

Thermo Catalytic Cracking of Waste Polyethylene Using a Hybrid Catalyst



By

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Thermo Catalytic Cracking of Waste Polyethylene Using a Hybrid Catalyst



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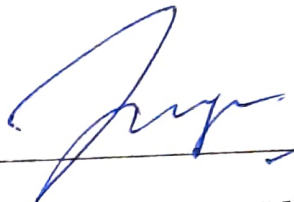
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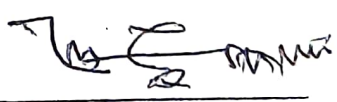
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Dedication

Devoted to Dearest Guardians

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Knowledge is limited to praise ALMIGHTY ALLAH, the Beneficent and the Merciful, who is the source of knowledge and whose blessing is the treasure of my thoughts. Peace and blessing of ALLAH on our beloved PROPHET HAZRAT MUHAMMAD (PBUH), the greatest social reformer, which is the cause of the creation of the universe and the forever source of knowledge and guidance for mankind.

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Abstract

Scientific advancements in the latest era have lead widespread and endless growth in the production of plastic materials. This exponential development has made public distress over the environmental effect instigated by the waste polymer produced. The transformation of plastic waste to valuable products is gaining increasing attention. The aim of this investigation was to examine the aspects of catalytic degradation of polymer utilizing Fuller's earth clay AKA (Multani Matti), Dolomite, HZSM-5 as catalyst and various metal oxides as an additive. A number of experiments were done using diverse catalysts and temperature conditions. The plastic used was waste polyethylene bags whereas blended mixtures of (ZnO + clay), (Fe (III) oxide +clay), (Ni oxide + clay) and (Dolomite + ZnO + HZSM-5) were used as a catalyst. The plastic catalytically cracked under controlled conditions of 400 °C to 500 °C. The gas products formed during the catalytic degradation of polyethylene were then analyzed in gas chromatograph mass spectrometer (GCMS). The product varied distinctly on the type of catalyst and conditions used. The proportion of gas products i.e. propene, 1-butene, butane, butene and 1-pentene produced using fuller's clay and dolomite zeolite mixture varied according to condition and w/w plastic to catalyst ratio. This is primarily due to different selectivity of dolomite mixture and fuller's clay mixture. 450°C gave the maximum amount of product in the temperature range of 400 °C to 500 °C. Furthermore, the experimental setup developed in this work appeared to be feasible to produce low molecular weight hydrocarbons.

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Abbreviation

SEM	Scanning Electron Microscope
FTIR	Fourier Transform Infra-Red
XRD	X-ray Diffraction
PE	Polyethylene
PP	Polypropylene
PS	Polystyrene
CPE	Cellulose Polyethylene Mixture
HDPE	High-Density Polyethylene
LDPE	Low-Density Polyethylene
GC	Gas Chromatography
MS	Mass Spectrometry
PVC	Poly Vinyl Chloride

Chapter 1

Introduction

At a certain point when we think about it, we have to admit that human beings are their own worst enemy. They create things of their own demise all the time. It's like their nature always drives them to self-destruct. There could be a list of things in this context but we are talking about one of the uncontrollable monsters they have created known as non-biodegradable plastic which formed a big mess in the whole world for quite some time now. We all have seen beautiful sandy beaches littered with plastic pollution and big cities facing massive plastic dumps. All this happened in the second half of the 20th century and still happening at a substantial rate around us in the 21st century as well. Plastic pollution is identified, alongside climate change, as an emerging issue that might affect biological diversity and human health[1]. Plastic pollutants include the buildup of plastic products inside the environment that influences wildlife, humans or wildlife habitat. Plastic wastes that act as pollution are classified into meso, micro or macroparticles on sized based totally. Plastic pollutants influence harmfully waterways, oceans, and lands, residing organisms in particular marine creatures can likewise be affected via direct ingestion and entanglement of plastic waste, or over chemical creation within the plastics that create disturbances in organic functions. Plastics can be characterized into two significant, categories as per their thermal course: thermoplastics and thermosets. Thermoplastics diminish when they are heated, and might be formed and molded, this heating procedure might be reused commonly. These plastics add to the cumulative plastic utilization by approximately 80 %, furthermore utilized as packaging, trash bags, containers and other merchandise.[2] Few cases are low and high-density polyethylene (LDPE, HDPE), polypropylene (PP), polyvinyl chloride (PVC) and polystyrene (PS). On the contrary, thermosets harden irreversibly during heating, since an irreversible system of cross-connected covalent bonds is developed, allowing a strong, hard and heat resistant items and products. The third category of plastics, elastic sort, rubber-type is termed elastomers, shaped by somewhat cross-connected polymer chains; in fewer extent than thermosets, providing for particular materials flexible and ductile properties and moderately worthy resistance. Plastic waste formation causes an adverse

environmental effect because these objects are typically non-biodegradable, furthermore, they usually stay as waste in the environment for quite a while; they can pose risks to the environment along with human health, and they could be hard to reprocess and additionally reprocess in extensive scale. The reclaiming of plastic waste is a crucial issue nowadays. The shrinking quantity of fossil assets of the world and the expanding measure of plastic waste show that plastic waste must be used again and again as raw materials. The degradation of plastic waste is the most convincing approach to resolve this reclaiming issue since it brings about hydrocarbon items similar to fuel either petrochemical feedstocks. **Figure 1** shows the global plastic production from 1950 to 2014 which indicates that plastic production in 2014 was 311 metric tons it is growing exponentially.

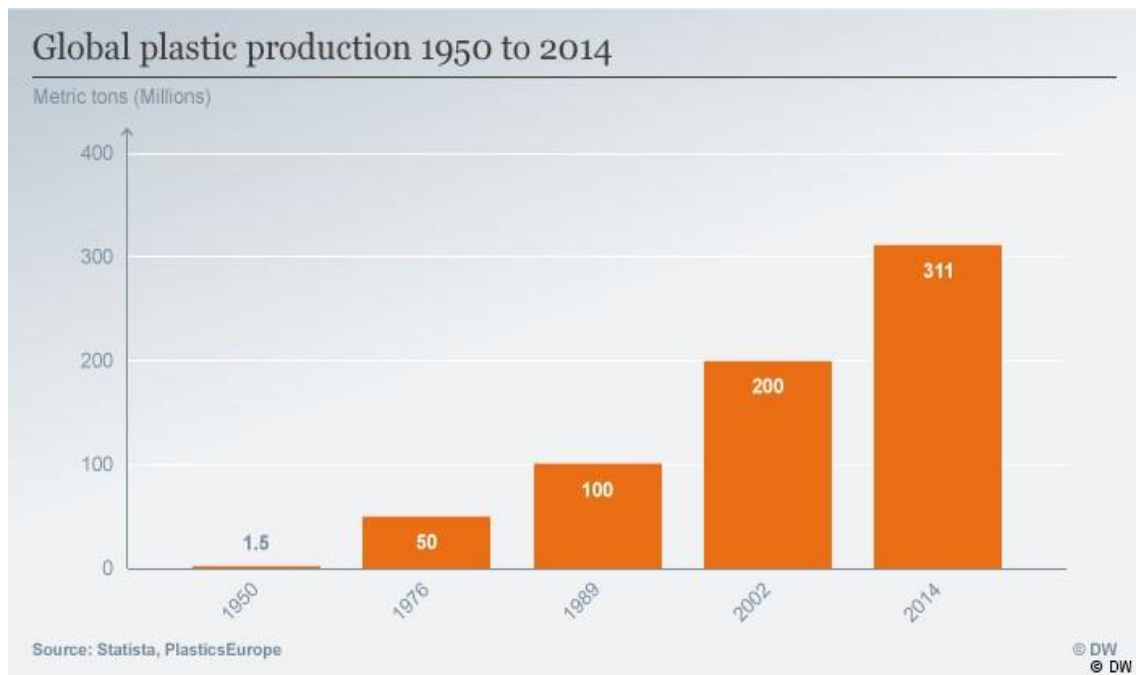


Figure 1: Global Plastic Production from 1950 to 2014

Figure 2 shows different types of plastics that are produced and from this, we can see that polyethylene (PE) covers a huge portion of the chunk.

Plastic around the globe

The term "plastic" covers many different types of polymers, each produced in many millions of tons in 2015.

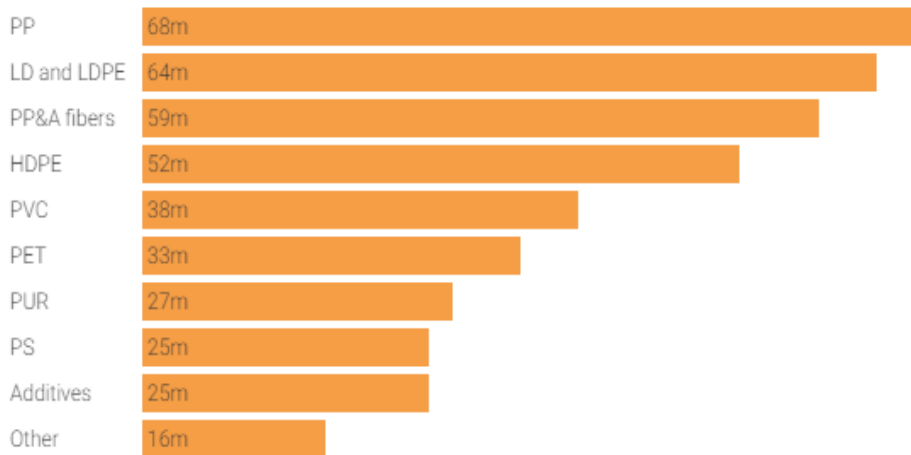


Chart: The Conversation, CC-BY-ND • Source: [Science Advances \(2017\)](#) • [Get the data](#)

Figure 2: Types of Plastic Waste in Million Tons

Recycling plastic waste gives important environmental advantages, for example:

1. **Decrease Disposal Areas:** The requirement to make novel disposal areas and to place extra junk in the earth is consistently expanding, and reusing is the main supportable answer to radically diminish the waste stored in landfills. In addition, as basic plastics are not degradable, they can stay for a considerable length of time without space liberation. One ton of plastic jugs free more than 7 cubic yards of landfills, at that point, reusing plastic means freeing a ton of room pointlessly utilized.
2. **Energy Management:** The reused material is utilized as a source, even if most, each reused bit of plastic changes into something totally different after the procedure.
3. **Reduction of Greenhouse Gases and Air Contamination:** A typical net decrease in harming substance releases greenhouse gas (GHG) of around 1.5 tons of CO₂ - eq of reused plastic has been evaluated [Department of Environment and Conservation (NSW), (2005)]. The reduction in GHG and hazardous waste

releases is basically a result of the exchange of virgin polymer generation, diminishing fuel consumption.

4. **Oil preservation:** The increasing cost of oil is extremely basic financial concern around the entire world; each ton of reused plastic saves just about 2000 pounds of oil. Saving can be because of the decrease of crude refinery materials in the manufacturing procedure, to the utilization of plastics as a source of ignition fuel in incinerators, and additionally fuel production from plastics by catalytic disintegration.[3]
5. **Improving Quality of Aquatic Life:** It has been reported that a plastic raft (bottle caps, toys, bottles, etc.) drifts on the ocean surface, trapping and killing marine life, as well as sea birds and turtles, unable to distinguish plastics from food, dying by malnutrition or asphyxia.[4]

A number of alternate solutions exist to manage plastic wastes. Four classifications can be considered for the treatment and reusing procedures of plastic wastes (**Table 1**) depending on the requirements of each territory or industry; every technique has its own advantages and disadvantages.

Out of all the options available, we ought to consider Tertiary (Chemical recycling) because it offers up a choice of:

- **Pyrolysis.** Polymer chains thermal deterioration in the absence of oxygen.
- **Gasification.** Degradation of polymer chains at high temperatures in an oxygen environment or steam action to produce a gas mixture.
- **Hydrogenation.** Chain breaking with hydrogen.
- **Catalytic cracking.** Breaking of polymer chain over the activity of a catalyst.

Catalytic thermal cracking is the most sustainable option of raw material reprocessing, with which exceptionally profitable substances could be produced. These innovations feasibly connected to LDPE, PP and HDPE, and that symbolize approximately 60% in plastic wastes. Additionally, on a fundamental level, any sort of plastic might be reused, giving the correct catalyst, the correct response framework and the correct reprocessing conditions.

Table 1: Plastic Recycling Methods

[Scheirs & Kaminsky, (2006); Al-Salem et al., (2009); Hopewell et al., (2009)]

Method	Description	Advantage	Disadvantage
R-extrusion (Primary)	Involves the reintroduction of clean, scrap of single polymer to the extrusion cycle in order to produce products of similar material.	Reusing plastic is preferable to recycling as it requires less energy and fewer resources, usually, they feed the secondary process.	Limited, since rarely possess the required quality. Sorting must be attempted within a short time. Removing paints is necessary.
Mechanical Recycling (Secondary)	Involves reprocessing of plastic by melting, shredding, or granulation. Separation, washing and preparation of wastes are essential.	It is an economic and Viable route for plastic wastes recovery. It is used mainly to manufacture fibers for carpets, apparel, and bottles.	Mechanical recycling of plastic solid waste can only be done on single polymer plastic, e.g PE, PP, PS, etc requires intense energy consumption.
Feedstock or Chemical Recycling (Tertiary)	Refers to techniques used to breakdown plastic polymers into their monomers or small molecules. It is the most sustainable method.	Can be used in petrochemical and chemical production plants; wastes are converted into valuable feedstock chemicals, useful as fuels or raw materials.	Costs of a feedstock plant are still high in comparison with oil plants. Still lacks the proper design and kinetic background to target certain products and chemicals.
Incineration and Energy Recovery (Quaternary)	Implies burning waste to produce energy in the form of heat, steam, and electricity.	Produce heat, power, and gaseous fuels. Plastic waste results in a volume reduction of 90–99% and reduce landfilling.	Health and environmental concerns due to the production of large amounts of air pollutants. E.g. toxic gas release.

