CHAPTER ONE

INTRODUCTION

1.1 Plastic

The word plastic is derived from the Greek πλαστικός (plastikos) meaning "capable of being shaped or moulded", from πλαστός plastosmeaning "moulded". It refers to their malleability or plasticity during manufacture that allows them to be cast, pressed, or extruded into a variety of shapes — such as films, fibers, plates, tubes, bottles, boxes, and much more.

Generic term used in the case of polymeric material that may contain other substances to improve performance and/or reduce costs. Plastic is a material consisting of any of a wide range of synthetic or semi-synthetic organics that are malleable and can be moulded into solid objects of diverse shapes. Plastics are typically organic polymers of high molecular mass, but they often contain other substances. They are usually synthetic, most commonly derived from petrochemicals, but many are partially natural.[1]

Plasticity is the general property of all materials that are able to irreversibly deform without breaking, but this occurs to such a degree with this class of mouldable polymers that their name is an emphasis on this ability.

Due to their relatively low cost, ease of manufacture, versatility, and imperiousness to water, plastics are used in an enormous and expanding range of products, from paper clips to spaceships. They have already

replaced many traditional materials, such as wood, stone, horn and bone, leather, paper, metal, glass, and ceramic, in most of their former uses. In developed countries, about a third of plastic is used in packaging and another third in buildings such as piping used in plumbing or vinyl siding. Other uses include automobiles (up to 20% plastic), furniture, and toys.

In the developing world, the ratios may be different - for example, reportedly 42% of India's consumption is used in packaging.[2] Plastics have many uses in the medical field as well, to include polymer implants, however the field of plastic surgery is not named for use of plastic material, but rather the more generic meaning of the word plasticity in regards to the reshaping of flesh.

1.2 History

Figure (1.1): Plastic (LDPE) bowl, by GEECO, Made in England, c. 1950

The development of plastics has evolved from the use of natural plastic materials (e.g., chewing gum, shellac) to the use of chemically modified, natural materials (e.g., natural rubber, nitrocellulose, collagen, galalite) and finally to completely synthetic molecules (e.g., Bakelite, epoxy, Polyvinyl chloride). Early plastics were bio-derived materials such as egg and blood proteins, which are organic polymers.

In 1600 BC, Mesoamericans used natural rubber for balls, bands, and figurines.[3] Treated cattle horns were used as windows for lanterns in

the middle Ages. Materials that mimicked the properties of horns were developed by treating milk-proteins (casein) with lye.[1]

In the 1800s, as industrial chemistry developed during the Industrial Revolution, many materials were reported. The development of plastics also accelerated with Charles Goodyear's discovery of vulcanization to thermoset materials derived from natural rubber.

Parkesine is considered the first man-made plastic. The plastic material was patented by Alexander Parkes, In Birmingham, UK in 1856.[4] It was unveiled at the 1862 Great International Exhibition in London. Parkesine won a bronze medal at the 1862 World's fair in London. Parkesine was made from cellulose (the major component of plant cell walls) treated with nitric acid as a solvent. The output of the process (commonly known as cellulose nitrate or pyroxilin) could be dissolved in alcohol and hardened into a transparent and elastic material that could be moulded when heated by incorporating pigments into the product; it could be made to resemble ivory.

In 1897, the Hanover, Germany mass printing press owner Wilhelm Krische was commissioned to develop an alternative to blackboards. The resultant horn-like plastic made from the milk protein casein was developed in cooperation with the Austrian chemist (Friedrich) Adolph Spitteler (1846–1940). The final result was unsuitable for the original purpose. In 1893, French chemist Auguste Trillat discovered the means to insolubilize casein by immersion in formaldehyde, producing material marketed as galalith.

In the early 1900s, Bakelite, the first fully synthetic thermoset, was reported by Belgian chemist Leo Baekeland by using phenol and formaldehyde.[1] After World War I, improvements in chemical

technology led to an explosion in new forms of plastics, with mass production beginning in the 1940s and 1950s (around World War II).[5]

Among the earliest examples in the wave of new polymers were polystyrene (PS), first produced by BASF in the 1930s and polyvinyl chloride (PVC), first created in 1872 but commercially produced in the late 1920s[2] In 1923, Durite Plastics Inc. was the first manufacturer of phenol-furfural resins.[1] In 1933, polyethylene was discovered by Imperial Chemical Industries (ICI) researchers Reginald Gibson and Eric Fawcett.

In 1954, Polypropylene was discovered by Giulio Natta and began to be manufactured in 1957. In 1954, expanded polystyrene (used for building insulation, packaging, and cups) was invented by Dow Chemical.[2]

1.3 Common Plastics and Uses

Table (1.1): plastic uses

Plastic	Abbreviation	Uses
Polyethylene	PE	Wide range of inexpensive uses including supermarket bags, plastic bottles.
High density polyethylene	HDPE	Detergent bottles, milk jugs and moulded plastic cases.
Low density polyethylene	LDPE	Outdoor furniture, siding, floor tiles, shower curtains, clamshell packaging.
polyethylene terephthalate	PET	Carbonated drinks peanut butter jars, plastic film, microwavable packaging.
polyvinyl chloride	PVC	Plumbing pipes and guttering shower curtains, window frames, flooring.

Polypropylene	PP	Bottle caps, drinking straws, yogurt containers, appliances, plastic pressure pipe systems.
Polystyrene	PS	Packaging foam/"peanuts", food container, plastic tableware, disposable cups, plates, cutlery, CD and cassette boxes.
High impact polystyrene	HIPS	Refrigerator liners, food packaging, vend cups.
Acrylonitrile butadiene styrene	ABS	Computer monitors, printers, keyboards, drainage pipe, Electronic equipment cases.
polycarbonate	PC	Compact discs, eyeglasses, riot shields, security windows, traffic lights, lenses.
Polyurethanes	PU	Cushioning foams, thermal insulation foams, surface coatings, printing rollers

Figure (1.2): A variety of plastic for different needs

1.4 Plastic Waste Management

1.4.1 Environmental Issues and Challenges:

The quantum of solid waste is ever increasing due to increase in population, developmental activities, changes in life style, and social-economic conditions, Plastics waste is a significant portion of the total municipal solid waste (MSW).

It is estimated that approximately 10 thousand tons per day (TPD) of plastics waste is generated i.e. 9% of 1.20 lacks TPD of MSW in the country. The plastics waste constitutes two major category of plastics; (i) Thermoplastics and (ii) Thermoset plastics. Thermoplastics, constitutes 80% and thermoset constitutes approximately 20% of total post-consumer plastics waste generated in India.

The Thermoplastics are recyclable plastics which include; Polyethylene Terephthalate (PET), Low Density Poly Ethylene (LDPE), Poly Vinyl- Chloride (PVC), High Density Poly Ethylene (HDPE), Polypropylene (PP), Polystyrene (PS) etc. However, thermoset plastics contains alkyd, epoxy, ester, melamine formaldehyde, phenolic formaldehyde, silicon, urea formaldehyde, polyurethane, metalized and multi-layer plastics etc.

The environmental hazards due to mismanagement of plastics waste include the following aspects: [6]

◆ Littered plastics spoils beauty of the city and choke drains and make important public places filthy.

◆ Garbage containing plastics, when burnt may cause air pollution by emitting polluting gases.

◆ Garbage mixed with plastics interferes in waste processing facilities and may also cause problems in landfill operations.

◆ Recycling industries operating in non-conforming areas are posing unhygienic problems to the environment.

1.5 Options for Plastic Waste Management

Recycling of plastics through environmentally sound manner: It should be carried in such a manner to minimize the pollution during the process and as a result to enhance the efficiency of the process and conserve the energy. Plastics recycling technologies have been historically divided into four general types -primary, secondary, tertiary and quaternary.[6]

■ Primary recycling involves processing of a waste/scrap into a product with characteristics similar to those of original product.

■ Secondary recycling involves processing of waste/scrap plastics into materials that have characteristics different from those of original plastics product.

■ Tertiary recycling involves the production of basic chemicals and fuels from plastics waste/scrap as part of the municipal waste stream or as a segregated waste.

■ Quaternary recycling retrieves the energy content of waste/scrap plastics by burning / incineration.

Steps Involved in the Recycling Process

Selection: The recyclers / reprocessors have to select the waste / scrap which are suitable for recycling /reprocessing.

Segregation: The plastics waste shall be segregated as per the Codes 1-7 mentioned in the BIS guidelines (IS:14534:1998).

Processing: After selection and segregation of the pre-consumer waste (factory waste) shall be directly recycled. The post-consumer waste (used plastic waste) shall be washed, shredded, agglomerated, extruded and granulated.

1 .6 Conversion of Plastics Waste Into Liquid Fuel

A research-cum-demonstration plant was set up at Nagpur, Maharashtra for conversion of waste plastics into liquid fuel. The process adopted is based on random de-polymerization of waste plastics into liquid fuel in presence of a catalyst. The entire process is undertaken in closed reactor vessel followed by condensation, if required. Waste plastics while heating up to 2700 C to 3000 C convert into liquid-vapour state, which is collected in condensation chamber in the form of liquid fuel while the tarry liquid waste is topped-down from the heating reactor vessel.

The organic gas is generated which is vented due to lack of storage facility.[6] However, the gas can be used in dual fuel diesel-generator set for generation of electricity. The process includes the steps shown ahead in figure (1.3):

Figure (1.3): Process steps

1.7 Environment Related Observations during the Process

There are no liquid industrial effluents and no floor washing as it is a dry process. There are no organized stack and process emissions. Odour of volatile organics has been experienced in the processing area due to some leakages or lack of proper sealing. Absolute conversion of liquid-vapour was not possible into liquid; some portion of gas (about 20%) is connected to the generator. However, the process will be improved in full-scale plant.

1.8 Benefits of Conversing Plastic Waste

Waste is not something that should be discarded or disposed of with no regard for future use. It can be a valuable resource if addressed correctly, through policy and practice. With rational and consistent waste management practices there is an opportunity to reap a range of benefits.[6] Those benefits include:

◆ Economic - Improving economic efficiency through the means of resource use, treatment and disposal and creating markets for recycles can lead to efficient practices in the production and consumption of products and materials resulting in valuable materials being recovered for reuse and the potential for new jobs and new business opportunities.

◆ Social - By reducing adverse impacts on health by proper waste management practices, the resulting consequences are more appealing settlements. Better social advantages can lead to new sources of employment and potentially lifting communities out of poverty especially in some of the developing poorer countries and cities.

◆ Environmental - Reducing or eliminating adverse impacts on the environmental through reducing, reusing and recycling, and minimizing resource extraction can provide improved air and water quality and help in the reduction of greenhouse gas emissions.

◆ Inter-generational Equity - Following effective waste management practices can provide subsequent generations a more robust economy, a fairer and more inclusive society and a cleaner environment.

◆ In order to understand, optimize the pyrolsis of plastic waste, know how we can produce the fuel, the properties and the effect of each

element in these systems. So I decided in research focus on the plastic waste especially HDPE, LDPE, PP for converting to fuel using pyrolysis system made locally, simple elements and easiest process.

CHAPTER TWO

LITERATURE REVIEW

A) WHAT ARE PLASTICS?

2.1 Composition Plastic

Most plastics contain organic polymers. The vast majority of these polymers are based on chains of carbon atoms alone or with oxygen, sulfur, or nitrogen as well. The backbone is that part of the chain on the main "path" linking a large number of repeat units together. To customize the properties of a plastic, different molecular groups "hang" from the backbone (usually they are "hung" as part of the monomers before the monomers are linked together to form the polymer chain). The structure of these "side chains" influences the properties of the polymer. This fine tuning of the repeating unit's molecular structure influences the properties of the polymer. [7]
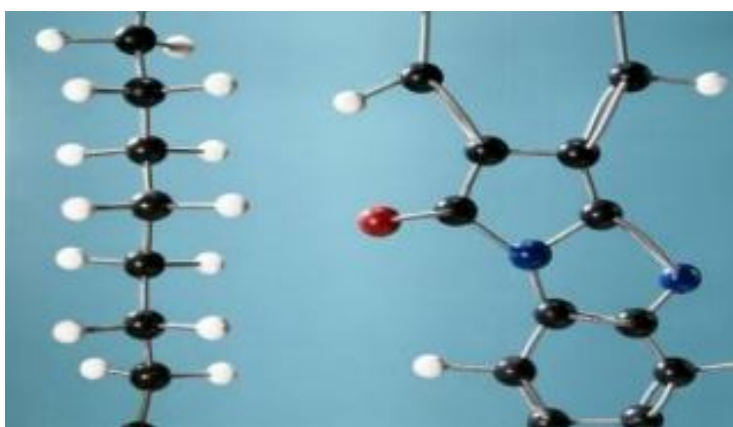
2.2 Monomers and Polymers

Figure (2.1): Types of monomers

Monomers are the building blocks of more complex molecules, called polymers. Polymers consist of repeating molecular units which usually are joined by covalent bonds. Here is a closer look at the chemistry of monomers and polymers.

Monomers

The word monomer comes from mono- (one) and -mer (part). Monomers are then chemically bonded into chains called polymers. There are two basic mechanisms for polymerization: addition reactions and condensation reactions. For addition reactions a special catalyst is added, frequently peroxide, that causes one monomer to link to the next and that to the next and so on. Catalysts do not cause reactions to occur, but cause the reactions to happen more rapidly. Addition polymerization, used for polyethylene and polystyrene and polyvinyl chloride among others, creates no by-products.

The reactions can be done in the gaseous phase dispersed in liquids. The second polymerization mechanism, condensation polymerization, uses catalysts to have all monomers react with any adjacent monomer. The reaction results in two monomers forming dimers (two unit cells) plus a by-product. Dimers can combine to form tetramers (four unit cells) and so on. For condensation polymerization the by-products must be removed for the chemical reaction to produce useful products. Some by-products are water, which is treated and disposed. Other by-products are raw materials and recycled for reuse within the process.

The removal of by-products is conducted so that valuable recycled raw materials are not lost to the environment or exposed to populations. Condensation reactions are typically done in a mass of molten polymer. Polyesters and nylons are made by condensation polymerization.

Different combinations of monomers can yield plastic resins with different properties and characteristics. When all monomers are the same, the polymer is called a homo-polymer. When more than one monomer is used, the polymer is called a co-polymer. Plastic milk jugs are an example of homo-polymer HDPE. Milk is satisfactorily packaged in the less expensive homo-polymer HDPE. Laundry detergent bottles are an example of Co-polymer HDPE. The aggressive nature of the detergent makes a Co-polymer the right choice for best service function. Each monomer yields a plastic resin with specific properties and characteristics.

Combinations of monomers produce co-polymers with further property variations. So, within each polymer type, such as nylons, polyesters, polyethylenes, etc., manufacturers can custom make plastics that have specific features. Polyethylenes can be made to be rigid or flexible. Polyesters can be made to be low temperature melting adhesives or high temperature resistant automobile parts.

