oil by the catalytic degradation of plastics can be attributed to the higher stability of carbon double bond (C=C) in the plastic materials as compared to single bond (C–C) (Achyut, 2018).

The presence of Decanoic acid, dodecyl ester (C20H40O2), Octacosyl trifluoroacetate (C30H57F3O2), Octadec-9-enoic acid (C18H34O2), Oleic acid (C18H34O2), 9-Octadecenoic acid, (E)- (C18H34O2) and E-15-Heptadecenal (C17H32O) from the GCMS characterization corroborate the alcohols, ethers, carboxylic acids and ester functional groups identified from the FTIR analysis of the zeolite catalysed plastic pyrolysis oil (Table 4.8). Likewise, the presence of Hexahydropyridine, 1-methyl-4-[4,5-dihydroxyphenyl]- (C12H17NO2), further confirms the presence of the nitrile functional group identified from the FTIR characterisation (Table 4.10). The GCMS characterization of the oil compared favourably with that reported by Achyut (2018) for calcium bentonite catalyzed plastics pyrolysis liquid.

4.4.2 Fourier transform infra-red spectroscopy of plastic pyrolysis fuel oil

The FTIR is used to determine the quantitative and qualitative analysis of functional group of organic and inorganic samples present in the plastic pyrolysis oils. The FTIR spectrum for the plastic pyrolysis oil in the presence of CaO catalyst is as shown in Figure 4.7 and the functional group identified from the transmittance spectrums are presented in Table 4.9. From Table 4.9, the constituent functional groups identified in the CaO catalyst plastic pyrolysis oil are mainly aliphatic, olefin, alkyne, vinyl and carbonyl functional group. The prominent absorption peaks identified from Figure 4.7 are correlated with their respective functional group vibration modes as shown in Table 4.9.