1.1 Objective of Work

Like the rest of the world, we are also consuming plastics in large amounts; the yearly utilization of polyethylene in Pakistan is more than one million tons per year [World Wide Fund for Nature (WWF) Pakistan (2018)], in this way creating a lot of waste plastic. The ecological risk by plastics waste is significantly higher because of increasing demand. Scientists have demonstrated that the atmosphere has been influenced incredibly by contamination. As the governments around the world are getting to be aware of the hazards of ecological contamination, so does the administration of Pakistan, in this way to handle the contamination caused by waste plastic, new avenues are investigated to take care of this issue. In any case, unfortunately, little has been done to address this issue, and we are lagging the world in such a manner. If the contamination issue isn't handled instantly, we will annihilate our biological community, which will incredibly influence us in the more drawn outrun. Entire mankind is influenced by the impacts of contamination and we are watching the ascent in earth's temperature, in this way causing numerous issues. In addition, the issues caused by contamination, Pakistan is likewise confronting an intense energy crisis. Pakistan mainly relies on its hydel power for energy generation, yet in spite of that, the quantity of significant dams in Pakistan is excessively few. Including, recuperating from this crisis, Pakistan is spending more than \$6 billion for every annum to import oil subsidiaries that significantly hampers the GDP development rate of Pakistan [United State Energy Administration]. Looking at the repercussions of the issues said above to the economy and society of Pakistan, we can see that much is to be picked up, in the event that we can discover an answer for these issues.

A lot of work has been done to recycle plastic waste into valuable products by using various catalysts i-e Zeolite and Clay. Polymer degradation while utilizing Zeolite-based catalysts gives valuable products but the main disadvantage of using these catalysts is that it's over cracked the polymer because of its high acidity. Clay catalyst usually cracks the polymer at high temperatures (700-800 °C). Such a high temperature leads to the deactivation of catalyst mainly by coking and poisoning [5].

This work basically intends to study the effect of gas product yield when catalytic thermal cracking is applied on polyethylene and the catalysts being used in the reaction are changed. The key objectives of this work are:

- Construction of experimental setup for catalytic thermal degradation of plastic waste.
- Conversion of polyethylene waste into lighter hydrocarbons.
- To investigate the performance of various catalysts.
- Compare the compositions of products produced with different catalysts.

1.2 Polyethylene (PE)

Polyethylene or polythene is the most widely recognized plastic. The yearly worldwide generation is approximately 80 million tones. The essential utilization of PE is in the packaging (plastic films, plastic bags, geomembranes, bottles along with containers, and so forth.). The chemical formula of Polyethylene is $(C_2H_4)_n$. PE is generally a blend of comparative ethylene polymers with different “n” estimations.

1.2.1 History

Polyethylene was firstly integrated by the German scientific expert Hans von Pechmann, who set it up unintentionally in 1898 whilst researching diazomethane. At the point when his partners Eugen Bamberger and Friedrich Tschirner described the white, waxy material he made, they perceived that it composed of lengthy $-CH_2-$ chains thus named it polymethylene. In 1933 at (ICI), the first industrial PE synthesis was found again unintentionally by Reginald Gibson and Eric Fawcett's works in England. They again created a waxy, white substance from benzaldehyde and ethylene blend after assigning intensively high pressure. Since initially, the experiment was hard to initiate but in their equipment, the reaction had been started by oxygen contamination flow. In 1939 the first industrial LDPE generation started by ICI scientific expert, Michael Perrin. Along with the advancement of catalysts, the materialistic PE generation started that at medium pressures and temperatures advanced the polymerization. In 1951 by R. Banks and J. P. Hogan the earliest of these was CrO_3 based catalyst. In 1953 K. Ziegler German scientific expert built up a catalytic framework in light of organoaluminium and titanium halides compounds that compared to Phillips catalyst operated at considerably medium

conditions. However, the two techniques are intensely utilized modernly as the Phillips catalyst is simpler to work with and more affordable. These catalysts were extensively utilized for HDPE generation. In the 1970s, by the embodiment of $MgCl_2$, the framework of Ziegler- sort catalysts were enhanced. By W. Kaminsky and H. Sinn in 1976, catalytic frameworks in light of solvent catalysts i-e metallocenes were accounted for. These catalysts were turned into the reason for the extensive variety of PE resins accessible today and were extremely adaptable at copolymerizing ethylene with different olefins. These resins include linear LDPE and very LDPE.

1.2.2 Properties

1.2.2.1 Mechanical Properties

PE has a nominal fraction, rigidity and strength. It senses waxy when contacted. Under constant force, it demonstrates intense creep but by the accession of small fibers, it can be diminished. PE has high malleability and impact strength.

1.2.2.2 Thermal Properties

By its melting point i-e $80\text{ }^{\circ}C$, the value of PE is restricted. The melting point of HDPE and LDPE is commonly in the domain of $120\text{ to }180\text{ }^{\circ}C$ for average materialistic evaluations. For normal, commercial LDPE, the melting point is commonly $105\text{ to }115\text{ }^{\circ}C$. With the different sorts of PE, these values differ unequivocally.

1.2.2.3 Chemical Properties

PE is mostly crystalline and its chemical conduct is like paraffin. They have a tendency to crystallize due to their regular sub atomic framework. PE comprises saturated, high molecular weight hydrocarbons, and non-polar. The distinctive macromolecules are not covalently connected. They have resistant to reducing agents and mild oxidants and are also not assaulted by solid bases or solid acids because of their great chemical resistance. They have good chemical and mechanical stability because of higher crystallinity. At room temperature, crystalline models do not liquidify. At elevated temperatures, for the most part, PE might be disintegrated in aromatic hydrocarbons, for example, xylene, and toluene or in chlorinated solvents, for example, trichlorobenzene or trichloroethane. Polyethylene retains no water. For most plastics, PE has lower water vapors and gas porousness. Flavorings, oxygen, and carbon dioxide and then again can pass it effectively.

When presented to sunlight, PE can emerge as brittle, as a UV stabilizer carbon black is typically utilized. PE consumes gradually emits a scent of paraffin having a blue flame with a yellow tip. The material creates a drip and keeps consuming on the evacuation of the source of flame. Without pretreatment, PE can't be fastened together or designated.

1.2.2.4 Electrical Properties

PE present decent tracking protection, and also have great electrical resisting characteristics, on the other hand, it becomes effectively electrostatically charged (which can be lessened by augmentations of carbon dark, graphite or antistatic agents).

1.2.2.5 Optical Properties

PE varies among milky-opaque (translucent), opaque, or almost clear (transparent) count on film thickness and thermal history. LDPE in this way claims the best, LLDPE somewhat less and HDPE the slightest transparency. Crystallites decreased the transparency is in the event that they are bigger than the wavelength of obvious light.

1.3 Classification

PE is typically characterized by its branching and density. The degree and sort of branching, the molecular weight, and the crystal structure are the factors on which the mechanical properties of the PE are mainly depended. PE has many types:

1. Linear low-density polyethylene.
2. Low-density polyethylene
3. Very low-density polyethylene
4. Chlorinated polyethylene.
5. High-density polyethylene.
6. Medium-density polyethylene.
7. High-density cross-linked polyethylene.
8. Cross-linked polyethylene.
9. Ultra-high molecular weight polyethylene.
10. Ultra-low molecular weight polyethylene.
11. High molecular weight polyethylene.

1.3.1 Low-Density Polyethylene (LDPE)

The characterization of LDPE is mainly based on its density domain of 0.91– 0.94 g/cm³. The chains of LDPE are not compact into the crystal framework because of its high level of the long and short-chain system. LDPE has less instantaneous dipole induced dipole attraction because of its average strong intermolecular forces. Due to this, LDPE has increased ductility and low tensile strength. Through free-radical polymerization, LDPE is formed. Liquid LDPE has novel and attractive stream characteristics because of its high level of fanning and long-chain branching. LDPE has a wide range of applications; typical utilization includes plastic sacks and film wrap. The worldwide market of LDPE in 2013 had an extent of nearly US\$34 billion [6].

1.3.2 High-Density Polyethylene (HDPE)

The branching level of HDPE is low. HDPE is characterized by a density of more prominent or equivalent to 0.94 g/cm³. HDPE has strong intermolecular forces because mainly the linear particles are pack firmly compare to high branched polymers. The little measure of branching that occurs can be structured by selecting reaction conditions and catalysts. High-density polyethylene might be delivered by metallocene catalysts Cr/Si catalysts or Ziegler-Natta catalysts. The development of PE particles mainly depends upon the free radical's arrangement which is favored by these catalysts. These catalysts make virgin monomers of ethylene add to the ends of the atoms, as opposed to with the center, forming the linear chain development. The elasticity of high-density polyethylene is high. It is utilized as a part of items and packaging, for example, butter tubs, detergent bottles, water pipes and garbage containers. 33% of all toys are fashioned from HDPE. The worldwide utilization of HDPE in 2007 achieved 30 million tons of volume.

1.4 Classification of Plastic Recycling

Plastic waste is made out of a few sorts of plastic. In this manner, it is essential to find out the incorporated in the life cycle of an item and what sort of reprocessing technique is the best one for every function with respect to financial and ecological rationalities. Life cycle appraisal is a target procedure to assess natural and assets influence related along with a product, procedure or action by recognizing and evaluating vitality and utilization of material and circumstantial discharges. "The environmental impact can be

evaluated in terms of local, regional and global influence"[7]. Recycling of plastic waste includes various techniques which are the following:

1.4.1 Primary Recycling

Primary reprocessing is also called mechanical recycling, in which from the fundamental material, the plastic waste is sustained into standard generation procedure. In this way, from the first one, once can get a product with an indistinguishable grade of the stipulation. (*Zahavich A. T et al, 1997.*)By the debased plastic waste, the new material is halfway alternated, therefore in the feed adulteration with an expanding reused plastic segment, the characteristics of the product diminishes. This type of plastic reusing technique needs uncluttered and not debased misuse of an indistinguishable sort from the virgin resin.

Therefore, the following advances from the particular reusing technique:

- The waste must be arranged by particular resins sorts and arranged by various colors.
- Washing of waste is necessary.
- The waste must be re-expelled into pellets for excelling melting characteristics results.
- The particular pellets are accumulated to the first rosin.

Due to the necessities with respect to the plastic properties said over, this sort of reusing is extremely costly contrasted with others. In the event that the waste is anything but difficult to sort by resin, however hard to pelletize because of contamination or coloring. With respect to the reactant's properties, it is conceivable that the waste is feed into a molding operation which is meagerly requesting.

1.4.2 Secondary Recycling

A few procedures to reuse plastic waste as a part of lower significance (less costly item) with respect to the item setup. In a generation procedure of clump, e.g. blended or adulterated waste is utilized to accomplish good outcomes because of various material characteristics. In this reprocessing technique to accomplish commercial benefits, the goal is to reserve a portion of the energy for plastic production utilization. This recycling

technique is agreeing to polluted or less isolated waste contrary to primary reusing. This waste must be purified in any case, (*Zahavich A. T et al, 1997*) the reusing procedure is distinctive contrasted with the standard production technique and includes an alternate item.

1.4.3 Tertiary Recycling

The alleged cracking procedure includes the degradation of plastic waste with or without utilizing catalyst (thermal and catalytic pyrolysis) retracts to raw material. The quantity of carbon molecules in an atom differs pretty much (the conveyance relies upon the catalyst) and the particular atoms consist of shorter chains of carbon than the un-broke molecules. In any chemical generation technique as fundamental material of low class, this raw material can be utilized (e.g. polymerization or fuel manufacture), with the goal that the standard esteem of the feedstock is extinct. Because of elevated amounts of waste contamination, the tertiary reusing process gets increasingly critical.

1.4.4 Quaternary Recycling

In this reprocessing technique, just the energy measure is recouped. As a result of the excessive heat measures of general plastics, most of the plastic waste is burned. This procedure produces reliable heat energy which is the main benefit of this recycling technique. The leftover of the particular burning, which shapes 21 wt % individually 9 vol % of the standard waste, is set in disposal areas. All things considered, this reusing procedure transfers the issue to an air contamination one, yet not resolves the substantial waste issue.

1.5 Thermal and Catalytic Degradation

Both catalytic and thermal degradation belongs to the group of tertiary recycling procedures. When the process temperature achieves a specific value, the structure of the polymer particles ends up noticeably temperamental. This causes the carbon chain to split into a few raw particles besides lesser carbon atoms having a place with every molecule than the paradigm. The product classification is usually extensive and operation temperatures approximately 890°C are needed by utilizing thermal cracking as a reusing technique. In the pilot plant experiments, this process is extremely notable because the thermal degradation technique utilizes fluidized beds or kilns. **Figure 3** shows the

thermal and catalytic energy requirement profile and we can see that catalytic degradation is energy efficient.

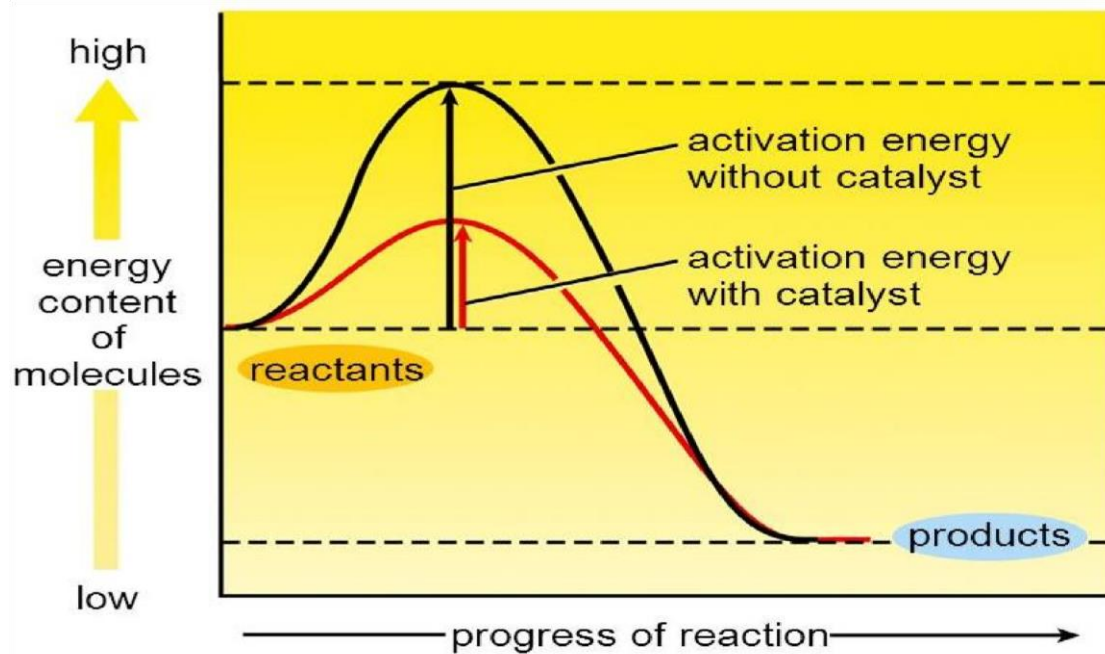


Figure 3: Thermal and Catalytic Process Energy Profile

Catalytic pyrolysis has following benefits over thermal cracking:

1. Cracking temperature is reduced.
2. The degrading capacity of plastics is superior,
3. The aggregation of solid deposition in the product is less
4. Furthermore, large selectivity to fluid items and the confined item classification with a pinnacle at light hydrocarbons in the boiling point ranges of engine fuel.