The resulting thermoplastic polymers may be melted to form many different kinds of plastic products with application in many major markets. The variability of the plastic either within plastic family types or among family types permits a plastic to be tailored to a specific design and performance requirements. This is why certain plastics are best suited for some applications while others are best suited for entirely different applications. No one plastic is best for all needs. [7]

2.3 The Structure of Polymers

As we have discussed, polymers can be homo-polymers or co-polymers.

If the long chains show a continuous link of carbon-to-carbon atoms, the structure is called homogeneous. The long chain is called the backbone. Polypropylene, polybutylene, polystyrene and poly-methylpentene are examples of polymers with homogeneous carbon structure in the backbone. If the chains of carbon atoms are intermittently interrupted by oxygen or nitrogen, the structure is called heterogeneous. Polyesters, nylons, and polycarbonates are examples of polymers with heterogeneous structure. Heterogeneous polymers as a class tend to be less chemically durable than homogeneous polymers although examples to the contrary are numerous.

Different elements can be attached to the carbon-to-carbon backbone. Polyvinyl chloride (PVC) contains attached chlorine atoms. How the links in thermoplastics are arranged can also change the structure and properties of plastics. Some plastics are assembled from monomers such that there is intentional randomness in the occurrence of attached elements and chemical groups. Others have the attached groups occur in very predictable order. Plastics will, if the structure allows, form crystals. Some plastics easily and rapidly form crystals, such as HDPE—high density polyethylene. HDPE can appear hazy from the crystals and exhibits stiffness and strength. Other plastics are constructed such that they cannot fit together to form crystals, such as low density polyethylene, LDPE. An amorphous plastic typically is clear in appearance.

By adjusting the spatial arrangement of atoms on the backbone chains, the plastics manufacturer can change the performance properties of the plastic. The chemical structure of the backbone, the use of co-polymers, and the chemical binding of different elements and compounds to a back-bone, and the use of crystallizability can change the

processing, aesthetic, and performance properties of plastics. The plastics can also be altered by the inclusion of additives.[7]

2.4 Additives

Most plastics contain other organic or inorganic compounds blended in. The amount of additives ranges from zero percentage (for example in polymers used to wrap foods) to more than 50% for certain electronic applications. The average content of additives is 20% by weight of the Polymer.

Additives are also used to protect the polymer from the degrading effects of light, heat, or bacteria; to change such polymer processing properties such as melt flow; to provide product colour; and to provide special characteristics such as improved surface appearance, reduced friction, and flame retardancy. [7]

2.4.1 Types of Additives:

· **Antioxidants:** for plastic processing and outside application where weathering resistance is needed.

· **Foaming agents**: for expanded polystyrene cups and building board and for polyurethane carpet under-layment.

· **Lubricants:** used for making fibers.

· **Antimicrobials:** used for shower curtains and wall coverings.

· **Flame retardants:** to improve the safety of wire and cable coverings and cultured marble.

· **Fillers:** improve performance and/or reduce production costs. Many plastics contain fillers, relatively inert and inexpensive materials that make the product cheaper by weight. Typically fillers are mineral in origin, e.g., chalk. Some fillers are more chemically active and are called reinforcing agents. Other fillers include zinc oxide, wood flour, ivory dust, cellulose and starch.[8]

· **Plasticizers:** Since many organic polymers are too rigid for particular applications, they are blended with plasticizers (the largest group of additives,[1] oily compounds that confer improved rheology.

· **Colorants :** are common additives, although their weight contribution is small.

2.5 Classification

Plastics are usually classified by their chemical structure of the polymer's back bone and side chains. Some important groups in these classifications are the acrylics, polyesters, silicones, polyurethanes, and halogenated plastics. Plastics can also be classified by the chemical process used in their synthesis, such as condensation, polyaddition, and cross-linking.[7]

2.5.1 Thermoplastics and Thermosetting Polymers

There are two types of plastics: thermoplastics and thermosetting polymers. Thermoplastics are the plastics that do not undergo chemical change in their composition when heated and can be molded again and again. Examples include polyethylene, polypropylene, polystyrene and polyvinyl chloride.[9]

Common thermoplastics range from 20,000 to 500,000 amu, while thermosets are assumed to have infinite molecular weight. These chains are made up of many repeating molecular units, known as repeat units, derived from monomers; each polymer chain will have several thousand repeating units. Thermosets can melt and take shape once; after they have solidified, they stay solid. In the thermosetting process, a chemical reaction occurs that is irreversible. The vulcanization of rubber is a thermosetting process. Before heating with sulfur, the poly-isoprene is a tacky, slightly runny material, but after vulcanization the product is rigid and non-tacky.[1]

2.5.2 Thermoplastic and Thermoset Processing Methods.

There are a variety of different processing methods used to convert polymers into finished products. Some include:

· **Extrusion:** This continuous process is used to produce films, sheet, profiles, tubes, and pipes. Plastic material as granules, pellets, or powder, is first loaded into a hopper and then fed into a long heated chamber through which it is moved by the action of a continuously revolving screw. The chamber is a cylinder and is referred to as an extruder. The plastic is melted by the mechanical work of the screw and the heat from the extruder wall. At the end of the heated chamber, the molten plastic is forced out through a small opening called a die to form the shape of the finished product. As the plastic is extruded from the die, it is fed onto a conveyor belt for cooling or onto rollers for cooling or by immersion in water for cooling. The operation's principle is the same as that of a meat mincer but with added heaters in the wall of the extruder and cooling of the product.

Examples of extruded products include lawn edging, pipe, film, coated paper, insulation on electrical wires, gutter and down spouting, plastic lumber, and window trim. Thermoplastics are processed by continuous extrusion. Thermoset elastomer can be extruded into weather stripping by adding catalysts to the rubber material as it is fed into the extruder.

· **Calendering:** This continuous process is an extension of film extrusion. The still warm extrudate is chilled on polished, cold rolls to create sheet from 0.005 inches thick to 0.500 inches thick. The thickness is well maintained and surface made smooth by the polished rollers. Calendering is used for high output and the ability to deal with low melt strength. Heavy polyethylene films used for construction vapor and liquid barriers are calendered. High volume PVC films are typically made using calendars.

· **Film blowing:** This process continuously extrudes vertically a ring of semi-molten polymer in an upward direction, like a fountain. A bubble of air is maintained that stretches the plastic axially and radially into a tube many times the diameter of the ring. The diameter of the tube depends on the plastic being processed and the processing conditions. The tube is cooled by air and is nipped and wound continuously as a flattened tube.

The tube can be processed to form saleable bags or slit to form rolls of film with thicknesses of 0.0003 to 0.005 inches thick. Multiple layers of different resins can be used to make the tube.

· **Injection Moulding:** This process can produce intricate three-dimensional parts of high quality and great re-producibility. It is predominately used for thermoplastics but some thermosets and

Elastomer are also processed by injection moulding. In injection moulding plastic material is fed into a hopper, which feeds into an extruder. An extruder screw pushes the plastic through the heating chamber in which the material is then melted. At the end of the extruder the molten plastic is forced at high pressure into a closed cold mould.

The high pressure is needed to be sure the mould is completely filled. Once the plastic cools to a solid, the mould opens and the finished product is ejected. This process is used to make such items as butter tubs, yogurt containers, bottle caps, toys, fittings, and lawn chairs. Special catalysts can be added to create the thermoset plastic products during the processing, such as cured silicone rubber parts. Injection moulding is a discontinuous process as the parts are formed in moulds and must be cooled or cured before being removed. The economics are determined by how many parts can be made per cycle and how short the cycles can be.

· **Blow Moulding:** Blow moulding is a process used in conjunction with extrusion or injection moulding. In one form, extrusion blow moulding, the die forms a continuous semi-molten tube of thermoplastic material. A chilled mould is clamped around the tube and compressed air is then blown into the tube to conform the tube to the interior of the mould and to solidify the stretched tube. Overall, the goal is to produce a uniform melt, form it into a tube with the desired cross section and blow it into the exact shape of the product.

This process is used to manufacture hollow plastic products and its principal advantage is its ability to produce hollow shapes without having to join two or more separately injection moulded parts. This method is used to make items such as commercial drums and milk bottles. Another blow moulding technique is to injection mould an intermediate shape

called a preform and then to heat the preform and blow the heat-softened plastic into the final shape in a chilled mould. This is the process to make carbonated soft drink bottles.

· **Rotational Moulding:** Rotational moulding consists of a mould mounted on a machine capable of rotating on two axes simultaneously. Solid or liquid resin is placed within the mould and heat is applied. Rotation distributes the plastic into a uniform coating on the inside of the mould then the mould is cooled until the plastic part cools and hardens. This process is used to make hollow configurations include shipping drums, storage tanks and some consumer furniture and toys.

· **Compression Moulding:** This process has a prepared volume of plastic placed into a mould cavity and then a second mould or plug is applied to squeeze the plastic into the desired shape. The plastic can be a semi-cured thermoset, such as an automobile tire, or a thermoplastic or a mat of thermoset resin and long glass fibers, such as for a boat hull.

Compression moulding can be automated or require considerable hand labor. Transfer moulding is a refinement of compression moulding. Transfer moulding is used to encapsulate parts, such as for semi-conductor manufacturing.

· **Casting:** This process is the low pressure, often just pouring, addition of liquid resins to a mould Catalysed thermoset plastics can be formed into intricate shapes by casting. Molten polymethyl methacrylate thermo-plastic can be cast into slabs to form windows for commercial aquariums. Casting can make thick sheet, 0.500 inches to many inches thick.

· **Thermoforming:** Films of thermoplastic are heated to soften the film, and then the soft film is pulled by vacuum or pushed by pressure to conform to a mould or pressed with a plug into a mould. Parts are thermoformed either from cut pieces for thick sheet, over 0.100 inches, or from rolls of thin sheet. The finished parts are cut from the sheet and the scrap sheet material recycled for manufacture of new sheet. The process can be automated for high volume production of clamshell food containers or can be a simple hand labor process to make individual craft items.[7]

2.5.3 Other Classifications

Plastics can also be classified by various physical properties, such as density, tensile strength, glass transition temperature, and resistance to various chemical products.

I. Biodegradability

Biodegradable plastics break down (degrade) upon exposure to sunlight (e.g., ultra-violet radiation), water or dampness, bacteria, enzymes, wind abrasion, and in some instances, rodent, pest, or insect attack are also included as forms of bio degradation or environmental degradation. Some modes of degradation require that the plastic be exposed at the surface, whereas other modes will only be effective if certain conditions exist in landfill or composting systems. Starch powder has been mixed with plastic as a filler to allow it to degrade more easily, but it still does not lead to complete breakdown of the plastic. Some researchers have actually genetically engineered bacteria that synthesize a completely biodegradable plastic, but this material, such as Bio-pol, is expensive at present. Companies have made biodegradable additives to enhance the biodegradation of plastics.

II. Natural vs synthetic

Most plastics are produced from petrochemicals. Motivated by the finiteness of petrochemical reserves and threat of global warming, bio-plastics are being developed. Bio-plastics are made substantially from renewable plant materials such as cellulose and starch.[1]

In comparison to the global consumption of all flexible packaging, estimated at 12.3 million tonnes/year, estimates put global production capacity at 327,000 tonnes/year for related bio-derived materials.[1, 10]

III. Crystalline vs amorphous

Some plastics are partially crystalline and partially amorphous in molecular structure, giving them both a melting points (the temperature at which the attractive inter-molecular forces are overcome) and one or more glass transitions (temperatures above which the extent of localized molecular flexibility is substantially increased).

The so-called semi-crystalline plastics include polyethylene, polypropylene, poly (vinyl chloride), polyamides (nylons), polyesters and some polyurethane. Many plastics are completely amorphous, such as polystyrene and its co-polymers, poly (methyl methacrylate), and all thermosets.

2.6 Properties of Plastics

The properties of plastics are defined chiefly by the organic chemistry of the polymer such as hardness, density, and resistance to heat, organic solvents, oxidation, and ionizing radiation. In particular, most plastics will melt upon heating to a few hundred degrees Celsius.[1] While plastics can be made electrically conductive.

UL Standards.[1]

Many properties of plastics are determined by tests as specified by Underwriters Laboratories, such as:

- Flammability - UL94

- High voltage arc tracking rate - UL746A

- Comparative Tracking Index

ISO

Many properties of plastics are determined by standards as specified by ISO, such as:

- ISO 306 - Thermoplastics

2. 7 The Effects of Plastic on Environment:

There are many of the damage caused by the plastic of living organisms (human, animal and plant). Plastic contains some chemicals that are difficult and constitute a threat to the ocean environment and living organisms. Plastic factories produce a great amount of greenhouse gases and carbon dioxide, which lead to significant increase in global warming that can change many species habitats therefore their numbers will decrease.

Another fact that most kind of plastic diffuse toxic pollutants to the atmosphere, besides burning plastic generate toxic fumes fuse with the air. In addition these toxics can leak to the soil and groundwater and cause contamination of soil and groundwater which makes it impossible to grow the plants. These harmful chemicals have the ability to conflict with hormones in the body which is a major reason of many disease and faultiest in cells functions.[1]

2.7.1 Climate Change

The effect of plastics on global warming is mixed. Plastics are generally made from petroleum. If the plastic is incinerated, it increases carbon emissions; if it is placed in a landfill, it becomes a carbon sink although biodegradable plastics have caused methane emissions.[1] Due to the lightness of plastic versus glass or metal, plastic may reduce energy consumption. For example, packaging beverages in PET plastic rather than glass or metal is estimated to save 52% in transportation energy.[11]

Figure (2.2): Effecting of plastic on climate

2.7.2 Incineration of Plastics

Controlled high-temperature incineration, above 850C for two seconds, performed with selective additional heating, breaks down toxic dioxins and furans from burning plastic, and is widely used in municipal solid waste incineration. Municipal solid waste incinerators also normally include flue gas treatments to reduce pollutants further.

This is needed because uncontrolled incineration of plastic produces Poly chlorinated dibenzo-p-dioxins, a carcinogen (cancer causing

chemical). The problem occurs as the heat content of the waste stream varies. Open-air burning of plastic occurs at lower temperatures, and normally releases such toxic fumes.[1]

2.7.3 The Effects of Plastic on Human:

Plastic contains chemicals that cause damage to the nervous system and immune system and some genetic diseases. If the plastic exposed to high temperature is produced from the melt poisonous substances called dioxins, causing this article some tumours, birth defects, genetic mutations, and cause gas vehicles pollution in the air and the earth, as well as causing chemicals resulting from the manufacture of plastics, such as oxide, ethylene, gasoline destruction of the nervous system and immune system and certain types of cancers, kidney disease, and this chemical pollution dangerous resulting in poisoning of food and causing health problems are complex, most important of which increase the chance of infertility and disease cancer.

2.7.4 The Effects of Plastic on the Plants:

Bags and volumes of plastic if stabilized volumes and bags on the plants to prevent the arrival of sufficient light to also prevent them from breathing at night and hinder its growth, if you reach this material to the soil to prevent it from breathing and ventilation, may reach hundreds of years, because most microorganisms cannot analysis of plastic materials, plastic bags that need to be 1000 years to decompose in the soil because they contain chemical analysis difficult.