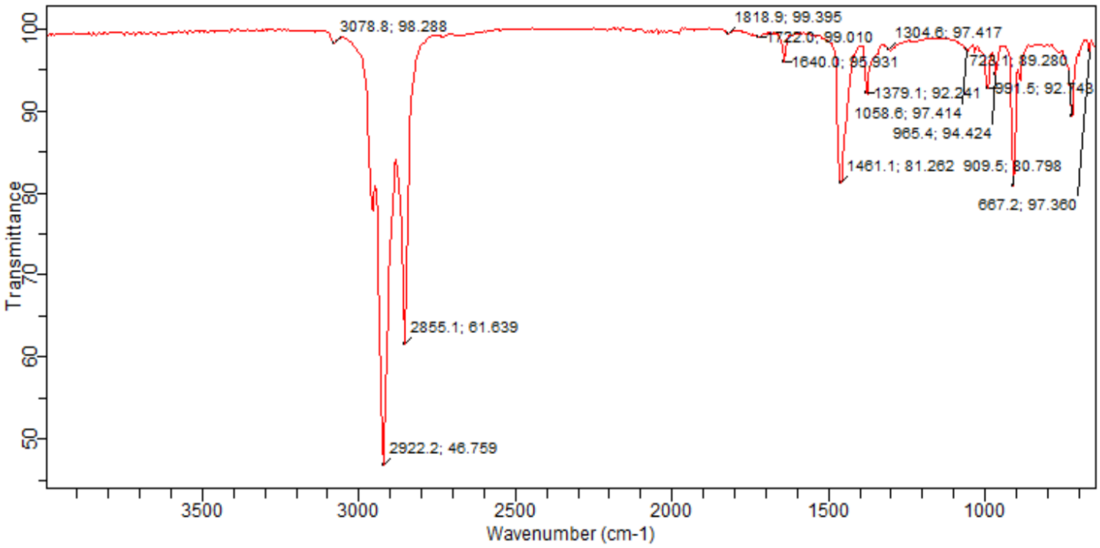

Figure 4.7: FTIR spectrum of CaO catalyst plastic pyrolysis oil

The region from about 1500 – 700 cm^{-1} is called the fingerprint region. The bands in region originate in interacting vibrational modes resulting in a complex absorption pattern. Usually, this region is quite complex and often difficult to interpret; however, each organic compound has its own unique absorption pattern (or fingerprint) in this region. From Figure 4.9, the spectra region from 1500 – 700 cm^{-1} can be referred to as the “fingerprint” region, which confirms the bands stemming from C–Br of aliphatic bromide stretching at 667.2 cm^{-1}, C–H rocking of aliphatic compound at 723.1 cm^{-1}, C–H bending of olefins compounds from 970 – 900 cm^{-1}, C–H stretching of cyclo-alkane compounds from 1060 – 995 cm^{-1}, C–H in plane bending of vinyl CH compounds at 1304.6 cm^{-1} and C–H bending of aliphatic compounds from 1500 – 1370 cm^{-1} of alkanes in the CaO catalyst plastic pyrolysis oil (Pawar and Lalitha, 2015). This bands correspond to similar “fingerprint” region spectrum of 1500 – 700 cm^{-1} reported by Achyut (2018) for CaO catalyst pyrolysis oil. The intermolecular bonded C=O groups at 1820 – 1700 cm^{-1} corresponds to the presence of carbonyl compound in the CaO catalyst plastic pyrolysis oil. The band in the range of 2930

– 2850 cm^{-1} is attributed to C–H stretching of Alkanes functional group and the band at 3078.8 cm^{-1} is attributed to =C–stretching of Alkenes. The FTIR analysis shows that the CaO catalyst pyrolysis oil comprises mainly of straight chain aliphatic and olefin functional groups hydrocarbon (Pawar and Lalitha, 2015).

Table 4.9: FTIR result of constituents functional group of CaO catalyst plastic pyrolysis oil

No.	Wavelength (cm^{-1})	Functional group	Class of compounds
1	667.2	C–Br stretching	Aliphatic bromo compounds,
2	723.1	C-H rocking	Alkanes (Methyl)
3	909.5	C-H bending	Alkene
4	965.4	C-H bending	Alkene
5	1060 – 995	C–H	Cyclo-Alkanes
6	1304.6	C–H in-plane bend	Vinyl CH
7	1379.1	C–H rocking	Alkanes (Methyl)
8	1461.1	C–H Scissor, bending	Alkanes (Methyl)
9	1527.67	C=C-C	Aromatic ring stretch
10	1640	C=C stretching	Alkenes
11	1820 – 1700	C = O	Carbonyl group of ethers
12	2855.1	C-H stretching	Alkanes (Methyl)
13	2922.2	C-H stretching	Alkanes (Methyl)
14	3078.8	C–H stretch, =C–H stretch	Alkenes

Also, the FTIR spectrum of ZSM-5 zeolite catalyst plastic pyrolysis oil was carried out to determine its functional group. The FTIR spectrum of the ZSM-5 zeolite catalyst plastic pyrolysis oil is as shown in Figure 4.8. and the identified functional group from the transmittance spectrums are presented in Table 4.10. From Table 4.10, the constituent functional groups identified in the ZSM-5 zeolite catalyst plastic pyrolysis oil are mainly aliphatic, olefin, alkyne, vinyl and carbonyl functional group. The major absorption peaks identified from Figure 4.8 are correlated with their respective functional group vibration modes as shown in Table 4.10.

