PYROLYSIS OF WASTE PLASTIC (PET) USING ZEOLITE CATALYST TO PRODUCE LIQUID FUEL.

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DEPARTMENT OF CHEMICAL ENGINEERING

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A PROJECT SUBMITTED TO THE DEPARTMENT OF
CHEMICAL ENGINEERING, FACULTY OF ENGINEERING,
UNIVERSITY OF BENIN, BENIN CITY

IN PARTIAL FULFILLMENT OF THE REQUIREMENT FOR THE
AWARD OF BACHELOR DEGREE IN CHEMICAL
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CERTIFICATION

This is to certify that this research project submitted to the Department of Chemical Engineering was carried out by MOMODU ABDULMALIK INUSA of the Department of Chemical Engineering, Faculty of Engineering, University of Benin, Benin City under the supervision of Dr. Mrs E.A OYEDOH.

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DEDICATION

This research project is dedicated to the ALMIGHTY GOD who is the source and giver of all wisdom. Special dedication to my ever-inspiring parents Mr and Mrs Momodu for encouraging me throughout my academic journey.

ACKNOWLEDGEMENT

With heartfelt exuberance, I express profound gratitude to the celestial source of all benedictions for the privilege of pursuing knowledge at the esteemed University of Benin, a milestone and blessing I will forever hold dear. My heartfelt appreciation goes to my father, Mr. Inusa Momodu, whose unwavering dedication has propelled me to this juncture. Father, your love and support are my life's blood. Equally, I am beholden to my mother, Mrs. Aisha Momodu, whose encouragement has been my unwavering anchor in times of trial.

I etend heartfelt thanks to my project supervisor, Dr. Mrs. E.A Oyedoh, whose mentorship has rendered this journey both enlightening and effortless. Your exceptional kindness and support are deeply cherished. Gratitude also extends to my brother, Friday, Gilbert, Samson, Victor, Riches, Patrick, and my fellow students, whose inspiration has been invaluable. I am also grateful to my companions at Uniben, including Florence, Bright, Joshua, Bro Samuel, Zino, and the occupants of Texas hostel, for their camaraderie and the imparted wisdom.

Throughout this expedition, I have been blessed with the unwavering support of my siblings, Amina, Ramat, Bekisu, and Jeminu. Your encouragement has been a ceaseless fountain of strength. To every individual who has contributed to my maturation and triumph, I express my deepest appreciation. Thank you all for being extraordinary companions on my life's passage.

ABSTRACT

This research endeavor seeks to develop an innovative catalyst for the pyrolysis procedure, transforming waste plastic (polyethylene terephthalate PET) into a liquid fuel source. The objectives include preparation of waste PET and clay specimens, the fabrication of a zeolite catalyst from clay, and the subsequent examination and characterization of this catalyst. The experimental setup entailed weighing 500 g of PET particles and 25 g of zeolite catalyst, purging the system with nitrogen gas to establish an oxygen-free milieu, and commencing pyrolysis at 450°C with a heating gradient of 15°C/min and a reaction duration of 30 min in a diminutive fixed-bed reactor.

The findings indicate the efficacy of calcined clay soil in the pyrolysis of discarded PET containers. Structural analysis revealed specific surface area, bulk density, particle size, and porosity values of 86.10 m^2/g, 1.285 g/cm^3, <100μm, and 48%, respectively. Spectroscopic analysis underscored a notable composition of calcium oxide in the catalyst, corroborating its catalytic prowess. Furthermore, the catalytic pyrolysis process yielded a greater volume of oil compared to non-catalytic pyrolysis, as exemplified in Table 4.3. The physiochemical attributes of the resultant oil conformed to ASTM standards, with caloric value, flash point, kinematic viscosity, and specific gravity measured at 16.42 kcal/kg, 78°C, 2.80 mm^2/s, and 0.8601, respectively.

In conclusion, this study proffers a promising approach to address the issue of plastic waste by converting PET bottles into a valuable liquid fuel source utilizing a novel clay-based catalyst. The developed catalyst exhibits advantageous structural and spectroscopic properties, enhancing the efficiency of the pyrolysis process. Moreover, the resulting fuel meets industry benchmarks, intimating its potential for practical applications in energy production and waste management.

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CHAPTER ONE

1 INTRODUCTION

1.1 BACKGROUND OF STUDY

Synthesized from petroleum derivatives, plastics comprise organic compounds with lengthy hydrocarbon chains. Due to their distinctive qualities, plastics have quickly gained widespread acceptance. The low cost, long-lasting nature, ease of accessibility and handling, and diverse applications have all significantly increased the production and consumption of plastics (Anandhu Vijayakumar et al., 2018)

Plastic is a high molecular weight material that was invented by Alexander Parkes in 1862. [Brydson, J.A. 1999] Polymers are other names for plastics. The term polymer describes a molecule formed by repeatedly repeating a simple unit. As an illustration, Figure 1.1 or Figure 1.2 depict the structure of polystyrene.

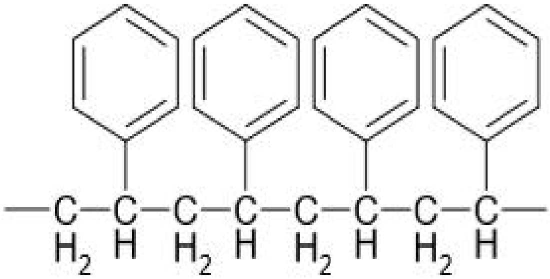


FIGURE 1. 1: COMMON EXPRESSION OF POLYSTYRENE MOLECULAR STRUCTURE

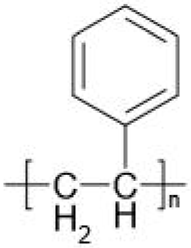


FIGURE 1. 2: A SIMPLIFIED EXPRESSION OF POLYSTYRENE MOLECULAR STRUCTURE

The polymer's repeating unit, [Unit], is enclosed in parentheses with a subscript, n, denoting the number of units within that polymer molecule. [Chanda, M., 2000].

The production of plastics globally has been increasing ever since its initial commercial production due to its ease of manufacturing and use, rising from 1.5 million tons in 1950 to 260 million tons in 2007 [Tencati, A., et al., 2016]. Plastic waste represents a serious environmental concern as it is a developing environmental pollutant (EEP) (Yalwaji et al., 2022) with the potential to harm life on land (Sustainable Development Goal (SDG 15) and in water (SDG 14).

In 2010, Nigeria, with a population of around 200 million, was the ninth-largest producer of plastic waste, contributing 830,000 metric tons of improperly managed plastic waste to the oceans (Jambek et al., 2015). This number is predicted to rise exponentially as the population grows, rural inhabitants migrate to cities, and infrastructure fails.

As seen in Figure 1.3, there has been a substantial and steady rise in plastic output and consumption in Nigeria (with little recycling). From 120 kilotons in 2007 to 436 kilotons in 2018, Nigeria's plastics output increased by 10.3% annually, reaching 523 kilotons in 2022. Consumption has also grown by 6.5% yearly, going from 578 kilotons in 2007 to 1.148 kilotons in 2017 and an estimated 1.478 kilotons in 2022, as seen in Figure 1.3.

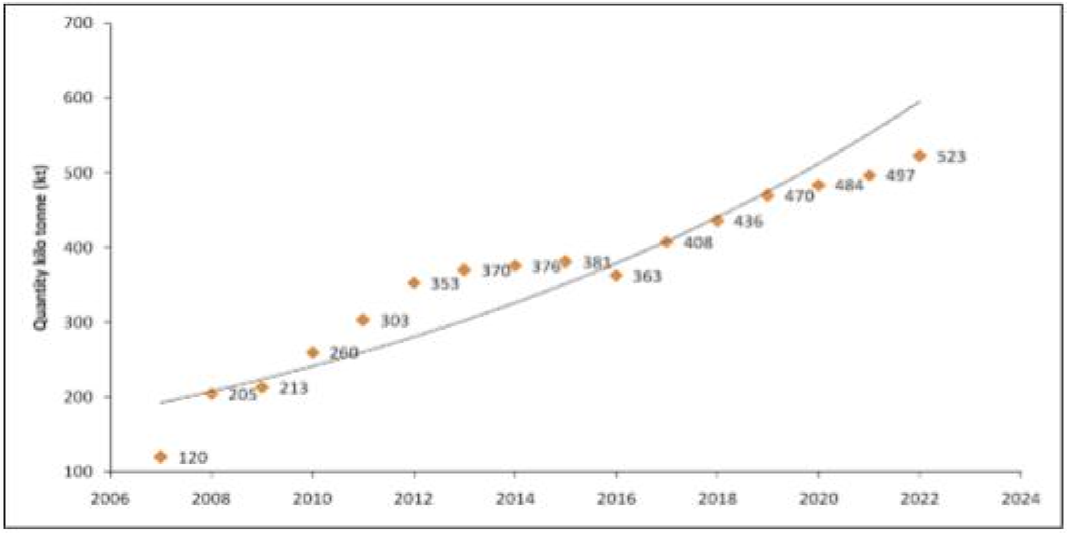


Figure 1. 3: plastic production in nigeria (data source: [j. Reisser, b. Slat et al, 12 (2015) 56–1249]).

Figure 1. 4: Plastic consumption in Nigeria (Data source: [J. Reisser, B. Slat et al, 12 (2015) 56–1249]).

Most plastic usage is concentrated in packaging (55%), with construction accounting for 16%, automotive 6%, and various industries consuming the remainder. This indicates that the problem of microplastic pollution is likely to worsen, as shown in Figure 1.5, given the current lack of waste reduction measures in Nigeria.

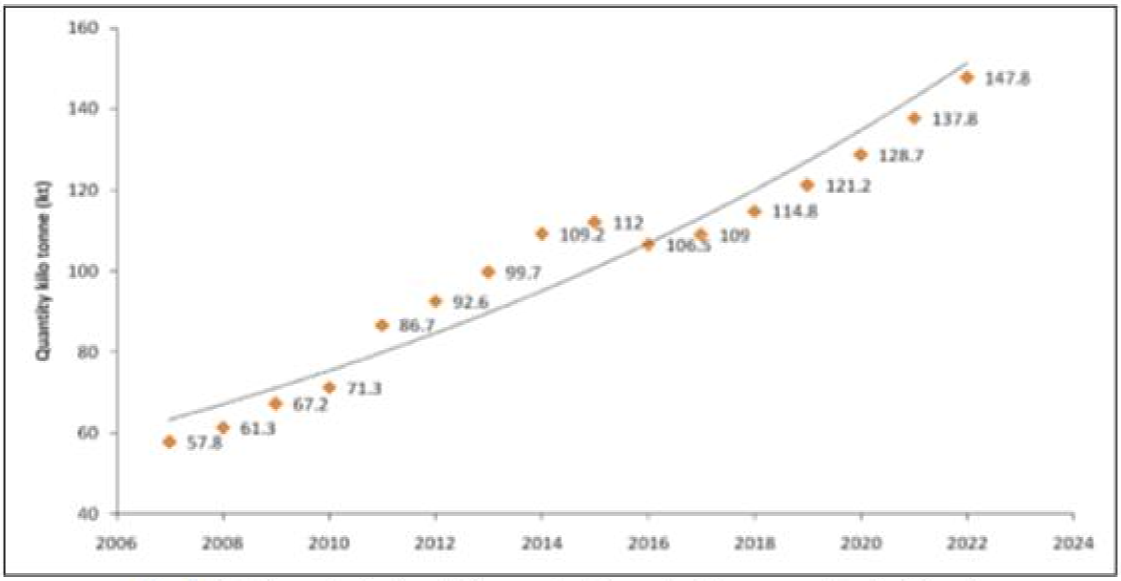


Figure 1. 5: Plastic waste (estimated) generated from plastic consumption in Nigeria

Thermoplastics dominate the global market, with polypropylene (PP) holding a significant share of 21%. Low-density polyethylene (LDPE) and linear low-density polyethylene (LLDPE) collectively make up 18%, while polyvinyl chloride (PVC) holds 17% and high-density polyethylene (HDPE) 15%. Polystyrene (PS) and expandable PS account for 8%, while polyethylene terephthalate (PET), excluding PET fiber, and the thermosetting plastic polyurethane have a 7% market share (Moses Jeremiah Barasa Kabeyi et al., 2023).

Waste plastic fuel shares similar characteristics with diesel fuel and can serve as its substitute. Both plastics and petroleum-derived fuels are hydrocarbons composed of carbon and hydrogen (I. Fahim, O. Mohsen, et al., 2021). The distinction lies in the longer carbon chains found in plastic molecules compared to liquidified petroleum gas (LPG), petrol, and diesel fuels. Consequently, it is feasible to convert waste plastic into fuels via the pyrolysis process (M. J.K. Kabeyi and O. A. Olanrewaju, 2021).

Pyrolysis, a thermochemical process that converts waste plastic into valuable products such as fuel, chemicals, and feedstock, offers a promising solution to these challenges.

1.2 PROBLEM STATEMENT

The primary challenge with plastic products is their short service life, with approximately 40% having a lifespan of less than a month.

The growing generation of plastic waste poses a significant environmental threat, contributing to pollution, resource depletion, and climate change concerns. Conventional waste management techniques, such as landfilling and incineration, exacerbate environmental degradation and greenhouse gas emissions.

Addressing these issues with pyrolysis technology, however, faces technical, economic, and environmental barriers. These hurdles include inefficient conversion processes, limited product quality and yields, high operational costs, and environmental impacts such as the emission of hazardous gases and residues.

1.3 AIM AND OBJECTIVES OF THE STUDY

The aim of this study is to develop a novel catalyst for the pyrolysis process for converting waste plastic (polyethylene terephthalate PET) into liquid fuel.

Objectives of this study are:

1. Collection and preparation of waste plastic (PET)
2. Collection and preparation of clay sample.
3. Synthesis of zeolite catalyst from clay.
4. Analysis and characterization of zeolite catalyst.
5. Pyrolysis of waste plastic (PET) with and without catalyst.
6. Analysis and characterization of waste plastic oil.

1.4 SCOPE OF THE STUDY

The scope of these study was restricted to only one type of waste plastic (polyethylene terephthalate PET) pyrolysis process with and without the use of catalyst,

1.5 SIGNIFICANCE OF THE STUDY

Plastic waste pollution has become a pressing global issue. However, the production and consumption of plastics continue to escalate, while recycling rates lag behind. Only around 15% of the 400 million tonnes of plastic produced annually is recycled globally [W. U. Eze et al., 2021]. The surge in plastic production over the past half-century has created a worldwide environmental crisis, with over 4.9 billion tonnes of plastics ending up in landfills [J. N. Hahladakis et al. 2018]. In light of the dwindling supply of fossil fuel energy sources such as gas, diesel, and petrol, there is a growing need to identify and develop alternative energy sources [K. Murthy et al 2020]. Plastic recycling offers the lowest environmental impact in terms of Global Warming Potential (GWP) and Total Energy Use (TEU) [C. A. Bernardo et al, 2016]. Chemical recycling of plastic waste is cost-effective and requires minimal sorting, utilizing high temperatures. Waste plastic pyrolysis can significantly benefit the fossil fuel industry by enhancing process sustainability, leading to a cleaner environment and reduced fossil fuel demand through the production of alternative oil.

CHAPTER TWO

2 LITERATURE REVIEW

2.1 OVERVIEW OF PLASTIC PYROLYSIS

Pyrolysis is a viable method for converting plastic waste into fuel. It involves complex chemical and thermal reactions that break down organic materials in the absence of oxygen [M.J.B. Kabeyi et al., 2022]. The process entails heating plastics to high temperatures, distilling the resultant volatile substances, and isolating them for use as energy sources [C. Pahl, 2021].

In plastic waste pyrolysis, plastic materials are exposed to elevated temperatures without oxygen or, in some cases, a catalyst to facilitate the controlled cracking of long-chain molecules. The gases generated are condensed into a low-sulfur-content waste plastic oil [M. Kabeyi et al., 2013]. Thermal degradation of plastics yields three primary fractions: gas, crude oil, and solid residue.