In this manner, the energy costs from one perspective and the expenses of resulting updating system [9] although are less, so compare to thermal cracking, catalytic cracking is less expensive. As opposed to the primary reprocessing technique, e.g., reprocessing of waste which is diverse to discrete or is just accessible in restricted amounts or plastics which hold remote issue and non-PVC rosins of polluted plastics are include in catalytic cracking. In spite of the fact that while burning, the heat rate of plastics is excessive, the nature of customary fuels is less awful than the nature of plastic-originated fuels with

respect to burning related maintenance and expenses. In this manner, plastics-derived fuels are just utilized as a part of energy profound applications and the goal of logical examinations is to expand the nature of the particular fuels. The catalyst and the plastic are in touch and these are incinerated to reaction temperature in the shut environment in pilot plant tests. The quantity of gas and liquid is removed after a specific time interval and analyzed in a GC (gas chromatography).

1.6 Catalysis

Because of the support of an extra material termed as a catalyst, a substance that changes the reaction rate but not consumed in the process. Catalyst isn't consumed in the catalyzed reaction and can keep on acting over and again. Regularly just little measures of catalyst are required on a fundamental level. Since catalyst needs a smaller extent of activation and initiation energy, this is the reason that they increase the reaction rate. In catalyzed processes, they normally operate and respond to structure a transitory intermediate which at that point recovers the standard catalyst in a periodical procedure. There are two forms of catalysts heterogeneous or homogeneous. In homogeneous catalysis, the reactants and the catalysts are present in the same phase. While in heterogeneous catalysis, the reactants and catalysts are not present in the same phase. Biocatalysts and enzymes are frequently considered as a third classification. **Figure 4** shows the activation energy profile and we can see that catalyst lowers the activation energy providing a different pathway for the reaction.

1.6.1 Types of Catalysts

The catalyst is classified into the following major types: [10]

1. Homogeneous catalysts
2. Heterogeneous catalysts
3. Electrocatalysts
4. Organ catalysts
5. Photocatalysts
6. Nanocatalysts
7. Enzymes and biocatalysts
8. Tandem catalysis

9. Autocatalysis

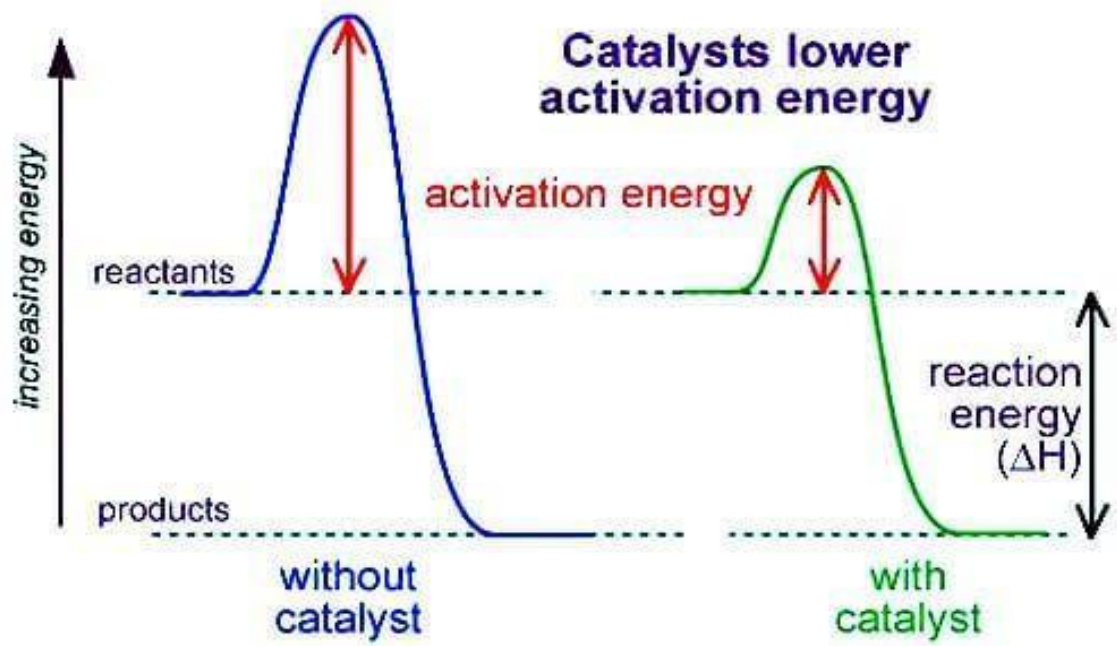


Figure 4: Activation Energy Profile with and Without Catalyst

Chapter 2

Literature Review

2.1 Previous Work on Recycling of Plastic Waste

In the mid- to late-nineties, Europe was creating 13.6 billion kgs (40 billion dollars) of post-consumer plastic waste every year and the U.S. was producing over 20 billion kgs (58 billion dollars) yearly [11]. The majority of indicated waste is arriving replete or burned; just 7% is reused (to poor quality plastic items) so limpidly enhance developed and worthwhile technique for reusing is required. while public interest elevates and government guidance turns into more stringent, advanced techniques, similar to the utilization of zeolite catalysts, do progressively investigated while methods for reprocessing plastic waste to an important frame. Customary reusing of plastics includes compounding blended post-consumer plastics and washing to create ordinary items with extensive properties, containing impurities and unappealing colors. Unconventional techniques (tertiary reusing strategies) depolymerize plastic waste, i.e. degradation of the polymer occurs back to the monomers or more to the unprocessed substances from which marketable plastics are formed [11]. On the off chance that this is accomplished, a vastly improved item might be produced from the reused substance (material). Recently developed systems have incremented the global quality of plastic, and that could be reused and also diminished the requirement for exorbitant disseverment of various plastic composes. The items acquired utilizing developed reusing methods are "virtually indistinguishable" against these produced using celibate materials. In contrast, reusing to virgin engenderment, 15.4 GJ of energy might be preserved per ton of plastic while engendering minor air ejections. The waste issue has generated an extensive variety of investigations containing the debasement of polyethylene to oils by utilization of critical water [12] and more inventive methodologies, for example, the debasement of plastics by the utilization of fungi capable for discharging and depolymerization [13]. Nowadays the reusing of plastic

substances is generally accomplished by utilizing homogeneous polymers. Consequently, a dissection from a domestic amassment of plastic items is compulsory since reusing activity. The most straightforward method for disjunction is by flotation in the water, i.e. the distinctive plastics disjunction in view of the diverse densities with regard to water. This implies all the plastic substances are isolated in a small portion for the most part of polyethylene and polypropylene and in an abundant division essentially of poly terephthalate and polyvinyl chloride (PVC). The reusing of the small fragment should, on a basic level, be simple in view of the comparative likeness of the component's chemical structure. The existence of modicum of polystyrene foam (lower density than water) in other words any polymer, for example, non-polymeric contaminations or PVC can, in any case, cause the properties of the auxiliary substance very poor. The integration of wood filaments (20-40 wt %) prompts a surprising increment in the elastic modulus whilst prolongation at rupture or impact strength reduction and the tensile strength practically unaltered. Thermo mechanical characteristics are additionally amended. In spite to amend particular characteristics, two functionalized models of polypropylene have been utilized as attachment promoters. The pairs of polypropylene grafted acrylic acid and polypropylene-grafted maleic anhydride ameliorate the mechanical properties specifically at the minor congregation. In order to get important items from plastic waste, it is essential to heat the plastic waste customarily in an inert atmosphere of hydrogen gas and permit to degrade plastic waste thermally. Thus, the technique is generally utilized to pristine or high-grade waste in a plastic-handing industrial facility, commonly known as mechanical reprocessing technique and, even after the characteristics of particular items incline to be of low quality. Mostly in modern large-scale plants usually plastic recycling is done, which are generally situated close centers of high populace density where sensible amounts of feedstock exist. Lately most mechanical reusing needs a flow of particular resins, which might be recycled into items, for example, pellets that bare nearby similarity with respect to the virgin counterparts. This viably implies that waste plastics compelled for reusing essentially be arranged within particular resins forms, arranged by color in some situations, cleaned and re-adjusted into pellets. This causes it a genuinely costly intensive

procedure. [Hardman et al.,] utilized a fluidized bed composed of silica, quartz sand or other refractory materials. The temperatures proposed were generally high in the domain of 450 °C to 550 °C. The thermal degradation items demonstrate a wide item distribution need to be more preparing for their characteristics to be redesigned [11] [14].

Over the years, Public demand for reprocessing and a customary want to occupy waste from disposal area or burning has prompted a noteworthy increment in roadside accumulation programs for reprocesses. An assortment of substances ranging from metal plastic to paper is gathered. Furthermore, a few jurisdictions handle household organics (kitchen squanders) and in addition compostable yard waste (brush and grass). By a wide margin, most plastics gathered are polyethylene milk jugs and PET soft drink bottles [14]. If a catalyst is included, anyhow, lesser exorbitant accomplishing circumstances can possibly be utilized and the cracking might be significantly faster.

2.2 Zeolite Based Catalysts

Zeolites are Microporous crystalline solids with all around characterized frameworks. For the most part, they accommodate aluminum, silicon and oxygen in their structure and cations, water as well as different molecules inside their pores. Most of these happen normally as minerals and are widely excavated across the world. Rest are manufactured and are fashioned economically for particular applications, or delivered by investigating researchers endeavoring to see further regarding their science. Due to their exceptional permeable characteristics, zeolites are utilized in many applications with a worldwide market of several million tons per annum. In the western world, significant applications are in, ion exchange (purification and water softening), petrochemical splitting and in the detachment and abstraction of gasses and solvents. Additional uses are in construction, horticulture and animal tillage. Zeolite is regularly exemplified as molecular sieves. They assign to safer, pure environment an incredible number of approaches. Indeed proximately each use of zeolites has been compelled by ecological interests, or performs a noteworthy part in diminishing energy consumption and reducing toxic [15].

In powder cleansers, zeolites superseded deleterious phosphate originators, presently prohibited in several regions of the world in view of water contamination dangers. Catalyst, by the statement, makes a chemical reaction likewise proficient, hence indirectly reducing pollution and saving energy [16].

Also, mechanisms might be completed in less advance, limiting by-products and unnecessary waste. Zeolites as strong acids decrease the requirement for acids corrosive fluid, and as sorbents and redox catalysts, might abstract air contaminants, for example, ozone-depleting CFCs and engine exhaust gases. Zeolites can likewise be utilized to isolate destructive constituents out of the water, and in expelling cumbersome metal particles, these created through atomic fission, out of water.

There are four properties which make zeolites particularly fascinating for heterogeneous catalysis:

- They contain replaceable cations permitting the induction of molecules accompanying different properties.
- Whenever H^+ is replaced, it produces a greater representation of extremely strong acid sites.
- The pore diameters of zeolites are less than 10\AA .
- The discrete sizes of particular pores are 1 or maybe more.

Zeolites have received a lot of consideration from researches as of late due to their shape selectivity and catalytic properties. ZSM-5 and Silicates.

The catalyst utilized in these experiments is a zeolite HZSM-5 (H implies this is the hydrogen form). This group of zeolites acquire average pore areas (cavities with a spherical diameter of 0.9nm , a critical diameter of 6.3\AA) and comprises of connected ten-component enclosure of interchanging oxygen and silicon atoms having general formula $Na_nAl_nSi_{96-n}O_{192}.16H_2O$ (where $n < 27$ and more often than not around 3. Over their channel framework zeolite give an excessive deal of chemical reaction and molecular transportation bias that comprises straight pores and intimate sinusoidal. The configuration of zeolite cannot be fundamentally influenced by the Si/Al proportion i-e 5-8000. However, the properties like hydrothermal, thermal and acid strength access by

increasing Si/Al proportion. The number of Al atoms existing identified the number of acid stability and thus acid sites. Hence by decreasing the Si/Al ratio, the strength of a zeolite's acidity increases and possibly as good as to strong inert acids such as concentrated sulphuric acid.

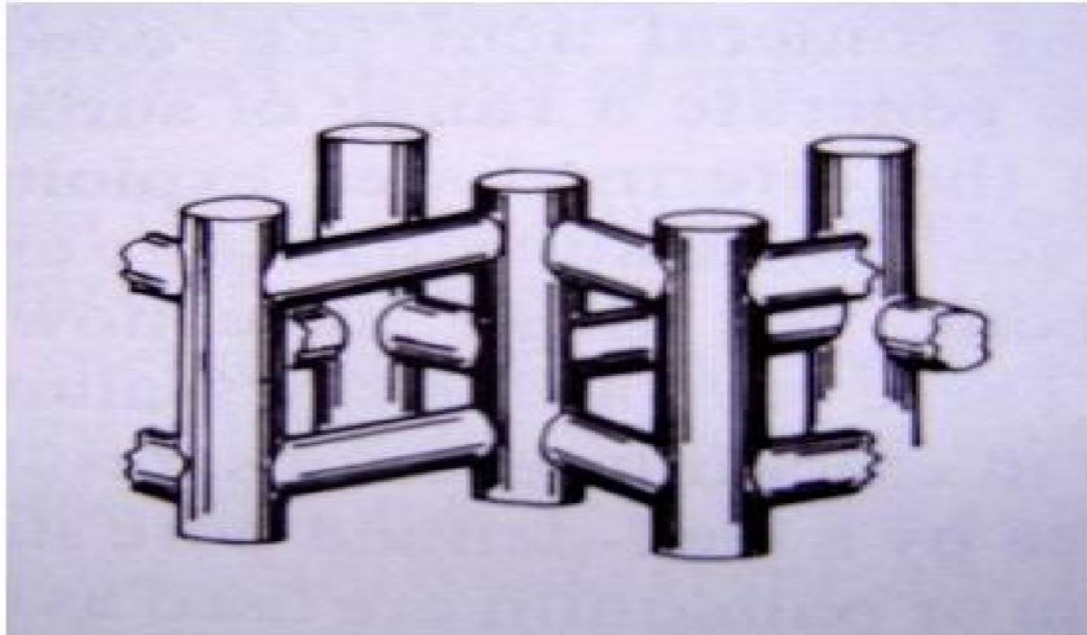


Figure 5: Illustration of the Two Types of Switching Pores of Zeolite

[Source: Toju S. Kpere-Daibo Department of Chemical Engineering University College London]

Silicalite is defined as, chain-type building, two dimensional, obstructs (secondary building segment) in whatever place SiO_4 -and SiO_2 -segments are individually collected. Additionally, ZSM-5 is a secondary building segment, but it is comprised of Al-atoms rather than it contains Si-atoms. ZSM-5 demonstrates a minor coking disposition and accommodate pores of roughly 5.2 to 5.8 Å. In FCC gasoline productions, the constitution of octane and olefin can be enhanced by the addition of ZSM-5. The interval of chain-type building segments can be increased by scorching O-atoms to shape a layer. The apertures of these layers comprise a size of very extensive molecules. The three-dimensional configuration of ZSM-5 and silicalite is representing in Figure 5. This configuration consists of intra-crystalline pores. In these

particular cavities, numerous little molecules can be dispersed, where they changed catalytically. The sizes of openings are greatly reliant on the amplitude of the encapsulated cations, which hinder the apertures most of the time. For any reactant, the acute molecular dimensions, the dimensions for the cavity area and the average channel size are essential to the different zeolite uses. Typical utilization of zeolites is molecular sieving accordingly of particular dimensions. This is correlated to channel molecules which are bigger than the basic molecular size. The average channel size is between 0.4 and 0.74 nm, the cavity size assort among 0.66 and 1.3 nm. Because of its little channel size (0.53 to 0.55 nm) and in this way less over cracking, the principal results of cracking polymers over these catalysts (ZSM-5) are olefins [17].