2.7.5 The Effects of Plastic on Animals:

The plastic is a danger to marine animals, when you get these materials to the seas and oceans is destroying the marine environment. When you get to work on the dam fish gills and prevent them from breathing and cause death. As well as causing damage to wildlife that may be addressed, causing blockage of the gastrointestinal tract and lead to death. Many animals eat the plastic bags by mistake this problem doesn't end in here because later when these animals died , the animal body will decompose but the plastic will not decompose and it will kill another victim.

2.7.6 The Effects of Plastic on Economy:

Plastic types are vary, some of them are petroleum -based plastic, which need more than 12 million barrels of petrol in its industry ,this type of plastic has a sharp increase in its price because of the petrol price. So scientists tried to find alternative materials for the petrol so they suggested to use oil shale and tar oil but it still expensive.

Besides people use plastic in big amount which can affect the economy of the individuals and country for example many people in the countries where water cannot be consume, they buy bottled water which cost a lot yearly and increase the amount of plastic waste, for that environmental groups like Clean Up the world suggest to find places of the good water to let the people use them instead of the bottled water. However, all of this cost a lot of money because finding alternatives require a lot of researches and studies which is expensive either.

B) WHAT IS THE PLASTIC WASTE?

Plastic waste is any substance which is discarded after primary use, or it is worthless, defective and of no use. Dozens of millions of tonnes of plastic debris end up floating in world oceans broken into micro plastic,

the so-called plastic soup. Micro plastics are found in the most remote parts of our oceans. Entanglement of turtles by floating plastic bags, sea mammals and birds that die from eating plastic debris and ghost fishing through derelict fishing gear produce shocking pictures. Moreover, plastic is not inert and chemical additives, some of them endocrine disruptors, can migrate into body tissue and enter the food chain.

The massive pollution of world oceans with plastic debris is therefore emerging as a global challenge that requires a global response. The European Union should be a showcase for how to build a coherent strategy to optimize plastic waste policy.

A second challenge is linked to resources conservation. Therefore, much energy and processed raw material is lost instead of being recycled into new products. Until now there is no comprehensive policy response to such challenges, specific aspects are addressed in various pieces of legislation, like the Waste Framework Directive with its 2015 separate plastic waste collection target or its 50% household waste collection target by 2020. The Packaging and Packaging waste Directive also has a specific plastic waste target.

Figure (2.3): Plastic waste in rivers

Plastic waste has started to attract increased public attention, notably due to a growing number of reports about marine litter. An estimated amount of more than 100.000 t, mostly so-called micro-plastics, is floating in the world's oceans. This is a great concern in particular since plastic and Pops concentrated on the surface of micro-plastics could enter the food chain. The potential environmental effects of this phenomenon are only beginning to be fully understood. In the light of the EU's policy objective of achieving a resource efficient recycling society it is hard to accept that in Europe we still landfill nearly 50% of plastic waste. On average nearly 80% of plastic in the marine environment is estimated to be coming from land.

Stepping up plastic waste prevention, preparation for re-use, recycling and separate plastic waste collection, as well as improving plastic design and plastic product design are all essential contributors to help achieve 'zero plastic to landfill' and move to a circular economy. Plastic products and plastic waste are two sides of the same coin and recycling already starts in the product design phase. Designers need to be involved in the reflection on the entire life cycle of products including the waste phase.

All actors designing, producing, using and disposing of plastic products and handling plastic waste will have to contribute to a less wasteful economy.

2.8 Plastic Waste Management Scenarios:

Waste management is all the activities and actions required to manage waste from its inception to its final disposal.[1] This includes among-st other things, collection, transport, treatment and disposal of waste

together with monitoring and regulation. It also encompasses the legal and regulatory framework that relates to waste management encompassing guidance on recycling etc.

The term usually relates to all kinds of waste, whether generated during the extraction of raw materials, the processing of raw materials into intermediate and final products, the consumption of final products, or other human activities, including municipal (residential, institutional, commercial), agricultural, and social (health care, household hazardous wastes, sewage sludge). Waste management is intended to reduce adverse effects of waste on health, the environment or aesthetics.[1]

Waste management practices are not uniform among countries (developed and developing nations); regions (urban and rural area), and sectors (residential and industrial).

2.8.1 Waste Hierarchy

The waste hierarchy refers to the "3 Rs" reduce, reuse and recycle, which classify waste management strategies according to their desirability in terms of waste minimization. The waste hierarchy remains the cornerstone of most waste minimization strategies. The aim of the waste hierarchy is to extract the maximum practical benefits from products and to generate the minimum amount of waste; see: resource recovery. The waste hierarchy is represented as a pyramid because the basic premise is for policy to take action first and prevent the generation of waste.

The next step or preferred action is to reduce the generation of waste i.e. by re-use. The next is recycling which would include composting. Following this step is material recovery and waste-to-energy. Energy can be recovered from processes i.e. landfill and combustion, at this level of

the hierarchy. The final action is disposal, in landfills or through incineration without energy recovery.

This last step is the final resort for waste which has not been prevented, diverted or recovered. The waste hierarchy represents the progression of a product or material through the sequential stages of the pyramid of waste management. The hierarchy represents the latter parts of the life-cycle for each product.[1]
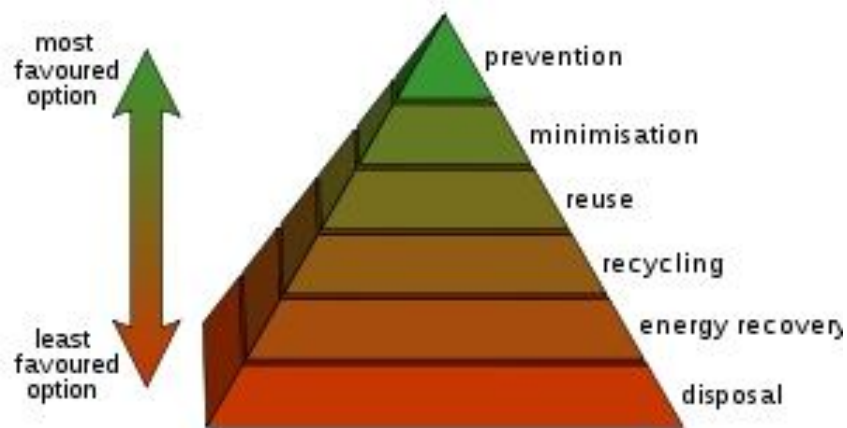

Figure (2.4): Diagram of the waste hierarchy

2.8.2 Life-cycle of a product

The life-cycle begins with design, then proceeds through manufacture, distribution, use and then follows through the waste hierarchy's stages of reuse, recovery, recycling and disposal. Each of the above stages of the life-cycle offers opportunities for policy intervention, to rethink the need for the product, to redesign to minimize waste potential, to extend its use. The key behind the life-cycle of a product is to optimize the use of the world's limited resources by avoiding the unnecessary generation of waste.

2.8.3 Landfill

A landfill site (also known as a tip, dump, rubbish dump, garbage dump or dumping ground and historically as a midden)[1] is a site for the disposal of waste materials by burial and is the oldest form of waste treatment (although the burial part is modern; historically, refuse was just left in piles or thrown into pits). Historically, landfills have been the most common method of organized waste disposal and remain so in many places around the world. Some landfills are also used for waste management purposes, such as the temporary storage, consolidation and transfer, or processing of waste material (sorting, treatment, or recycling).

Figure (2.5): A landfill site

Operations:

Typically, operators of well-run landfills for non-hazardous waste meet predefined specifications by applying techniques to:

- Confine wastes to as small an area as possible.

- Compact waste to reduce volume.

- Cover waste (usually daily) with layers of soil.

Advantages:

Landfills are often the most cost-efficient way to dispose of waste, especially in countries like the United States with large open spaces.

While resource recovery and incineration both require extensive investments in infrastructure, and material recovery also requires extensive manpower to maintain, landfills have fewer fixed—or ongoing—costs, allowing them to compete favorably. In addition, landfill gas can be upgraded to natural gas—landfill gas utilization—which is a potential revenue stream.

Disadvantages:

Social and environmental impact: cause a number of issues. Infrastructure disruption, such as damage to access roads by heavy vehicles, may occur. Pollution of local roads and water courses from wheels on vehicles when they leave the landfill can be significant and can be mitigated by wheel washing systems. Pollution of the local environment, such as contamination of groundwater or aquifers or soil contamination may occur, as well.

Dangerous gases: Methane is naturally generated by decaying organic wastes in a landfill. It is a potent greenhouse gas, and can itself be a danger because it is flammable and potentially explosive. In properly managed landfills, gas is collected and utilized. This could range from simple flaring to landfill gas utilization. Other potential issues include Wildlife disruption, dust, odor, noise pollution, and reduced local property values.

2.8.4 Incineration:

Incineration is a disposal method in which solid organic wastes are subjected to combustion so as to convert them into residue and gaseous products. This method is useful for disposal of residue of both solid waste management and solid residue from waste water management. This process reduces the volumes of solid waste to 20 to 30% of the original

volume. Incineration and other high temperature waste treatment systems are sometimes described as "thermal treatment". Incinerators convert waste materials into heat, gas, steam, and ash.

Incineration is carried out both on a small scale by individuals and on a large scale by industry. It is used to dispose of solid, liquid and gaseous waste. It is recognized as a practical method of disposing of certain hazardous waste materials (such as biological medical waste).

Incineration is a controversial method of waste disposal, due to issues such as emission of gaseous pollutants. Incineration is common in countries such as Japan where land is scarcer, as these facilities generally do not require as much area as landfills. Waste-to-energy (WtE) or energy-from-waste (EfW) is broad terms for facilities that burn waste in a furnace or boiler to generate heat, steam or electricity. Combustion in an incinerator is not always perfect and there have been concerns about pollutants in gaseous emissions from incinerator stacks. Particular concern has focused on some very persistent organic compounds such as dioxins, furans, and PAHs, which may be created and which may have serious environmental consequences.

2.8.5 Recycling

It is the process of collecting and processing materials that would otherwise be thrown away as trash and turning them into new products. Recycling can benefit your community and the environment.

Ⅰ-Benefits of Recycling

· Reduces the amount of waste sent to landfills and incinerators.

· Conserves natural resources such as timber, water and minerals.

・ Prevents pollution by reducing the need to collect new raw materials.

・ Saves energy.

・ Reduces greenhouse gas emissions that contribute to global climate change.

・ Helps sustain the environment for future generations.

・ Helps create new well-paying jobs in the recycling and manufacturing industries in the United States.

Ⅱ - Steps to Recycling Materials:

Recycling includes the three steps below, which create a continuous loop, represented by the familiar recycling symbol.

・ **Step 1: Collection and Processing**

There are several methods for collecting recyclables, including curbside collection, drop-off centers, and deposit or refund programs.

After collection, recyclables are sent to a recovery facility to be sorted, cleaned and processed into materials that can be used in manufacturing.

Recyclables are bought and sold just like raw materials would be, and prices go up and down depending on supply and demand in the United States and the world.

・ **Step 2: Manufacturing**

- **Step 3: Purchasing New Products Made from Recycled Materials**

In 1988, to assist recycling of disposable items, the Plastic Bottle Institute of the Society of the Plastics Industry devised a now-familiar scheme to mark plastic bottles by plastic type. A plastic container using this scheme is marked with a triangle of three "chasing arrows", which encloses a number giving the plastic type.
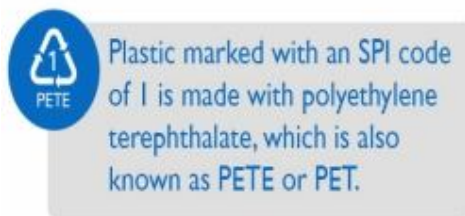
Plastic marked with an SPI code of 1 is made with polyethylene terephthalate, which is also known as PETE or PET. PETE-based containers sometimes absorb odors and flavors from foods and drinks that are stored inside of them. Items made from this plastic are commonly recycled. PETE plastic is used to make many common household items like beverage bottles, medicine jars, peanut butter jars, combs, bean bags, and rope. Recycled PETE is used to make tote bags, carpet, fiberfill material in winter clothing, and more.

The SPI code of 2 identifies plastic made with high-density polyethylene, or HDPE. HDPE products are very safe and are not known to leach any chemicals into foods or drinks. Plastic Milk Jugs (However, due to the risk of contamination from previously held substances, please note: it is NEVER safe to reuse an HDPE bottle as a food or drink container if it didn't originally contain food or drink!) HDPE products are commonly recycled. Items made from this plastic include containers for milk, motor oil, shampoos and conditioners, soap bottles, detergents, and bleaches.

Many personalized toys are made from this plastic as well. Recycled HDPE is used to make plastic crates, plastic lumber, fencing, and more.

Plastic labeled with an SPI code of 3 is made with polyvinyl chloride, or PVC. PVC is not often recycled and can be harmful if ingested. PVC is used for all kinds of pipes and tiles, but it's most commonly found in plumbing pipes. This kind of plastic should not come in contact with food items. Recycled PVC is used to make flooring, mobile home skirting, and other industrial-grade items.

Plastic marked with an SPI code of 4 is made with low-density polyethylene, or LDPE.

Plastic marked with an SPI code of 4 is made with low-density polyethylene, or LDPE. LDPE is not commonly recycled, but it is recyclable in certain areas. It tends to be both durable and flexible. It also is not known to release harmful chemicals into objects in contact with it, making it a safe choice for food storage. Plastic cling wrap, sandwich bags, squeezable bottles, and plastic grocery bags all are made from LDPE. Recycled LDPE is used to make garbage cans, lumber, furniture, and many other products seen in and around the house.

Consumers will find the SPI code of 5 on plastic items made with polypropylene, or PP.

Plastic marked with an SPI code of 6 is made with polystyrene, also known as PS and most commonly known as Styrofoam. PS can be recycled, but not efficiently; recycling it takes a lot of energy, which means that few places accept it. Disposable coffee cups, plastic food boxes, plastic cutlery, packing foam, and packing peanuts are made from PS. Recycled PS is used to make many different kinds of products, including insulation, license plate frames, and rulers.

Plastic marked with an SPI code of 6 is made with polystyrene, also known as PS and most commonly known as Styrofoam. PS can be recycled, but not efficiently; recycling it takes a lot of energy, which means that few places accept it. Disposable coffee cups, plastic food boxes, plastic cutlery, packing foam, and packing peanuts are made from PS. Recycled PS is used to make many different kinds of products, including insulation, license plate frames, and rulers.

The SPI code of 7 is used to designate miscellaneous types of plastic that are not defined by the other six codes. Polycarbonate and polylactide are included in this category. Plastic CD's and DVDs These types of plastics are difficult to recycle. Polycarbonate, or PC, is used in baby

bottles, large water bottles (multiple-gallon capacity), compact discs, and medical storage containers. Recycled plastics in this category are used to make plastic lumber, among other products.