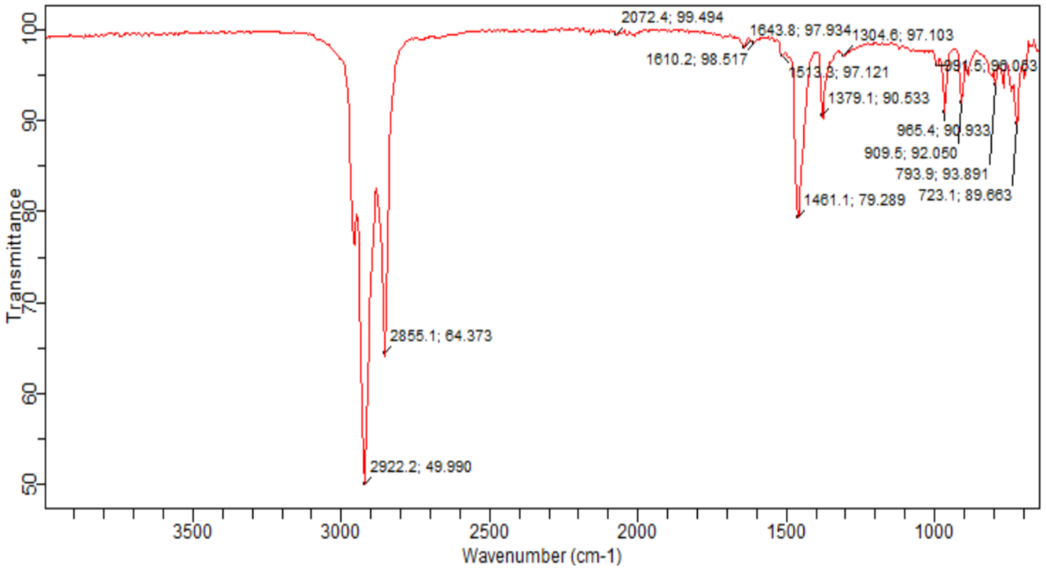

Figure 4.8: FTIR spectrum of ZSM-5 zeolite catalyst plastic pyrolysis oil

The region from about 1500 – 700 cm^{-1} also shows the fingerprint region for the ZSM-5 zeolite catalyst plastic pyrolysis oil spectrum which is usually quite complex region and often difficult to interpret. From Figure 4.10, the spectra region of 1500 – 700 cm^{-1} is the “fingerprint” region which confirms the bands stretching from C–H functional group of aliphatic and olefins compound in the ZSM-5 zeolite catalyst plastic pyrolysis oil. This bands correspond to similar “fingerprint” region spectrum of 1500 – 700 cm^{-1} reported by Panda and Sing (2013) and Achyut (2018) for ZSM-5 zeolite catalyst plastic pyrolysis oil. The band at 1610.2 cm^{-1} corresponds to conjugated C=C functional group of Olefins and aromatics compounds; the band at 1643.8 cm^{-1} corresponds to C=O stretching functional group of alcohols, ethers, carboxylic acids or esters while the band at 2072.4 cm^{-1} corresponds to C ≡ C or C ≡ N stretching functional group of alkyne and nitrile for zeolite catalyst plastic pyrolysis oil (Pawar and Lalitha, 2015). The band in the range of 2965 – 2850 cm^{-1} corresponds to C–H stretching of Alkanes functional group for zeolite catalyst plastic pyrolysis oil. The FTIR analysis shows that the ZSM-5 zeolite catalyst pyrolysis oil comprises mainly of aliphatic, olefin, nitrile and carbonyl functional groups hydrocarbon (Achyut, 2018). Comparatively, CaO and ZSM-5 zeolite catalyzed plastic pyrolysis oil have similar functional group which comprises mainly of aliphatic, olefins, carbonyl and nitrile compounds.

Table 4.10: FTIR result of constituents functional group of ZSM-5 zeolite catalyst plastic pyrolysis oil

No.	Wavelength (cm^{-1})	Functional group	Class of compounds
1	723.1	C-H rocking	Alkanes
2	793.9	C-H bending	Alkene
3	909.5	C-H out of plane bending	Alkene
4	965.4	C-H bending	Alkene
5	991.5	C-H Bending	Alkene
6	1304.6	C–H in-plane bend	Vinyl CH
7	1379.1	C–H Scissoring and Bending	Alkanes
8	1461.1	C=C stretching	Alkenes
9	1513.8	C – C	Alkanes
10	1610.2	Conjugated C=C	Olefins, Aromatics
11	1643.8	C=O stretching	Alcohols, Ethers, Carboxylic acids, Esters
12	2072.4	C ≡ C, C ≡ N	Alkyne and nitrile
13	2855.1	C-H stretching	Alkanes
14	2922.2	C-H stretching	Alkanes
15	2964.2	C-H stretching	Alkanes

Therefore, both the FTIR and GCMS analysis affirms that the ZSM-5 zeolite catalyzed plastic pyrolysis oil comprises of better hydrocarbon mixture range of alkane, alkenes, cycloalkanes, aromatics and very minute organic acid compounds compared to CaO catalysed plastic pyrolysis oil.