The configuration of aluminosilicate gets Al^{3+} , Si^{4+} and O^{2-} ions. To accomplish ZSM-5, Si^{4+} is supplanted by Al^{3+} . In order to keep the particle electric neutral, positive non-structure particles (atoms) must be accumulated. The charges of these ions are different. The properties of the zeolite-construct catalyst are intensely reliant with respect to these embedded cations. In this way, one can alter the catalyst's properties effectively through ion exchange. The catalyst configuration is critical with respect to the ion exchange capacity, e.g. catalyst comprising numerous Al^{3+} ions contrasted with Si^{4+} ions allow excessive catalytic site concentrations than others, in light of the fact that the atoms accommodate innumerable encapsulated cations. Because of a greater concentration of inserted and encapsulated cations, the ion exchangeability and the acidity of the molecule are escalating with a diminishing Si/Al proportion. All of these atoms demonstrate an extraordinary affinity to water. Si/Al proportion is usually a function of hydrophilicity of a material. With an escalating Si/Al proportion,

- In the presence of concentrated acid, the strength of the crystal anatomy is escalating.
- In subsistence of solutions, the strength of the crystal anatomy is diminishing.
- The atomization temperatures are escalating.
- The proton donor's ability is finally escalating.

Stability at high temperatures and the high number of catalytic sites are the two considerations why zeolites are extensively and mostly utilized industrial catalysts.

2.3 Dolomite

Though pyrolysis is a good option for the recovery of petroleum products from plastic waste, the process requires high investment and process cost and yield obtained is comparatively low. The use of expensive catalysts makes the process more expensive, so there is a need to find out cost-effective catalysts which will help to minimize the process costs and will enhance the quantity and quality of the liquid product. Dolomite is a very cost-effective catalyst with calcium and magnesium source. There is one study on the effect of dolomite in pyrolysis of plastic waste [18]. It shows a good effect of dolomite on the pyrolysis of plastic waste after heating at 900°C. The present research focuses on the use of raw dolomite for enhancing the quantity and quality of liquid fuel in the pyrolysis of HDPE, LDPE. Waste low-density polyethylene milk carry bags were used as raw material. Screening and selection of catalysts were done depending on cost-effectiveness, easy availability, and stability of the material and for enhancing quantity and quality of liquid fuel product at low temperature. It was observed that among the Scolecite and Dolomite, Dolomite is the best catalyst in pyrolysis as it fulfills most of the criteria decided during the study. Liquid fuel samples obtained without catalyst and with catalysts were characterized for GC-MS and calorific values. It showed an increase in the concentration of C10-C20 hydrocarbon fractions and calorific values of liquid fuel samples obtained with Dolomite as compared to Scolecite and without catalyst [19]. Shwedaung clay, Mabisan clay, Bentonite clay, Dolomite and zinc oxide were used as catalysts for the pyrolysis of mixed plastic wastes. Mixed plastic wastes include HDPE, LDPE, PP, PS and PET. Pyrolysis processes were carried out at the temperature range of 32 – 380 °C for 1.5 hours [20][21].

Table 2 is a brief summary of some of the previous work on waste polyethylene plastic conversion to useful products using catalytic and thermal degradation.

Table 2: Previous Work Done on PE Degradation

Plastic	Pre-Process Conditions	Catalyst	Operating Conditions	Gas Yield	Liquid Yield	Ref.
HDPE, PS, PP, and PET	10 g plastic mixed with 1 g catalyst	Fe-, Ti-, Zr- and Al-pillared clays	300-500 °C	30 % H ₂ , CH ₄ , CO, CO ₂ , and C ₂ , C ₃ gases.	70 % heavy hydrocarbons > C ₁₃ and some fraction of alkenes	[22]
LDPE	NiO catalyst mixed with 15 g LDPE and 500 g SiC.	NiO and HY zeolite		H ₂ , light alkenes, and alkanes about 30-40%.	Liquid products in gasoline range about 50-60% over different ratios of catalyst.	[23]
Cellulose/PE Mix	A 200 mg of CPE mixed with catalyst	3 Clays (K10 – montmorillonite K10, KSF – montmorillonite KSF, B – Bentonite)	400–500 °C		Bio-oil obtained contains cellulosic products as well hydrocarbons > C ₁₀	[24]
Polyethylene (PE)	_____	Ni-Ce bimetallic catalyst	600-800 °C	The major fraction of H ₂ and		[25]

				smaller fractions of CO CO ₂ and CH ₄		
HDPE, LDPE And PP	_____	Alumina, scolecite, dolomite, ceramic powder, white cement, sand and red brick powder.	400-450 °C		Alkanes and alkenes in range of C ₈ and bigger molecules	[26]
PE and PP Mix	_____	HZSM-5, USY and NH ₄ ZSM-5	450 °C	Gaseous products in range C3-C7	Alkyl benzenes, naphthalene.	[27]
Yellow Paper and HDPE	_____	Microporous HZSM-5 and mesoporous Al-MCM-41	600 °C	C ₂ -C ₄ Alkenes, C ₁ -C ₄ Alkanes CO and CO ₂	Benzene, Toluene and Xylene.	[28]

Chapter 3

Materials and Method

3.1 Experimental Equipment

The pilot plant fabricated for the complete pyrolysis of the plastics and collection of the products consisted of the following equipment:

3.1.1 Reactor

The reaction conditions for these particular reactions were not very severe, requiring a temperature of around 400 °C and atmospheric pressure. Therefore, the material of construction for the reactor was chosen to be standard carbon steel. The reactor was cylindrical in shape, with a diameter of 6 inches and a length of 12 inches as shown in **Figure 6**.

The reactor was fixed with a lid having a diameter of 8 inches and a thickness of 1 inch which could be flanged shut when the reaction was in progress. A round sieved plate of diameter 6 inches and 1 cm thickness was installed in the middle of the reactor acting as catalyst and material bed. This sieved plate allowed the liquid to pass through and exit at the bottom. The flanged lid allowed easy access to the inside of the reactor which aided in the cleaning of the reactor. This also served as the entry point for the feed and the catalyst. Additionally, there was a PVC gasket attached to the lid that prevented any gases, evolving during the reaction, to escape the reactor through the lid.

3.1.2 Expansion Chamber

Even though the reaction did not have any pressure requirements for its completion, allowing the gases to build up in the reactor, constantly checking the pressure inside the reactor in order to allow the production of the gases. As a result, the gases, when allowed to leave the reactor were at a pressure around 2 bars. This pressure was more than what the condenser fitted after the reactor; therefore, an expansion chamber was installed to relieve some of the pressure of the gases. The material of construction of this chamber was the same as the reactor. This chamber was also cylindrical, with a diameter of 3 in. and a length of 9 is shown in **Figure 7**.



Figure 6: Reactor

3.1.3 Condenser

The main purpose of the condenser was to cool the mixture of gases evolving from the reactor so that it could be collected for further tests. A shell-and-tube type condenser has been used for this purpose, with one shell pass and two tube passes, the hot gases were passed in from the tube side, while the coolant (water at r.t.p.) was passed in from the shell side. Both the shell and tube were made of silica glass shown in **Figure 8**.



Figure 7: Expansion Chamber



Figure 8: Condenser

3.2 Instrumentation

For the proper monitoring of the conditions of the products and reactants alike, the pilot plant was fitted with a number of temperatures, pressure, and level indicators at numerous locations. Although the reaction conditions (pressure and temperature requirements) of the process are not very harsh in order to enhance the efficiency and conversion of the products, these instrumentations are required. The reactor assembly was fitted with various temperature, pressure and level indicators as follows:

3.2.1 Pressure Indicators

The process required the monitoring of pressure at three different locations on the pilot plant, therefore, each of these locations was fitted with a pressure gauge. The specifications of the gauges varied according to their use and location. The gauges were labeled P1, P2, and P3. The details are given in **Table 3** below.

3.2.2 Temperature Indicators

The process required monitoring of temperature at certain locations, so these locations were fitted with bimetallic strip temperature gauges. There was a total of 2 temperature gauges installed (T1 and T2). The specification is given in **Table 4** below.

Table 3: Pressure Gauge Specifications

Pressure Gauge	Location	Dial Diameter/in	Pressure Unit	Range	Graduation	Port Size/in	Port Location
P1	On Reactor	2	Bar (psi)	0-35 (0-500)	1 (10)	0.5	Bottom
P2	On Expansion Chamber	2	Bar (psi)	0-35 (0-500)	0.05 (0.5)	0.5	Bottom
P3	After the Condenser	2	Bar (psi)	0-35 (0-500)	0.05 (0.5)	0.5	Bottom

Table 4: Temperature Indicators Specifications

Pressure Gauge	Location	Dial Diameter/in	Pressure Unit	Range	Graduation	Port Size/in	Port Location
T1	On Reactor	3	°C (°F)	0-500 (30-930)	5 (10)	1	Back
T2	After Condenser	4.5	°C (°F)		1 (2)	1	Back

3.2.3 Flow Indicators

There was two positions in the assembly where a flow indicator was needed. The flow meters used were rotameter and were located after the condenser and after the nitrogen cylinder. One point was the position of the discharge of the products; therefore, a flow meter we needed to calculate the yield of the process. And after the nitrogen cylinder to control the flow of nitrogen in the reaction chamber. The specifications of both rotameters are given in **Table 5**.

Table 5: Rotameter Specifications

Dial Length/in	Flow Rate Unit	Range	Graduation	Port Size/in	Port Location
3	L/min	0-1	0.1	0.75	Back

3.3 Assembly

All of this equipment was connected together, to form a complete setup, with rubber pipes of an inside diameter of 0.5 in. according to the following process flow diagram (PFD) **Figure 9**:

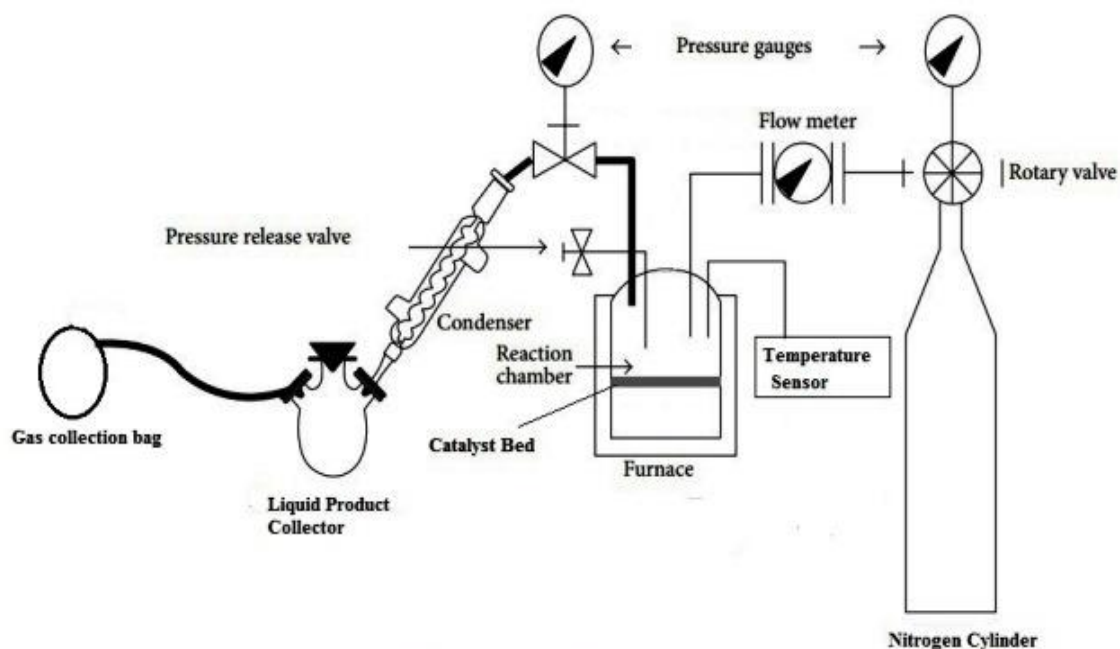


Figure 9: Process Flow Diagram (PFD)

Furthermore, this assembly was mounted on a frame, made up of mild steel rods, with the following dimensions given in **Table 6** here.

Table 6: Assembly Frame Specifications

Length/ft.	Width/ft.	Height/ft.
5	2	4

Figure 10 shows all of the equipment mentioned combined to form a complete reactor assembly mounted on an iron frame specification mentioned in **Table 6**.



Figure 10: Reactor Assembly Mounted on Frame

3.4 Experimental Procedure

3.4.1 Fuller's Clay and Metal Oxides Mixture as Catalyst

For the first four experiments with fuller's clay and metal oxides, 20-gram fuller's clay for first-run then 10 g of fuller's clay and 10 g of each metal oxide (ZnO, Fe (III)Oxide, Ni Oxide) was blended together in a powder mixture for 30 minutes in order to ensure the homogenous mixtures. These mixtures are then dried in an oven. After drying the samples at 150 °C for 35 mins and allowing it cool to room temperature, 20 g of catalyst and 100 g of polymer shards were weighed and fed into the reactor. Before feeding, the reactor was first purged to remove possible contamination. The mixture is heated with a 4000 W jacket heater to a temperature of 400 °C. **Figure 11 (a)** depicts cut up pieces of waste plastic bags. **Figure 11 (b)** is the reactor covered with insulation and heating jacket

before loading it with catalyst and plastic mixture and **Figure 11 (c)** is solid ash remains in the reactor after the process was completed and the reactor was opened to collect ash content for further analysis.