2.8.6 Pyrolysis

Plastics can be pyrolyzed into hydrocarbon fuels, since plastics have hydrogen and carbon. One kilogram of waste plastic produces roughly a litter of hydrocarbon. Pyrolysis is a process with relatively low cost from which a wide distribution of products can be obtained. In the process of pyrolysis, where heating occurs in the absence of oxygen, the organic compounds are decomposed generating gaseous and liquid products, which can be used as fuels and / or sources of chemicals. Traditional treatments for post-consumed plastics were landfills or incineration. HDPE, LDPE, PP and PS are all hydrocarbons consisting entirely of carbon and hydrogen, which are similar to hydrocarbon fuels such as liquefied petroleum gas (LPG), petrol and diesel. Plastics are derived from petroleum and have calorific values in a similar range as those of LPG, petrol and diesel as given in Table (2.1).[12]

This method can be improved by the addition of catalysts, which will reduce the temperature and reaction time and allow the production of hydrocarbons with a higher added value, such as fuel oils and petrochemical feed stocks.[1, 9] That is, the use of catalysts gives an added value to the pyrolysis and cracking efficiency of these catalysts depends both on its chemical and physical characteristics. These particular properties, promote the breaking of C-C bonds and determine the length of the chains of the products obtained.[1, 12]

Table (2.1): Comparison of energy density of plastics and different types of fuel [1]

Material	Calorific value (MJ/kg)
Polyethylene	46.3
Polypropylene	46.4
Polystyrene	41.4
Polyvinyl chloride	18.0
Liquefied petroleum gas	46.1
Kerosene	43.4
Diesel	43.0
Light fuel oil	41.9
Heavy fuel oil	41.1

Table (2.2):   Hydrocarbon range in commercial fuels

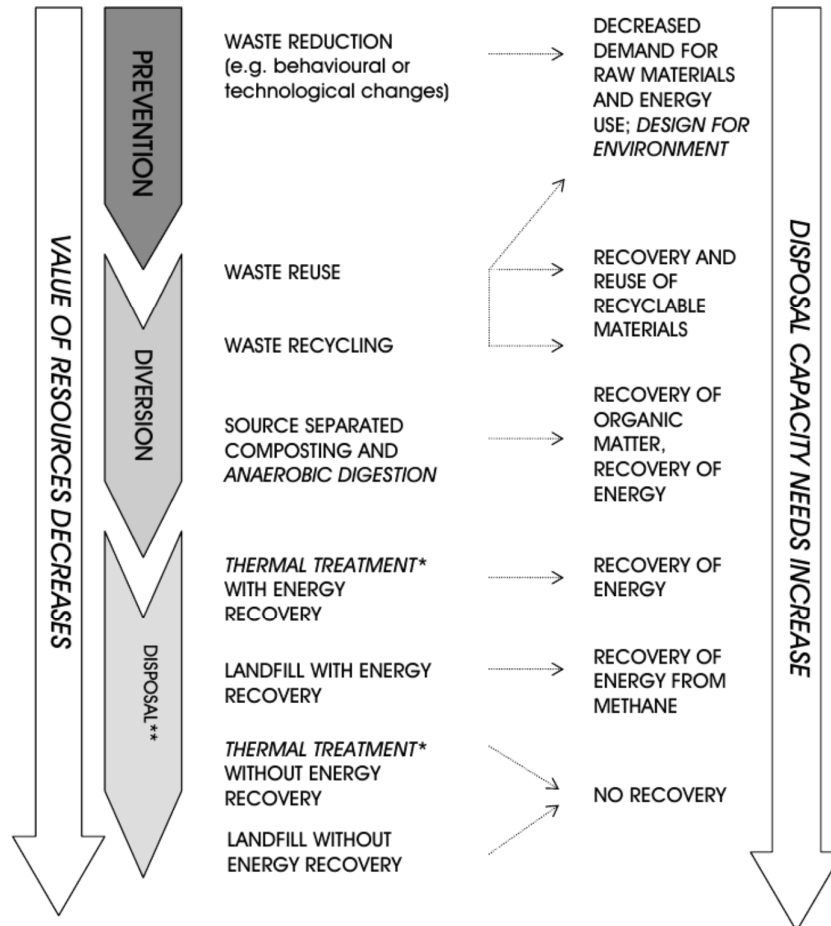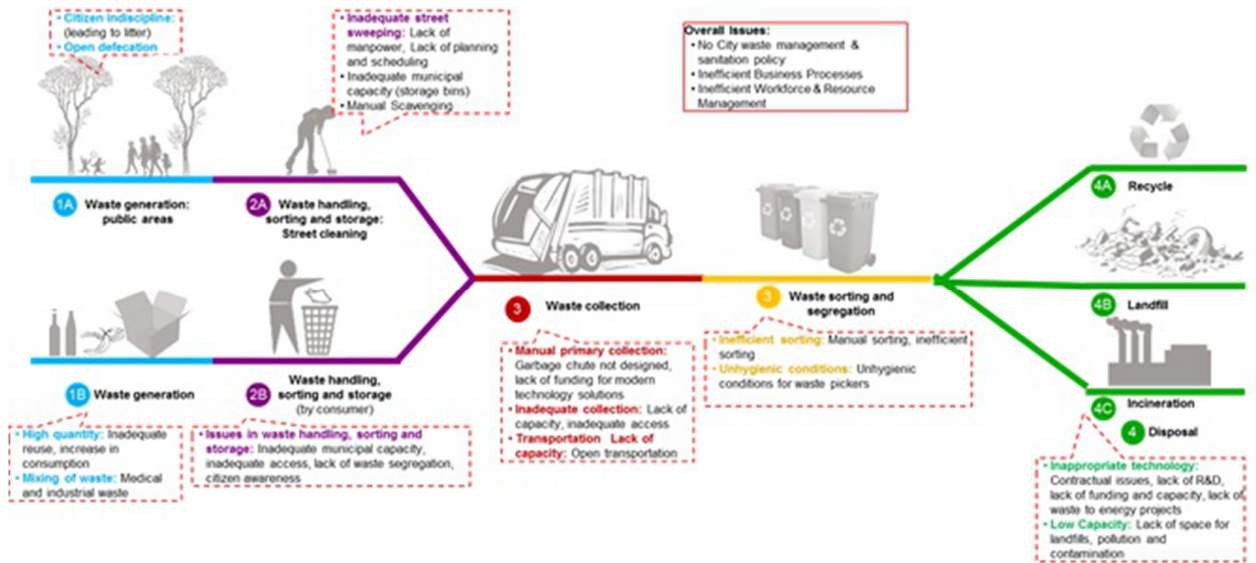| Fuels	LPG	Petrol	Kerosene	Diesel	Heavy Fuel oil
Hydrocarbons	C3 to C4	C4 to C12	C12 to C15	C12 to C24	C12 to C70

Figure (2.6): Waste management hierarchy

Figure (2.7): waste management scenarios
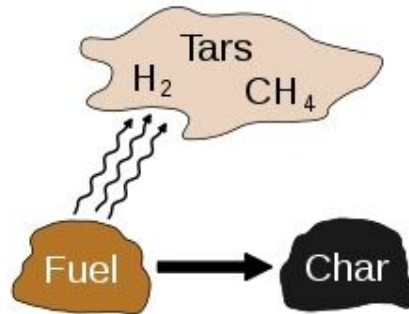
C) PYROLYSIS

Figure (2.8): Simplified depiction of pyrolsis chemistry.

Pyrolysis is the thermochemical decomposition of biomass at temperatures between 400 and 650 °C in the absence of O2. The decomposition process releases volatile species, while the solid, non-volatiles are collected as bio-char. A portion of the gas-phase volatiles condense into a black, viscous fluid termed bio-oil[10] that has a variety of synonyms including pyrolsis oil, bio-crude oil, bio-fuel oil, wood liquid, wood oil, liquid smoke, wood distillates, pyroligneous tar, and pyroligneous acid. Pyrolysis methods differ in their residence time, temperature, and heating rate, which in turn greatly affect the percentages of gas, char, and liquid products in a semi-predictable manner, while the resulting, individual chemical species remain hard to predict and quantify.[1] Pyrolysis methods can be grouped into two large categories, slow and fast (or flash) pyrolsis.[13]
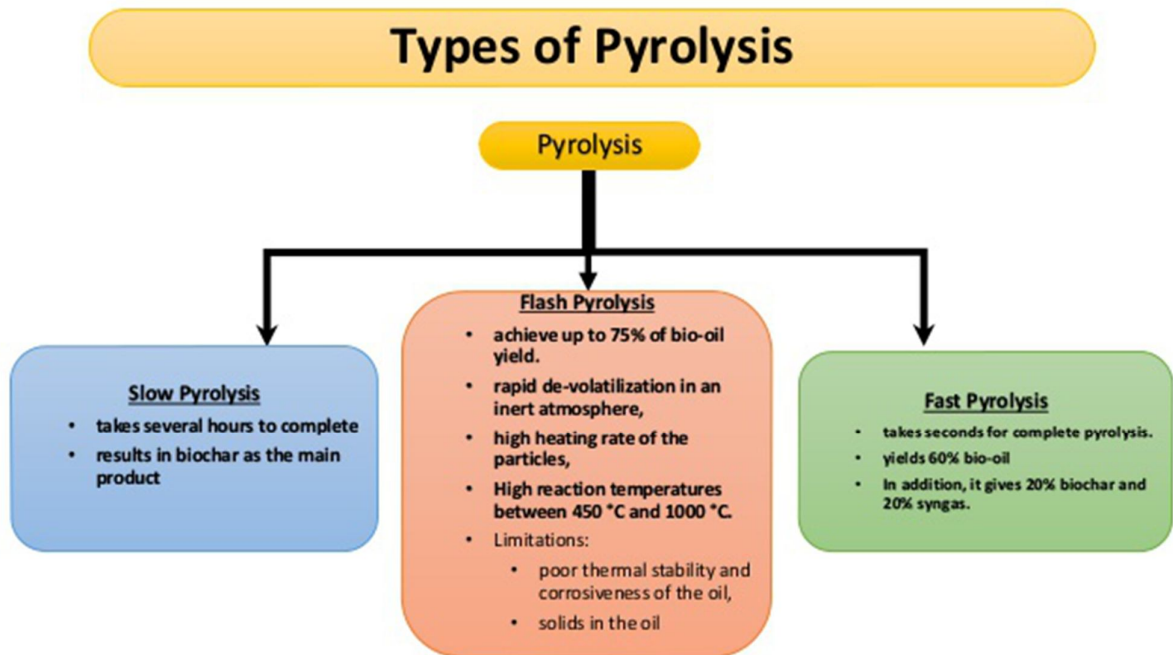
Figure (2.9): Types of pyrolysis

Slow pyrolysis consists of slow heating rates of 0.1–1 °C/s, a residence time anywhere from hours to minutes, and a temperature range of 400–60 °C. It has been used for centuries to produce methanol and yields approximately equal quantities of char, gas, and liquid.

Fast pyrolysis is a relatively new, promising technology involving a high liquid yield achieved through rapid heating rates of 10 to >1000 °C/s, short residence times of <2 s, temperatures of 400–650 °C, and rapid quenching of the vapors.[1]

2.9 Processes

Since pyrolysis is endothermic, various methods to provide heat to the reacting biomass particles have been proposed:

- Direct heat transfer with a hot gas, the ideal one being product gas that is reheated and recycled. The problem is to provide enough heat with reasonable gas flow rate.

- Indirect heat transfer with exchange surfaces (wall, tubes): it is difficult to achieve good heat transfer on both sides of the heat exchange surface.
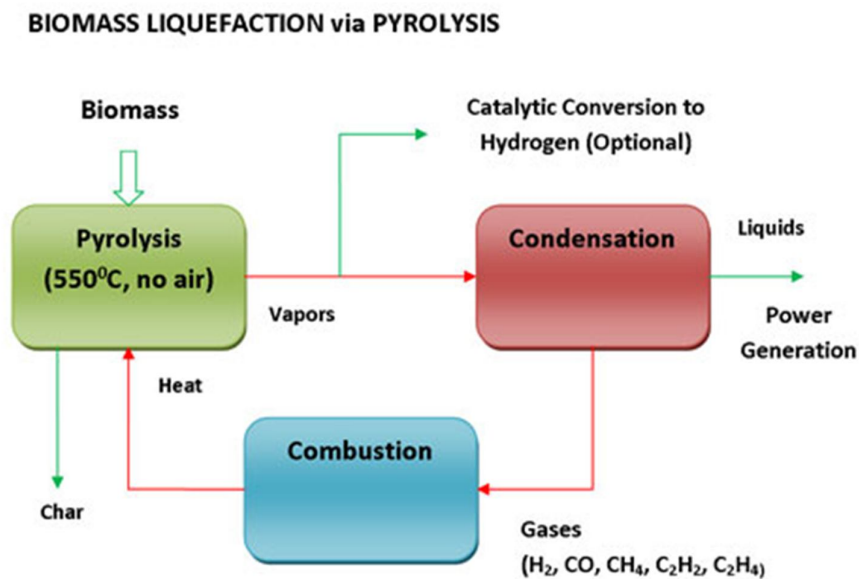

Figure (2.10): Pyrolysis diagram

Bio-oil varies according to process conditions and feed stock. Most studies have focused on fast pyrolysis oil that can be generalized as consisting of hydroxyaldehydes, hydroxyketones, carboxylic acids, furan/pyran ring containing compounds, anhydrosugars, phenolic compounds and oligomeric fragments of lignocellulosic polymers with some examples represented in figure(2.11). These products stem from the original biomass composition consisting of cellulose, hemicelluloses,

lignin, extractives, lipids, proteins, simple sugars, starches, water, hydrocarbons, ash, and other compounds.[14]
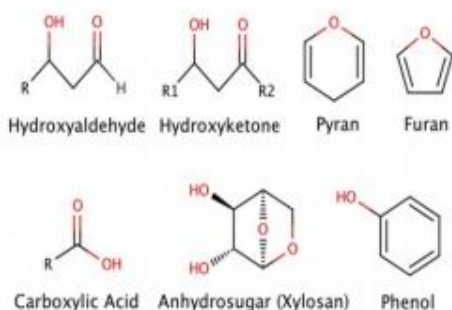

Figure (2.11):   Representative compounds of bio-oil.

Reactions under pyrolsis conditions are complex and not fully understood due to the range of reaction temperatures and the complex biomass composition, but they can be generally classified as asimultaneous mix of dehydration, depolymerization, re-polymerization, fragmentation, rearrangement, and condensation, as represented by some examples in figure (2.12).