4.5 Analysis of Properties of Catalysed Plastic Pyrolysis Oil

The plastic pyrolysis oil obtained using CaO and ZSM-5 zeolite catalyst were characterized to determine its suitability for use as an alternative source of diesel. The density, specific gravity, kinematic viscosity, flash point, heating value and cetane number of pyrolysis oil from the two catalyst were evaluated and compared with the ASTM standards. Table 4.11 shows the physical property of the pyrolysis oil.

Table 4.11: Fuel Performance Characterization of Pyrolysis Oil

S/N	Properties	Diesel Standard (D–6751)	CaO Catalyzed Oil	ZSM-5 Zeolite Catalyzed Oil
1	Density at 40 ºC (g/cm^3)	0.820 – 0.900	0.931	0.839
2	Specific gravity	–	0.938	0.846
3	Kinematic viscosity (mm^2/sec)	1.3 – 6	7.46	3.81
4	Flash point, (ºC)	> 38	59.2	44.8
5	Heating value (MJ/kg)	42 – 44.5	37.852	42.193
6	Cetane Number	> 40	41.75	50.82

The fuel properties of the pyrolysis oil were analyzed and compared with ASTM D–6751 diesel fuel standard value. From Table 4.11, the fuel performance characterization shows that the density and specific gravity of the CaO catalyzed pyrolysis oil was determined as 0.931 g/cm^3 and 0.938 respectively compared 0.839g/cm^3 and 0.846 respectively for ZSM-5 zeolite catalyzed pyrolysis oil. The density and specific gravity obtained for the CaO catalyzed pyrolysis oil were higher than those of ZSM-5 zeolite catalyzed oil. The study also, found that the density of ZSM-5 zeolite catalyzed oil (0.846g/cm^3) is within the range of value recommended by D–6751 for diesel fuel (Table 4.11) while that of CaO catalyzed pyrolysis oil is higher than 0.931 D–6751 recommended density for oil used as diesel fuel, hence upgrading of CaO catalyzed pyrolysis oil would enhance its density. The high density for the CaO could be attributed to the present of high hydrocarbon compound in the oil (C_{32} and C_{54}) identify from the GCMS characterization and the high density and specific gravity could affect the level of engine power. Conversely, the density obtained for ZSM-5 zeolite catalyzed plastic pyrolysis oil compared favorably with 0.820 – 0.845 g/cm^3 reported for plastic pyrolysis oil according to EN ISO 12185 (Stella *et al.*, 2017). Hence the high density of the CaO catalyzed pyrolysis oil is attributed to the presence of heavier compounds in the oil.

Viscosity which is a measure of the fuel spray atomization and fuel system lubrication was evaluated for both CaO and ZSM-5 zeolite catalyzed pyrolysis oil. From Table 4.11, that kinematic viscosity of CaO catalyzed plastic pyrolysis oil 7.46 mm^2/sec which is slightly higher than value recommended by D–6751 for diesel fuel while that of ZSM-5 zeolite catalyzed pyrolysis oil is 3.81 mm^2/sec which is within the acceptable range of value recommended by D–6751 for diesel fuel. This indicated that CaO catalyzed pyrolysis oil contains higher hydrocarbon fraction as seen from the GCMS characterization (C_{32} and C_{54}). Whereas, the value obtained for the ZSM-5 zeolite catalyzed pyrolysis oil which is with the recommended D–6751 value, shows the positive quality in the handling and transporting of the oil (Miandad *et al*., 2016; Punkkinen *et al*., 2017; Suhartono *et al*., 2018).

Flash point, which is the minimum temperature at which a liquid gives sufficient vapours to ignite momentarily when a flame of standard dimension is brought near the surface of the liquid. It is used to characterize the fire hazards associated with a fuel and measure of the safety in handling of fuel oil. The flash point of the CaO and ZSM-5 zeolite catalyzed pyrolysis oil were also evaluated as shown in Table 4.11. The flash point obtained for CaO catalyzed pyrolysis oil is 59.2^{o}C which is higher than the minimum recommended value by D–6751 for diesel fuel while that of ZSM-5 zeolite catalyzed pyrolysis oil is 44.8^{o}C, also higher than the minimum recommended value by D–6751 for diesel fuel. The relatively high flash point obtained for both CaO and ZSM-5 zeolite catalyzed pyrolysis oil can be attributed to the presence of mixture of different heavier compounds in the oils as identified from the GCMS characterization. Similarly, the high flash point indicates the absence of volatile constituents in the oil and as such, the oils do not pose any serious safety concerns in handling and transport.