Various processes can be employed to convert plastics into fuels, including gasification, pyrolysis, plasma processing, and incineration. Pyrolysis, in particular, involves breaking down plastic waste into solid, liquid, or gaseous fuels through the thermal degradation of long-chain polymers into smaller molecules in the absence of oxygen. The primary products of pyrolysis are combustible gas with high calorific value, fuel-grade oils, and carbonized char [Agency, Waste Plastics to Fuel Oil, EE Publishers, South Africa, 2018).

Pyrolysis entails the conversion of plastics into solid, liquid, or gaseous fuels by thermally degrading long-chain polymers into simpler molecules in the absence of oxygen. The process yields high calorific gas, high-quality oils, and carbonized char. Pyrolysis can produce yields as high as 80wt.% under moderate conditions and typically requires temperatures ranging from 300 to 900°C [R. Miandad, M. Rehan, M. A. Barakat et al., 2019].

Over the years, pyrolysis technology has evolved to produce valuable liquid oils by leveraging the valorization of organic materials. However, challenges persist due to the utilization of diverse feedstock types. Crucially, the advancement of pyrolysis hinges upon the design of innovative reactor systems to maximize product yields while simultaneously reducing energy consumption and production costs. Pyrolysis technology has matured, with numerous commercial plants operating for both biomass and plastic feedstock.

Pyrolysis offers an effective means of treating various plastic waste streams, including packaging waste and more complex materials such as rubber, WEEE (waste electrical and electronic equipment), ELV (end-of-life vehicle), and hospital waste, which often contain toxic and hazardous substances. Pyrolysis of plastic waste yields pyrolysis oil, a hydrocarbon-rich gas with a heating value of 25–45MJ/kg, making it ideal for process energy recovery and char. This pyrolysis gas can be reintroduced into the process to provide heat for process heating, significantly reducing reliance on external heating sources [M. S. Qureshi, A. Oasmaa, H. Pihkola et al., 2020].

Figure 2.1 below illustrates a pyrolysis process with its inputs and product outputs. Waste plastics are combined and heated in the absence of oxygen in a process known as cracking, which generates a gas. The gas or vapor is further refined into products ranging from heavy waxes and oils to light oils and gas. Many of these products possess the potential to serve as building blocks for new polymers or as fuel sources [C. Middlehurst, 2021]. Figure 2.2 depicts the plastic pyrolysis process. As shown in Figure 2, the primary components of a plastic pyrolysis process plant are the reactor, condenser, fractionating tower, and condenser.

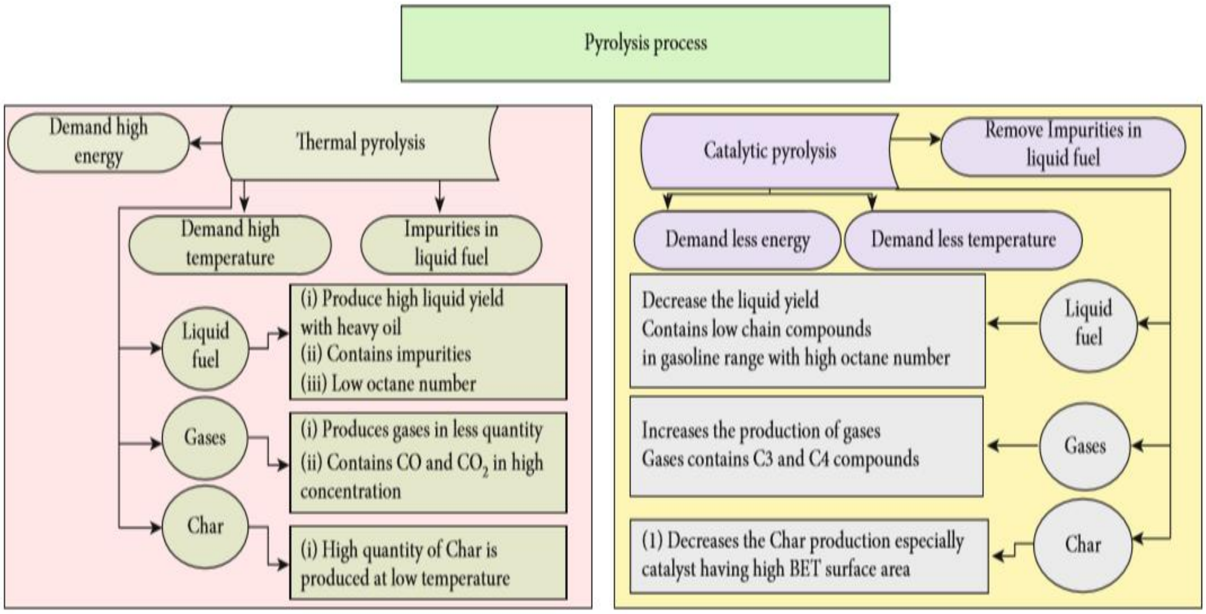


Figure 2. 1: Industrial waste plastic-to-oil pyrolysis plant [E.R.Larson, 2015].

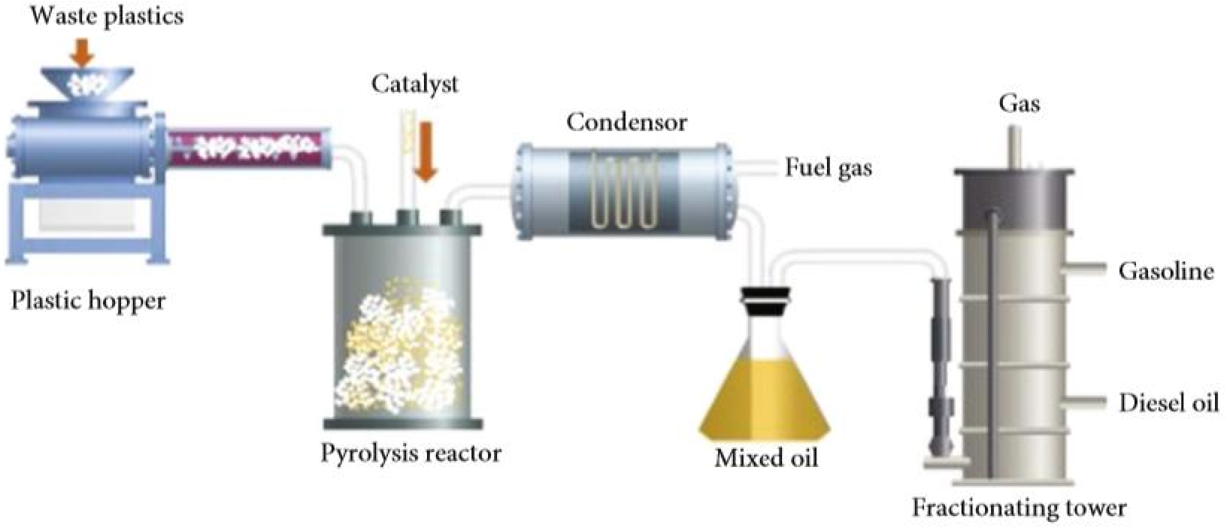


Figure 2. 2: Plastic pyrolysis process description [C. Middlehurst, 2015].

A pyrolysis facility can repurpose even challenging plastics like polystyrene and flexible packaging into 75% liquid oil, which can be utilized as sustainable fuel and feedstock for plastic production. The remaining 25% can be employed as a wax equivalent in the manufacture of candles and paints, while the generated gas and char can serve as energy sources for the plant [C. Middlehurst, 2021]. Thermal treatment, which produces heat for either process-heating applications or steam generation and power production, is the most common technology used in plastic waste disposal [L. Lombardi, E. Carnevale, and A. Corti, 2015].

2.2 FACTORS AFFECTING PLASTIC PYROLYSIS.

The major factors influencing the plastic pyrolysis process and pyrolysis product molecular distribution include chemical composition of the feedstock, cracking temperature and heating rate, operation pressure, reactor type, residence time and application of catalyst. These factors are summarized in this section as follows. Figure 2.3 below gives a pictorial summary

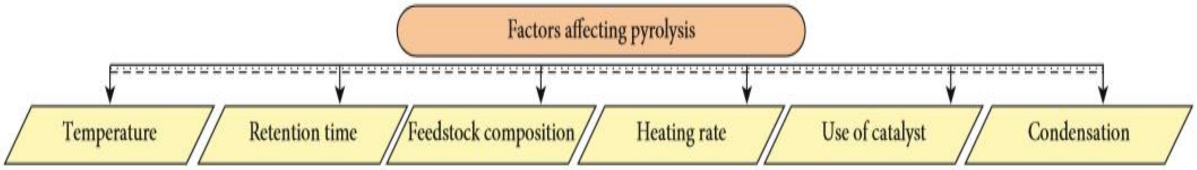


Figure 2. 3: factors affecting plastics pyrolysis (M.J.B Kabeyi et al., 2022).

2.2.1 CHEMICAL COMPOSITION OF FEEDSTOCK

The pyrolysis results are directly correlated to the chemical composition and structure of the plastics. Feedstock composition also impacts the pyrolysis process. Realistically, waste plastics may be contaminated prior to recycling, which can affect the pyrolysis process and products.

Plastics can be categorized based on polymer molecule structure as linear, branched, or cross-linked (as depicted in Figure 2.4). Linear polymers have units linked only to two others. Polymer structures become branched when chains extend randomly from the main polymer, while side groups are considered part of the unit but not branches. For instance, polystyrene (PS) is classified as a linear polymer despite containing functional groups. Branched polymers have monomers connected to more than two functional groups due to branching. Functional side groups and branching affect pyrolysis products significantly. Styrene, a dominant component in PS pyrolysis products, originates from the PS carbon backbone. (Karaduman, A., et al. 2001)

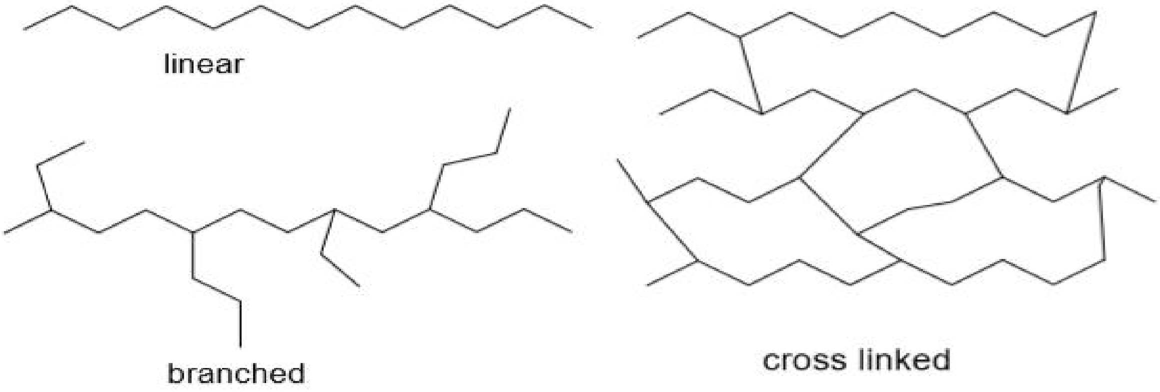


Figure 2. 4: Polymer structure, linear, branched and cross linked

Cross-linked polymers are interconnected branched polymers with chains linked to form larger molecules. In theory, cross-linked polymers have infinite molecular weight. In practice, molecular weight is limited by the breakdown of molecular inter-connections. Cross-linked polymers crack during pyrolysis instead of melting or evaporating, unlike linear or branched polymers.

2.2.2 CRACKING TEMPERATURE AND HEATING RATE

Temperature is a crucial operating factor, influencing polymer cracking. Not all polymers can be cracked solely by temperature increase. Van der Waals force attracts molecules, preventing their collapse. When molecular vibrations are sufficient, molecules evaporate from the surface. However, if the energy induced by Van der Waals force exceeds the C-C bond enthalpy, the carbon chain breaks. This explains why high molecular weight polymers decompose instead of boiling upon heating.

Theoretically, thermal C-C bond breaking temperatures should be consistent for specific plastics. However, studies have reported varying results. For example, the cracking temperature of PP was reported as 380 ºC by Ciliz et al. and 650 ºC by Demirbas. Both studies employed similar batch process reactors and thermo gravimetric analysis. The most probable cause for the discrepancy is the variation in temperature measurement locations. Significant temperature gradients exist within the apparatus, with lower temperatures at the bottom and higher temperatures at the top. Vaporized products also influence the temperature within the pyrolyzer. Karaduman et al. examined temperature profiles within an externally heated tube. Significant temperature differences were observed between the tube's ends and center (Figure 2.5). Heat loss was evident at both tube ends. Varying sensor placements among studies are believed to contribute to the reported differences in cracking temperatures.

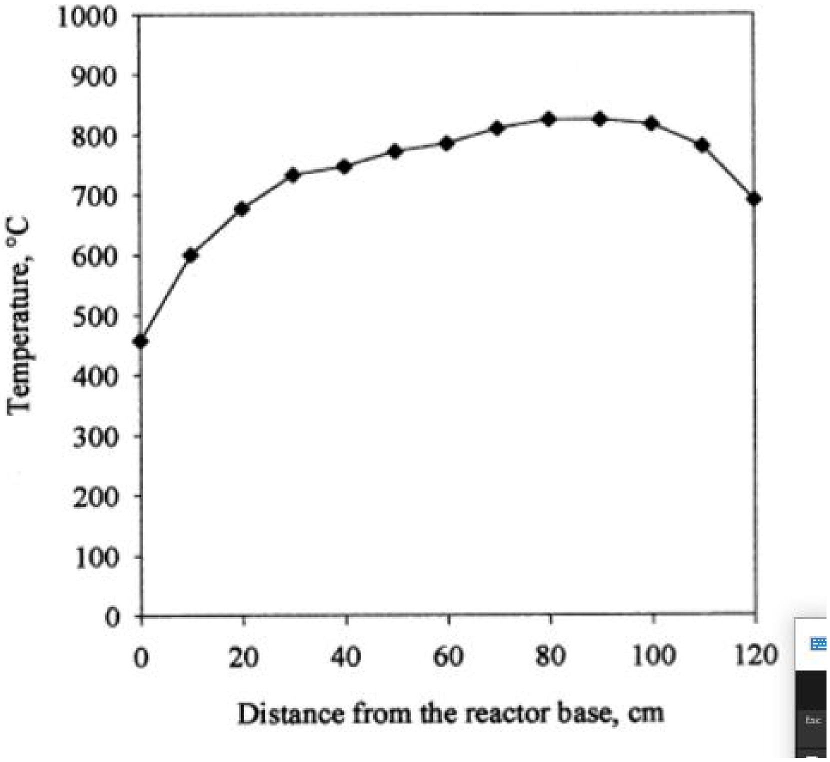


Figure 2. 5: Temperature profile along the tube reactor [Karaduman, A., et al., 2001]

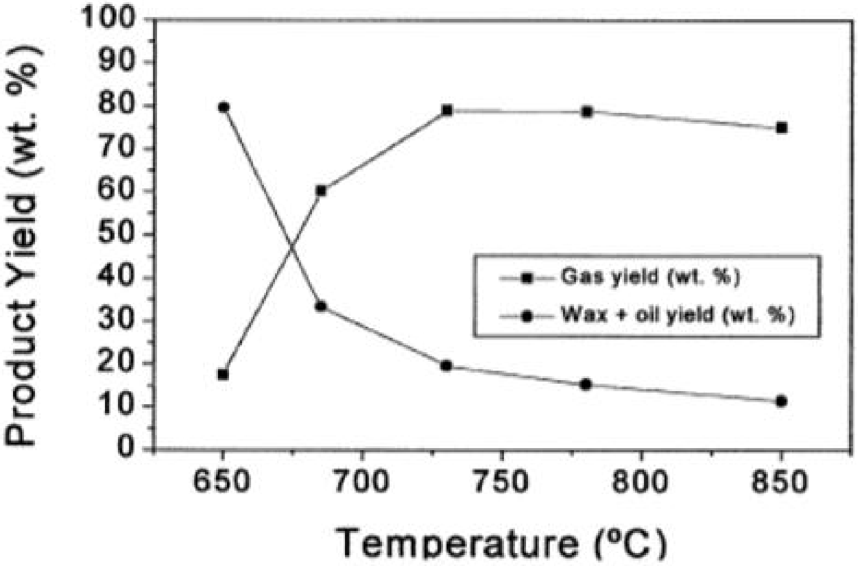


Figure 2. 6: Influence of temperature on product distribution [Mastral, F.J., et al., 2004]

In a comparative study, Karaduman, A., et al. recorded the temperature difference between the plastic's surface in contact with the heating element and the plastic's interior. This difference was found to be minimal and consistent throughout the study. As a result, the temperature at the reaction surface was utilized to monitor the cracking temperature of the plastics. In a separate investigation, Shah, N., J. Rockwell, and G.P. Huffman (1999) subjected a mixture of post-consumer plastics (PE, PP, PS) to pyrolysis in a fixed-bed batch reactor at various temperatures for one hour. Their findings indicated that higher reaction temperatures favored gas production while also increasing the molecular weight of liquid products. Notably, the overall gas yield grew with increasing cracking temperature (up to 730oC), whereas the liquid product yield diminished across the entire temperature range employed (as shown in Figure 2.6).