These reactions result in a bio-oil containing over 300 individual compounds. For more extensive reviews of the elemental and chemical composition of biomass and bio-oil see Yanik et al. , Branca et al. , Lu et al. , Valtiner et al. , Ralph et al., Evans et al. , Marsman et al. , and Sipila et al. .
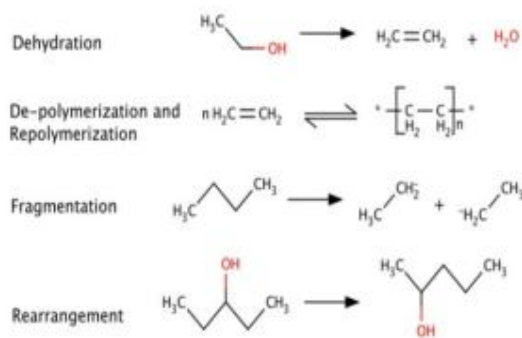
Figure (2.12): Representative pyrolysis reactions.

To overcome these issues, bio-oil must be modified chemically or 'upgraded' by the removal and modification of unwanted compounds, most of which contain oxygen. Many times, the final product is evaluated by its O/C ratio and H/C ratio, with low O/C and high H/C ratios indicating a higher quality liquid product. These ratios are especially important if the bio-oil is to be used as a substitute for demanding petrochemical applications such as transportation fuels that need a clean, homogenous fuel stream. To achieve these results, bio-oil can be re-volatilized in a catalytic environment, generally referred to as catalytic upgrading, or biomass can be pyrolyzed in the presence of catalysts that affect the desired changes before the initial condensation, generally referred to as catalytic fast pyrolsis. Ideally, a single reactor would fulfill all process requirements and produce a quality liquid fuel from the initial, solid biomass [38,39]. Due to its potential in a wide variety of situations, many consider catalytic fast pyrolsis to be the most promising way to improve the final, liquid composition.[1] The challenge is to design catalysts that positively affect all of the over 300 volatilized, organic compounds through various cracking and reforming reactions. This is important for biorefineries and will help them become cost competitive

with current infrastructure. Improving catalysts' activity, selectivity, and stability is essential for progress in the field of biomass utilization.

In McMurrys study, the branched polyethylene is also called low density polyethylene (LDPE), which is different from linear polyethylene that is called high density polyethylene (HDPE). [1, 15]

Table (2.3): Bio-oil vs. Crude oil characteristics

| Composition	Bio-oil	Crude Oil
Water (wt %)	15–30	0.1
pH	2.8–3.8	-
density (kg/L)	1.05–1.25	0.86
viscosity 50 °C (cP)	40–100	180
HHV (MJ/kg)	16–19	44
C (wt %)	55–65	83-86
O (wt %)	28–40	<1
H (wt %)	5–7	11–14
S (wt %)	<0.05	<4
N (wt %)	<0.4	<1
Ash (wt %)	<0.2	0.1
H/C	0.9–1.5	1.5–2.0
O/C	0.3–0.5	≈0

2.10 Factors affecting Plastic pyrolsis

The major factors influencing the plastic pyrolysis process and pyrolysis product molecular distribution include chemical composition of the feed stock, cracking temperature and heating rate, operation pressure, reactor type, residence time and application of catalyst. These factors are summarized in this section as follows.[16]

2.10.1. Chemical composition of feed stock

The pyrolysis products are directly related to the chemical composition and chemical structure of the plastics to be pyrolysis. In

addition, the chemical composition of the feed stock also affects the pyrolysis processes. As mentioned in Chapter 1, PE and PP are most commonly used polymeric hydrocarbons and were selected as the investigated materials in this study. Polyethylene is formed from ethylene through chain polymerization which is shown in Formula 2-1.

n CH2= CH2   polymerization   -(CH2 -CH2-)n
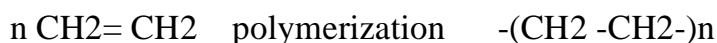
Ethylene   Polyethylene

Formula (2.1) Polymerization of ethylene to polyethylene

Plastics can be classified, according to structural shape of polymer molecules, as linear, branched, or cross-linked in Figure (2.13). The units in linear polymer are linked only to two others, one to each ends. The polymer is termed branched when branches extend beyond the main polymer chain randomly. In branched polymers, at least one of the monomers is connected to more than two functional groups due to the branching points produced from the polymerization process.

There is a significant relationship between the density and the branching intensity of polymers. The PE with more branches has relatively lower density.
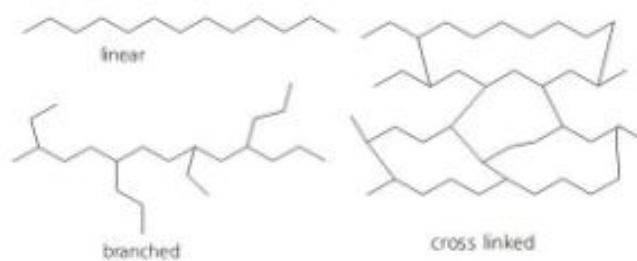

Figure (2.13): Polymer structure, linear, branched and cross linked

A cross linked polymer can be described as an interconnected branched polymer with all polymer chains are linked to form a large molecule. Thus, the cross linked polymer constitutes large molecule. The cross linked polymer cannot be dissolved in solvents or be melted by heat because of their network structure. For example, PEX, a common abbreviate of cross-linked polyethylene, is widely used in oil and water piping. In pyrolysis process, cross linked polymer will crack rather than melt or evaporate. This is different from the reactions of linear or branched polymers in pyrolysis process.[1]

2.10.2. Cracking temperature and heating rate

Temperature is one of the most important operating variables, since the temperature dominates the cracking reaction of the polymer materials. Van der Waals force is the force between the molecules, which attracts molecules together and prevents the collapse of molecules. When the vibration of molecules is great enough, the molecules will evaporate from the surface of the object. However, the carbon chain will be broken if energy induced by van der Waals force along the polymer chains is greater than the enthalpy of the C-C bond in the chain.[1]

This is the reason why high molecular weight polymer is decomposed rather than is boiled when it is heated. In theory, the temperature of thermal breaking the C-C bonds should be constant for a given type of plastic (polymer). However, this temperature has been found to differ in different studies. Different locations of the temperature sensors in different studies are believed to be one of the most important factors on the different cracking temperature reported. Karaduman et al. investigated the temperature profile along a tube heated by external furnace.[1] Large

temperature variation was observed between the ends and the centre of the tube. (Figure 2.14) Clearly, there was significant heat loss at both ends of the tube reactor.
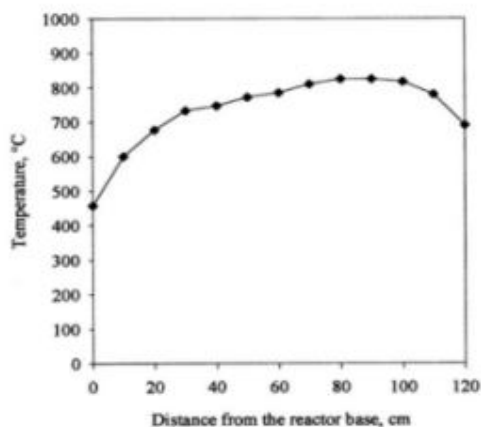

Figure (2.14): Temperature profile along the tube reactor
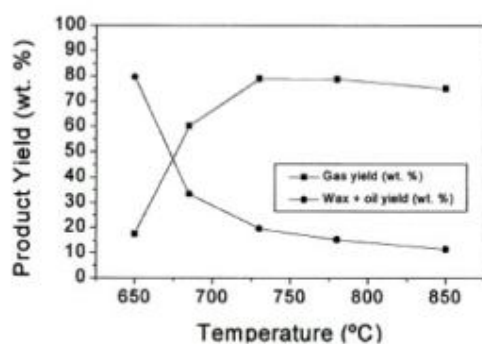

Figure (2.15): Influence of temperature on product distribution

However, the overall gas proportion of gas product increased with increasing cracking temperature up to 730°C while the liquid product proportion decreased with the cracking temperature in the full range of temperature used. (Figure 2.15)

51

2.10.3. Type of reactor

The reactor type for the plastic pyrolysis significantly influences on the heat transfer rate, mixing of plastics with pyrolsis products, residence time and the reflux level of the primary products. Reactors can be classified into batch, semi-batch and continuous or classified based on types of reactor bed.[16]

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. Batch and semi-batch reactors are mainly applied on research,[1, 10] and continuous reactor is mainly for industrial production such as Mitsui R21, Fuji, Toshiba, Veba Oel, PKA, etc.

Fixed bed and fluidized reactors

Based on the heat transfer methods and flow patterns of the feed stock and products, the pyrolysis reactors can be classified into fixed bed reactor, fluidized bed reactor and screw kiln reactor. In the fixed bed reactor, the pyrolysis occurs on a stationary bed which is easy to design and operate.

The fluidized bed reactor has been used in most commercial plants in which gaseous products or inert gas flow through an expanded bed of feed stock and other bed materials, forming bubbles or eddies. The advantages of fluidized bed reactor are the homogeneity of both temperature and composition. Heat and mass transfer rates are much higher than the fixed bed thus the low thermal conductivity in fluidized bed reactors is no longer a problem. In the fluidized bed reactor, the dimensions and the material of the bed material are the key parameters affecting the pyrolysis and products. Bed materials loss and separation from the gases are other issues which need consideration.[17]

2.10.4. Residence time

The definition of residence time differs in various studies. In fast pyrolysis or continuous pyrolysis process, it refers to the contact time of the plastic on the hot surface throughout the reactor. However in slow pyrolysis and batch process, the residence time means the duration from the time when feed stock plastic start to be heated to the time when the products are removed. Longer residence time favours a further conversion of the primary products thus yielding more thermal stable products such as light molecular weight hydrocarbons, non-condensable petroleum gases. In a slow pyrolysis, long residence time encourages the carbonization process and produces more tar and char in the products. The pyrolysis conditions, residence time and target products are given in Table (2.4).

Table (2.4): The pyrolsis conditions, residence time and target product

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)

Except for the batch pyrolysis reactor in a closed system, residence time is difficult to be controlled directly but scan be adjusted by altering other operation parameters such as feeding rate, carrier gas flow rate and product discharge rate. Residence time was, then, calculated for these controllable operation parameters.

Secondary pyrolysis cracking occurs when residence time is long enough, which enhances the yield of gaseous product.[1, 15] Higher value of V/m represents longer residence time in Figure (2.16). The Y axis is the conversion of HDPE to gaseous product. There is a significant effect on the conversion when the residence time varies in a certain range during the non-catalyst thermal reaction.
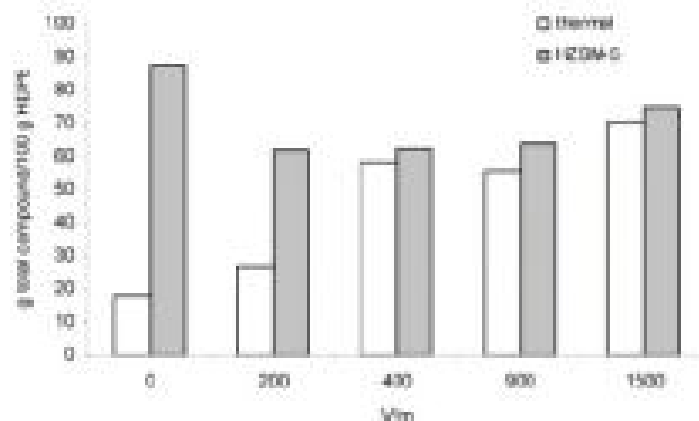
Figure (2.16): Influence of residence time on the production of gaseous
product (from HDPE thermal and catalytic cracking)

2.10.5. Use of catalyst

Advantages of using catalyst

In order to optimize plastic pyrolysis reactions and modify the distribution of pyrolysis products, catalysts are widely used in research and industrial pyrolysis processes. Petroleum fuels, such as LPG, petrol, kerosene, and diesel, are hydrocarbons from C1 to C24. The PE pyrolysis products are mainly straight hydrocarbons from C1 up to C80, which contain much more heavier molecular weight components.[1] One of the main purposes of using catalysts is to shorten the carbon chain length of the pyrolsis products and thus to decrease the boiling point of the products.

Catalysts are found to be mainly applied to PE pyrolsis because the primary product from other plastics, such as PP is mainly light hydrocarbons, with similar carbon chain length to the range of commercial fuels. The products from non-catalytic PE pyrolsis contain high proportion of 1-alkenes and dialkenes. Moreover, it is reported that

activation energies (Ea) measured in the PE pyrolsis with catalysts (such as HZSM-5, HY, and MCM-41) were much lower than those when no catalyst was added.[1]

Catalyst classification Homogeneous and heterogeneous catalysts have been studied for the catalytic cracking of plastics. Homogeneous catalysts used for polyolefin pyrolsis have mostly been classical Lewis acids such as AlCl3. Generally, heterogeneous catalysts are preferred due to their easy separation and recovery from the reacting medium.

Heterogeneous catalysts can be summarized as nanocrystalline zeolites, aluminium pillared clays, conventional acid solids, mesostructured catalysts, superacid solids, gallosilicates, metals supported on carbon, and basic oxides. Among the mentioned catalysts, nanocrystalline zeolites have been extensively studied for polyolefin pyrolsis and this type of catalysts will be discussed in more details as follow.

Zeolite properties: pore size (structure) and Si/Al ratio (acidity) A zeolite is a crystalline aluminosilicate with a three-dimensional framework structure that forms uniform pores of molecular dimensions. Zeolites act as sieves on a molecular scale and exclude molecules that are too large to pass through the pores. The 23 three-dimensional frame structures significantly increases the area of the sieves and absorbs molecules that have similar sizes as the pores. According to the structure of zeolites, 176 zeolite framework types have been confirmed.

A three-letter code, such as MFI, is assigned to framework types by the Structure Commission of the International Zeolite Association. The codes are normally derived from the name of the zeolite, for example, MFI from ZSM-5 (Zeolite Socony Mobil-five). The MFI framework type

of ZSM-5 is described as shown in Figure (2.17), with pentasil chains running parallel to z.[1]

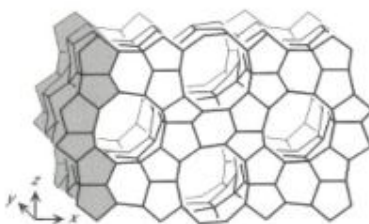**Figure (2.17):The framework type ZSM-5 with pentasil chain parallel to z**

2.11 Catalytic Upgrading

2.11.1 Introduction

The addition of catalysts to the pyrolsis system enhances reactions that include cracking, decarbonylation, decarboxylation, hydrocracking, hydrodeoxygenation, and hydrogenation[1] as summarized in figure (2.18).
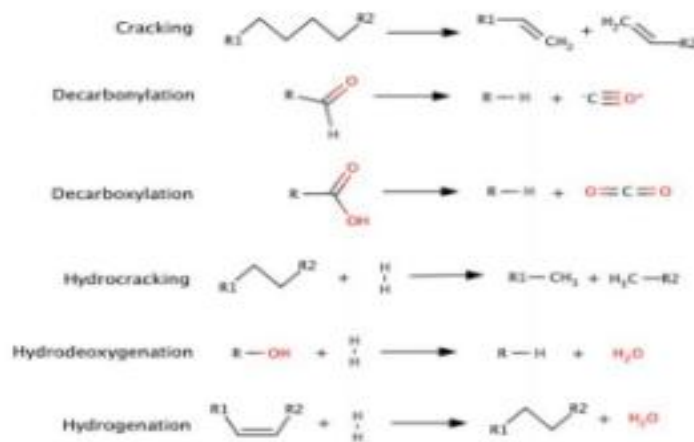

Figure (2.18): Representative catalytic upgrading reactions.