Heating value, which is a measure of the fuel economy was evaluated for both CaO and ZSM-5 zeolite catalyzed pyrolysis oil as shown in Table 4.11. The heating value obtained for CaO catalyzed pyrolysis oil is 37.852 MJ/kg which is less than the minimum recommended value of 42 MJ/kg by D–6751 for diesel fuel while the heating value obtained for ZSM-5 zeolite catalyzed pyrolysis oil is 42.193 MJ/kg which is within the recommended range of value of 42 – 44.5 MJ/kg by D–6751 for diesel fuel. The low heating value obtained for the CaO catalyzed pyrolysis oil is attributed to the presence of mixture of different compounds of low calorific value in the oil. However, the 42.193 MJ/kg obtained for ZSM-5 zeolite catalyzed pyrolysis oil relatively compares with 44.34 MJ/kg reported by Suhartono *et al.* (2018) and 43.55 MJ/kg reported by Punkkinen *et al*. (2017) as well 43.83 MJ/kg reported by ASTM International (2016) for pyrolysis oil from waste plastics.

Cetane number, which is a measure of the ignition, smoking and emission quality of fuel oil was determined for the CaO and ZSM-5 zeolite catalyzed plastic pyrolysis oil. From Table 4.11, the cetane number obtained for CaO and ZSM-5 zeolite catalyzed pyrolysis oil are 41.751 and 50.882 respectively which are higher than the minimum recommended value of 40 by D–6751 for diesel fuel (Table 4.11). The obtained cetane number is higher than the minimum recommended range. The high cetane number obtained for the ZSM-5 zeolite catalyzed pyrolysis oil is attributed to the presence of mixture of different compounds (naphthalenes and aromatics) in the pyrolysis oil. The obtained cetane number for ZSM-5 zeolite catalyzed plastic pyrolysis oil is comparable to 51 reported by Suhartono *et al.* (2018) for plastic pyrolysis and lower than 60.7 reported by Stella *et al.* (2017).

The most important properties for diesel fuel are ignition quality, viscosity among other few, which the zeolite catalyzed satisfied the D–6751 recommended standard for diesel fuel. However, the CaO catalyzed pyrolysis oil required some preliminary upgrade and treatment to enhance it fuel properties to meet the D–6751 recommended standard for diesel fuel. The fuel properties of the ZSM-5 zeolite catalyzed plastic pyrolysis oil compared favorably with diesel fuel oil, while CaO required upgrade to meet recommended diesel fuel standard, hence ZSM-5 zeolite catalyzed plastic pyrolysis oil show better fuel performance than CaO catalyzed plastic pyrolysis oil and the oil may be considered as a valuable component for use with automotive diesel fuels and may be directly used as fuels for industrial boilers, furnaces and power plants.

4.6 Comparative Study of the Pyrolysis Oil Product from CaO and ZSM-5 Zeolite

Table 4.11 presents a comparison between the CaO and of ZSM-5 zeolite catalysed plastic pyrolysis oil at the same temperature and heating rate. The oil yield obtained from ZSM-5 zeolite catalysed plastic pyrolysis oil were much higher than those obtained for CaO catalysed plastic pyrolysis oil at 400^{o}C and 15^{o}C/min; 400^{o}C and 30^{o}C/min, 500^{o}C and 22.5^{o}C/min and 600^{o}C and 15^{o}C/min while the yield at 600^{o}C and 30^{o}C/min were very close for both CaO catalysed plastic pyrolysis oil (55.3 wt.%) and ZSM-5 zeolite catalysed plastic pyrolysis oil (58.34 wt%). The high yield recorded for ZSM-5 zeolite could be attributed to the catalyst activity and its selectivity for hydrocracking process (Miandad *et al.*, 2016; Punkkinen *et al.*, 2017). The different oil yields between CaO and ZSM-5 zeolite catalysed plastic pyrolysis oil shown in Table 4.11 is due to the difference in catalysts pore size and active sites present in the catalyst as well as the silica/alumina ratio which influenced the number of catalytically active sites on the ZSM-5 zeolite catalyst surface (Miteva *et al.*, 2016).