Another key operational parameter is the heating rate, which refers to the temperature rise per unit time. The influence of heating rate on the plastic pyrolysis process and product distribution varies across studies due to differences in reactor design, operating conditions (temperature and pressure), and temperature measurement location. In fast or flash pyrolysis, heating rate typically describes the temperature change experienced by the plastic from the moment it is deposited on the hot surface until it decomposes and vaporizes. The hot surface maintains a constant temperature while the amount of plastic deposited on it remains relatively low. Under these conditions, the heating rate can be extremely high, reaching up to 10,000 K/s [Williams, P.T. and E.A. Williams, 1998]. In batch processes, the plastic is typically heated from room temperature to the cracking temperature over several minutes, making it a slow pyrolysis process. Once the plastic feedstock reaches the cracking temperature, the temperature remains relatively stable until all feedstock has undergone pyrolysis. Consequently, in slow pyrolysis processes, heating rate is often used as a temperature indicator rather than reaction temperature. Previous slow pyrolysis studies have shown that heating rates typically range from 10 to 100 ºC/minute [Williams, E.A. and P.T. Williams, 1998]. Saha and Ghoshal (2005) investigated the impact of heating rate on the pyrolysis process of Coca-Cola drink PET bottles using thermogravimetric analysis (TGA), as depicted in Figure 2.7. The figure plots dAlpha/dT, which represents the rate of reaction (K-1), against absolute temperature for varying heating rates (10 to 25 K/min). The results suggest that a higher heating rate accelerates the rate of pyrolysis reactions [Williams, P.T. and E.A. Williams, 1998].

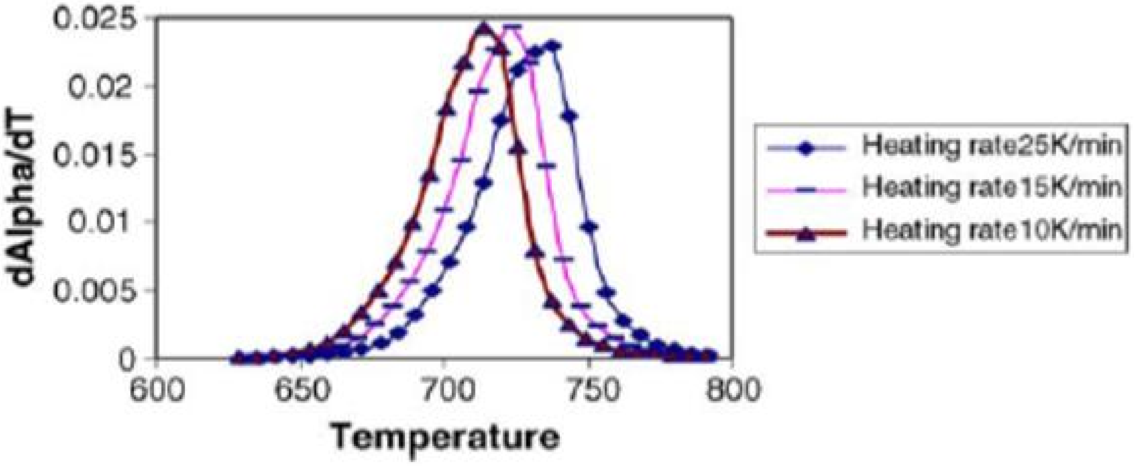


Figure 2. 7: Reaction rate as a function of temperature and heating rate in pyrolysis of Coca Cola soft drink PET bottle [Saha, B. and A.K. Ghoshal, 2005]

2.2.3 TYPE OF REACTOR

The choice of reactor for plastic pyrolysis significantly impacts heat transfer efficiency, the intermixing of plastics and pyrolysis products, residence time, and the reflux level of primary products. Reactors can be categorized based on their operation mode (batch, semi-batch, continuous) or based on the type of reactor bed they employ.

2.2.3.1 Batch, semi-batch and continuous reactors

According to the feeding and product removal processes, the pyrolysis reactor is categorized into batch, semi-batch and continuous reactors. In the batch reactor, the materials are fed into the reactor in batches for pyrolysis either at the start of the process or after all of the fed materials are processed. In the continuous reactor, the feed materials are input from one part and the products are led out from the other part of the reactor. A semi-batch reactor removes the pyrolysis products continuously once they are generated but the feed materials are added initially before the pyrolysis process starts. Some semi-batch process uses inert carrier gas to help remove the pyrolysis products. Batch and semi-batch reactors are mainly applied on research, [Arena, U. and M.L. Mastellone, 2006] and continuous reactor is mainly for industrial production such as Mitsui R21, Fuji, Toshiba, Veba Oel, PKA, etc. [Lee, K.H., 2006] Particular reactions and phenomenon such as Particular reactions and phenomenon such as secondary pyrolysis may occur in semi-batch reactors and does not occur in batch reactors. [Arena, U. and M.L. Mastellone, 2006]

2.2.3.2 Fixed bed, fluidized bed and screw kiln reactors

Based on heat transfer methodology and feedstock/product flow characteristics, pyrolysis reactors fall into categories: fixed bed, fluidized bed, and screw kiln. Fixed bed reactors entail pyrolysis on an immobile bed, offering ease of design and operation. However, uneven feedstock particle sizes can hinder continuous processes, and low thermal conductivity may lead to temperature gradients in batch processes. Fixed beds often serve as secondary reactors for primary pyrolysis products in liquid or gas form. [Uemichi, Y et al., 1999]

Screw kiln reactors have gained prominence recently in plastic processing. [Mastral, F.J., et al., 2002] They feature an extruder that propels feedstock from a feeder in an oxygen-free environment, heated by external sources. Solid residues and pyrolysis products are separated and collected at the other extruder end. Plastic viscosity does not affect flow in screw kiln reactors due to external drive, allowing for the processing of melted or solid plastic particles. The extruder's small diameter and efficient mixing minimize radial temperature gradients. The process is stable and does not require bed material like fluidized bed reactors. Control over feed rate is achieved by adjusting extruder rotation speed, which also influences plastic residence time.

2.2.4 RESIDENCE TIME

Residence time definitions vary. In fast/continuous pyrolysis, it denotes feedstock contact time with the reactor's hot surface. In slow/batch pyrolysis, it spans from the onset of feedstock heating to product removal. Extended residence times enhance primary product conversion, resulting in more stable products like light hydrocarbons and non-condensable gases. [Hernández, M.d.R., et al., 2006] Conversely, in slow pyrolysis, prolonged residence times promote carbonization, increasing tar and char content. [Buekens, A., 2006] Pyrolysis conditions, residence times, and target products are detailed in Table 2.1.

Table 2. 1: Pyrolysis processes and target products [Jung, C.G. and A. Fontana, 2004]

Process	Heating rate	Residence time	Temperature (°C)	Target Products
Slow carbonization	Very low	Days	450-600	Charcoal
Slow pyrolysis	10-100K/min	10-60 min	450-600	Gas, oil, char
Fast pyrolysis	Up to 1000K/s	0.5-5 s	550-650	Gas, oil, (char)
Flash pyrolysis	Up to 10000K/s	<1 s	450-900	Gas, oil, (char)

2.2.5 USE OF CATALYST

2.2.5.1 Advantages of using catalyst

Catalysts are widely employed in pyrolysis processes to optimize reactions and alter product distribution. A primary aim is to shorten the pyrolysis products' carbon chain length, reducing their boiling point.

In catalytic pyrolysis, catalysts facilitate cracking reactions, lowering their temperature and duration. [M. J. B. Kabeyi and O. A. Olanrewaju, 2021] Its cost-effectiveness makes it economically viable. [63] The focus is on minimizing catalyst usage through reuse and low quantities. Catalytic pyrolysis offers advantages such as cost savings, reduced plastic waste pollution, and diminished solid residues. [M. J. B. Kabeyi and O. A. Olanrewaju, 2021]

Catalytic-cracking pyrolysis involves heating plastic materials in an inert environment with catalysts. The temperature range for this process is 350°C to 550°C. It can be applied to both pure and mixed plastics and yields higher-quality fuel oils than thermal pyrolysis. Catalysts promote decomposition at lower temperatures, reducing energy consumption, accelerating cracking reactions, enhancing process selectivity, and increasing the output of value-added products. [S. M. Al-Salem, et al., 2017]

2.2.6 CATALYST CLASSIFICATION

Research has delved into homogeneous and heterogeneous catalysts for the catalytic cracking of plastics. Lewis acids like AlCl3 have been commonly employed as homogeneous catalysts in polyolefin pyrolysis [Ivanova, S.R., et al., 1990]. However, heterogeneous catalysts are often preferred due to their ease of separation and retrieval from the reaction medium. These catalysts encompass nanocrystalline zeolites, pillared clays of aluminum, conventional acidic solids, mesostructured catalysts, superacid solids, gallosilicates, carbon-supported metals, and basic oxides. Nanocrystalline zeolites have been extensively studied for polyolefin pyrolysis and merit further examination.

2.2.6.1 Zeolite properties: pore size (structure) and Si/Al ratio (acidity)

Zeolites are crystalline aluminosilicates with three-dimensional frameworks that form uniform pores of molecular scale [Maesen, T., 2007]. They act as molecular-scale sieves, excluding molecules that exceed the pore size. The three-dimensional structure exponentially increases the sieve area, facilitating absorption of molecules comparable in size to the pores. Currently, 176 confirmed zeolite framework types exist [McCusker, L.B. and C. Baerlocher, 2007]. The International Zeolite Association's Structure Commission assigns each framework type a three-letter code, such as MFI [Kayacan, I. and O.M. Dogan, 2008]. ZSM-5's MFI framework type is illustrated in Figure 2.8, with pentasil chains aligning parallel to the z-axis.

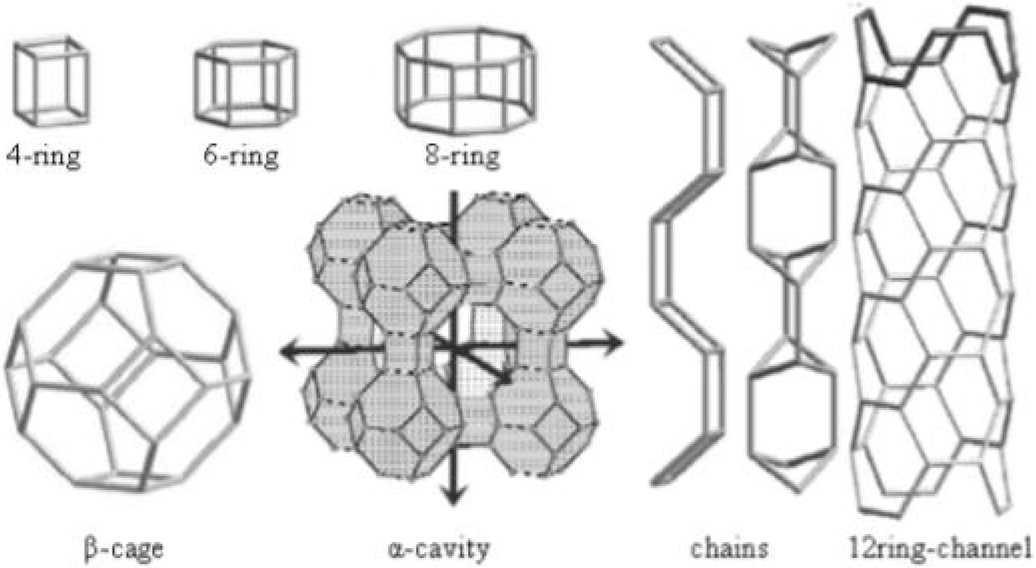


Figure 2. 8: Framework types of zeolite [Faravelli, T., et al., 1999]

2.2.7 PRESSURE

Pressure significantly impacts both the pyrolysis process and its products. Elevated pressure increases the boiling points of pyrolysis products, leading to further pyrolysis of heavy hydrocarbons under pressurized conditions instead of their vaporization at a given temperature [Murty, M.V.S., et al., 1996]. Figure 2.9 demonstrates the impact of pressure on hydrocarbon count and their proportions in pyrolysis products of PE. Essentially, pressurized pyrolysis necessitates additional energy for intensified hydrocarbon cracking. High pressure has also been observed to enhance the yield of non-condensable gases while diminishing the output of liquid products (Figure 2.10). Additionally, pressure reduces the average molecular weight of gas products [Murata, K., K. Sato, and Y. Sakata, 2004]. However, Murata et al. [Murata, K., K. Sato, and Y. Sakata, 2004] reported an insignificant influence of pressure on the double bond (C=C) concentration in liquid products. In summary, pressure has a profound effect on the pyrolysis reaction and the distribution of PE pyrolysis products but minimally impacts double bond components.