As shown in fig. (2.18), catalytic upgrading can enhance the properties of bio-oil by removing oxygenated compounds via H_2O and CO_2, reducing molecular weight, and altering chemical structures to resemble those of petrochemical products. Interestingly, biomass has within its chemical framework naturally present ions that can have catalytic effects under pyrolsis reaction conditions, such as reducing the bio-oil yield in favor of char and gaseous species. This effect was observed with the most abundant inorganic components of biomass, including silica, Na, K, Mg, and Ca. Both the cations and anions present were shown to have an effect on the pyrolsis products, while demineralization was shown to increase the yield of anhydrosugars.

Catalytic effects of inorganics found in ash have also been studied. Patwardhan et al. studied the pyrolysis of pure cellulose in the presence of switchgrass ash, a representative mix of water-soluble salts of alkali and alkaline earth metals. It was discovered that as little as 0.5% ashes resulted in a tripling of the formic acid and quadrupling of glycoaldehyde, whereas the levoglucosan yield was halved. The comparative yields of each chemical species were changed, but the individual species themselves were unaffected. Most of these inorganic salts can be extracted with an acid wash, even though some alkaline earth metals associated with organic macromolecules are resistant to extraction.

It is therefore important to take into consideration that pyrolsis is inherently a catalytic process unless pretreated, and when studying the selectivity of additional catalysts, the catalytic effects of various naturally occurring minerals should be evaluated.

Catalysts should be highly active, selective to particular products, resistant to deactivation, readily recycled, and cheap. Most catalysts used

in the upgrading of bio-oil are supported, meaning the metal catalyst is dispersed on a different and cheaper material such as carbon, silica, or alumina. Supported catalysts are cost effective and can generally be used at higher temperatures due to the dispersed metal particles' resistance to sintering, or melting together. Furthermore, the support itself can act as a catalyst. Different catalysts have different mechanisms for eliminating oxygen and catalyzing other desired reactions as shown in formula (2.12) and (2.18). Two main routes for upgrading have dominated the research and development fields, hydro-deoxygenation and zeolite cracking.

Current research focuses on improving catalyst effectiveness and longevity. The petroleum industry has been eliminating sulfur from petrochemicals for years using a similar hydrogenolysis process called hydrodesulfurization (HDS).

A possible mechanism for HDO of a lignin-derived compound such as guaiacol on a supported metal catalyst is given in fig. (2.19).[1]
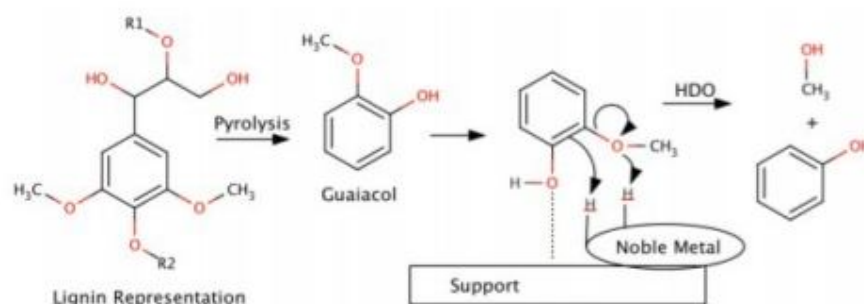

Figure (2.19): **Possible mechanism for HDO of guaiacol**

HDO of guaiacol was studied using zirconia-supported mono- and bimetallic noble metal catalysts in a batch reactor at 80 bar. Rh, Pd, Pt, RhPd, RhPt, and PdPt all performed better in the hydrogenation of

guaiacol at 100 °C and at 300 °C than the conventional sulfided CoMo/
Al2O3 catalyst which deactivated due to carbon deposition and
contaminated the product with sulfur. Rh and RhPt completely converted
the guaiacol at 100 °C to a variety of products, but deoxygenation only
took place at 300 °C. The bimetallic catalysts containing Rh gave better
results than the monometallic Pt and Pd catalysts in terms of guaiacol
hydrogenation. The PdPt catalyst was less reactive than that of the
separate monometallic catalysts. This indicates that catalysts react with
each other in a variety of ways when used simultaneously, in addition to
reacting with the biomass. For a comparison of several methods for
characterizing HDO oils see Oasmaa et al.. Table (2.5) provides a
summary of the yield, product quality, and operating conditions for
several catalysts investigated for HDO. DOD (%) stands for degree of
deoxygenation.[1]

Table (2.5): Summary of catalysts investigated for HDO.

Catalyst	Temp. (°C)	Pressure (bar)	DOD (%)	O/C	H/C	Oil Yield (wt %)	Ref.
Co-MoS$_2$/Al$_2$O$_3$	350	200	81	0.8	1.3	26	[58]
Co-MoS$_2$/Al$_2$O$_4$	370	300	100	0	1.8	33	[64]
Ni-MoS$_2$/Al$_2$O$_3$	350	200	74	0.1	1.5	28	[58]
Ni-MoS$_2$/Al$_2$O$_4$	400	85	28	.	.	84	[65]
Pd/C	350	200	85	0.7	1.6	65	[58]
Pd/C	340	140	64	0.1	1.5	48	[55]
Pd/ZrO$_2$	300	80	.	0.1	1.3	.	[56]
Pt/Al$_2$O$_3$/SiO$_2$	400	85	45	.	.	81	[65]
Pt/ZrO$_2$	300	80	.	0.2	1.5	.	[56]
Rh/ZrO$_2$	300	80	.	0	1.2	.	[56]
Ru/Al$_2$O$_3$	350	200	78	0.4	1.2	36	[58]
Ru/C	350–400	230	73	0.1	1.5	38	[66]
Ru/C	350	200	86	0.8	1.5	53	[58]
Ru/TiO$_2$	350	200	77	1	1.7	67	[58]

2.11.2 Catalytic Cracking with Zeolites

Zeolites are complex, three-dimensional porous structures with varying elemental compositions that exhibit catalytic activity in up to 50% of their volume. Cracking and dehydration are the main reactions seen.

Adsorption of the oxy-compound occurs on an acid site. This is followed by either decomposition or bimolecular monomer dehydration, as determined by pore size. As with sulfide/oxide and transition metal catalysts, the acidity of the zeolite affects the reactivity and yields, with high acidity leading to a higher affinity for C and water formation. In HZSM-5, one of the most widely used zeolites; acidity is linked to the Si/Al ratio, with a low ratio indicating high acidity. Pore blockage from polymerization and polycondensation reactions causes deactivation of the catalyst. Zeolites should have correct pore size and acidic sites to promote desired reactions while minimizing carbon formation. A possible mechanism for dehydration of hydroxyl containing compounds (i.e.,carbohydrates) on an aluminosilicate zeolite is given in figure(2.20).

Zeolites produce aromatics at atmospheric pressures without H2 requirements. The final product generally has a low heating value. This is due both to its low H/C ratio and high O/C ratio as compared to HDO oils.[1] Research is generally conducted at temperatures from 350 to 600 °C. For HZSM-5, yields are in the 15% range with predictions of 23%. Excessive C production and therefore catalyst coking is a problem. In one study, coke deposition at all temperatures led to a decrease in the catalytic activity after only 30 min time on stream.

Furthermore, coke has been shown to significantly increase at temperatures above 400 °C. Some coke can be burned off, but irreversible

dealumination and loss of acid sites occurs at temperatures as low as 450 °C in the presence of water Research on the reduction of coking is important, with a variety of approaches showing promise. For example, the recycling of non-condensable gases into a catalytic reactor has the potential to reduce char/coke yields while increasing oil yields.[1]
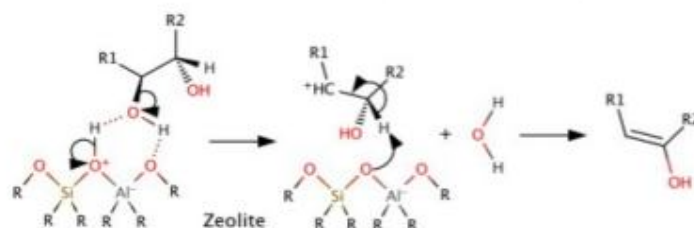

Figure (2.20): Aluminosilicate zeolite dehydration of model compound.

The elemental composition of the fast pyrolysis bio-oil feedstock, as measured by its H/Ceff ratio has been determined to have a large impact on the production of olefins, aromatics, and coke. Experiments have shown that pyrolytic bio-oil feedstocks with a ratio of at least 1.2 or higher perform better in zeolite cracking upgrading. Ten feed stocks were studied over HZSM-5. Yields of olefins and aromatics increased while coke production decreased with increasing H/Ceff ratios. Catalyst life increased as coke yield decreased. This suggests that it may be beneficial to increase the H/Ceff ratio to 1.2 through hydrogenation of the bio-oil feedstock before upgrading with a zeolite catalyst.

Other zeolites have been studied in comparison to HZSM-5 with mixed results. In one study using a fixed bed micro-reactor operating at 1 bar, 3.6 weight hourly space velocity (WHSV), and 330–410 °C, HZSM-5 was found to yield more hydrocarbons than HY, H-mordenite, silicalite, and other silica-alumina zeolites. HZSM-5 and H-mordenite

also showed higher selectivity for aromatics than aliphatics while the other catalysts produced the opposite effect. However, other zeolites do have some advantages. In a similar study, silicalite produced the least coke. Silica-alumina best converted the non-volatile fraction of the bio-oil. HZSM-5 produced the most yields in the gasoline boiling point range while HY and H-mordenite produced fewer yields and in the kerosene boiling point range. In another study, catalytic pyrolysis of pinewood over zeolites HBeta-25, HY-12, HZSM-5-23, and HMOR-20 was conducted in a fluidized bed reactor at 450 °C. Quartz sand was used for non-catalytic pyrolysis. Oil from each bed was chemically characterized and compared. Overall, ketones and phenols were produced. HZSM-5 produced more ketones and less alcohols and acids than other catalysts. It also produced more liquid, similar in quantity to the quartz bed but containing more water. Mordenite and quartz produced almost no PAHs. One major advantage noted is that the catalysts were regenerated successfully.

Table (2.6): Summary of catalysts investigated for zeolite cracking.

Catalyst	Temp. (°C)	Feedstock	Catalyst Effects	Ref.
HZSM-5 with varying Si/Al$_2$O$_3$ ratios	500–764	Kraft Lignin	Decreasing the SiO$_2$/Al$_2$O$_3$ ratio from 200/1 to 25/1 and increasing the catalyst-to-lignin ratio from 1:1 to 20:1 decreased the oxygenates and increased the aromatics. Aromatics yield increased from 500 to 650 °C and then decreased at higher temperatures. Under optimal reaction conditions, the aromatic yields were 2.0% (EHI 0.08) and 5.2% (EHI 0.35).	[88]
HZSM-5, Na/ZSM5, HBeta, and HUSY	650	Alkaline lignin	H-USY had the largest pore size and lowest Si/Al ratio (7) and had the best liquid yield of 75% and aromatic yield of 40%.	[89]
ZSM-5, Al/MCM-41, Al-MSU-F, ZnO, ZrO$_2$, CeO$_2$, Cu$_2$Cr$_2$O$_5$, Criterion-534, alumina-stabilized ceria-MI-575, slate, char and ashes derived from char and biomass	500	Cassava rhizome	ZSM-5, Al/MCM-41, Al-MSU-F type, Criterion-534, alumina-stabilized ceria-MI-575, Cu$_2$Cr$_2$O$_5$, and biomass-derived ash were selective to the reduction of most oxygenated lignin derivatives. ZSM-5, Criterion-534, and Al-MSU-F catalysts enhanced the formation of aromatic hydrocarbons and phenols. No single catalyst was found to reduce all carbonyl products but ZSM-5, Criterion-534 and MI-575 could reduce most of the carbonyl products that contained hydroxyl groups. ZSM-5, Criterion-534, Al/MCM-41, Al-MSU-F, copper chromite, char and ashes increased acetic, formic, and lactic acid. MI-575 did not increase acids.	[90]
Dolomite	500–800	Waste olive husks	Dolomite increased cracking and gas production.	[91]
HZSM-5, Al/MCM-41, Al-MSU-F, and alumina-stabilized ceria MI-575, pore sizes 5.5, 31, 15, and NA respectively	500	Cassava rhizome	HZSM-5 was the most effective catalyst for the production of aromatic hydrocarbons, phenols, and acetic acid and the reduction of oxygenated lignin-derived compounds and carbonyls containing side chain hydroxyl groups. Only MI-575 showed a decrease in acetic acid yields. MI-575 also showed the most increase in methanol with HZSM-5 a close second.	[81]

Catalysts can either be mixed with the biomass prior to pyrolysis or separated as to only interact with the gaseous reactants. It was discovered that separation of the catalyst and biomass was more effective for the conversion to desirable products. This study involved a catalyst containing Fe and Cr in their oxide forms, chromite (FeCr2O4) in the combined active phase. It showed promising results in terms of limited water production. Chromite produces hydrogen from water and carbon

monoxide in the WGS reaction. The catalyst therefore consumes water produced from deoxygenation through the WGS reaction while producing large quantities of hydrogen.Chromite also showed selectivity in converting the heavy phenolic compounds to phenol and light phenolics.[1]

2.11.3 Pressure

Operating pressure has significantly effect on both the pyrolsis process and the products. The boiling points of the pyrolsis products are increased under higher pressure, therefore, under pressurised environment heavy hydrocarbons are further pyrolyzed instead of vaporized at given operation temperature. Figure (2.21) shows the effect of pressure on hydrocarbon number and their fractions in the pyrolysis products of PE.