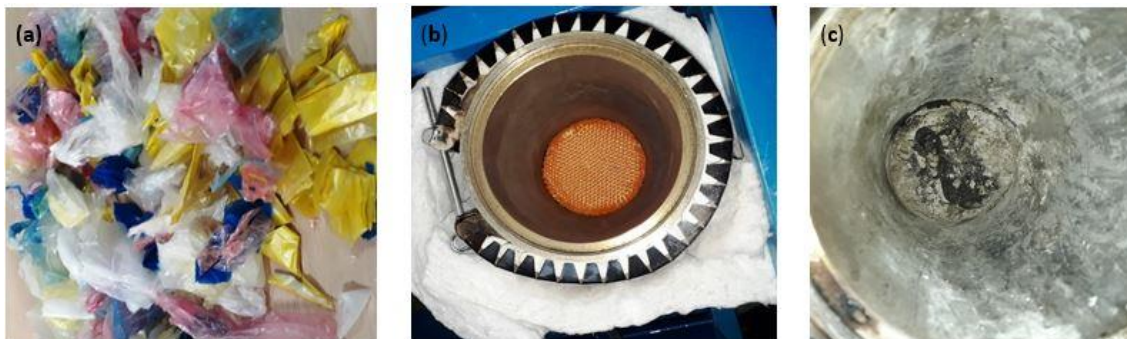


Figure 11: (a) Waste Plastic Bags (b) Reactor Before Loading (c) Solid Ash and Residue

3.4.2 Dolomite Zeolite and ZnO Mixture as Catalyst

For the next four experiments with Dolomite HZSM-5 and ZnO mixture, 10 g of Dolomite and 5 g of HZSM-5 and ZnO were used along with 100 g plastic keeping the plastic to catalyst w/w ratio 1:0.2. 20 g of catalyst and 100 g of polymer shards were weighed and fed into the reactor. Before feeding, the reactor was first purged to remove possible contamination. The mixture is heated with a 4 KW jacket heater to a temperature of 400 °C.

3.4.3 Altering Temperature Conditions

Next five experiments were done using different temperature conditions, and the plastic waste to catalyst w/w ratio was kept constant at 1: 0.2 (100-gram plastic 20-gram catalyst mixture) and the temperature was set at 400 °C first, then 425 °C, 450 °C, 475 °C and 500 °C in next four runs.

3.4.4 Different w/w Plastic to Catalyst Ratio

The next five experiments were done using different w/w plastic to catalyst ratio e.g. (1:0.1, 0.2, 0.3, 0.4 and 0.5. 10-gram catalyst mixture in which Dolomite (5 gram), ZnO (2.5 gram), and HZSM-5 (2.5 gram) mixture with 100-gram waste plastic bag shards, 1:0.1 plastic to catalyst weight ratio. Similarly, next four runs were done using 1:0.2, 1:0.3, 1:0.4 and 1:0.5 w/w plastic to catalyst fraction.

Chapter 4

Results and Discussion

4.1 Physical and Chemical Analysis of Catalyst Mixtures

The main polymer feed was waste polyethylene bags collected from different sources like the cafeteria, hostels, and garbage disposal bins. The feed was washed, dried and then cut into smaller shards manually. The catalysts utilized in this investigation were Fuller's earth clay (density 0.512-0.592 g/cm³) and Dolomite. Zinc oxide, Iron(III) oxide, Nickel(III) oxide and HZSM-5 were used as additives. The purpose of these metal oxides (Zinc Oxide, Fe(III) Oxide, Ni(III) Oxide) with Fuller's clay was to use as an additive to reduce the acidity of Fuller's earth clay having PH value in between 5 and 5.5. Furthermore, HZSM-5 as seen in past work helps the production of low boiling hydrocarbons. Dolomite and ZnO also have the benefit of increasing gas yield.

4.1.1 XRD Analysis of Fuller's clay and Metal oxide Mixture

X-ray powder diffraction (XRD) is a swift analytical method mostly used for the phase investigation of a crystalline solid sample. Unit cell dimensions information can also be collected by this method. The analyzed material is finely pulverized, mixed and homogenized and average bulk configuration is determined. When clay catalyst is blended with different metal oxides (Fe₂O₃, ZnO, NiO), it shows almost equal compositions of clay and metal oxides components which ensure the homogeneity and purity of the catalysts.

Catalyst phases were analyzed by the X-ray diffraction technique at room temperature. Clay and homogenous mixtures of Clay + ZnO, Clay + Fe₂O₃ and Clay + NiO show different phase profiles. Clay catalyst presents one high-intensity peak at 26.62 which is a characteristic line of quartz as shown in Figure 12. The homogenous mixture of clay and Fe₂O₃ gives a peak at 26.62 because the presence of Fuller's clay and all other peaks are consistent with the standard XRD pattern of α -Fe₂O₃ (hematite, JCPDS No. 24-0072)[29]. The homogenous mixture of clay and ZnO shows a peak at 26.62° consistent with the presence of Fuller's clay and all the other nine distinctive peaks detected in the 30–80 range is in agreement with the characteristic diffraction pattern of wurtzite

structured ZnO of hexagonal phase (JCPDS file: 36–1451) [30]. The blended mixture of clay and NiO presents one peak at 26.62° because of quartz (fuller’s clay) in the mixture. All the other peaks are in accordance with the typical diffraction pattern of cubic NiO (JCPDS 47-1049) [31]. The common peak in all four results at 26.62° confirms the presence of quartz in fuller’s clay and in all three blends. It also indicates the homogeneous mixing of metal oxides with clay.

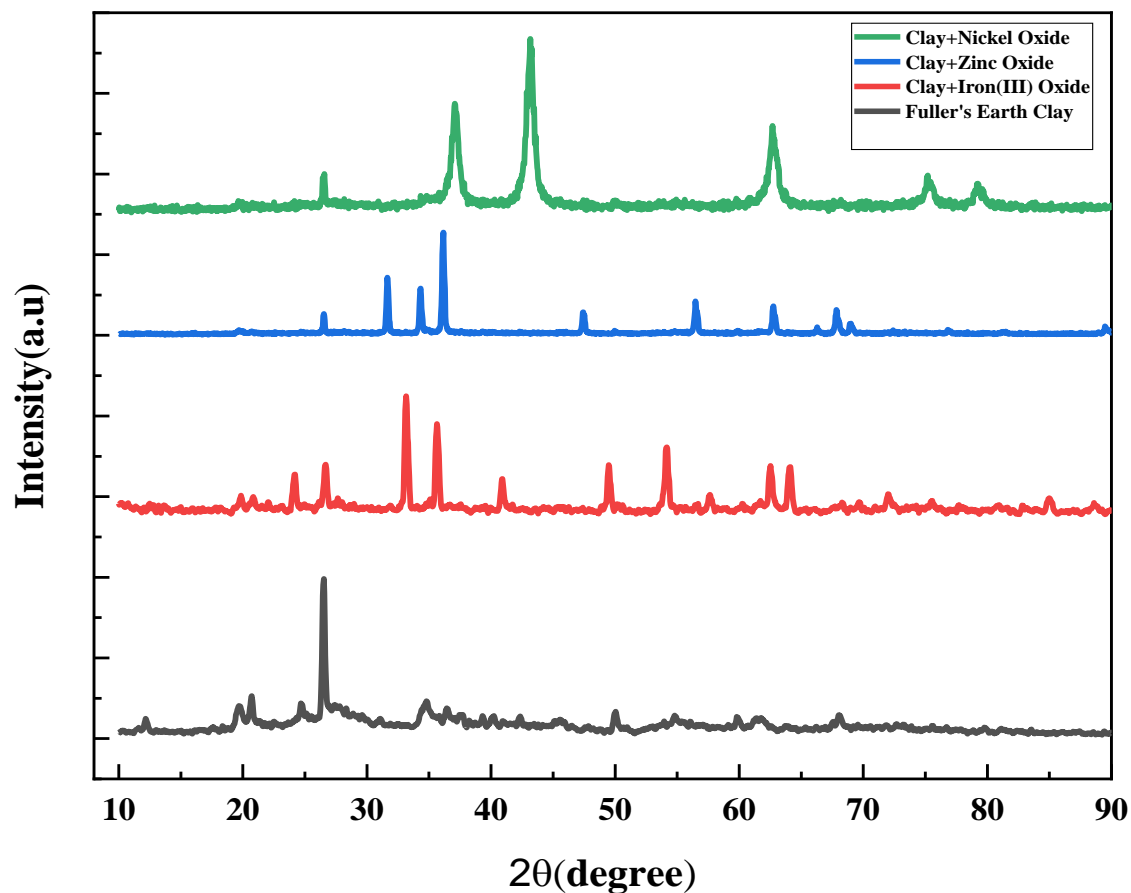


Figure 12: XRD Peaks of Fuller’s Clay and Metal Oxide Mixtures

4.1.2 XRD Analysis of Dolomite, ZnO, HZSM-5, and Mixture

XRD of dolomite, ZnO, and HZSM-5 show typical peaks of all the materials as expected in Figure 13. Dolomite shows its characteristic peak near 30° and four smaller peaks between 40° and 50° which confirms the presence of dolomites crystalline structure according to (JCPDS files card 11-78). Nine distinctive peaks detected in the 30° – 80° range are in agreement with the characteristic diffraction pattern of wurtzite structured ZnO of

hexagonal phase (JCPDS file: 36–1451) [30]. The XRD patterns of samples exhibit a small doublet at 6–10° 2θ along with a triplet at 22–25° 2θ representing the HZSM-5 framework [32][33]. The peaks in the mixture confirm the presence of all three materials. It also indicates the homogeneous mixing of HZSM-5 and ZnO with dolomite.

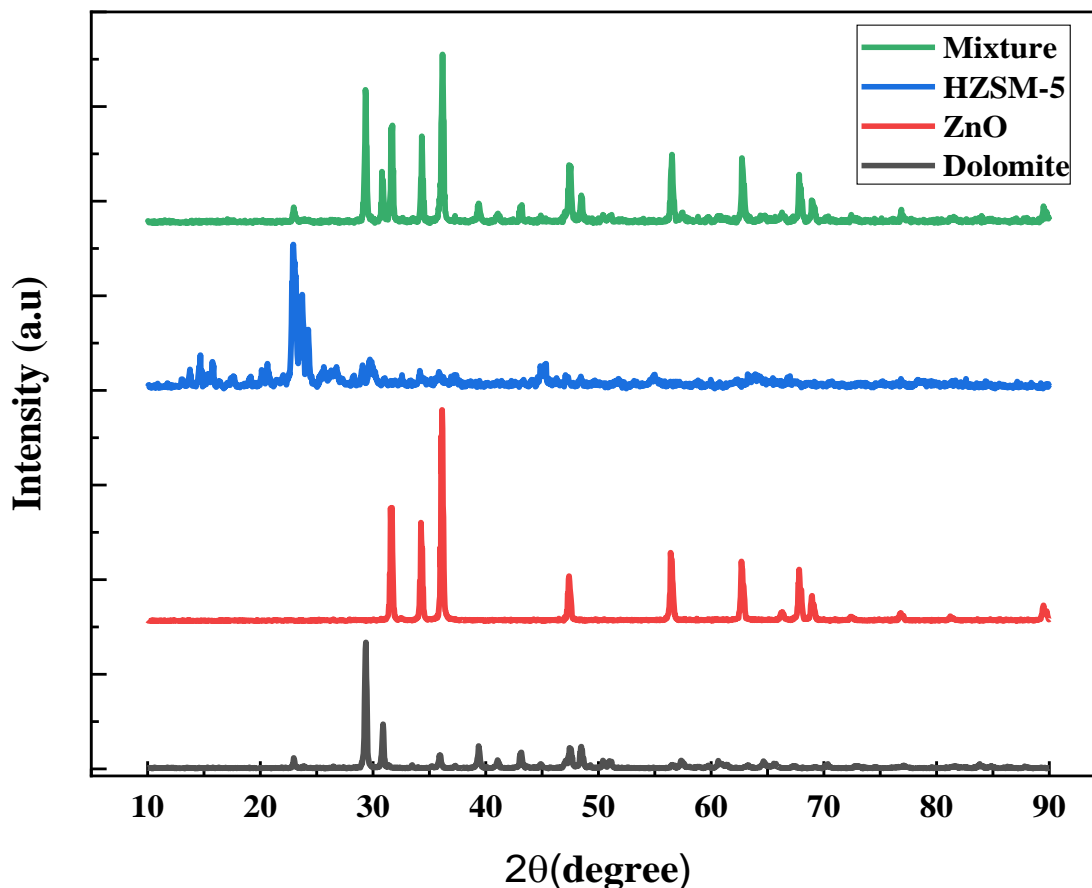


Figure 13: XRD Peaks of Dolomite, ZnO, HZSM-5, and Mixture

4.1.3 SEM Analysis of Clay and Metal Oxide Mixture

Some characteristic features of clays and clay minerals are more easily seen on the SEM than by other common techniques. These features involving surface and 3-dimensional aspects of clay minerals, such as the morphology (configuration) of samples.

The exterior surface morphology of Fuller’s earth clay is shown in **Figure 14 (a)** is Fuller’s earth exhibited plate-like arrangement with a coarse surface. **Figure 14 (b) (c)** and **(d)** is an SEM image of clay + zinc oxide, clay + iron (III) oxide and clay + nickel

oxide blend respectively showing a homogenous mixture is formed and metal oxide particles are dispersed on clay particles in a uniform manner.