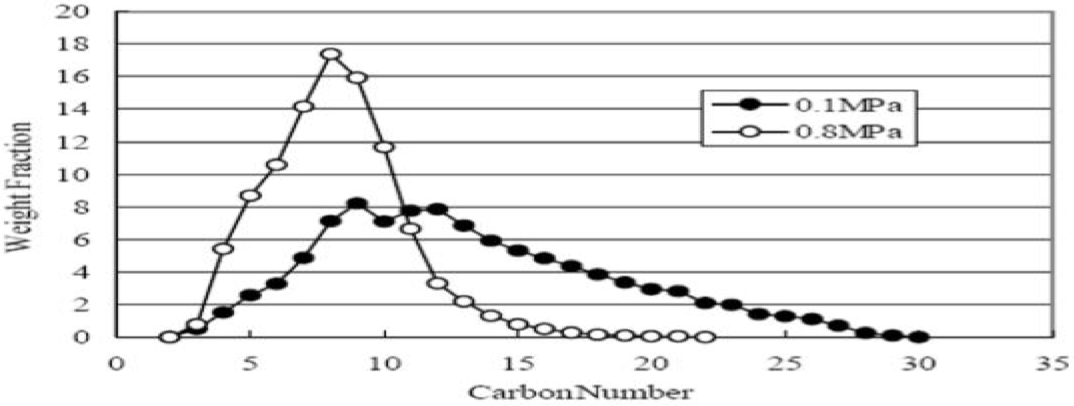


Figure 2. 9: Effect of pressure on the distribution of PE pyrolysis products [Murata, K., K. Sato, and Y. Sakata, 2004]

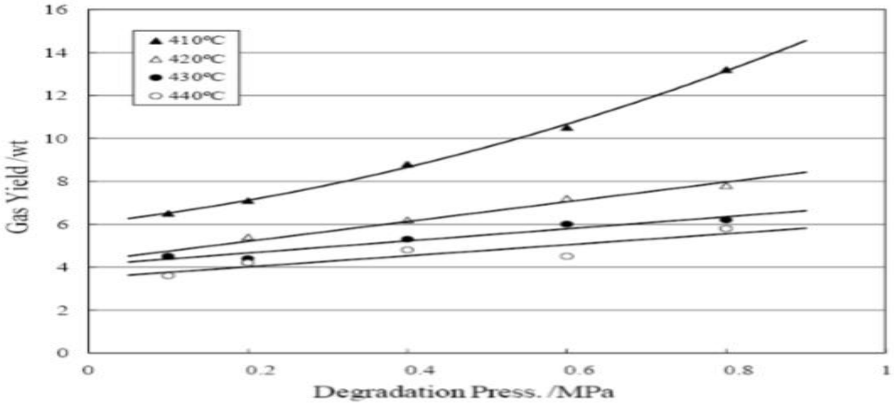


Figure 2. 10: Effect of pressure on the yield of gas at different temperature [Murata, K., K. Sato, and Y. Sakata, 2004]

2.3 QUALITY COMPARISON OF PYROLYSIS PRODUCTS AND PETROLEUM FUELS

2.3.1 *REVIEW OF PYROLYSIS MONITORING AND PRODUCT ANALYSIS*

2.3.1.1 Pyrolysis process monitoring

In plastic pyrolysis, variations exist in plastic types and operating conditions utilized in research and industry. Accordingly, the literature reveals significant discrepancies in the yield and quality of pyrolysis products. However, with the use of identical plastics and operating conditions, similarities emerge in product yield and production distribution. In numerous research endeavors, thermogravimetric analysis (TGA) in a fixed-bed batch pyrolysis reactor has been adopted for measuring the pyrolysis rate of feedstock plastics [Regnier, N. and B. Mortaigne, 1995]. Certain studies have employed high-pressure pyrolysis, utilizing a pressure gauge to regulate and monitor operating pressure. These monitoring tools enable process control by adjusting operating parameters, such as heating power, feed rate, pressure, and carrier gas flow rate, as necessary.

2.3.1.2 Product analysis method

Under standard conditions of 25 ºC and 100 kPa, the pyrolysis byproducts of plastics are primarily hydrocarbons existing as gases, liquids, and solid waxes. Gas chromatography (GC) can be utilized to separate these hydrocarbon products, followed by identification through comparison with hydrocarbon standards or mass spectrometry (MS). The composition and proportions of individual components are examined in laboratory analyses. [Uemura, Y., et al., 1999].

2.3.2 COMPARISON OF DIESEL WITH PLASTIC DERIVED FUELS

In diesel fuel regulations, cetane number (or its substitute, cetane index) is a critical thermodynamic property that reflects the fuel's auto-ignition characteristics. [Gerpen, J.V., 1998] Cetane index is determined based on fuel density and distillation range, both of which are listed in regulatory requirements. Thus, cetane number, density, and distillation range are significant properties for diesel fuel.

Fuel flow properties, such as viscosity, cloud point, pour point, cold filter plugging point, and flash point, are also important. Their significance depends on the availability of information on fundamental properties like density and distillation range. If these fundamental properties are known, flow properties become less critical.

Miscellaneous properties indicate the impact of minor constituents in diesel fuels, including carbon residues, sulfur content, water content, ash content, and polycyclic aromatic hydrocarbon content. Carbon residues are fine solid particles that can accumulate as combustion chamber deposits. Sulfur content beyond a certain threshold causes excessive engine wear and damages catalysts. Water content contributes to corrosion in fuel storage tanks and injection equipment, while ash content is the solid residue left after fuel combustion. Polycyclic aromatic hydrocarbons are added to enhance cetane number due to their low boiling point and high density (Feng Gao., 2010).

The quality of liquid fuels derived from plastic pyrolysis varies based on the pyrolysis operating conditions, reactor type, and feedstock composition. However, comparisons between plastic pyrolysis fuels and petroleum-based fuels have been documented, prompting this study to investigate this in detail.

The quality of plastic-derived fuels varies considerably depending on the process and feedstock. The diesel range components in LDPE-derived fuels consist of the same linear chain alkanes found in fresh diesel. However, the alkene content in LDPE-derived products is significantly higher than in diesel, reducing the fuel's storage stability. [Scheirs, J., 2006] Compared to naphtha, aromatic compounds, and branched hydrocarbons, linear alkanes have a higher cloud point at the same carbon number or density. Therefore, various catalysts and processes are employed to transform linear hydrocarbons into other types. [Scheirs, J., 2006] Plastic-derived diesel has a high proportion of linear alkanes, which have low solubility in diesel. This can significantly increase the cloud point, the temperature at which crystals first appear in diesel. Dewaxing, hydrogenation, isomerization, and cyclization are commonly used in pyrolysis processes to modify the products' chemical composition. [Williams, P.T., 2006] Other properties of plastic-derived fuels, such as distillation range and carbon residue, are controlled during the production process.

2.4 EXISTING COMMERCIAL PLASTIC PYROLYSIS TECHNOLOGIES AND PROCESSES

Plastic pyrolysis plants have been established and operated in several countries. The choice of process and plant design is primarily influenced by the feedstock composition and desired products.

2.4.1 FEEDSTOCK EFFECTS

A study by Arena and Mastellone identified the presence of PVC as the most critical feedstock property. [Arena, U. and M.L. Mastellone, 2006] The thermal cracking process for PVC pyrolysis differs from that of other common waste plastics, including PE, PP, and PS, yielding distinct products. HCl-containing products from PVC pyrolysis pose a particular hazard for fuels. [Kim, S., 2001] If the feedstock contains PVC, the plants must incorporate a re-treatment system to remove HCl and a solvent scrubber to extract it from the pyrolysis products.

The size of the feedstock is another crucial consideration for certain current processes. This requirement aims to prevent feedstock blockage and promote heat exchange between the heating medium and plastic particles.

In most cases, the feedstock constitutes a blend of various waste plastics sourced from municipal solid waste or industrial waste. During the pyrolysis of mixed plastics, interactive effects may arise among the different plastic types due to variations in cracking temperatures and resulting products. Nonetheless, no literature has been identified where pyrolysis technology is specifically designed for a particular type of waste plastic. [Arena, U. and M.L. Mastellone, 2006]

2.4.2 TECHNOLOGY

Typically, a pyrolysis technology comprises three components: feeding system, pyrolysis reactor, and separation system.

2.4.2.1 Feeding system

In commercial processes, raw materials are typically heated and melted in the feeding system prior to entering the reactor. Impurities such as air, moisture, and other solid materials can be removed from the raw plastic materials in the feeding system. Furthermore, pre-treatment may be necessary for the cracking of PVC at 250 ºC. [Bagri, R. and P.T. Williams, 2002]. Most feeding systems employ gravity or an extruder to convey the highly viscous melted plastic into reactors. However, a gradual temperature gradient must be maintained from the feeding system to the pyrolyzer. For instance, PS has a cracking temperature of 420 ºC, thus overheating in the feeding system must be avoided. Free-fall feeding systems are commonly utilized in fixed bed and fluidized bed reactors (Feng Gao., 2010).

2.4.2.2 Pyrolysis

Continuous pyrolysis processes are employed in most commercial plants, allowing for the use of catalysts and resulting in relatively short plastic retention times. High-pressure operating conditions are rarely implemented in commercial plants, with most operating at or slightly above atmospheric pressure. The operating temperature within reactors varies significantly, ranging from 250 ºC (Mazda fixed-bed catalytic process in Japan) to 800 ºC (Compact Power fixed-bed pyrolysis in the United Kingdom), although the majority of pyrolysis reactors operate between 400 ºC and 550 ºC. [Scheirs, J. and W. Kaminsky, 2006]

2.4.2.3 Product separation and collection

Plastic pyrolysis primarily yields combustible gases and liquids. The liquids can either be combusted for power generation or further refined to produce high-quality fuels. In certain plants, pyrolysis products are simply separated into liquid, gas, and solid forms, while others employ a more comprehensive separation system, directing the mixture of liquid and gas into distillation columns. This process enables the distillation of diesel range products, similar to an oil refinery process. The non-condensable gases consist predominantly of hydrocarbons, with minor amounts of hydrogen and carbon monoxide. These gases can be liquefied for use as fuels, employed to heat the pyrolysis reactor, or if their quantity is insignificant, disposed of in an incinerator or flared off with air [Okuwaki, A., 2004]. Non-condensable gases may contain ash, necessitating the use of gas scrubbers in most commercial processes to eliminate impurities.

2.5 THEORY OF PYROLYSIS REACTIONS

This thermal degradation process is frequently referred to as depolymerization of polymers in various literature and research [Lee, K.H., 2006]. The fundamental phenomena underlying pyrolysis are explored from both physical and chemical perspectives. Further literature review examines the reaction kinetics of pyrolysis reactions and analyzes the heat associated with these reactions and the energy requirements for pyrolysis.

2.5.1 EFFECT OF THERMODYNAMIC ON PHYSICAL PROPERTY OF POLYMER

The physical properties of plastics can undergo significant alterations at various temperatures before the plastic decomposition temperature is attained. Exceeding this temperature causes the carbon backbone of the plastic to fragment into shorter carbon chains. The chemical structure of the plastics also undergoes changes. These phenomena have been extensively understood since the advent and study of thermal plastics for over a century [Miller, E., 1996]. Under the same temperature conditions, different types of plastics exhibit varying physical properties, and their decomposition processes may also differ.

As temperatures increase, polymers undergo three key thermal transformations: vitreous transition, liquefaction, and decomposition, as depicted in Figure 2.11 for PET's temperature-dependent state changes. At ambient conditions, polymers solidify into rigid structures, known as the glassy state. When temperatures surpass the vitreous transition temperature, Tg, thermoplastics gain sufficient energy to facilitate chain mobility, transitioning them into a rubbery state. [Chanda, M., 2000] Further temperature elevation converts the rubbery polymer into a liquid-like substance.

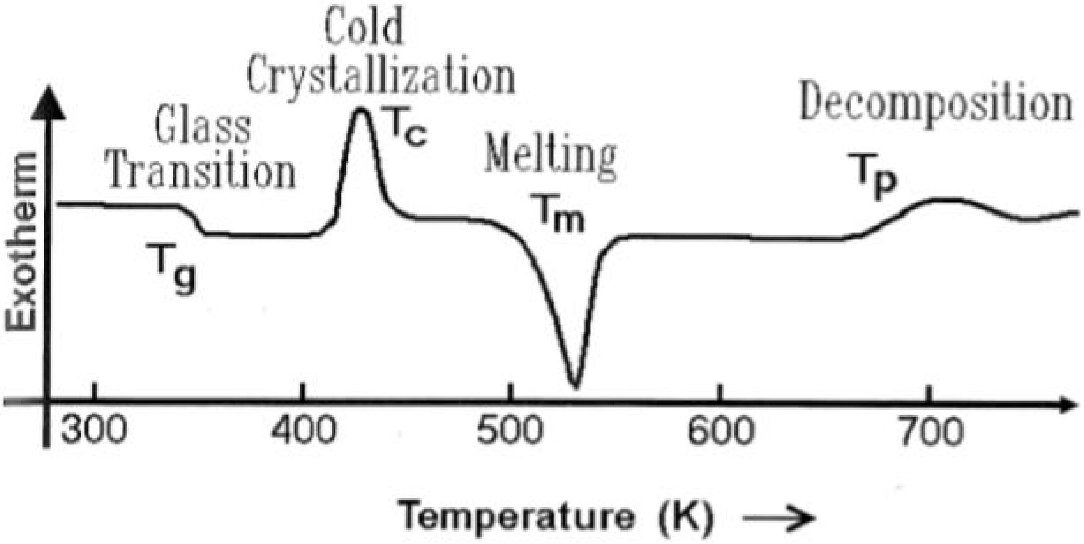


Figure 2. 11: The phase transitions of PET by differential thermal analysis [Wunderlich, B., 2005]

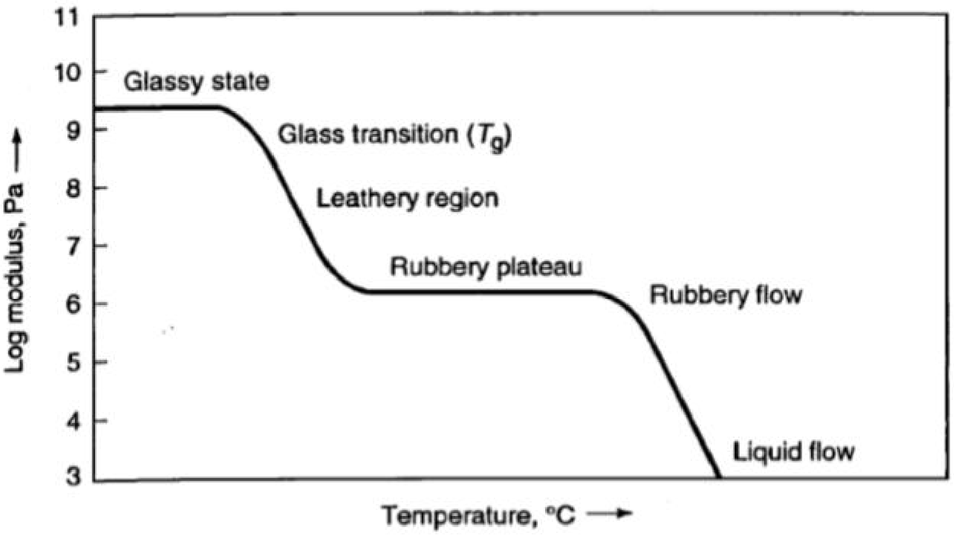


Figure 2. 12: Effect of temperature on elastic modulus of polymers [Baker, A.-M.M. and J. Mead, 2000]

2.5.2 PYROLYSIS REACTION PROGRESSES

Polymer cracking is a crucial process in plastic pyrolysis. However, the complete sequence involves additional reactions. This section examines the entire pyrolysis reaction process. The plastic pyrolysis process encompasses myriad reactions, divisible into three stages: initiation, propagation, and cessation [Regnier, N. and B. Mortaigne, 1995].

(1) Initiation: This stage entails the haphazard severing of the C– C bond on the main chain, triggered by heat, generating hydrocarbon radicals.

(2) Propagation: The hydrocarbon radical decomposes into smaller hydrocarbons, such as propylene, followed by β-scission and extraction of H-radicals from other hydrocarbons, resulting in a new hydrocarbon radical.

(3) Cessation: This stage involves the disproportionation or recombination of two radicals, including catalytic degradation with iron-activated charcoal in the presence of hydrogen. Hydrogenation olefin, i.e., hydrocarbon ion, and the abstraction of the H-radical in HC

(hydrocarbon) or HC radical, would foster significantly enhanced degradation. When reactions occur below 400°C and are swift, concluding within an hour, numerous hydrocarbon radicals exist in the reactor, readily recombining due to their diminished mobility [D. Almeida, 2016].