In effect, under pressurized pyrolsis, more energy is required for further hydrocarbon cracking. It was also found that high pressure increases the yield of non-condensable gases and decreases the yield of liquid products. (Figure 2.21) The average molecular weight of gas product also decreases with the increase of pressure.[1]
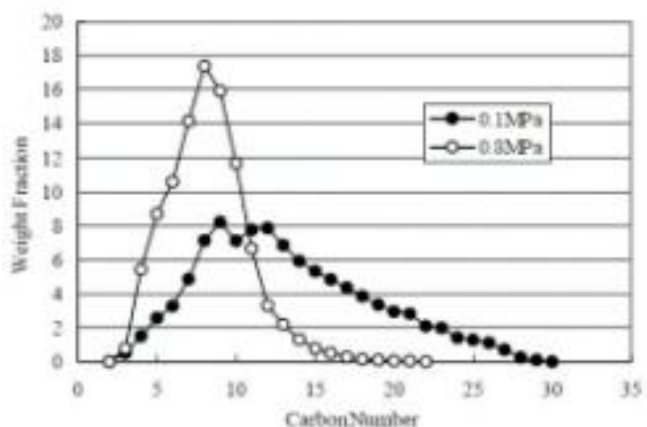

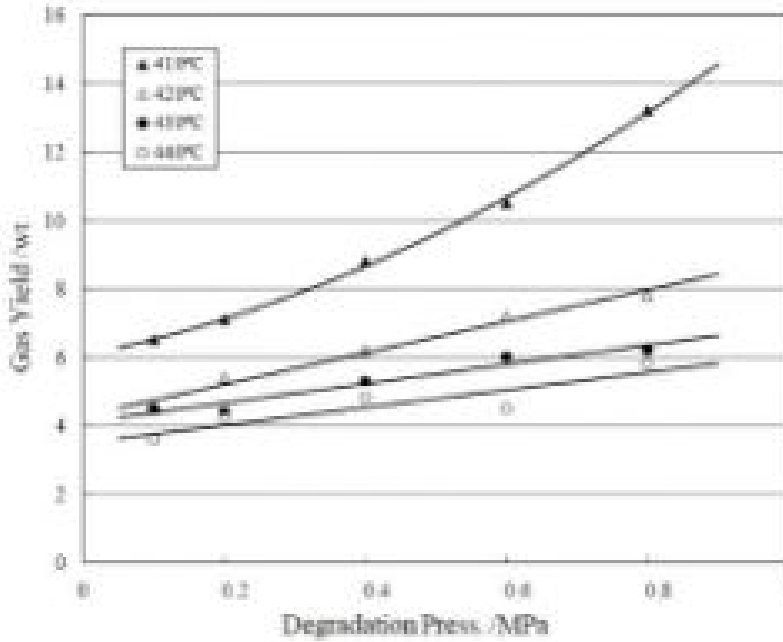**Figure (2.21): Effect of pressure on the distribution of PE pyrolysis products**

Figure (2.22): Effect of pressure on the yield of gas at different temperature
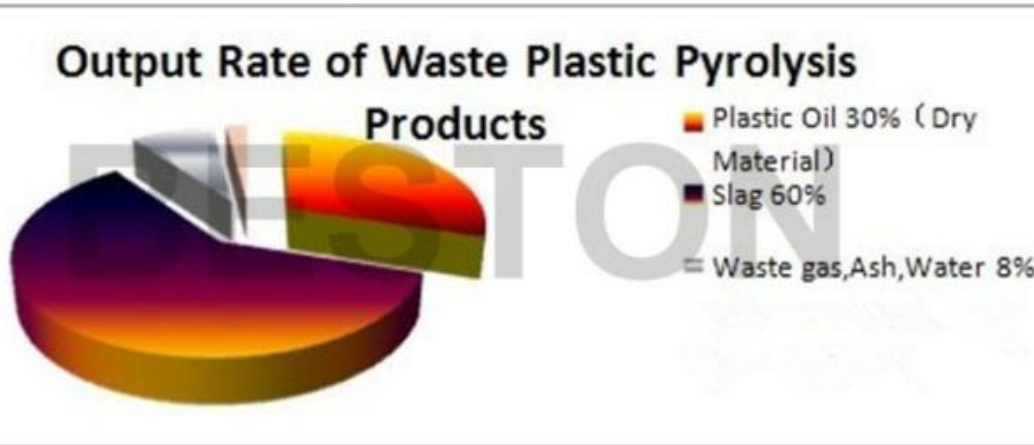

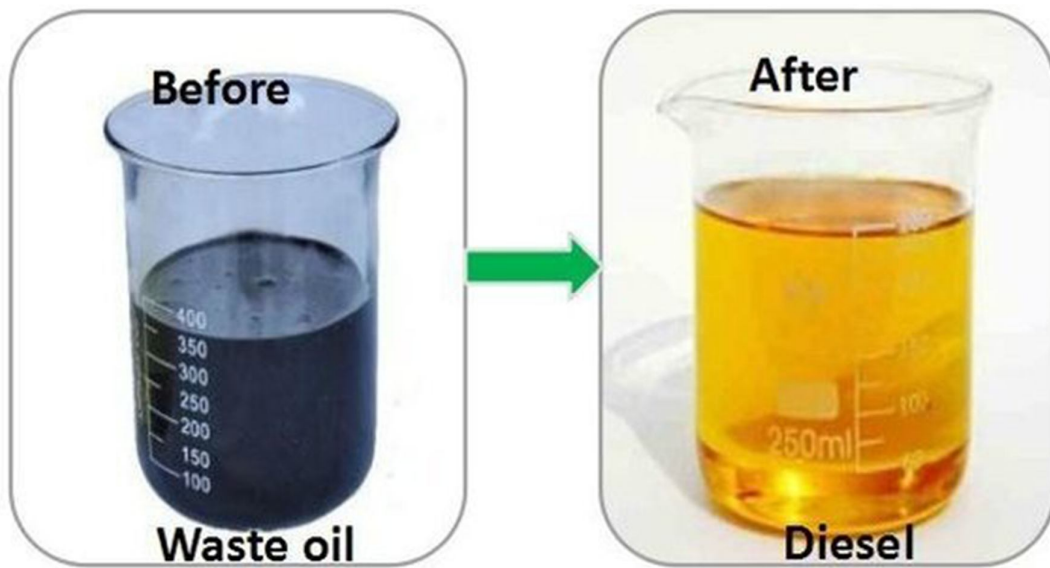**Figure (2.23): The output rate of waste plastic pyrolsis**

Figure (2.24): The end product of pyrolsis process

Previous Work and Studies

◆ M. Sarker and M. M. Rashid (April 2013) had performed Black color non coded food container hard shape waste plastic to fuel product into laboratory scale in the batch process at temperature 400 ºC. 125 gm Sample was used for experimental purpose and fuel product production conversion rate was 87.3%. Product fuel density is 0.76 g/ml. fuel color is light yellow and fuel is ignited. Product fuel was analyzed by GC/MS, and Chromatogram analysis compounds carbon range showed C3 to C27. They proposed that their product fuel can be used for internal combustion engine because fuel has short chain to long chain hydrocarbon compounds.[18]

◆ M. Dohare Devendra1 and M. Nagori Kaustubh2 (July 2014) had worked on new technologies to treat the plastic waste. Batch reactor is used in pyrolsis process in which temperature ranges between 350 to 5000C in atmospheric pressure. The aim of the study is to convert the mixed plastic waste into crude oil which can be used as hydrocarbons fuel. In the present paper waste plastic pyrolsis oil and its blend with diesel has been introduced as an alternative fuel. Waste plastic oil (W.P.O.) was tested as a fuel in a D.I. diesel engine and it is observed that the engine could operate with 100% waste plastic oil and can be used as fuel in diesel engines.[19]

◆ M. Seyed Alireza Sakaki, M. Behrooz Roozbehani, M. Mohammadreza Shishesaz and M. Nasrin Abdollahkhani (11 November 2013) had used Mixture of polymers (HDPE/LDPE/PP) to pyrolyze over a silico-alumina catalyst using a laboratory semi batch reactor operating isothermally at ambient pressure. The experiments we're discussed and show that the used of catalyst provides proper

selectivity in the liquid product distributions and improved the yield of light hydrocarbon productions. The liquid samples were ana- lyzed using GC/FID to find out their composition. The liquid collected at optimum condition (420 °C, 40 cat/pol ratios) was distilled at different temperatures to discretize light and heavy fractions. Octane number, color, Reid vapor pressure, specific gravity, and density are further analyised to determine extra physicochemical properties of the liquids at optimum reaction condition. Also, results were compared with the physical properties of commercial gasoline which imply that the liquid somewhat matches with standard gasoline. By using Arrhenius's law, a kinetic model at optimum reaction conditions has been developed and activation energy determined. The reaction follows the first-order kinetic rate relationships. This model equation gives a suitable match with experimental results.[20]

◆ Behrooz Roozbehani,1 Bagher Anvaripour, Zahra Maghareh Esfahan, 2 Mojtaba Mirdrikvand,1 and Saeedeh Imani Moqadam1 (January 2013) had We have studied the effect of temperature and catalyst loading on the product yield in cracking of high density polyethylene (HDPE).[21]

We have identified the optimal temperature and catalyst loading that results in maximum conversion. We have constructed a kinetic model of the process and have determined the activation energy.

◆ M. Nagori Kaustubh and M. Dohare Devendra (September 2014) had converted the mixed (selected) plastic waste into crude oil which can be used as hydrocarbons fuel using   pyrolsis in Batch reactors and temperature ranges between 370 to 550 0C under atmospheric pressure. Waste plastic oil (W.P.O.) was tested as a fuel in a D.I.

diesel engine and it is observed that the engine could operate with 100% waste plastic oil and can be used as fuel in diesel engines.[11]

◆ M. Sunbong Lee1, M. Koji Yoshida2 and M. Kunio Yoshikawa1,2 (March 2015) had focused on plastics from municipal wastes that were converted into oil through the pyrolsis and the catalytic reforming process in a commercial facility. Compared with diesel fuel, the raw pyrolsis oil showed slightly lower kinematic viscosity than the minimum level of diesel fuel and almost the same heating value. Its carbon class differed from diesel, gasoline and kerosene and is mainly composed of naphethenes and olefins which have poor self-ignition quality. The pyrolsis oil was blended with diesel fuel with different mixing ratios. A single cylinder small size direct injection diesel engine was used for the test. The full load performance, the exhaust emissions and the thermal efficiency were investigated from the view point of the compatibility to diesel fuel based on the US EPA regulation mode.[22]

◆ M. Devaraj J, M. Y. Robinson, and M. P.Ganapathi (April-June 2015) had investigated the effect of variable compression ratio on the performance and emission characteristics of a single cylinder, direct injection diesel engine powered by waste plastic pyrolsis oil blended with diethyl ether. Experiments were conducted with different compression ratios of 15, 16, 16.5 and 17 at various load conditions with a constant speed of 1500 rpm. Two blends of WD05 and WD10 on volume basis have been tested and compared with respect to waste plastic pyrolsis oil and diesel fuel. Brake thermal efficiency was slightly higher with respect to diesel fuel. It was observed that the exhaust emissions are significantly decreased with increase in diethyl ether waste plastic pyrolysis oil (DEE –WPPO) at full load

conditions. By increasing the compression ratio from 15 to 17, produces lower smoke opacity, hydro carbon (HC), Oxides of nitrogen (NOx) and carbon monoxide (CO) respectively.

◆ M. CEYLA GÜNGÖR1,M. HASAN SERIN1, M. MUSTAFA ÖZC NLI1, M. SELAHATTIN SERIN2, and M. KADIR AYDIN (Dec 2015) had evaluated the use of various blends of plastic oil produced from waste polyethylene (WPE) with diesel fuel (D). WPE was degraded thermally and catalytically using sodium aluminum silicate as a catalyst. The oil collected at optimum conditions (414◦C–480◦C rangeand1hreaction time) was fractionated at different temperatures and fuel properties of the fractions were measured. Plastic oil was blended with diesel fuel at the volumetric ratios of 5%, 10%, 15%, 20%, and 100%. Fuel properties of blends are found comparable with those of diesel fuel within the EN 590 Diesel Fuel standard and they can also be used as fuel in compression ignition engines without any modification. Engine performance and exhaust emission studies of 5% WPE-D (WPE5) blend were performed. Experimental results showed that carbon monoxide (CO) emission is decreased by 20.63%, carbon dioxide (CO_2) emission is increased by 3.34%, and oxides of nitrogen (NOx) emission is increased by 9.17% with WPE-D (WPE5) blend compared to diesel fuel.[23]

◆ Prof.Vikas Mukhraiya, M. Raj Kumar Yadav and M. Brajesh raikawar (Dec 2015) had used high density polythene and low density polythene to converted into recycled fuel by pouring in the close combustion chamber, then by heating the close combustion chamber in temperature range of 110 to 300 degree celsius for approximately 30 minute to 1 hour. Then the sample converted into fuel and was used in four stroke petrol engine. It was observed that 8ml fuel run

bike of 110 cc bajaj caliver for approx 2 minute. Also different properties of the fuel are calculated namely viscosity, density, specific gravity, flash point, fire point, cloud point, or pour point .then these properties of the fuel and petrol fuel are compared. It give similar properties like petrol fuel.[24]

◆ M. Raj Kumar Yadav and Prof. Yogesh Kumar Tembhurne (Jan-Feb 2016) had used plastic wastes for the pyrolsis to get fuel oil that has the same physical properties as the fuels like petrol, diesel etc. Pyrolsis runs without oxygen and in high temperature of about 300°C which is why a reactor was fabricated to provide the required temperature for the reaction. The waste plastics are subjected to depolymerisation, pyrolsis, thermal cracking and distillation to obtain different value added fuels such as petrol, kerosene, and diesel, lube oil etc. Converting waste plastics into fuel hold great promise for both the environmental and economic scenarios.[25]

CHAPTER THREE

MATERIALS AND METHODS

3.1 INTRODUCTION

In this work, several types of reactor were designed and constructed as shown in figures below. The goal of these experiments was to customize the process of the plastic pyrolysis through monitoring and analyzing the temperature profile and the type of oil according to the plastic type. In the system, a gas stove was applied to heat the reactor as an external heating resource. The reactor was made of iron pipe with inner diameter 27mm and thickness of 5mm. The system also consists of water cooling condenser connected to the reactor with pipe diameter 1.27mm.

The materials supplied by plastic recycling factories which were: HDPE, LDPE, PP in addition to a mixer of them with different percentages as post-consumer plastic chips was supplied by a plastic recycling factories Johnson, Swalif and Poly tech.

3.2 MATERIALS

Materials used in this research work were as follows:

1. High density polyethylene, (HDPE)
2. Low density polyethylene, (LDPE)
3. Polypropylene, (PP)
4. Mixture of the above three single resins with variable percentages.

High Density Polyethylene (HDPE):

HDPE is a polyethylene thermoplastic made from petroleum. It is sometimes called "polythene" when used for pipes. It characterized with a

high strength-to-density ratio, HDPE is used in the production of plastic bottles, corrosion-resistant piping, geo-membranes, and plastic lumber. HDPE is commonly recycled, and has the number "2" as its resin identification code. In 2007, the global HDPE market reached a volume of more than 30 million tons.

Mechanical properties:

Stiffness, strength, toughness, resistance to chemicals and moisture, permeability to gas, ease of processing, and ease of forming.

Physical properties:

Table (3.1): Properties of HDPE

Density	0.93 to 0.97 g/cm3 or 970 kg/m3
Melting point	259-267 ºC
Tensile strength	0.20 - 0.40 N/mm2

HDPE used in this work was shredded bags and jars from poly tech plastic factory and Johnson plastic factory.