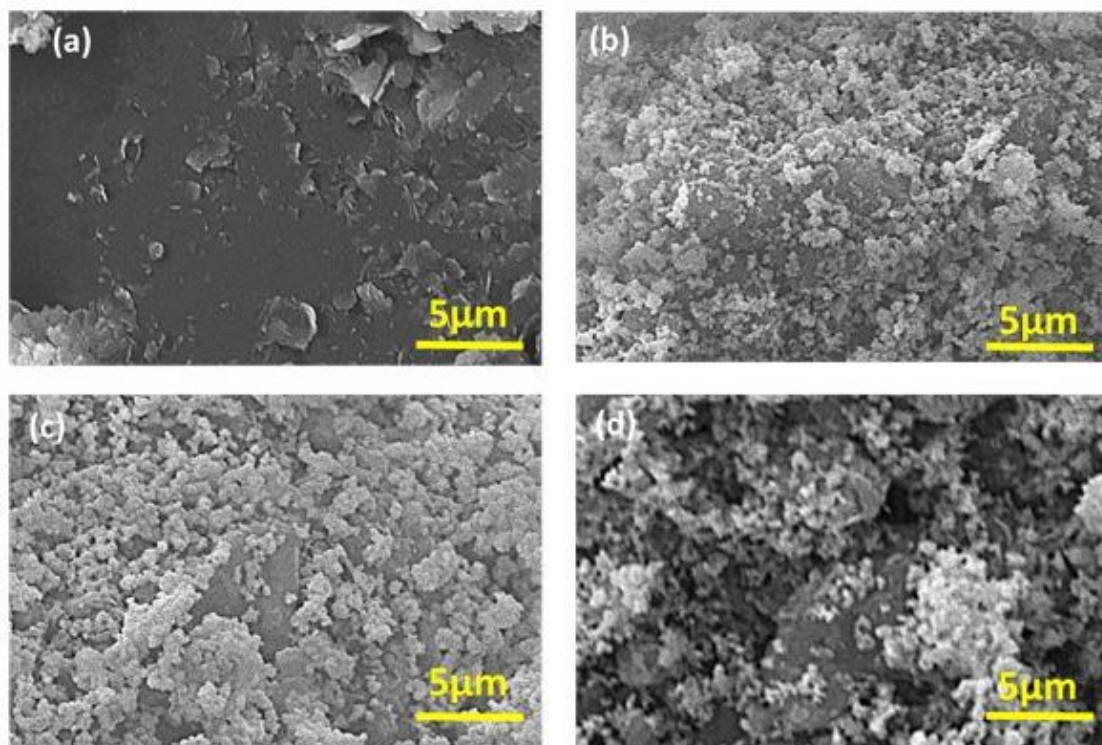


Figure 14: SEM image of (a) Fuller's Earth (b) Clay + ZnO (c) Clay + Fe₂O₃ (d) Clay + NiO

4.1.4 SEM Analysis of Dolomite, ZnO, HZSM-5, and mixture

Surface and 3-dimensional aspects of Dolomite and mixture catalyst, such as the morphology (configuration) of samples is shown in **Figure 15**.

Figure 15 (a) is an SEM image of ZnO particles and it can be seen that the particles possess a somewhat geometrical rhombic shape with some granules. **Figure 15 (b)** is dolomite's micrograph and dolomite particles are agglomerated and have granular morphology. **Figure 15 (c)** is SEM of HZSM-5 and it shows coarse particles of various sizes and powder-like distribution. **Figure 15 (d)** is an SEM image of a mixture of all three materials and it can be seen all particles are mixed together in a uniform manner and are dispersed over each other.

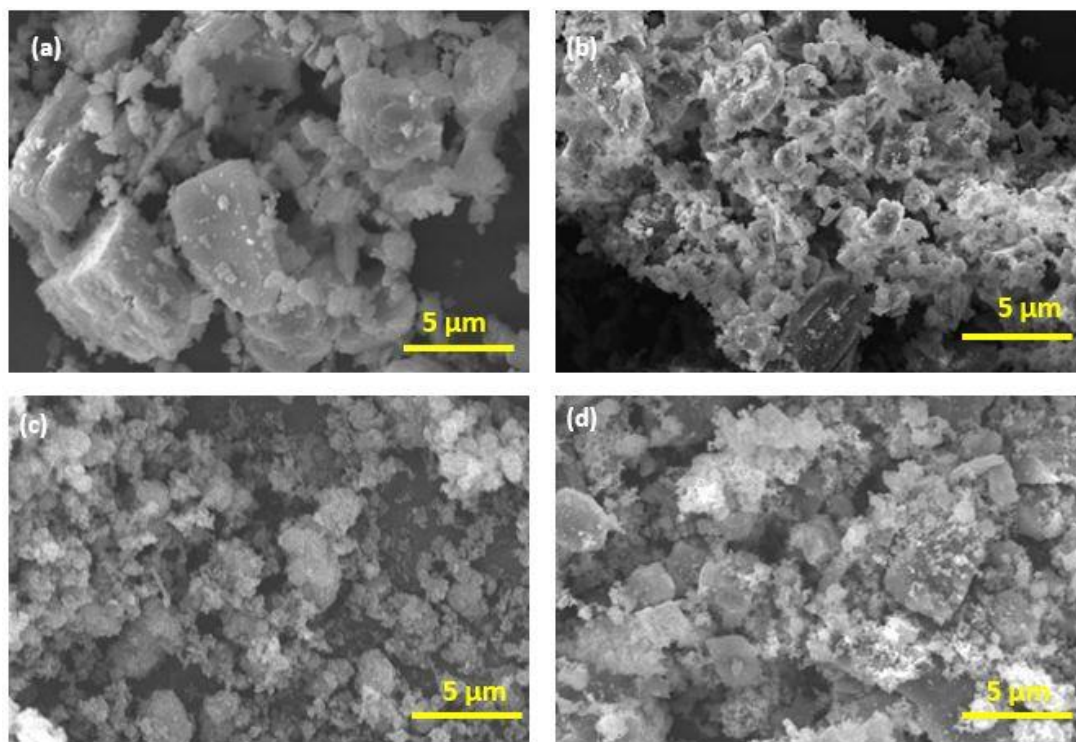


Figure 15: SEM image of (a) ZnO (b) Dolomite (c) HZSM-5 (d) Mixture

4.1.5 FTIR Analysis of Fuller's Clay and Mixtures

Changes in the functional group and the possibility of different interactions between fuller's earth clay and metal oxide particles were detected by FTIR spectroscopy. The spectrum of fuller's earth in **Figure 16** indicates absorption bands positioned at 3423, 1640, 1031 and 798 cm^{-1} due to the H-O-H bond expansion of physisorbed water on the surface of fuller's earth, Si-O-Si broadening and Si-O bond, respectively. All the other three spectrum lines of the mixture of clay and metal oxides show slight variation in values from the fuller's earth numbers indicating that mixing of metal oxides changed the absorption of Si-O-Si, H-O-H and Si-O bonds having involved Fe-O, Ni-O and Zn-O bonds in the mixture.

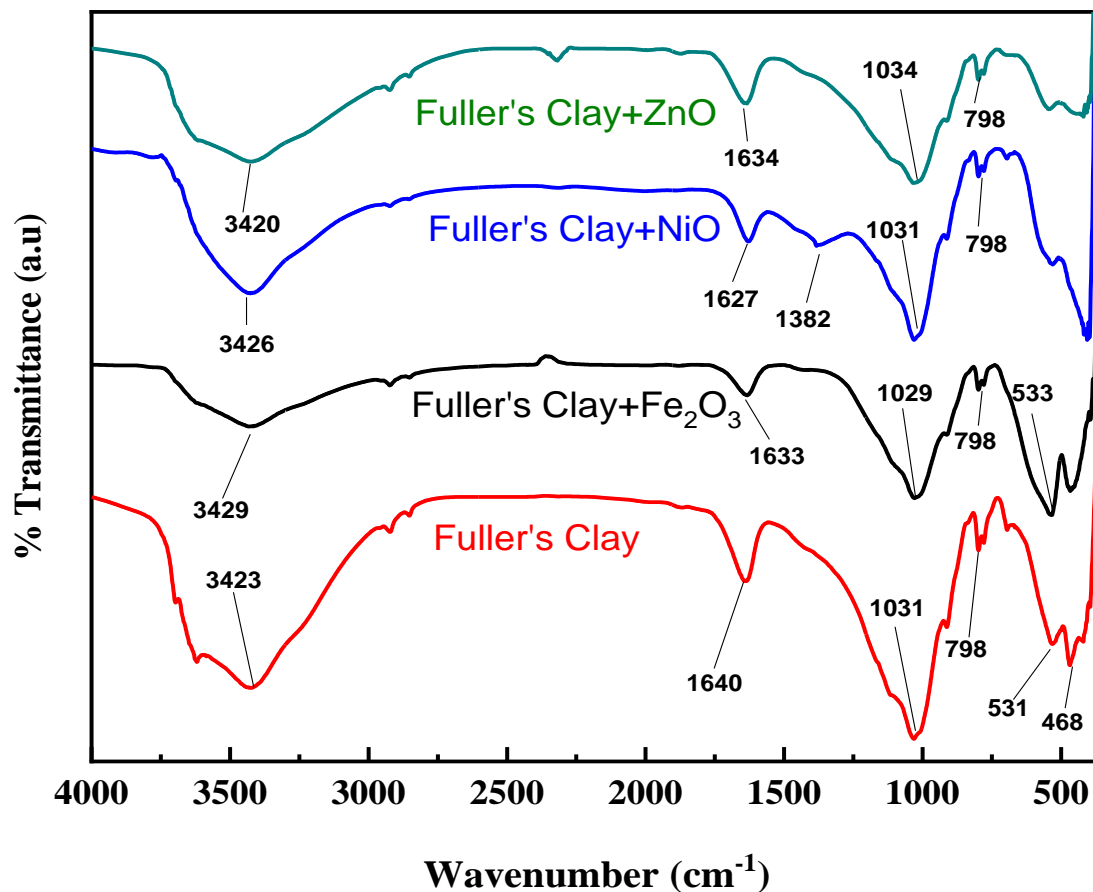


Figure 16: FTIR Spectra of Fuller's Earth and Metal Oxide Mixtures

4.1.6 FTIR Analysis of Dolomite, HZSM-5, and Mixture

The possibility of different interactions between Dolomite, ZnO, and HZSM-5 mixture was detected using FTIR spectroscopy shown in **Figure17**. FTIR spectra of minerals display characteristic features that can be related qualitatively to variations in the constituent minerals. Absorption features result from the detection of vibrational modes, i.e., lattice vibrations and/or molecular group vibrational modes. The amount of calcium and magnesium in most specimens of dolomite is equal, but occasionally one element may have a slightly greater presence than the other which can cause absorption bands to shift values. The spectrum of dolomite shows prominent absorption bands at 3423, 2519, 1799, 1417, 875 and 712. Some of these absorption bands like 712, 875, 1417, and 2519 are typical features of dolomite [21].

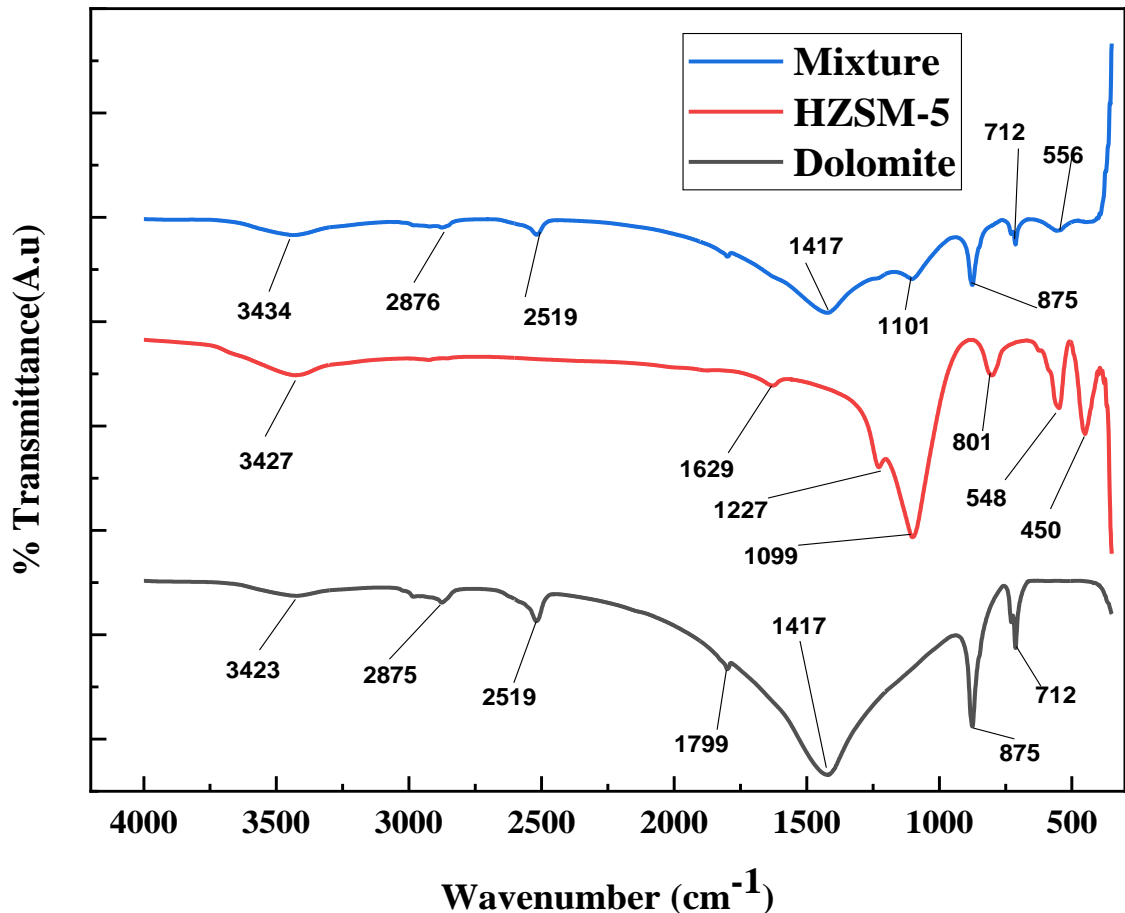


Figure 17: FTIR Spectra of Dolomite, HZSM-5, and Mixture

HZSM-5 shows bands at 450, 548, 801, 1099, and 1227. These values are very near to a characteristic FTIR spectrum of HZSM-5. Bands near 1080 cm^{-1} (internal asymmetric stretch), 801 cm^{-1} (external symmetric stretch), 548 cm^{-1} (double ring vibration) and 450 cm^{-1} (Si-O band) were apparent. Additional evidence for the HZSM-5 zeolite was the asymmetric stretch vibration of the band at 1227 cm^{-1} , which has been assigned to external linkages (between the SiO_4 tetrahedral) and is a structure-sensitive IR band of HZSM-5 zeolite [34] and the mixture of Dolomite, ZnO and HZSM-5 shows absorption bands at 556, 712, 875, 1101, 1417 and 2519. These somewhat changed values in the mixture's FTIR specifies that mixing of ZnO and HZSM-5 changed the absorption of bonds of dolomite having involved HZSM-5 zeolite and Zn-O bonds in the mixture.

4.2 Gas Products Obtained Using Clay and ZnO Catalyst

The product distributions of gaseous fractions over clay and ZnO catalyst are presented in **Figure 18** which shows a high proportion of propene, 1-butene and 1-pentene and small proportions of other products like hexane, hexene, heptane, heptene, 1-pentanol and many more.