2.6 KINETICS OF PLASTIC PYROLYSIS REACTION

2.6.1 *REACTION KINETICS*

Plastic pyrolysis reactions are intricate. Moreover, several factors impact the process and reactions, including catalysts, reactor type, plastic type, and secondary cracking. Non-catalytic thermal degradation of plastics can generally be described by the Arrhenius equation. [Uemichi, Y., et al., 1999]

$$-\frac{dm}{dt} = km^{n} \qquad (1)$$

The reaction kinetic constant in the above equation can be determined by

$$k = A_{o}e^{-\frac{Ea}{RT}} \qquad (2)$$

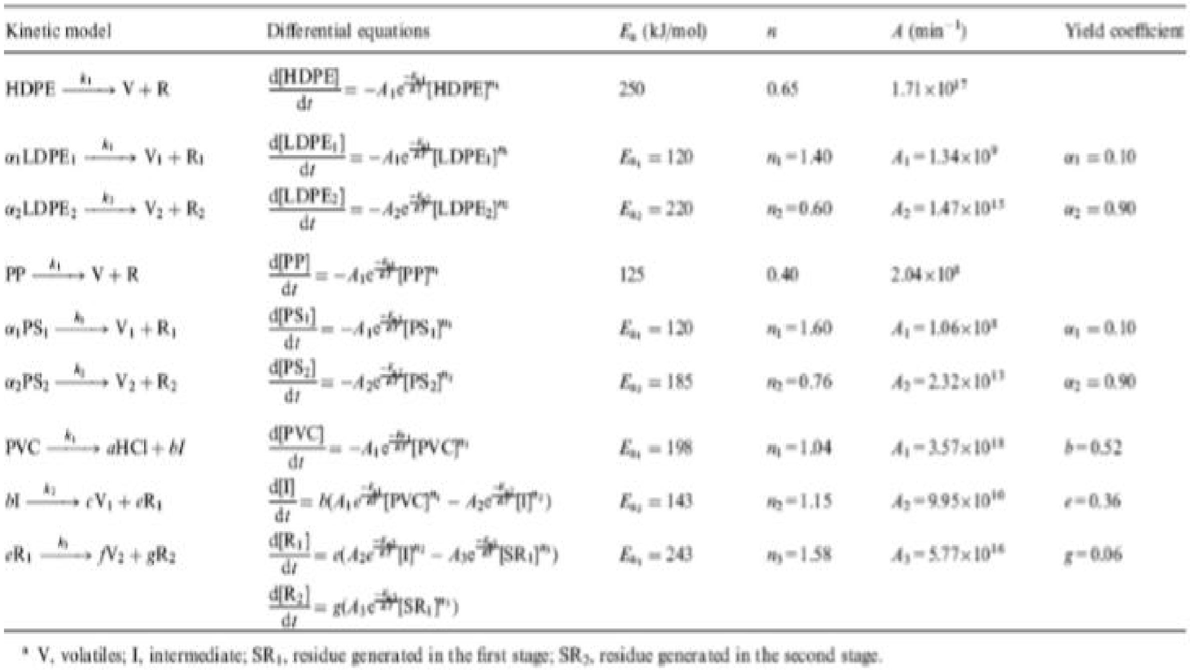
Here, m denotes the mass ratio of unreacted sample residue to the initial material before reaction, while n signifies the reaction order. Ea is the activation energy (kJ/mol), and Ao is the pre-exponential constant in the standard Arrhenius form. R represents the gas constant (J K-1 mol-1), and T is the temperature in Kelvin (K).

Conjoining Equations (1) and (2) yields: [Sobko, A.A., 2008]

$$\frac{d\alpha}{dt} = A_{o}\, exp\left[\frac{E_{a}}{RT}\right](1-\alpha)^{n} \qquad (3)$$

Where α denotes the conversion ratio equivalent to (1-m). The kinetic parameters and reaction order are experimentally determinable [Bagri, R. and P.T. Williams, 2002]. Marongiu et al. implemented kinetic models for diverse plastics under non-catalytic pyrolysis, obtaining values for Ea, n, and A0 presented in Table 2.2. [Marongiu, A., et al., 2017] Products originating from primary cracking reactions may undergo further cracking in subsequent reactions, decomposing into hydrocarbons of lower molecular weight. [Wallis, M.D. and S.K. Bhatia, 2007] The latter, termed secondary cracking, occurs in both non-catalytic and catalytic pyrolysis reactions.

Table 2. 2: Reaction kinetic parameters and values in pyrolysis of different plastics [Ranzi, E., et al., 1997]



Kinetic model	Differential equations	E_a (kJ/mol)	n	A (min^{-1})	Yield coefficient
$\mathrm{HDPE} \xrightarrow{k_1} \mathrm{V} + \mathrm{R}$	$\frac{d[\mathrm{HDPE}]}{dt} = -A_1 e^{\frac{-E_a}{RT}}[\mathrm{HDPE}]^{n}$	250	0.65	1.71×10^{17}	
$\alpha_1\mathrm{LDPE}_1 \xrightarrow{k_1} \mathrm{V}_1 + \mathrm{R}_1$	$\frac{d[\mathrm{LDPE}_1]}{dt} = -A_1 e^{\frac{-E_{a_1}}{RT}}[\mathrm{LDPE}_1]^{n_1}$	$E_{a_1} = 120$	$n_1 = 1.40$	$A_1 = 1.34 \times 10^{9}$	$\alpha_1 = 0.10$
$\alpha_2\mathrm{LDPE}_2 \xrightarrow{k_2} \mathrm{V}_2 + \mathrm{R}_2$	$\frac{d[\mathrm{LDPE}_2]}{dt} = -A_2 e^{\frac{-E_{a_2}}{RT}}[\mathrm{LDPE}_2]^{n_2}$	$E_{a_2} = 220$	$n_2 = 0.60$	$A_2 = 1.47 \times 10^{15}$	$\alpha_2 = 0.90$
$\mathrm{PP} \xrightarrow{k_1} \mathrm{V} + \mathrm{R}$	$\frac{d[\mathrm{PP}]}{dt} = -A_1 e^{\frac{-E_a}{RT}}[\mathrm{PP}]^{n}$	125	0.40	2.04×10^{8}	
$\alpha_1\mathrm{PS}_1 \xrightarrow{k_1} \mathrm{V}_1 + \mathrm{R}_1$	$\frac{d[\mathrm{PS}_1]}{dt} = -A_1 e^{\frac{-E_{a_1}}{RT}}[\mathrm{PS}_1]^{n_1}$	$E_{a_1} = 120$	$n_1 = 1.60$	$A_1 = 1.06 \times 10^{8}$	$\alpha_1 = 0.10$
$\alpha_2\mathrm{PS}_2 \xrightarrow{k_2} \mathrm{V}_2 + \mathrm{R}_2$	$\frac{d[\mathrm{PS}_2]}{dt} = -A_2 e^{\frac{-E_{a_2}}{RT}}[\mathrm{PS}_2]^{n_2}$	$E_{a_2} = 185$	$n_2 = 0.76$	$A_2 = 2.32 \times 10^{13}$	$\alpha_2 = 0.90$
$\mathrm{PVC} \xrightarrow{k_1} a\mathrm{HCl} + b\mathrm{I}$	$\frac{d[\mathrm{PVC}]}{dt} = -A_1 e^{\frac{-E_{a_1}}{RT}}[\mathrm{PVC}]^{n_1}$	$E_{a_1} = 198$	$n_1 = 1.04$	$A_1 = 3.57 \times 10^{18}$	$b = 0.52$
$b\mathrm{I} \xrightarrow{k_2} c\mathrm{V}_1 + e\mathrm{R}_1$	$\frac{d[\mathrm{I}]}{dt} = b(A_1 e^{\frac{-E_{a_1}}{RT}}[\mathrm{PVC}]^{n_1} - A_2 e^{\frac{-E_{a_2}}{RT}}[\mathrm{I}]^{n_2})$	$E_{a_2} = 143$	$n_2 = 1.15$	$A_2 = 9.95 \times 10^{16}$	$c = 0.36$
$e\mathrm{R}_1 \xrightarrow{k_3} f\mathrm{V}_2 + g\mathrm{R}_2$	$\frac{d[\mathrm{R}_1]}{dt} = e(A_2 e^{\frac{-E_{a_2}}{RT}}[\mathrm{I}]^{n_2} - A_3 e^{\frac{-E_{a_3}}{RT}}[\mathrm{SR}_1]^{n_3})$	$E_{a_3} = 243$	$n_3 = 1.58$	$A_3 = 5.77 \times 10^{16}$	$g = 0.06$
	$\frac{d[\mathrm{R}_2]}{dt} = g(A_3 e^{\frac{-E_{a_3}}{RT}}[\mathrm{SR}_1]^{n_3})$				

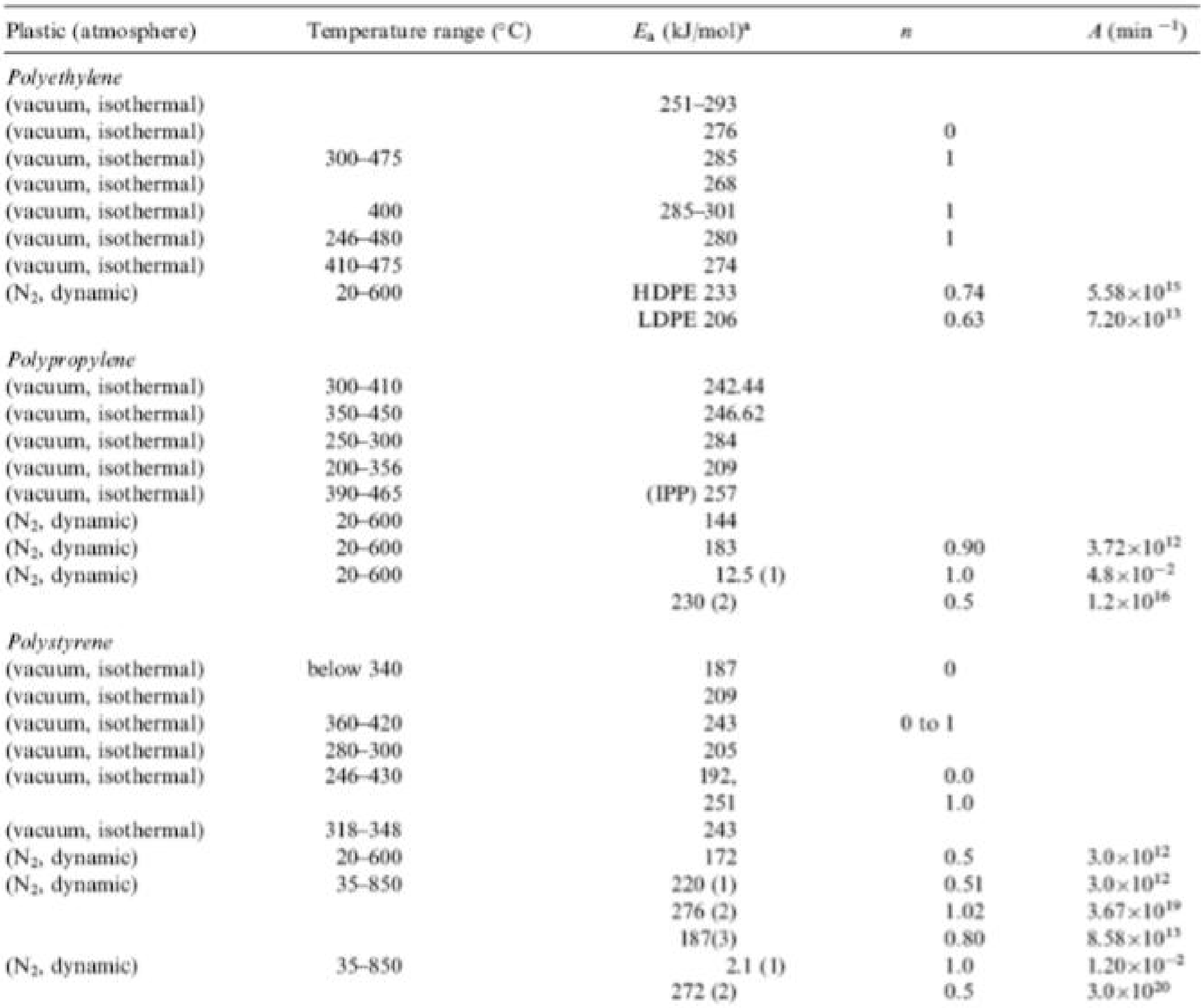
[a] V, volatiles; I, intermediate; SR_1, residue generated in the first stage; SR_2, residue generated in the second stage.

Examining Table 2.2, it is evident that Ea values range from 120 to 250 kJ/mol, potentially reflecting disparities in experimental conditions and materials utilized in the application of the kinetic reaction model. Parameters including activation energy (Ea), the coefficient of n, and A within the kinetic reaction model (Equations 2 and 3) are summarized for different plastic types and operational conditions in Table 2.3, which also specifies plastic types and cracking temperature [Ranzi, E., et al., 1997].

For pyrolysis reactions, Ea represents the total activation energy for all pyrolysis reactions. The pyrolysis process and individual reactions influence the Ea value. Collectively, these factors exert a significant impact on the Ea value, complicating its evaluation. Table 2.3 [Staggs, J.E.J., 2005] highlights that the cracking process and temperature are crucial factors affecting the Ea value.

Table 2.2 indicates that the Ea value rises with increasing cracking intensity of the products. The Ea value for LDPE cracking, which includes secondary crackings, is 220 kJ/mol, exceeding 150% of the Ea value for LDPE cracking into solely primary products. Temperature also impacts the Ea value due to its significant effect on product distribution. Various studies have extensively investigated the effects of temperature on Ea values (e.g., Miranda et al.). However, accurately determining the influence of temperature change on the Ea value remains challenging due to the wide variation in experimental methodologies employed in different literature sources (Table 2.3). Drawing inferences from the differential equations (Table 2.2), it can be concluded that factors affecting the Ea value indirectly influence the product composition, with products containing a higher proportion of small hydrocarbons requiring greater activation energy [Miranda, R., et al., 2001].

Table 2. 3: Literature data on kinetic parameters for plastic pyrolysis [Miranda, R., et al., 2001]



Plastic (atmosphere)	Temperature range (°C)	E_a (kJ/mol)^a	n	A (min^{-1})
Polyethylene				
(vacuum, isothermal)		251–293		
(vacuum, isothermal)		276	0	
(vacuum, isothermal)	300–475	285	1	
(vacuum, isothermal)		268		
(vacuum, isothermal)	400	285–301	1	
(vacuum, isothermal)	246–480	280	1	
(vacuum, isothermal)	410–475	274		
(N_2, dynamic)	20–600	HDPE 233	0.74	5.58×10^{15}
		LDPE 206	0.63	7.20×10^{13}
Polypropylene				
(vacuum, isothermal)	300–410	242.44		
(vacuum, isothermal)	350–450	246.62		
(vacuum, isothermal)	250–300	284		
(vacuum, isothermal)	200–356	209		
(vacuum, isothermal)	390–465	(IPP) 257		
(N_2, dynamic)	20–600	144		
(N_2, dynamic)	20–600	183	0.90	3.72×10^{12}
(N_2, dynamic)	20–600	12.5 (1)	1.0	4.8×10^{-2}
		230 (2)	0.5	1.2×10^{16}
Polystyrene				
(vacuum, isothermal)	below 340	187	0	
(vacuum, isothermal)		209		
(vacuum, isothermal)	360–420	243	0 to 1	
(vacuum, isothermal)	280–300	205		
(vacuum, isothermal)	246–430	192,	0.0	
		251	1.0	
(vacuum, isothermal)	318–348	243		
(N_2, dynamic)	20–600	172	0.5	3.0×10^{12}
(N_2, dynamic)	35–850	220 (1)	0.51	3.0×10^{12}
		276 (2)	1.02	3.67×10^{19}
		187(3)	0.80	8.58×10^{13}
(N_2, dynamic)	35–850	2.1 (1)	1.0	1.20×10^{-2}
		272 (2)	0.5	3.0×10^{20}

- Numbers in brackets indicate the step of pyrolysis of single plastics in literatures.

Pyrolysis of hydrocarbon polymers is a highly intricate process involving numerous reactions and products. Several factors significantly impact these reactions and products. This chapter explores the fundamental processes and reactions involved in plastic pyrolysis, building on prior research. As temperature increases, plastic transitions from glassy state to rubbery state to liquid state, eventually decomposing. Decomposition of plastics in an inert environment into liquid form is referred to as pyrolysis. Four stages of reactions occur during plastic pyrolysis: initiation, propagation, hydrogen transfer, and termination reactions. In the initiation reactions, polymer molecules experience three cracking types: random, end chain, and chain strip cracking, determined by the side functional group on the plastic molecular carbon backbone. Propagation reactions, particularly β-scission, involve the decomposition of large molecular weight free radicals, generating smaller compounds. Hydrogen transfer reactions increase the diversity of free radicals and the final product. Termination reactions combine all free radicals into molecules. With a comprehensive understanding of the fundamental pyrolysis process and reactions, a kinehtic model was established for calculating the energy of these reactions. Based on the kinetic model and estimated products, the theoretical energy requirement for PE pyrolysis was determined to be 1047.62 kJ/kg. The net energy gain from the process is 42.3 MJ/kg.