Table 4.11: Comparison between the yield of CaO and of ZSM-5 zeolite catalyzed plastic pyrolysis oil at the same temperature and heating rate

Run	Temperature (°C)	Heating Rate (°C/min)	Zeolite Yield (%)	CaO Yield (%)
1	400	15	45.24	19.94
2	400	30	40.56	25.16
3	500	22.5	57.78	43.54
4	500	22.5	57.24	45.2
5	600	30	58.34	55.3
6	600	15	40.08	19.9

Further comparison of the fuel properties shows that the properties of the ZSM-5 zeolite catalyzed plastic pyrolysis oil meets the D–6751 recommended standard for diesel fuel (ASTM International, 2016) while that obtained from CaO catalyzed pyrolysis requires further treatment to meet D–6751 recommended diesel fuel standard. Therefore, ZSM-5 zeolite catalyzed plastic pyrolysis oil show better fuel properties than CaO catalyzed plastic pyrolysis oil.

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATION

5.1 Conclusion

From the study carried out, the following conclusion are drawn;

1. The XRD analysis shows that the crystalline structure of the CaO catalyst contains mainly CaO and small quantity of $Ca(OH)_2$ with typical diffraction peak of portlandite (CaO) and lime phase ($Ca(OH)_2$) in the CaO catalyst with 98.848 wt.% CaO and <1% of other oxide identified from XRF analysis while the zeolite catalyst contains mainly silicate crystals with the presence of a highly crystalline zeolitic structure with well-defined diffraction peaks of a high structural order that are indication of those of ZSM-5 and a silica to alumina ratio of 29.50:1 from the XRF analysis.
2. The pyrolysis oil produced shows that ZSM-5 zeolite catalyst gives much higher yield of 58.34% with better quality at lower temperature compared 43.54% for CaO catalyst with oil quality requiring improvement.
3. The optimum temperature, heating rate and catalyst type for maximum plastic pyrolysis oil yield (58.385%) are 597 ^{o}C temperature, 29.909 ^{o}C/min and ZSM-5 zeolite catalyst type respectively while the optimum temperature and heating rate for CaO catalyst are 600 ^{o}C and 30 ^{o}C/min respectively for a maximum oil yield of 54.868% with temperature, heating rate and catalyst type as well as interaction between this parameters having predominant effect on the amount of liquid product yield.
4. Therefore, both the FTIR and GCMS analysis affirms that the zeolite catalyzed plastic pyrolysis oil comprises of better hydrocarbon mixture range of alkane,

alkenes, cycloalkanes, aromatics and very minute organic acid compounds compared to CaO catalysed plastic pyrolysis oil.

5. The fuel properties of the zeolite catalyzed plastic pyrolysis oil compared favorably with diesel fuel oil, while CaO required upgrade to meet recommended diesel fuel standard, hence zeolite catalyzed plastic pyrolysis oil show better fuel performance than CaO catalyzed plastic pyrolysis oil and zeolite catalyzed pyrolysis oil may be considered as a valuable component for use with automotive diesel fuels and may be directly used as fuels for industrial boilers, furnaces and power plants

5.2 Recommendation

From the study carried out, it is recommended that further study should be carried out to examine the comparative study of the effect of CaO and zeolite catalyst on biomass pyrolysis as well as a combination of biomass and waste plastic at different ratio.

5.3 Contribution to Knowledge

The study has established the optimum condition for fuel oil yield from the catalytic pyrolysis of plastic waste in the presence of CaO calcium oxide and zeolite ZSM-5 catalyst and have compared the effect of the two catalyst and discovered Zeolite ZSM-5 to give high fuel yield (58.385%) at the optimum condition of temperatue ($600^{o}C$), heating rate ($30^{o}C$/min) at a desirability of 1 however having compared to CaO calcium oxide which gave the lowest oil yield (54.868%) at the optimum condition of temperature ($600^{O}C$), heating rate ($30^{O}C$/min) at the desirability function of 0.9