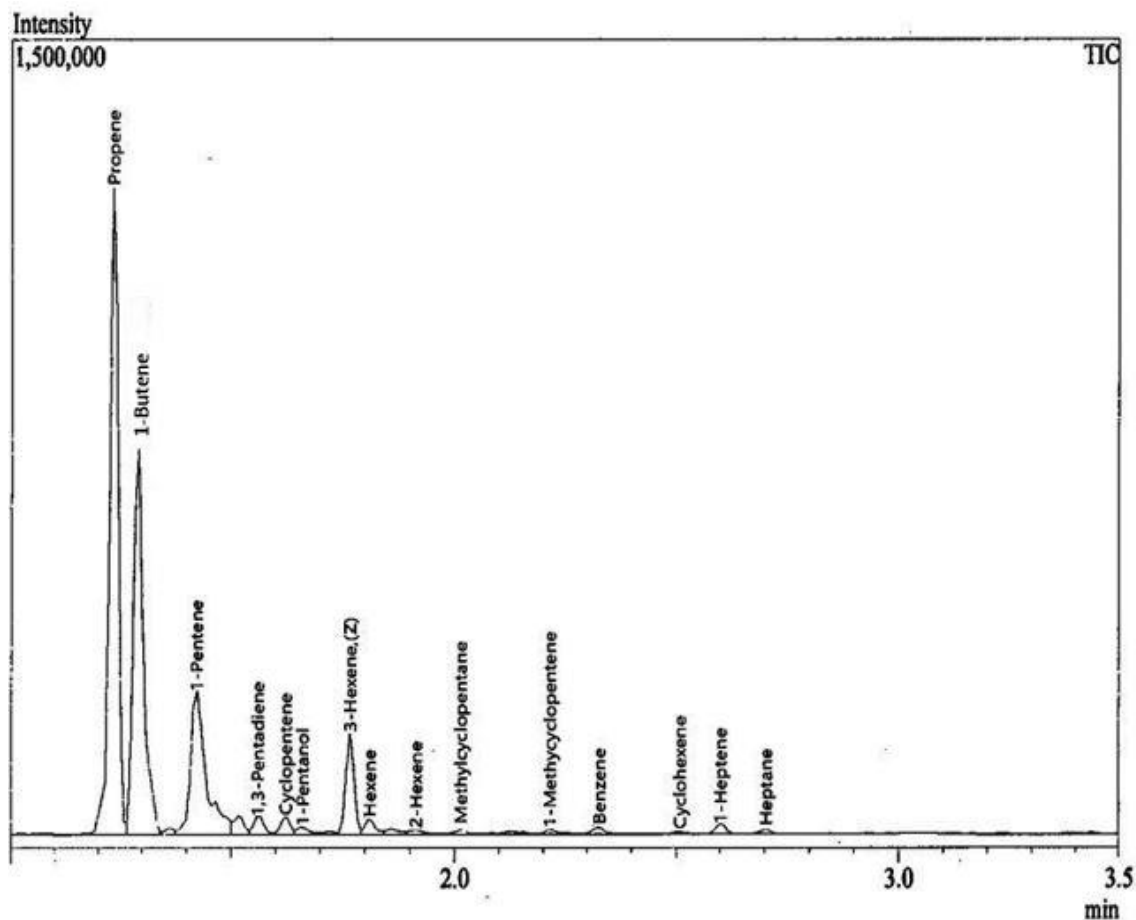


Figure 18: GC Analysis of Gas Products (Clay + ZnO)

4.3 Gas Products Obtained Using Clay and Fe(III) Oxide Catalyst

The gas chromatographic analysis of polyethylene cracking is shown in **Figure 19**. It is clear that in a highly efficient column, chromatogram obtained contains three dominant products i.e propene, 1-butene and 1-pentene and small proportions of other products.

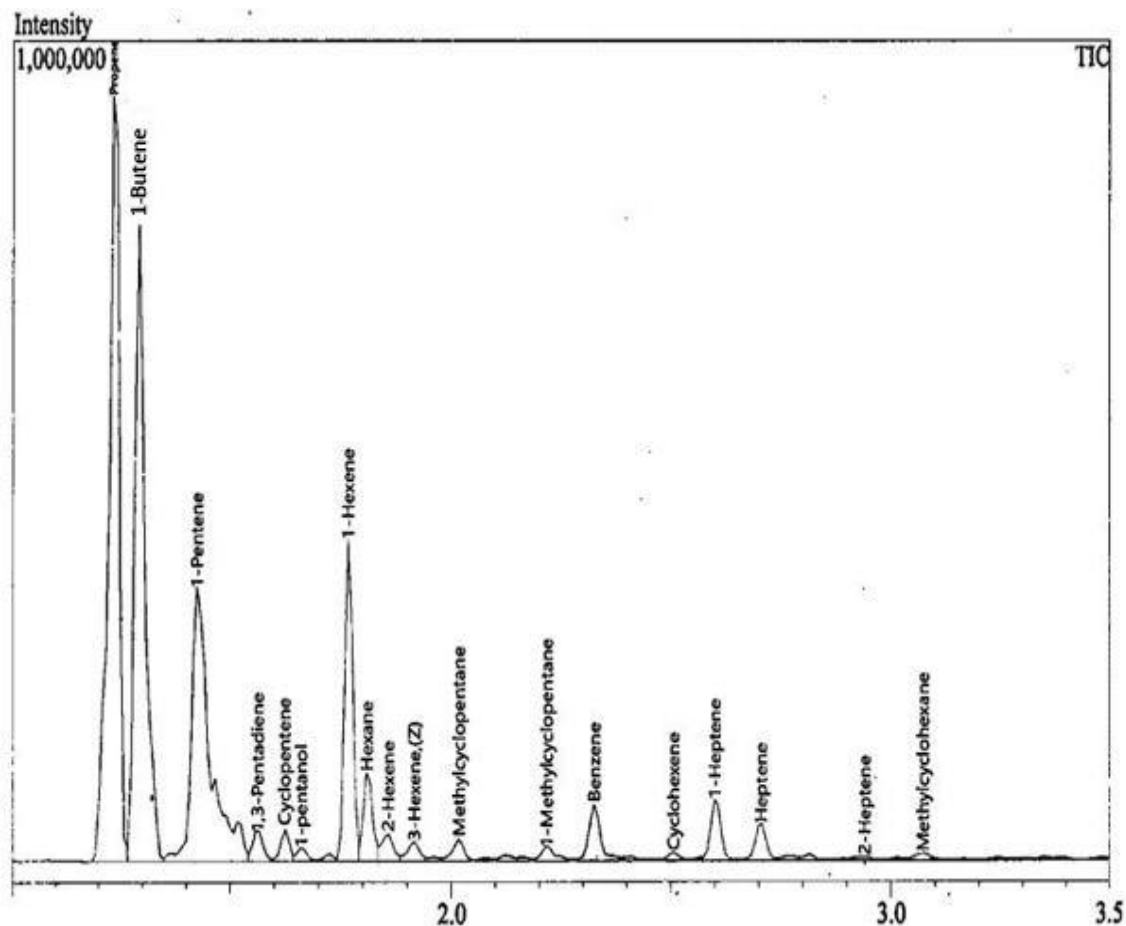


Figure 19: GC Analysis of Gas Products (Clay+Iron(III) Oxide)

4.4 Gas Products Obtained Using Clay and NiO Catalyst

The gas chromatographic results of high-density polyethylene cracking using clay and Ni(III) oxide catalyst is shown in **Figure 20**. This figure presents three high-intensity peaks i.e propene, 1-butene and 1-pentene and moderate and small intensity peaks of other gaseous products.

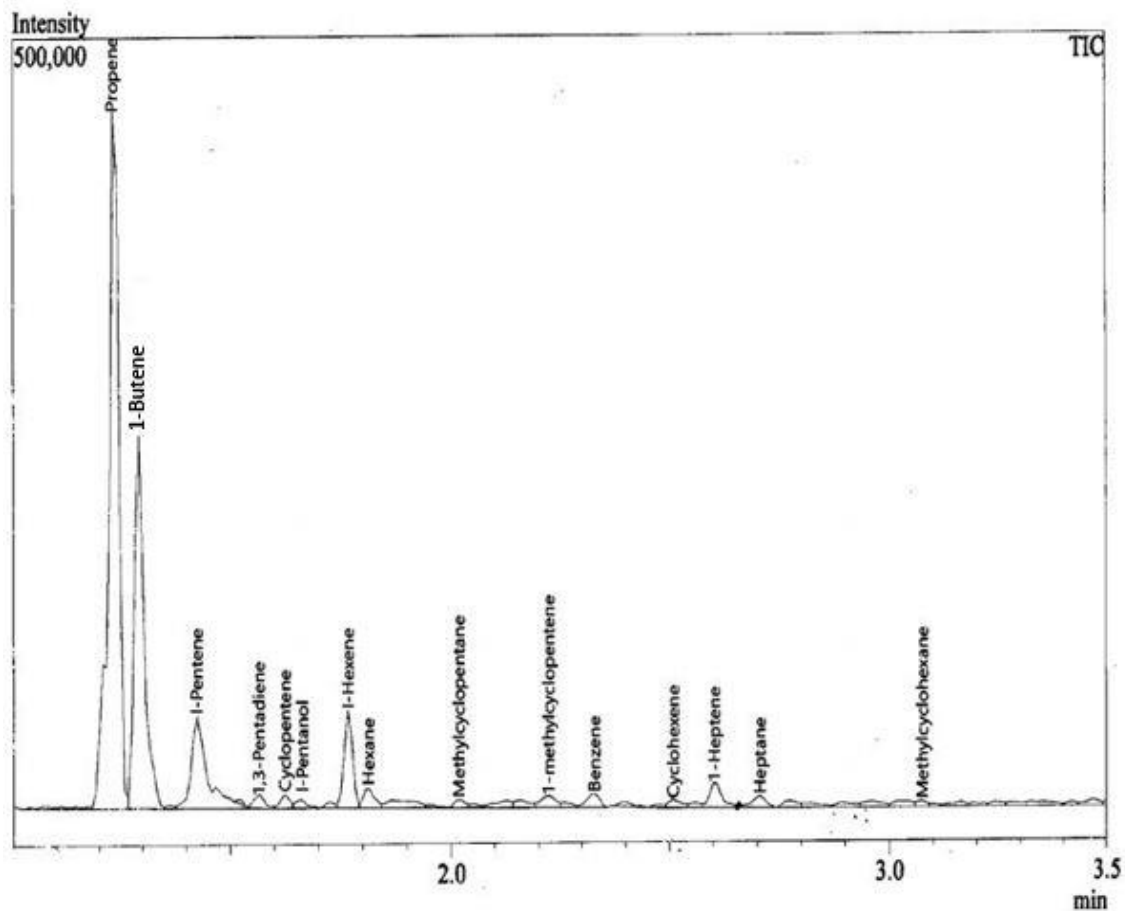


Figure 20: GC Analysis of Gas Products (Clay + NiO)

4.5 Products

The first four experiments were done on different catalysts Fuller's Clay, (Clay + ZnO, Clay + Fe(III) Oxide, Clay + Ni oxide) to study the variability in the products. The gaseous products obtained are then analyzed with the aid of a Gas Chromatograph Mass Spectrometry (GCMS). **Figure 21** shows the GCMS data of the product obtained in the process. Considerable compounds in gas products can be obtained such as propene, 1-butene and 1-pentene. The distribution of gaseous products obtained depends strongly on the catalyst. By using the homogenous mixture of Clay and ZnO catalysts, the main products obtained are propene, 1-butene, 1-pentene and very small amounts of hexane, cyclohexene and heptane. By utilizing the same reaction conditions, the gaseous products obtained using Clay + Fe(III) Oxide and Clay + Ni Oxide were propene, 1-pentene, 1-butene, 1-hexene and small amounts of heptene, heptane and hexane.

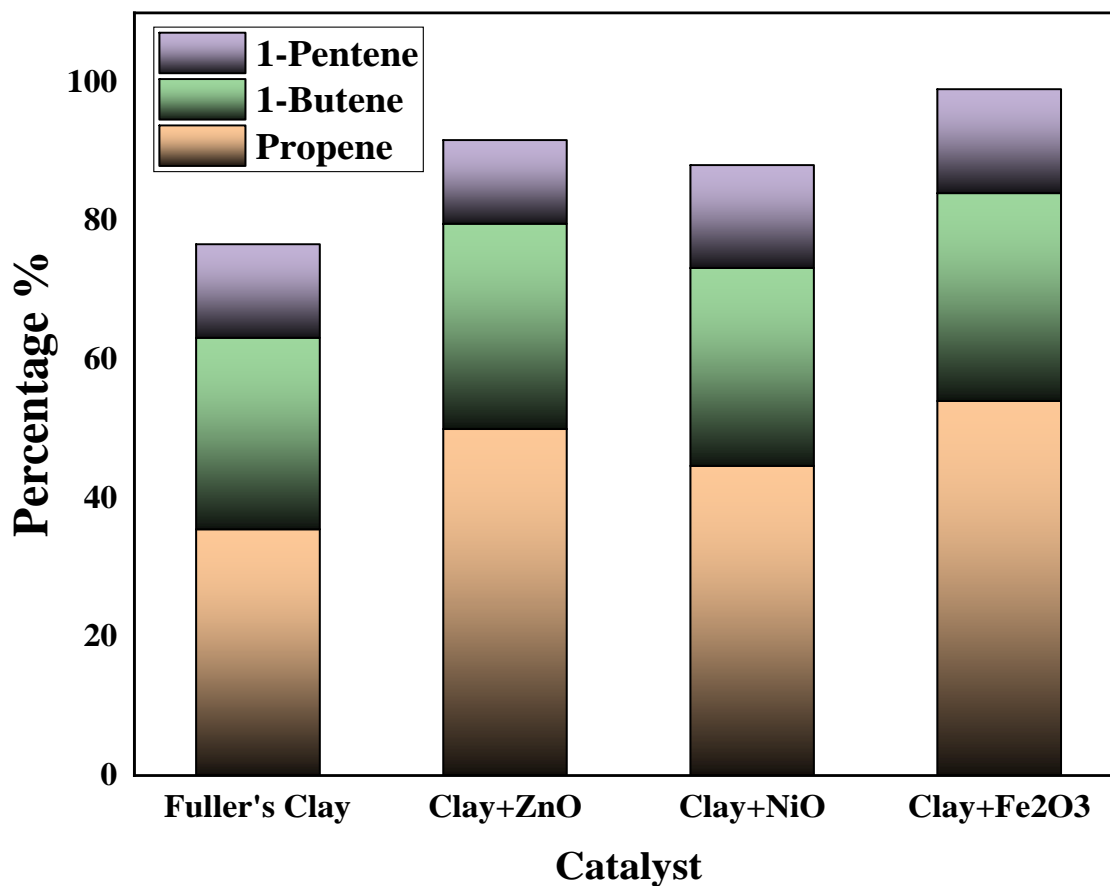


Figure 21: Proportions of Gas Products Using Fuller's Clay and Metal Oxides Mixture

The next four experiments were done with dolomite, HZSM-5, and ZnO mixture, 10 g of Dolomite and 5 g of each HZSM-5 and ZnO was used along with 100 g plastic keeping the plastic to catalyst w/w ratio 1:0.2. The product percentage changed as shown in **Figure 22** by using the different catalyst mixture because the dolomite and presence of zeolite changed the reaction sites and pore size of available catalyst so we also observe an addition of butane among the products as well some quantity of 1- Hexene.