CHAPTER THREE

3 MATERIAL AND METHODS

3.1 MATERIAL

Table 3. 1: Materials and their Uses

MATERIALS	**USES**
Polyethylene terephthalate (PET) plastics waste	The feedstock that was pyrolyzed to give the pyrolysis oil product.
Clay sediment.	Used for the catalyst preparation.
Tap water	Used for washing and rinsing the the PET waste to remove impurities before their preparation.

Table 3. 2: Reagents and their sources

REAGENTS	**SOURCES**
Hydrochloric acid (HCL)	37% pure analytical grade produced by loba-chemie, india.
Sodium hydroxide (NaOH)	96% pure, produced y CDH, new Delhi, India
Nitrogen gas(N_2)	china
Deionized/ Distilled water	Central labouratory university of benin

Table 3. 3: Equipments and uses

EQUIPMENT	**USES**
Laboratory muffle furnaces	Used for calcination of the ground eggshell
Pestle and mortar	Used for grinding the eggshells into tiny particles
Desiccator	Used for cooling the eggshells in the absence of air
Sieve	For sieving the ground eggshell particles to obtain an even size distribution
Digital weighing balance	For weighing purposes
Constant temperature electric-powered pyrolysis reactor.	For pyrolysis of the PET for bio-oil production
Thermocouple	For temperature measurement
Electric heater	For heating purposes
Condenser	Used for condensing the vapor produced in the pyrolysis reactor to obtain our bio-oil.
Filtering paper	Used to filter out the catalyst for recoverable purposes after the pyrolysis reaction
X-ray fluorescence spectrometer	used to analyze the composition of the solid eggshell catalyst
X-ray diffractometer	was used to analyze the prepared catalyst crystal structure and phase composition
Fourier Transform Infrared Spectroscopy	Used to examine the structure and functional groups present in the eggshell samples

Thermogravimeter	used for the analysis of water loss in eggshells
Gas Chromatography-Mass Spectrometry	to analyze the composition of the pyrolysis oil obtained.

3.2 METHODOLOGY

3.2.1 WASTE PLASTICS (PET) COLLECTION AND PREPARATION

The waste plastic was sourced from eateries and lecture halls waste bins within the faculty of engineering university of Benin then it was cleaned of residual water and dirt, then dried using sunlight. After which the PET plastics waste is dry, the plastic waste was cut so that the size was reduced to about 2cm.

3.2.2 CLAY COLLECTION AND PREPARATION

Clay was sourced from ikpeshi akoko-edo LGA edo state.

Clay was obtained from ikpeshi river bed, it was laid to dry under the sun for two days to remove moisture content and then crush using the laboratory mortar and pestles, using a sieve of mesh size 200 microns to reduce it to fine particles. The fine clay particles were placed in small crucibles and place in the muffle furnace for calcination at 900^{o}C for 24hrs. The reason for the calcination was to help remove surface contaminant, enhance surface area and porosity, and to create active sites necessary for catalytic reactions (Vijayakumar and Sebastian, 2018)

3.2.3 SYNTHESIS OF ZEOLITE CATAYLST FROM CLAY.

3.2.3.1 ACID LEACHING

500 g of the calcinated clay was transfer into a 1000 ml beaker and a 25% 500 ml HCl was added to the beaker containing the sample(Mgbemere, Ekpe and Lawal, 2017). The solution was stirred continuously in a magnetic stirrer hot plate at a temperature of 100℃ for 1hr. It was then

allowed to cool and was constantly wash with de-ionized water to a pH of approximately 7.0. The resulting solid was then dried in an ovum.

3.2.3.2 AUTOCLAVING

The dried acid leached clay was transfer into a 1000 ml beaker and a solution of 3.0 M NaOH was added to saturate the clay. It was transfer to an autoclave operating at a temperature of 120°C and was sealed. The autoclave was then switched on and the synthesis was allowed to proceed for duration of 3hr. After the hydrothermal treatment, the autoclave was cooled to room temperature. The solid product was then collected and was constantly washed with deionized water to neutral pH of about 7.0. The collected solid product was dried in an oven at a temperature of around 100°C to remove any remaining moisture.

3.3 ANALYSIS AND CHARACTERIZATION OF ZEOLITE CATALYST

The synthesized zeolite catalyst was characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), and Brunauer-Emmett-Teller (BET) analysis to determine its crystal structure, morphology, and surface area.

1. **X-Ray diffraction (XRD) analysis:** This is used to analyze the prepared catalyst crystal structure and phase composition. It was performed using an X-ray diffractometer, which consists of an X-ray source, a sample holder, and a detector
2. **X-Ray Fluorescence (XRF) analysis:** This is used to analyze the composition of the zeolite catalyst. It was performed using an XRF spectrometer, which consists of an X-ray source, a sample holder, and a detector. XRF analysis was used to quantify the concentrations of various elements present in the catalyst, such as aluminum oxide (AlO), silicate oxide (SiO), and potentially other trace elements.

3. **Fourier Transform Infrared (FTIR) analysis:** This was done on the catalyst using Fourier Transform Infrared Spectroscopy to examine the structure and functional groups present in the zeolite sample. The analysis provided information about the absorption profile and characteristic peaks corresponding to different vibrational modes of the molecules present in the eggshell catalyst. The analysis helped in understanding the modifications and transformation of the ZEOLITE structure during the calcination process and provided valuable insights into the catalyst's composition and properties.

3.4 REACTOR SET-UP

The Constant temperature electric-powered pyrolysis reactor was modified in accordance with Miandad (2019). The Constant temperature electric-powered pyrolysis reactor is capable of performing thermal and catalytic pyrolysis utilizing a variety of feedstocks, including biomass and plastic. In this study, zeolite catalysts were added to the reactor along with the feedstock. The pyrolysis reactor can accommodate up to 20 L of feedstock and can reach a maximum working safe temperature of up to 600 C with the required heating rates. As the temperature exceeds certain values, the plastic waste transforms into monomers that are conveyed to the condenser, where these vapors are condensed into liquid oil. To maintain the condensation temperature below 10°C and ensure maximum conversion of vapor to liquid oil, a continuous condensation system utilizing a water bath and ACDelco Classic coolant was employed. The produced liquid oil is collected in the oil collection tank and undergoes further analysis to determine its chemical makeup and properties for potential applications (Miandad et al., 2019; Miandad, Barakat, Rehan, et al., 2017)

3.5 EXPERIMENT PROCEDURE/ METHOD

Commencing the experiment, 500 g of PET particles and 25g of zeolite catalyst were weighed using a four decimal place Mettler AE 200 balance and placed into the pyrolysis reactor. Subsequently, the system was sealed and purged with nitrogen gas for one minute to create an oxygen-free environment. Following this, the furnace was turned on to full capacity with control scale at 100, corresponding to a heating power of 881 W. The pyrolysis process was carried out in a small fixed-bed reactor. It was heated to reach a temperature of approximately 450°C, using a heating rate of 15°C/min and a reaction time of 30min. The products of this process include gas vapor, which passes through a condenser to produce liquid fuel (waste plastic oil).

3.6 ANALYSIS AND CHARACTERIZATION OF WASTE PLASTIC OIL.

The chemical compound and functional group were obtained by Gas Chromatography-Mass Spectrometry (GC−MS) technique. GC−MS is a powerful analytical technique used to separate and identify individual components in complex mixtures of liquid fuel derived from the pyrolysis process. It provided information about the types and concentrations of various hydrocarbon, oxygenates, and organic compounds present in the liquid fuel.

The physical properties of the liquid fuel were determined, including the pour point, flash point, calorific value, density, viscosity, and specific gravity.

3.6.1 THE POUR POINT

The pour point refers to the lowest temperature at which the pyrolysis oil will flow under specified conditions. To determine the pour point, a pour point apparatus is used to gradually cool a sample of the oil until it ceases to flow. The temperature at which the oil stops flowing is recorded as the pour point.

3.6.2 FLASH POINT

Flashpoint refers to the temperature at which sufficient vapor is released from pyrolysis oil to ignite briefly. The American Society for Testing and Materials (ASTM) D93 or similar methods are generally employed to determine flashpoint. A small oil sample is heated at a controlled rate in an enclosed or open vessel, and a flame or electrical spark is periodically passed over its surface. The temperature at which a flash or flame is observed constitutes the flashpoint.

3.6.3 CALORIFIC VALUE

Calorific value, also known as heating value or energy content, is the amount of heat released per unit mass of pyrolysis oil upon combustion. ASTM D240 or equivalent methods are used to measure calorific value. The oil is combusted in a calorimeter, and the heat released is measured and calculated based on temperature changes. Calorific value is typically reported in units such as BTU/lb or MJ/kg.

3.6.4 VISCOSITY

Viscosity gauges the resistance of pyrolysis oil to flow. ASTM D445 or analogous methods are commonly employed to measure viscosity. The oil is placed in a viscometer, and the time it takes for the oil to traverse a capillary tube under specific conditions is recorded. Viscosity is generally reported in units such as centistokes (cSt) or mm^2/s.

3.6.5 SPECIFIC GRAVITY.

Specific gravity represents the ratio of the density of pyrolysis oil to the density of a reference substance (typically water). ASTM D1298 or equivalent methods are commonly used to measure specific gravity. The oil is weighed and its volume is determined; specific gravity is then calculated by dividing the density of the oil by the density of water. Specific gravity is a dimensionless quantity.

CHAPTER FOUR

4 RESULT AND DISCUSSION

4.1 CATALYST CHARACTERIZATION

The thorough examination of catalyst properties is crucial in the development and utilization of catalysts across a spectrum of chemical processes, encompassing industrial production and environmental cleanup efforts. This examination aims to comprehensively evaluate catalyst behavior, effectiveness, and appropriateness for particular reactions.

4.1.1 PROPERTIES OF CLAY SOIL DERIVED CATALYST

Figure 4.1 outlines the physical characteristics of the catalyst derived from clay soil. These properties were found to contribute significantly to the catalyst's high activity during reactions.

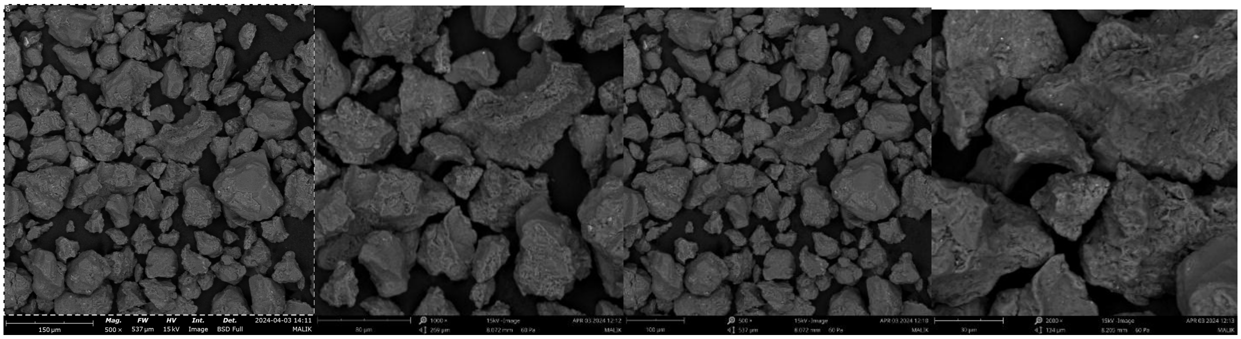


figure 4. 1: FOV: 537 µm, Mode: 15kV - Image, Detector: BSD Full

Analysis demonstrated that the catalyst exhibited a considerable surface area of 86.1m²/g, facilitating the effective diffusion of reactants within the catalyst's structure (Bharti et al., 2019). Jain and Sharma (2010) assert that attaining a large surface area is beneficial for improving the diffusion of both reactant and product molecules, a viewpoint supported by the findings of Ordóñez and Díaz (2009) who reported a slightly higher pore volume (0.76cm³/g) for CaO catalysts.

4.1.2 ELEMENTAL COMPOSITION OF CALCINED CLAY SOIL

Table 4. 1: Properties of Clay soil derived properties

Element Number	**Element Symbol**	**Element Name**	**Atomic Conc.**	**Weight Conc.**
14	Si	Silicon	63.14	60.94
13	Al	Aluminium	19.93	18.48
26	Fe	Iron	5.90	11.32
11	Na	Sodium	10.33	8.16
22	Ti	Titanium	0.55	0.90
17	Cl	Chlorine	0.17	0.20
12	Mg	Magnesium	0.00	0.00
20	Ca	Calcium	0.00	0.00
19	K	Potassium	0.00	0.00
15	P	Phosphorus	0.00	0.00
16	S	Sulfur	0.00	0.00

The elemental composition analysis of the clay soil derived catalyst was conducted using X-ray fluorescent (XRF) equipped with energy dispersive spectrometer (EDS). From Table 4.1, the results obtained revealed the presence of Silicon (Si) at 91.783% in its oxide form at a peak of 173418 cps/mA, making Silicon the most predominant element followed by Aluminum (Al), Iron (Fe) and Sodium (Na) both with the same concentration of 0.984% at peaks 80 cps/mA and 16 cps/mA respectively. Titanium (Ti) was present at 0.71% as the first peak to be obtained, and Chlorine (Cl) was present at 0.2718% with a peak of 281 cps/mA.

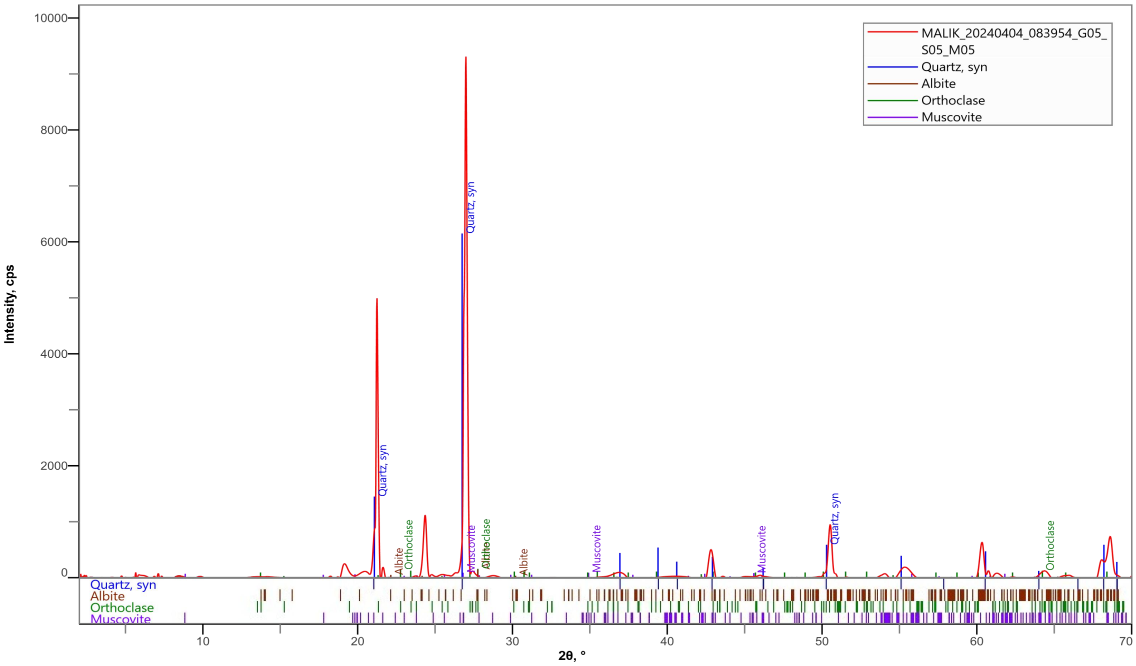


figure 4. 2: EDXRF Spectrum Of Calcined Clay Soil

4.1.3 CRYSTALLINITY OF CALCINED CLAY SOIL

The crystallinity of the calcined clay soil catalyst was assessed using X-ray diffractometry. The results obtained revealed the characteristic reflections of lime (CaO) and portlandite (Ca(OH)2) with cubic and hexagonal crystalline phases, respectively. The presence of these distinct crystalline phases was confirmed by their crystallographic parameters, with alpha = beta = gamma = 90° for lime and alpha = beta = 90°, gamma = 120° for portlandite. Notable peaks for lime (CaO) were observed at 2θ = 32.5°, 35.0°, 37.5°, 54.0°, 65.0°, and 67.5°, while characteristic peaks for portlandite were noted at 2θ = 18.0°, 34.0°, 51.0°, and 65.0°. The calculated densities were 3.34 g/cm³ and 2.20 g/cm³, with corresponding cell volumes of 111.35 x 10^6 pm³ and 54.46 x 10^6 pm³, respectively. The narrow and highly intense peaks observed in the spectrum (Figure 4.2) of the calcined clay soil catalyst further validate its crystalline structure, with calcium (Ca) identified as the predominant element.