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APPENDICES

APPENDIX A

DETERMINATION OF PYROLYSIS LIQUID YIELD

	Weight of Plastic Materials (Wo) =				50kg	
Temperature ^{o}C	Catalyst Type	Heating Rate ^{o}C/min	W_1 (Empty Container)	W_2 (Oil+W_1) kg	W3 (Oil), kg $W_3 = W_2 - W_1$	Yield (%)
600	Zeolite	30	13.08	42.25	29.17	58.34
400	CaO	30	13.1	25.68	12.58	25.16
400	Zeolite	15	13.09	35.71	22.62	45.24
400	Zeolite	30	13.08	33.36	20.28	40.56
500	CaO	22.5	13.08	34.85	21.77	43.54
500	CaO	22.5	13.1	35.7	22.6	45.2
600	CaO	30	13.06	40.71	27.65	55.3
500	Zeolite	22.5	13.03	41.92	28.89	57.78
400	CaO	15	13.14	23.11	9.97	19.94
600	CaO	15	13.08	23.03	9.95	19.9
500	Zeolite	22.5	13.09	41.71	28.62	57.24
600	Zeolite	15	13.02	33.06	20.04	40.08

$$Yield\ (\%) = \frac{W_3}{W_0} x\ 100$$

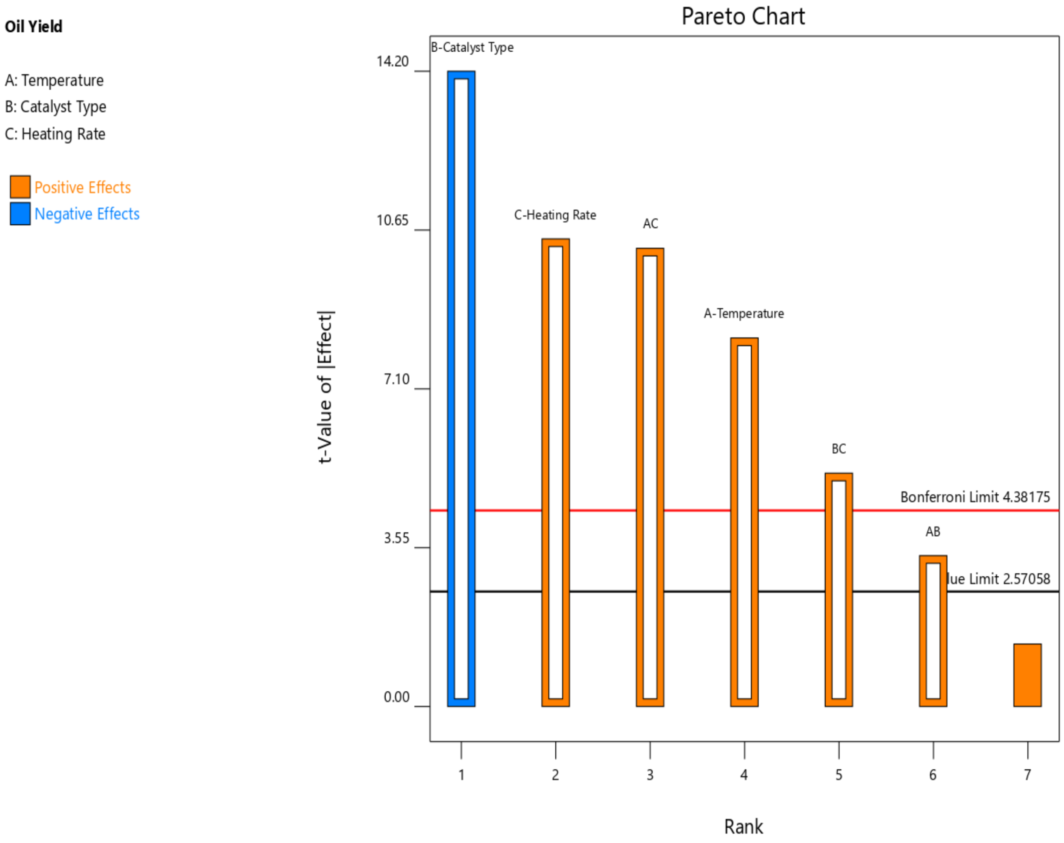

Figure D.1: Pareto Chart

APPENDIX B

INSTRUMENT AND MATERIALS USED, AND EXPERIMENTAL PROCEDURES

Plate D.1a: Pyrolysis Setup

Plate D.1b: Pyrolysis Setup

Plate D.2: Waste Raw Materials

Plate D.3: Pyrolysis Solid Products

Plate D.4: (a) Zeolite Catalyst and (b) Pyrolysis Liquid Product

Plate D.5: Weighing Balance

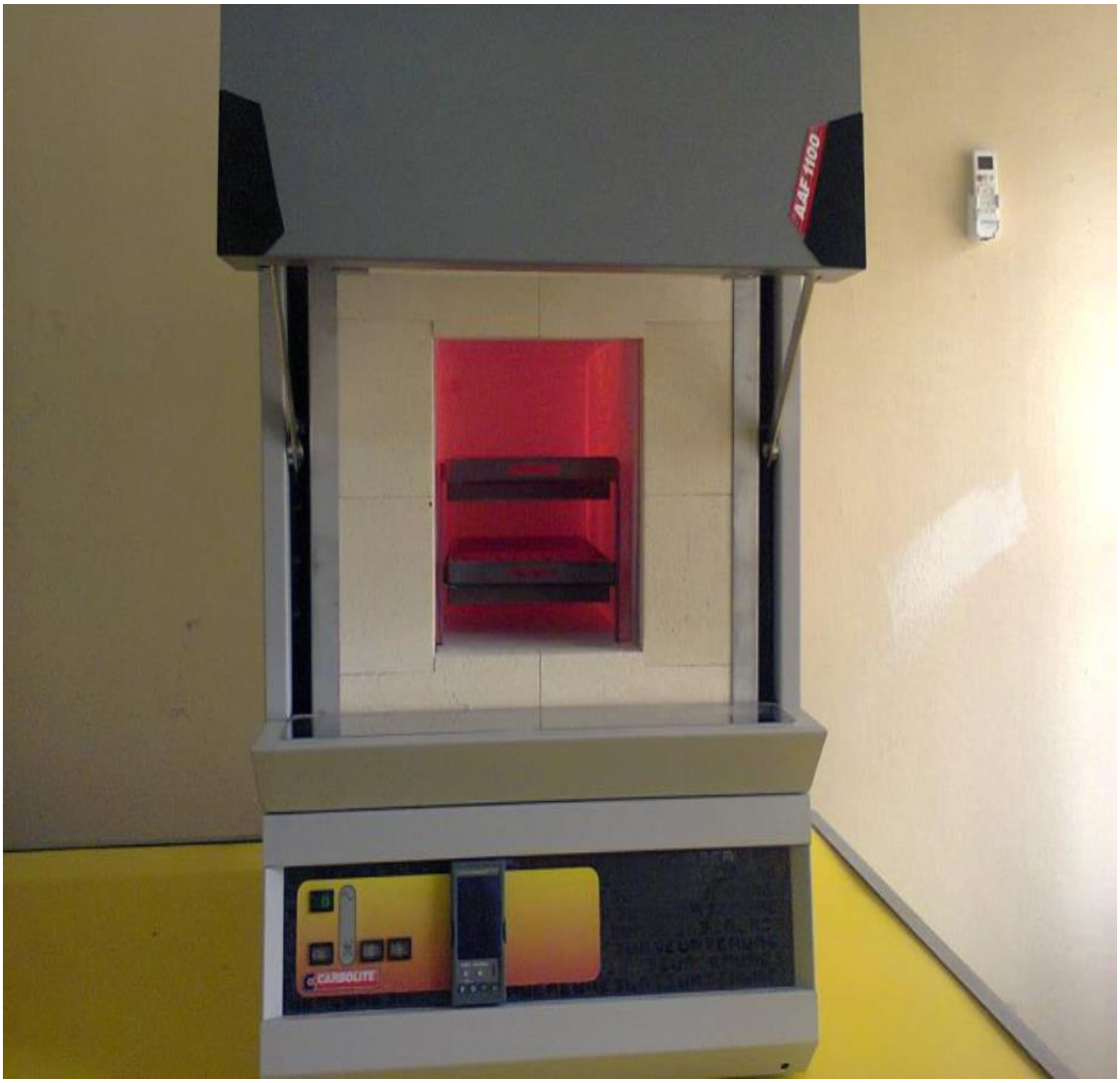

Plate D.6: Carbolite Furnace