The next five experiments were done using different temperature conditions and catalyst mixture (Dolomite, ZnO and HZSM-5) in constant ratio 0.2 to check the optimum temperature to increase the product yield and out of five different conditions, 450 °C temperature condition gave the maximum yield of products **Figure 23**. In these five runs,

a considerable percentage of n-butane, 1-butene and 1-Hexene were present in the mixture differently than the last three runs with fuller's clay and metal oxide mixtures.

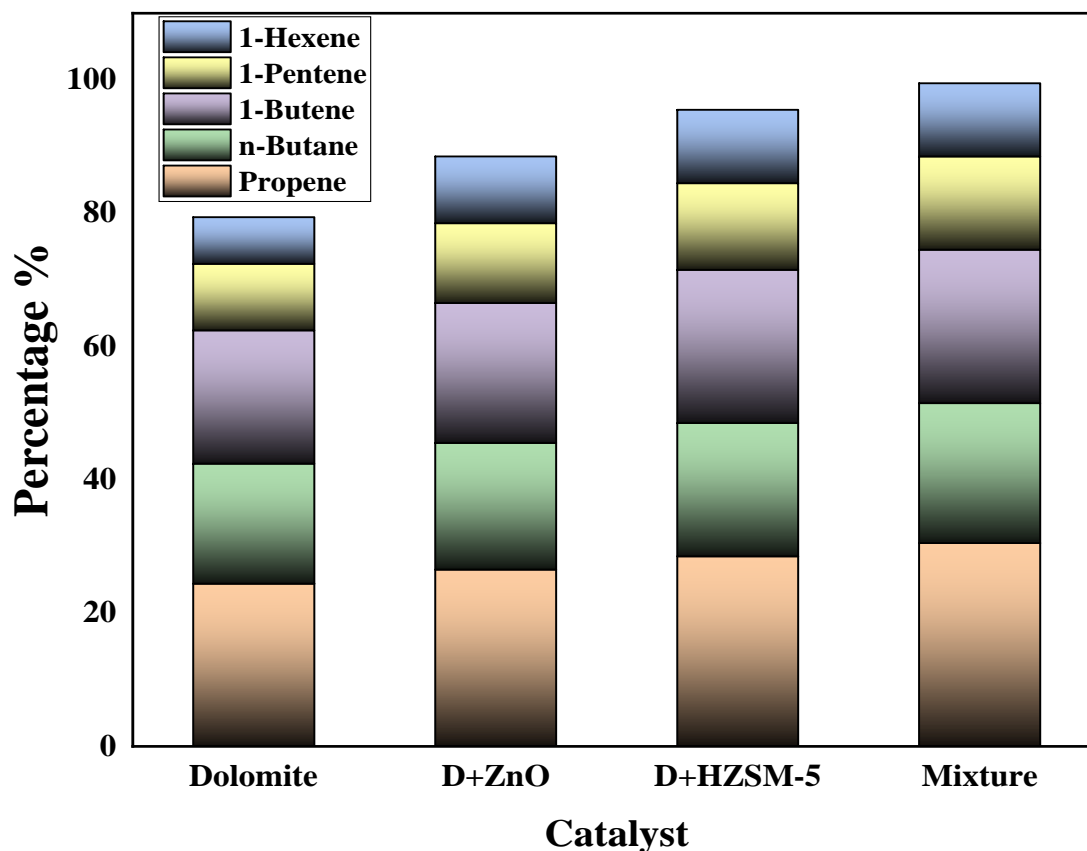


Figure 22: Proportions of Gas Products Using Dolomite, HZSM-5 and ZnO Mixture

The next five experiments were done using different plastic to catalyst ratio w/w e.g. (1:0.1, 0.2, 0.3, 0.4 and 0.5) to check which fraction of catalyst gives us the maximum gaseous product and better compounds and as we increase the amount of catalyst mixture, the number of products increased relatively, as in 0.1 gave the least product and 0.5 gave the maximum amount of all gases. In these runs' product gases were the same as the previous five runs but their amounts increased. A direct relation can be observed in **Figure 24**.

Like in [35] we can see that clay C-27 Saponite and Zenith-N (montmorillonite) gives about 66% and 70% alkenes in gaseous products. In another study done on the pyrolysis of PE, we see that the catalytic process yields C₁ to C₆ alkanes and alkenes gaseous

products. Similar to our process two clays Dolomite and Scolecite were used as catalysts in catalytic pyrolysis of PE to produce fuel range hydrocarbons [26].

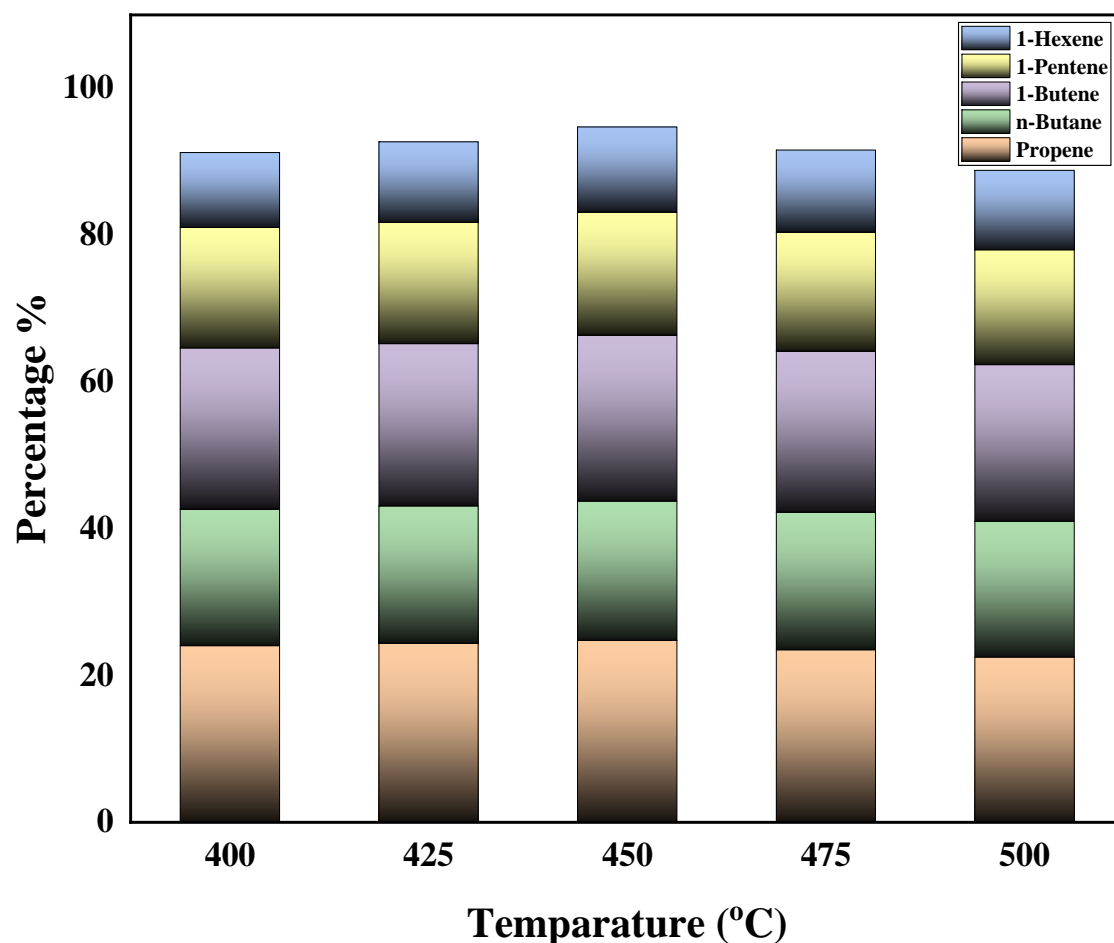


Figure 23: Proportions of Gas Products Using Variable Temperatures

In a review, it is said that the pyrolysis process is appropriate and a potential method to produce energy from plastic waste. This process produces valuable liquid oil, gaseous fuel and char from waste plastics which otherwise would have ended up in a landfill increasing environmental pollution. To find an economical catalyst another study was done using $\text{AlCl}_3\text{-NaCl}$ eutectic salt as a catalyst for waste PE pyrolysis and it concluded that this catalyst lowers the temperature demand of the process as well as produces $\text{C}_4\text{-C}_{12}$ fuel range hydrocarbons [36].

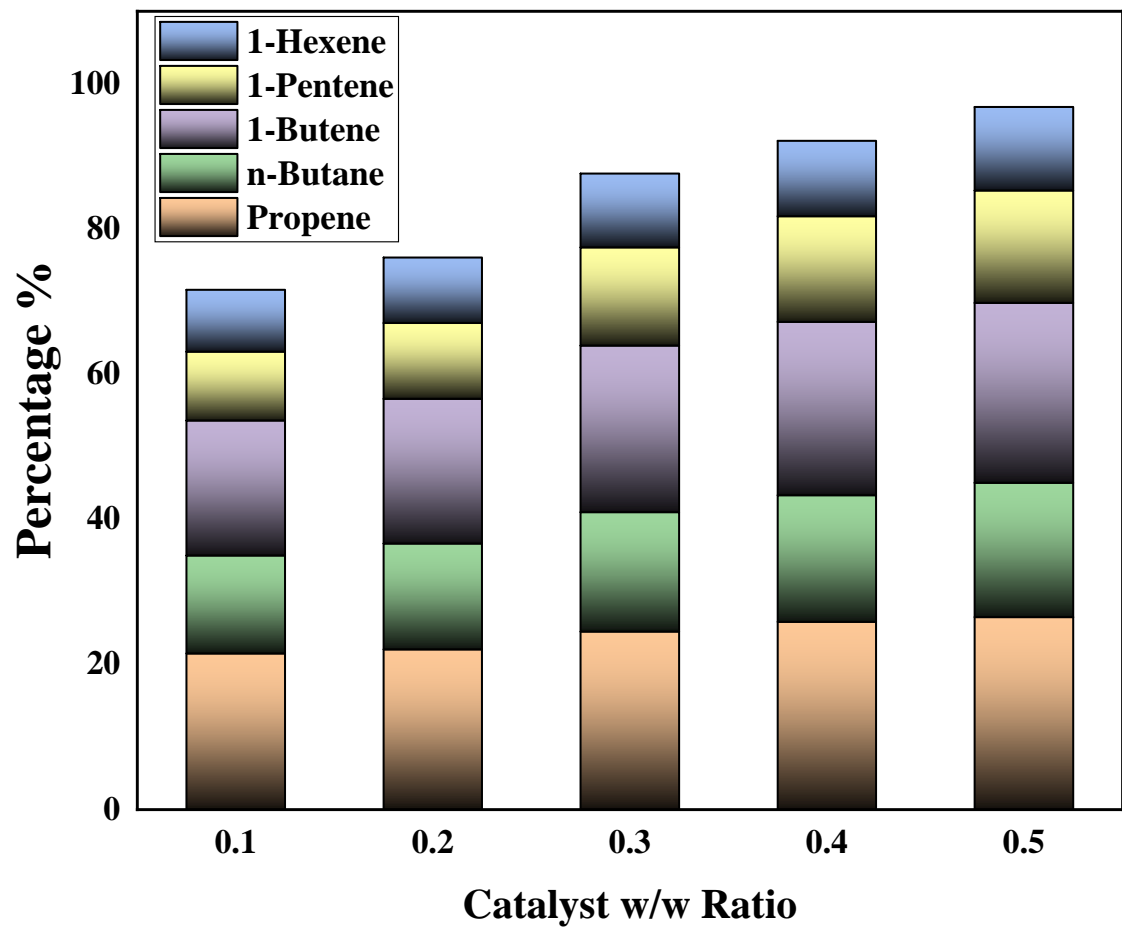


Figure 24: Proportions of Gas Products Using Different Catalyst w/w Ratio

Conclusion

A laboratory-scale catalytic bed reactor has been used to obtain a range of volatile hydrocarbons by catalytic cracking of waste PE bags in the temperature range 400 °C-500 °C. From the results shown above, we can conclude that this method is feasible to produce valuable low molecular mass hydrocarbons. The product varied distinctly on the type of catalyst used and conditions provided for the reaction. Type of catalyst affects the product because different materials like dolomite, fuller's clay, and HZSM-5 have diverse active sites and pores for polymeric chains to crack. This changes the selectivity towards light hydrocarbons as well as saturated and unsaturated hydrocarbon yield. Temperature variation also affects the product yield because too high a temperature may cause coking of catalyst and we see a decrease in the fraction of gases. In the past, various catalysts were utilized for the catalytic degradation of polyethylene. The most widely used catalyst for polyethylene cracking is Clay. The major disadvantage of using Clay is that it cracks the polymer at a relatively high temperature (700-800 °C). In this work, a high proportion of propene and other gases are produced by using metal oxides and Fuller's Clay catalyst mixture. On the other hand, a less proportion of propene and other gases are obtained while utilizing Dolomite, ZnO and HZSM-5 catalysts. The high proportion of gas products produced using Fe(III)Oxide and Fuller's clay catalyst mainly because of the milder acidity of the blended mixture. The basic purpose to use these metal oxides as an additive to reduce the high acidity of Fuller's earth Clay. Dolomite, HZSM-5 zeolite and ZnO mixture is useful when the purpose of cracking is to produce alkane as well because HZSM-5 has selectivity for butane. Zeolite gives valuable products during polymer cracking but at the same time disadvantage associated with the Zeolite, the catalyst is that it's very expensive. At the external dynamic sites catalytic cracking reaction of polymer begins and more valuable products can be obtained by manipulation of these sites. We can say that Fe(III) Oxide and clay is the most suitable catalyst for polymer degradation and production of propene under these conditions and this process is feasible to convert plastic waste into light hydrocarbon and should be employed for eliminating waste plastics.

Recommendations

There are territories in which future work could be sought after and these included the following:

- The investigation could be extended to study polymer mixtures and in addition another waste municipal, for example, food, refuse and paper.
- The selectivity of products can undoubtedly be different by changing catalysts to suit the request of the market. We can likewise observe from the information in the literature that we can shift selectivity from light hydrocarbons to heavier ones by utilizing some other catalyst.
- This procedure can turn out to be amazingly essential against the exceptionally harming issues of contamination and energy crisis. The plant's ability can be expanded to treat waste on an industrial scale.

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