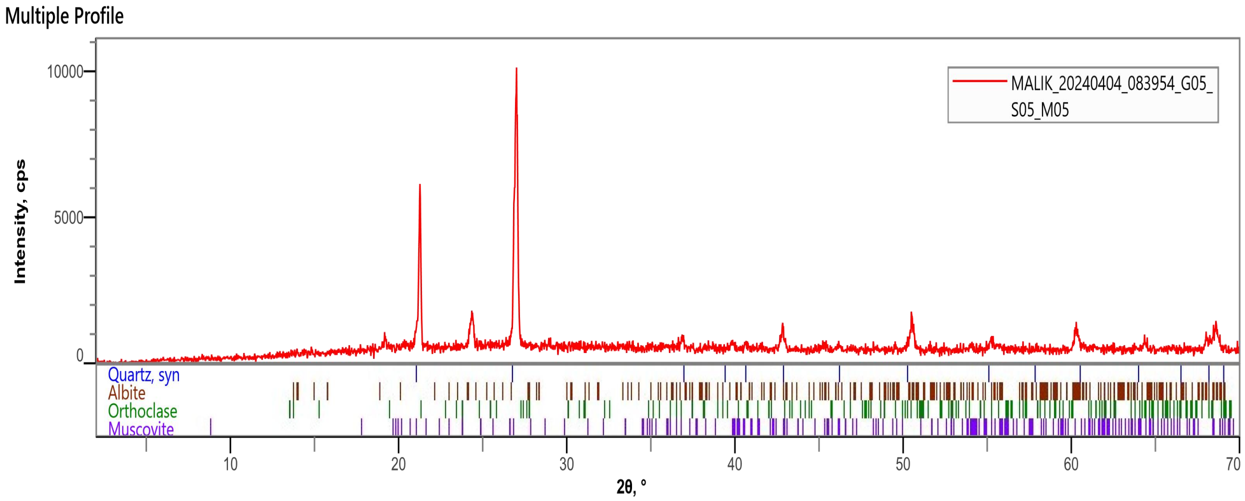


figure 4. 3: XRD analysis of calcined clay soil catalyst

4.1.4 FUNCTIONAL GROUP OF CALCINED CLAY SOIL

The existence of surface functional groups containing oxygen plays a crucial role in defining the surface characteristics and adsorption tendencies of activated carbons (Dawood & Sen, 2014). The development of these groups, whether through the activation procedure or through oxidation following the preparation of activated carbon, is significant. Figure 4.3 illustrates the FTIR spectra of the resulting adsorbent, highlighting three primary absorption bands within the 1600 – 1400 cm^{-1} range.

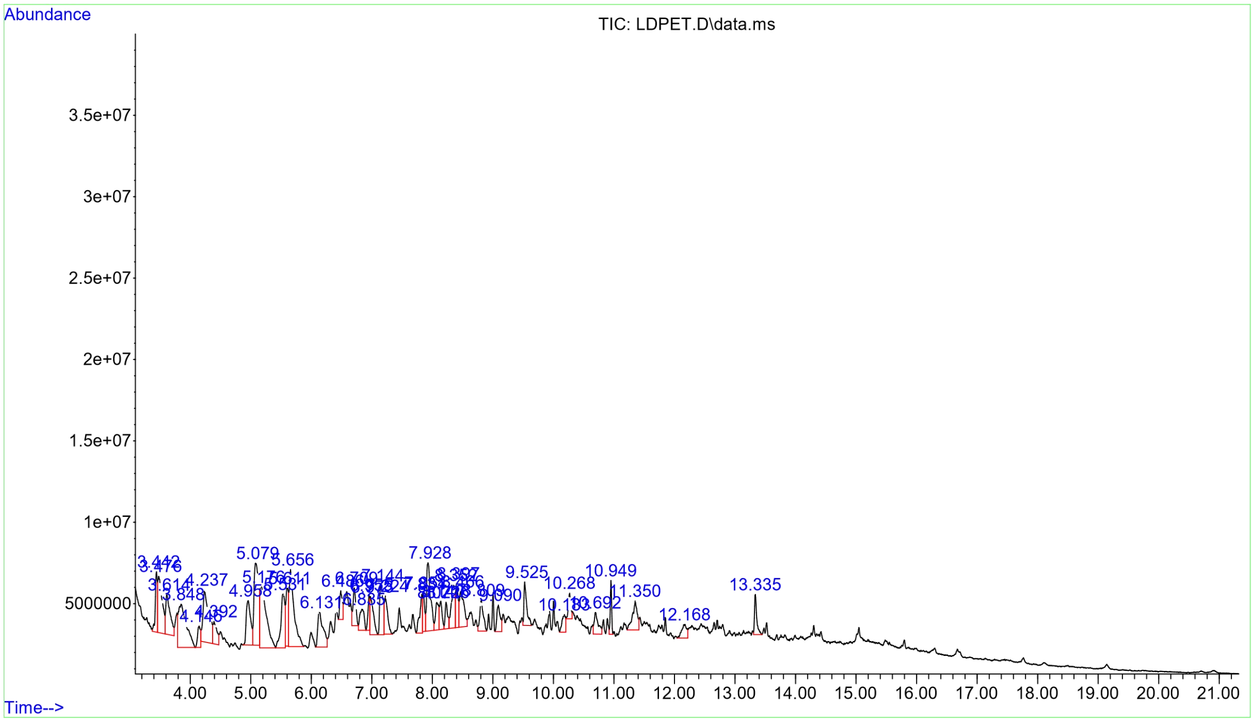


figure 4. 4: LDPET Spectrum Analysis Calcined clay soil

Figure 4.3 illustrates that the prominent peak at 1416 cm⁻¹ is indicative of the stretching vibrations of Carbonate ion (CO_3^{2-}) bonds, a characteristic often found in calcined clay soil. Furthermore, the lesser peak at 3641 cm⁻¹ is linked to the stretching vibrations of Heterocyclic amine (N – H) bonds. These findings are concisely presented in Figure 4.3.

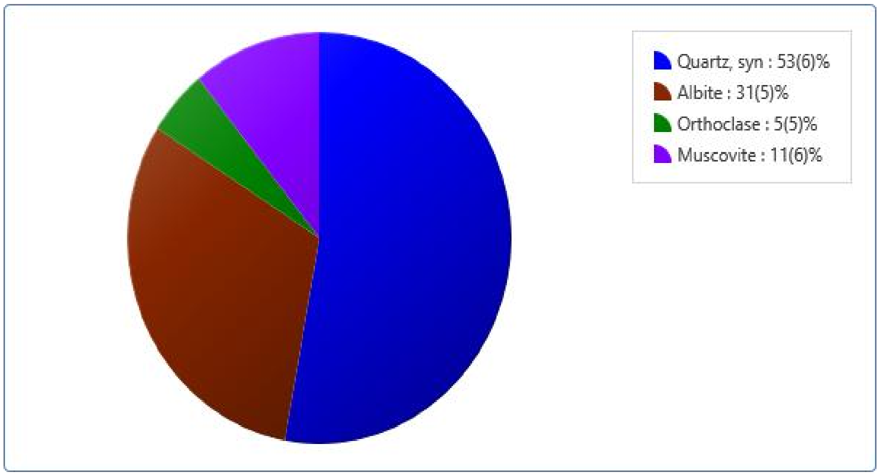


figure 4. 5: LDPET result analysis

Table 4. 2: Summary of spectrum peaks of calcined clay soil

Peak Number	**Wavenumber (cm^{-1})**	**Intensity**	**Functional group**	**Comment**
1	872.19705	74.81318	Epoxy and oxirants (C – O –)	Weak Stretch
2	1416.38838	63.10627	Carbonate ion (CO_3^{-2})	Strong stretch
3	3641.60907	71.88433	Heterocyclic amine (N – H)	Weak stretch

4.1.5 RESULTS OF THERMAL STABILITY OF CATALYSTS

Through the analysis of TGA/DTA thermograms, depicted in Figure 4.4, we could trace the thermal degradation process of the treated catalyst. The TGA thermogram exhibited three distinct phases of weight loss for the processed catalyst. Initially, spanning from 23.19°C to 320°C, the processed catalyst experienced a weight loss of less than 10%. This initial phase primarily corresponded to the release of absorbed organic molecules and moisture from the catalyst.

The second phase, occurring between 320°C and 560°C, contributed to a significant weight loss, approximately 80% of the total. This substantial reduction in weight during this phase was largely attributed to the further removal of moisture content from the processed catalyst.

The third weight loss phase began after 560°C and coincided with the thermal disintegration phase of the processed catalyst. Beyond 800°C, the rate of weight loss remained relatively constant, eventually leading to the complete decomposition of the processed catalyst around 846°C. Examination of the DTA thermogram revealed a subtle peak at around 200°C, indicating energy absorption, corresponding to the 10% weight loss observed in the TGA thermogram.

Furthermore, a more pronounced and sharper peak was observed at 480°C, indicating an endothermic reaction curve, likely representing the thermal decomposition of the catalyst. This sharp peak was also consistent with the thermal disintegration phase observed in the TGA thermogram.

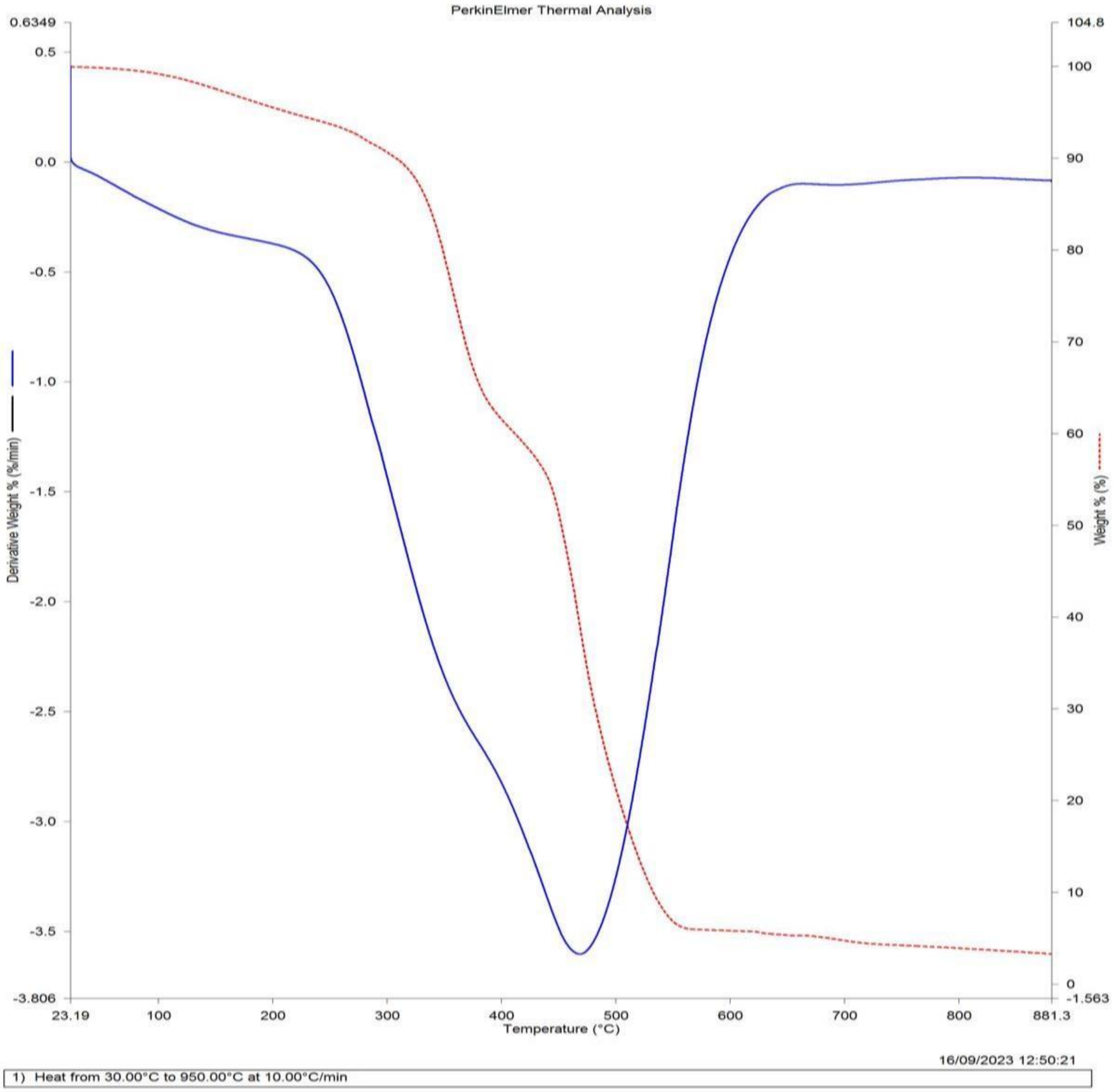


figure 4. 6: DTA/TGA of calcined clay soil

4.2 RESULTS OF PYROLYSIS OF WASTE PET BOTTLES

Table 4.3 presents the cumulative oil recovery from the pyrolyzed waste PET bottles. The thermochemical process was conducted within the temperature range of 200°C to 400°C, both with and without the catalyst (Calcined Clay soil). It is evident from Table 4.3 that the volume of oil recovered increases with temperature, and notably, the presence of the catalyst enhances oil recovery compared to its absence. This difference is visually depicted in Figure 4.5.

Table 4. 3: Cumulative Oil Recovery of Pyrolysis of PET

Temperature (^oC)	**Oil recovery (ml) without catalyst**	**Oil recovery (ml) with catalyst**
200	0	1
210	0	7
254	1	13
300	12	28
320	28	39
350	49	67
360	67	86
380	91	108
400	123	147

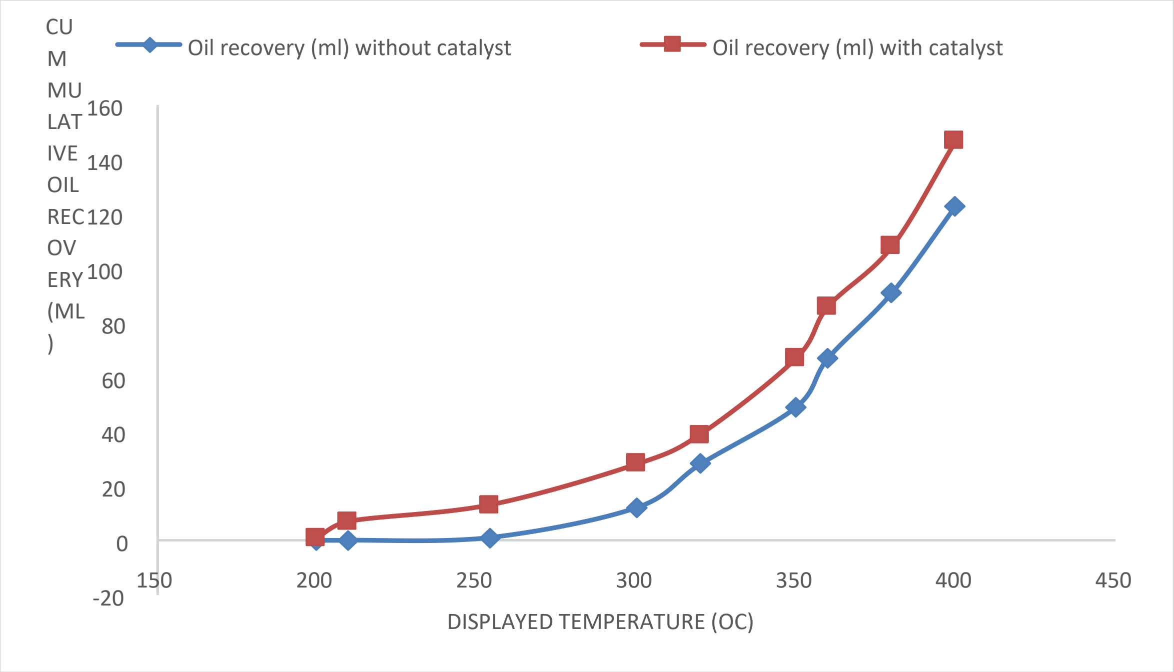


Illustration on the Cumulative Oil Recovery of Pyrolysis of PET

4.3 PHYSICAL AND CHEMICAL PROPERTIES OF PYROLYSIS OIL

The laboratory characterization of the oil derived from the pyrolyzed waste PET bottles yielded the physiochemical properties, which are detailed in Table 4.4.

Table 4. 4: Physiochemical properties of the pyrolyzed waste BET bottle

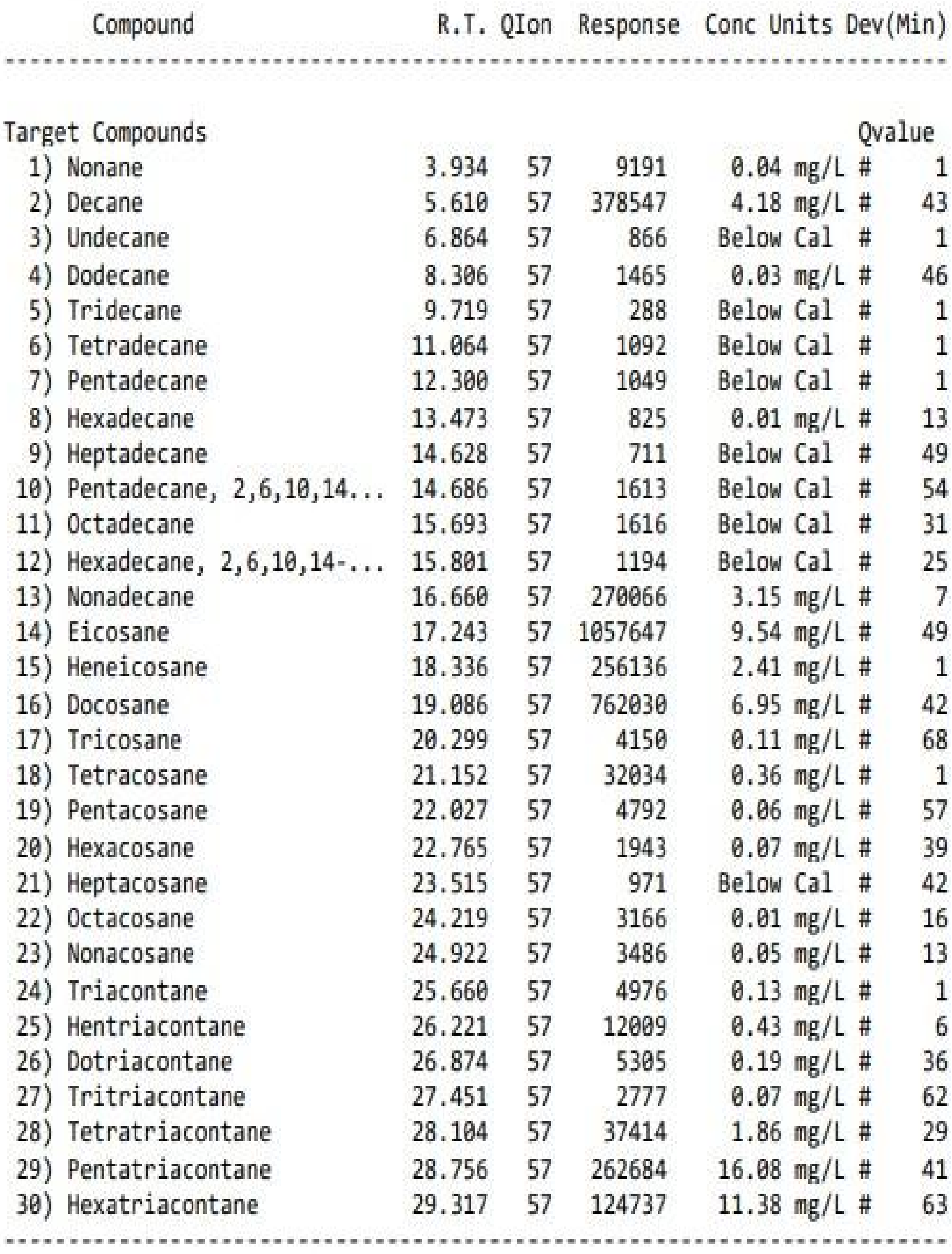
PROPERTY	**VALUE**
Caloric Value (kcal/kg)	16.42
Flash Point (^{O}C)	78
Viscosity Kinematic (mm^2/s)	2.80
Specific Gravity	**4.8601**

4.3.1 GC-MS RESULT ON THE OIL OBTAINED FROM THE PYROLYZED WASTE PET BOTTLES

The Gas-Chromatography and Mass-Spectroscopy analysis performed on the oil extracted from the pyrolysis process revealed the presence of various compounds, including n-tatriacontane (retention time: 29.317 minutes), Hexatriacontane (retention time: 28.756 minutes), Tetratriacontane (retention time: 28.104 minutes), Triacontane (retention time: 27.451 minutes), Hentriacontane (retention time: 26.874 minutes), Dotriacontane (retention time: 26.221 minutes), Tritriacontane (retention time: 25.660 minutes), Nonacosane (retention time: 24.922 minutes), Tricosane (retention time: 24.219 minutes), Tetracosane (retention time: 22.765 minutes), Pentacosane (retention time: 22.027 minutes), Hexacosane (retention time: 21.152 minutes), Octacosane (retention time: 20.299 minutes), Docosane (retention time: 19.086 minutes), Heneicosane (retention time: 18.336 minutes), Eicosane (retention time: 17.243 minutes), Nonadecane (retention time: 16.660 minutes), Hexadecane (retention time: 13.473 minutes), Dodecane (retention time: 8.30 minutes), Decane (retention time: 5.610 minutes), and Nonane (retention time: 3.934 minutes) in significant concentrations.

The chromatogram depicted in Figure 4.6 illustrates that Dodecane exhibited a prominent cluster between 8-10 minutes of retention time. Furthermore, as indicated in Table 4.5, Pentatriacontane was notably more abundant than other compounds, given its higher concentration unit compared to the rest.

Table 4. 5: Compounds analyzed from the pyrolyzed oil through GC-MS Analysis



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      Compound                      R.T. QIon  Response  Conc Units Dev(Min)
---------------------------------------------------------------------------

Target Compounds                                                    Qvalue
  1) Nonane                        3.934   57      9191    0.04 mg/L #     1
  2) Decane                        5.610   57    378547    4.18 mg/L #    43
  3) Undecane                      6.864   57       866   Below Cal  #     1
  4) Dodecane                      8.306   57      1465    0.03 mg/L #    46
  5) Tridecane                     9.719   57       288   Below Cal  #     1
  6) Tetradecane                  11.064   57      1092   Below Cal  #     1
  7) Pentadecane                  12.300   57      1049   Below Cal  #     1
  8) Hexadecane                   13.473   57       825    0.01 mg/L #    13
  9) Heptadecane                  14.628   57       711   Below Cal  #    49
 10) Pentadecane, 2,6,10,14...    14.686   57      1613   Below Cal  #    54
 11) Octadecane                   15.693   57      1616   Below Cal  #    31
 12) Hexadecane, 2,6,10,14-...    15.801   57      1194   Below Cal  #    25
 13) Nonadecane                   16.660   57    270066    3.15 mg/L #     7
 14) Eicosane                     17.243   57   1057647    9.54 mg/L #    49
 15) Heneicosane                  18.336   57    256136    2.41 mg/L #     1
 16) Docosane                     19.086   57    762030    6.95 mg/L #    42
 17) Tricosane                    20.299   57      4150    0.11 mg/L #    68
 18) Tetracosane                  21.152   57     32034    0.36 mg/L #     1
 19) Pentacosane                  22.027   57      4792    0.06 mg/L #    57
 20) Hexacosane                   22.765   57      1943    0.07 mg/L #    39
 21) Heptacosane                  23.515   57       971   Below Cal  #    42
 22) Octacosane                   24.219   57      3166    0.01 mg/L #    16
 23) Nonacosane                   24.922   57      3486    0.05 mg/L #    13
 24) Triacontane                  25.660   57      4976    0.13 mg/L #     1
 25) Hentriacontane               26.221   57     12009    0.43 mg/L #     6
 26) Dotriacontane                26.874   57      5305    0.19 mg/L #    36
 27) Tritriacontane               27.451   57      2777    0.07 mg/L #    62
 28) Tetratriacontane             28.104   57     37414    1.86 mg/L #    29
 29) Pentatriacontane             28.756   57    262684   16.08 mg/L #    41
 30) Hexatriacontane              29.317   57    124737   11.38 mg/L #    63
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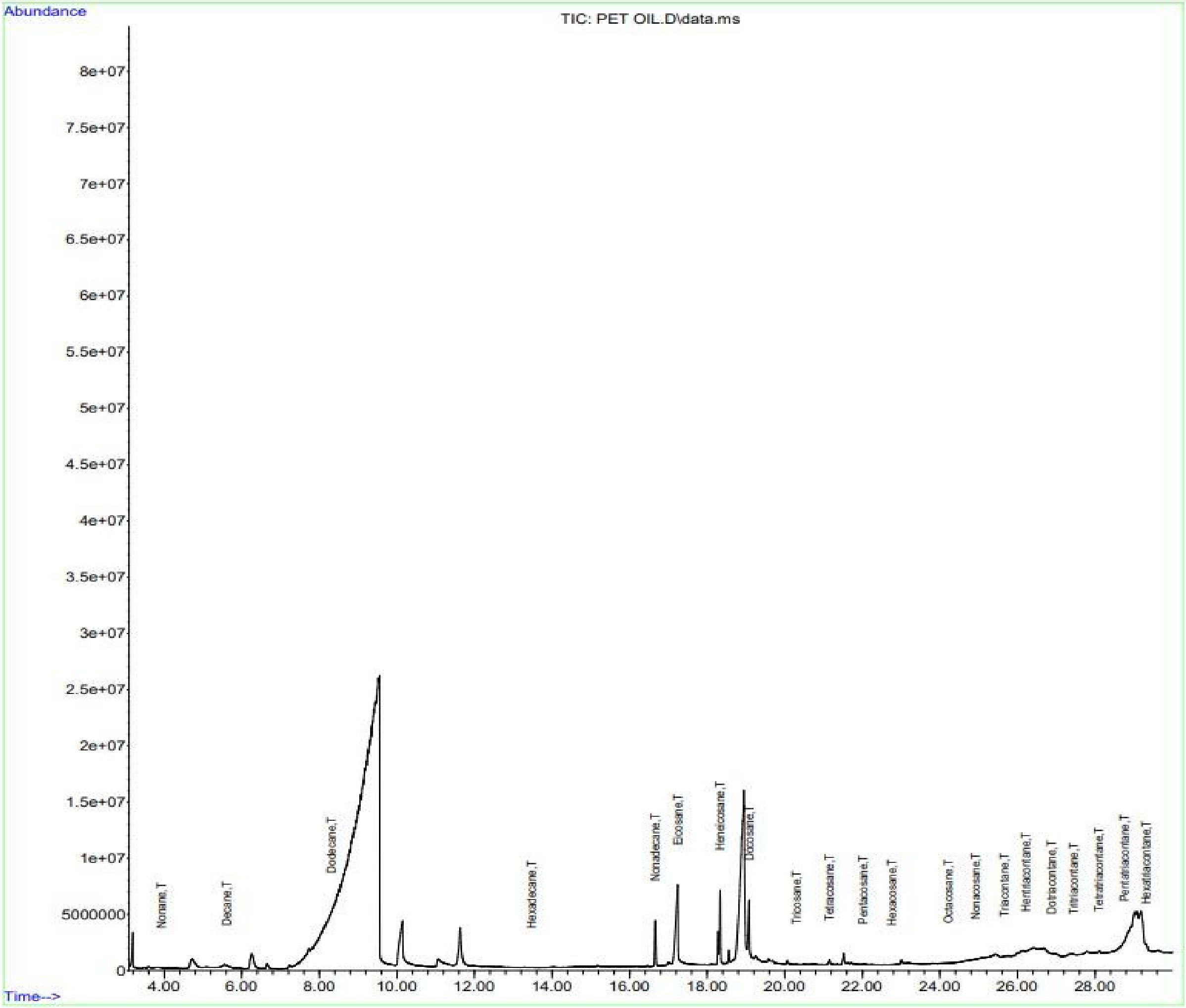

Figure 4. 7: Chromatograph Of The GC-MS Analysis

CHAPTER FIVE

5 CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

In our research pursuit, the primary objective was to develop a catalyst sourced from a readily available biomass, namely clay soil, with the aim of facilitating the pyrolysis process of waste PET bottles. This catalyst was envisioned to play a crucial role in converting plastic waste into valuable products efficiently.

I am delighted to announce that our diligent efforts and meticulous experimentation have led to successful outcomes. We have achieved the production of the desired catalyst from clay soil, marking a significant milestone in our study. This catalyst has proven effective in enhancing the pyrolysis of waste PET bottles, a vital step toward addressing plastic waste management challenges and promoting sustainable recycling practices.

The successful execution of this research not only demonstrates the feasibility of utilizing biomass-derived catalysts in waste-to-energy processes but also highlights the potential for sustainable and eco-friendly waste management solutions. Our findings make a valuable contribution to the fields of catalysis and environmental sustainability, offering a more efficient and sustainable approach to tackling plastic waste challenges.

The conclusions drawn from this study are as follows:

1. The calcined clay soil proved to be effective in the pyrolysis of waste PET bottles. Structural analysis of the catalyst revealed a surface area, bulk density, particle size, and porosity of 86.10 m^2/g, 1.285 g/cm^3, <100µm, and 48%, respectively. Spectroscopic analysis indicated a high composition of calcium oxide, indicating its efficacy.

2. The study demonstrated that catalytic pyrolysis of waste PET bottles resulted in a greater volume of oil compared to non-catalytic pyrolysis, as shown in Table 4.3.
3. The physiochemical properties of the oil from the pyrolysis of waste PET bottles were found to meet ASTM standards. Caloric value, flash point, kinematic viscosity, and specific gravity were determined to be 16.42 kcal/kg, 78°C, 2.80 mm^2/s, and 0.8601, respectively.

5.2 RECOMMENDATION

To gain a deeper understanding of this research, which centers on catalytic pyrolysis of discarded PET bottles using calcined clay soil, it is beneficial to explore the following areas:

1. Reaction kinetics of the involved reactions.
2. Influence of the catalyst's particle size on the pyrolysis process.
3. Investigation into optimizing the catalytic pyrolysis of waste PET bottles.

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