Low Density Polyethylene (LDPE):

LDPE is a thermoplastic made from the monomer ethylene. It was the first grade of polyethylene, produced in 1933 by Imperial Chemical Industries (ICI) using a high pressure process via free radical polymerization. The EPA estimates 5.7% of LDPE (recycling number 4) is recycled Despite competition from more modern polymers, LDPE continues to be an important plastic grade. In 2013 the worldwide LDPE market reached a volume of about US$33 billion.

Physical Properties:

Table (3.2): Properties of LDPE

Density	0.917 - 0.930 g/cm3
Tensile Strength	0.20 - 0.40 N/mm2
Thermal Coefficient of expansion	100 - 220 x 10-6

Chemical resistance:

- Excellent resistance (no attack / no chemical reaction) to dilute and concentrated acids, alcohols, bases and esters.
- Good resistance (minor attack / very low chemical reactivity) to aldehydes, ketones and vegetable oils.
- Limited resistance (moderate attack / significant chemical reaction, suitable for short-term use only) to aliphatic and aromatic hydrocarbons, mineral oils, and oxidizing agents.
- Poor resistance, and not recommended for use with halogenated hydrocarbons.

LDPE used here was a small cutting of bags from poly tech plastic factory.

Polypropylene (PP):

PP is a thermoplastic polymer used in a wide variety of applications. An addition polymer made from the monomer propylene, it can be produced in a variety of structures giving rise to applications including packaging and labeling, textiles, plastic parts and reusable containers of various types, laboratory equipment, automotive components, and medical devices. It is a white, mechanically rugged material, and is resistant to many chemical solvents, bases and acids. Polypropylene is the

world's second-most widely produced synthetic plastic, after polyethylene. Also is the most important plastic with revenues expected to exceed US$145 billion by 2019. The sales of this material are forecast to grow at a rate of 5.8% per year until 2021.

Physical Properties:

Table (3.3): Properties of PP

Density	0.855 g/cm^3, amorphous ,0.946 g/cm^3, crystalline
Melting point	130 to 171 °C (266 to 340 °F; 403 to 444 K)
Young's modulus	Between 1300 and 1800 N/mm².

PP used was recycled ropes in small pieces from sawalif plastic factory.

3.3 EQUIPMENT

Domestic pressure cooker

50 litter pressure cooker as shown in figure (3.1) was used for first reactor trials. The condensation unit was copper pipes connected to glass condenser with flask to receive the final product. The reactor was heated by gas stove with electrical heater connected to electrical temperature control.

Figure (3.1): Domestic pressure cooker

Vertical Reactor V1

5 litter vertical reactor as shown in figure (3.2) was designed and constructed from iron using local facilities. The condensation unit was a jar of water, heating unit was gas stove only.

Figure (3.2): vertical reactor V1

Vertical Reactor V2

In this version the 5 litter vertical reactor was heated by electrical heater instead of the gas stove to maintain temperature control in the system. Three electrical heaters were made one in the bottom of reactor

and two around it, all of this was connected to electric circuit, as shown in Figure (3.3).

Figure (3.3): Vertical reactor V2

Horizontal Reactor V3

A new design of the same vertical unit reactor in a horizontal direction was used. A motor was used to rotate the unit to facilitate material mixing and smooth melting beside good temperature distribution and increased the white gas outcome. V3 is shown in figure (3.4)

Figure (3.4): Horizontal reactor V3

Vertical Reactor V4

In this version vertical reactor V1 was developed by adding new condenser made of iron as intermediate stage of condensation to decrease the losses of condense-able gases in addition to give good pure oil quality. Two temperature measuring watches were added, one at the reactor exit pipe were the gas pass through it to measure the temperature of gas leaving the reactor, and the another watch after the condenser to measure the temperature of the gas leaving the condenser. Then converted gas to oil was complete in a jar full of water as shown in figure (3.5).

Figure (3.5): Reactor V4

Vertical reactor V5

In this version, vertical reactor V4 was again developed by taking out the condenser and the watch after condensation as shown in figure (3.6)

Figure (3.6): Reactor V5

3.4 METHODS

Domestic cooker:

Several experiments were accomplished using domestic cooker as follows:

1) Cooker was filled with water and heated up to 100ºc by gas stove. After a while some steam leakage was observed in the connection between the copper pipe and the top of pressure cooker. Then steam release was fixed and cooker was reheated up again to 107ºc, another leakage of steam was observed in the sensor connection so the test was stopped. After fixing the sensor connection by welding the sensor at the top, cooker was heated again to 117ºc then the pressure indicator rose up and the temperature was stable. The pressure indicator hole was closed, cooker was filled again with water and heated and the temperature raised to 79ºc the steam was given out and temperature continued rising to 102ºc and then stopped.

2) 1.5 kg LDPE was loaded into the pressure cooker then heated, when the temperature raised to 225ºC the sensor turned off, but the condenser holder was broken and the gas inside the condenser escaped to air, Fixed the condenser holder and raised the temp again to 225ºc when the gas was detected in the condenser, the pressure watch melted so test stopped.

3) Changed the pressures watch and re-use the process by using same plastic. After the plastic melted the gases started passing in the condenser but the condensation was not good, some of gases did not condensed. Also some of gas was released through the hands of cooker. In spite of we continuing the process for two hours by increasing the water compression inside the condenser to collect the output. After all this trials few output yield compared to the quantity of plastic used.

4) fixed the cooker by brushing the nails and loaded it with 1 kg of LDPE, the process started at 10:55 am, when the temperature raised up to 225ºc at 11:07 am the gases begin inside the condenser and all the stuck oil around the glass from the previous process will passed to the receiving flask shown in fig (4.2), then continue the condensation of gas to oil. This process was better than the others also the outcome was better and continuous shown in fig (3.4); but there was some problem in condensation some the gases does not condense, some of it became as thick viscous substance shown in fig (4.2) and a little amount of gas escaped through the nails . The process was ended up at 11:30 am.

5) Closed all the holes in cooker to prevent the gases escaping and reloading cooker with 1 kg LDPE then started, when the temperature reached 70oc the pressure cooker exploded.

Vertical reactor V1

It is assumed that the pressure cooker did not meet the requirements of these procedures. Then if changed with another material can hold and continue at the high temperature using reactor V1. Several experiments were accomplished using V1 reactor as follows:

1) Started the first trial at 11:20 am by adding 1Kg of HDPE until 3:50 pm, the product was approximately 70 ml shown in fig (4.3) with plastic remained unconverted.

2) Reactor was loaded with 850g of HDPE at 11:45 am, after half an hour the bubbles begin at the surface of water then the white gas observed after an one hour, 14 minutes. The white gas automatically started and condenses to oil in jar of water. After 2 hour the percentage of oil was little due to the rate of heating and thickness of reactor, increasing the rate of heating increased the gas subsequently, but the water became too hot, ice was added to help in cooling. An hour later the oil amount increased quickly. The procedure was stopped after 3 hours at 2:45 pm, then separated the oil from water by making a small hole at the bottom of jar allowing the water to pass out and the oil remain in the jar then place it in the glass flask shown in fig (4.4).

3) 1kg of HDPE were adding to a reactor and started at 11:35 am, after half an hour the bubbles started and white gases condense to oil . The

test ended at 1:05 pm then we separate the oil from water the product shown in fig (4.6). This trail was better than before.

4) 1kg of PP were used at 4:30 pm, the bubbles of white gases started after half an hour from beginning and the operation stopped at 5:30 pm. then oil was separated from water. After finished the reactor opened and a residual plastic shown in figure (3.7).which was not converted was collected.

Figure (3.7): Pyrolsis Residues for HDPE using V1 reactor

5) 1Kg of PP were added at 12:26 am and stopped at 1:54 pm. This operation was very quick and the final product was very good shown in figure (4.7).

Vertical reactor V2

Operation on V2 started using 1kg of HDPE at 11am. and continued for three hours without reaction happened although the temperature reached $450^{\circ}c$.

Horizontal reactor V3

V3 loaded with 1 kg of LDPE and heated as before but heavy wax was resulted due to the low temperature. The experiment was repeated

using HDPE and PP in same condition and resulted for all cases heavy wax as shown in figures (4.8) and (4.9).

Vertical reactor V4

Same procedure used for V1 was used but long time without positive results.

Vertical reactor V5

1) First trail was 1kg of PP run about 1 hour from 11 am to 12 pm, the final product was green oil from 170°c to 380°c.

2) Repeated the test (1) above with the same condition to check the unit doing well. Again the product was also green oil about 950ml in same temperature where the percentage of conversation was the best (95%).

3) 1 kg mixture (1:1) of PP and HDPE started at 12 pm to 12:45pm, temperature in range $150^{o}C$ to $350^{0}C$, the final product was almost 950 ml light green oil as shown below in figure (4.10).

4) 1 kg mixture (1:1) of LDPE and HDPE added to the unit started at 2:45 pm ended at 3:20 pm, the gases started at 150°c to 350°c when the gases complete out the temperature also decrease gradually to know the processed done. Where the result is pure and light yellow oil in spite of wax due to LDPE shown in figure (4.11). Oil was separated in a glass which was 960 ml.

5) 1.5 kg mixture (1:1:1) of LDPE, HDPE and PP added to the unit at 11:45 am to 12:30 pm at same temperature, the result was 900ml green light oil. Increased white gases coming so the losses in condensation bigger than others were noticed in this process as shown in figure (4.12).

3.5 EXTRA TRIALS

After every process finished separated oil normally placed in a glass that was kept in the office until analysed. When the oil exposed to cold air from A/C then started to solidify into wax completely in run (4), and some blocks and heavy dense oil in run (5) as shown in figures (4.13) and (4.14).

Wax and heavy viscous oil were reloaded to the unit and re-heated as second pyrolysis stage.

● PP oil from previously processed in unit V4 was run at 11 am to 11:30 am where the green heavy oil turn to very light oil and the colour was also very light green as shown in figure (4.14).

● The HDPE wax from previously processed in unit V4 loaded in the unit and run again for an hour which yielded light oil.   As shown in figure (4.15).

3.6 PLASTIC OIL ANALYSIS

The following tests were conducted on plastic oil (liquid samples) according to the relevant standards as specified for each:

1. GCMS for PP oil sample done by University of Medical Science and Technology.

2. Density at 15°c using ASTM D4052 (g /cm$^{3)}$. [26]

3. Kinematic viscosity at 50°c using ASTM D445-12. [26]

4. Flash point using ASTM D93-12 ^{o}C. [26]

5. Gross calorific value using ASTM D4868-00 or calculation (Mj /Kg).[26]

6. Viscosity @ 40oc using ASTM D445 cSt.[26]

7. Water by distillation using ASTM D95 (V /V).[26]

8. Micro Carbon residue using ASTM 4530 (Wt. %).[26]

● All the above tests conducted in Petroleum Research and Studies Laboratories, Sudan (PLRS).

9. Dioxin and furan test according to PCDD /PCDF method which determination of tetra -through Octa- chlorinated dioxins and furans by isotope dilution HRGC /MS. EPA 1613-B (1994). Tests conducted in Agricultural Research Center, Egypt.

10. Total sulfur content using ASTM D4294 (mg /l) and Total lead content using ASTM D4691 (mg /l). Tests were conducted in Egyptian Petroleum Research Institute (EPRI), EPRI central analytical labs.

3.7 APPLICATION OF THE PLASTIC WASTE OIL

Five trials were made to apply the plastic waste oil as fuel to TukTuk, these were as following:

1. 500 ml of the resulting HDPE oil from reactor V1 was used as fuel to replace the traditional fuel of tuktuk. Distance travelled by was measured for both HDPE and traditional oil. HDPE oil were 13 Km compared to 10 Km for the domestic fuel. Fortunately, tuktuk travelled distance 1.3 times the distance travelled by same amount of traditional fuel.

2. 500 ml of LDPE oil from reactor V5 was used as fuel to replace the traditional fuel of tuktuk. Distance travelled was measured for both LDPE and traditional oil. LDPE oil used in tuktuk travelled 11 Km

while the traditional fuel travelled 10 Km. Fortunately, tuktuk travelled distance 1.1 times the distance travelled by same amount of traditional fuel.

3. 600 ml of PP oil from reactor V5 was used as fuel to replace the traditional fuel of tuktuk. Distance travelled was measured for both PP and traditional oil. PP oil used in tuktuk travelled 11 Km while the distance travelled by same amount of traditional fuel was 9 Km. Fortunately, tuktuk travelled distance 1.2 times the distance travelled by same amount of traditional fuel, Which was less than the first trial due to the density of it was less than above oil where the burning characteristics was fast.

4. Small amount of domestic oil used to be added to benzene was added to PP oil and reused again in tuktuk Distance travelled by was measured compared to distance in (2) above and to traditional oil the result being very excellent. Where the distance differ between PP oil plus oil and the PP oil only 1 Km.

5. 600 ml of (LDPE + HDPE) oil when adding fuel to the tuktuk the engine deactivated and didn't work due to properties of oil.

6. 100 ml of mixed plastic oil (HDPE, LDPE, PP) where adding to the Cresset and lighting duration was recorded for 9 hours. Shown in figure (4:19).

CHAPTER FOUR

RESULT AND DISCUSSIONS

4.1 INTRODUCTION

In this chapter the products from each type of reactor and their analysis will be discussed. Comparison of the plastic oils products with the benzene and diesel specifications will take from Khartoum refinery Co. Ltd. Central Laboratory.

4.2 REACTOR DESIGN

Domestic pressure cooker:

When using domestic pressure cooker, it is noticed that, the final product was very thick, viscous, dark and small amount as shown in figure (4.2). This may be due to the excessive heat, oxygen inside the pressure cooker and the gases escaped through the nail, thus oil was stocked in the condenser as shown in figure (4.1). It is concluded that the Domestic cooker is not suitable and a new design should be found out.

Figure (4.1): oil stuck inside the condenser

Figure (4.2): Thick and dark product

Vertical reactor V1:

For HDPE trial, the problem was that the time of heating was very long due to its rate and the thickness of reactor walls. A little sludge remained in the reactor shown in fig (4.5). Oil given was 70 ml oil as shown in figure (4.3) below.

Figure (4.3): Oil from remain HDPE

The amount of oil yielded was 695 ml out of 850 gm. of HDPE, so the percentage of conversion is: 695 /850 * 100 = 81.7 %

Figure (4.4): Oil from 850g of HDPE

Figure (4.5): HDPE sludge remain in the reactor

When 1 Kg of HDPE was used, clear yellow oil yielded as shown in figure (4.6) and luckily the percentage of converting was 950 /1000 * 100 = 95%

Figure (4.6): Oil from 1 Kg of HDPE

When 1 Kg of PP was used, clear green oil yielded as shown in figure (4.7) and luckily the percentage of converting was 822.2 /1000 * 100 = 82.2%

Figure (4.7): Oil from 1Kg of PP

Horizontal reactor V3:

All result was heavy wax as clearly shown in figures (4.8) and (4.9). This is due to low temperature and distribution of heat around the reactor during rotating is not enough.
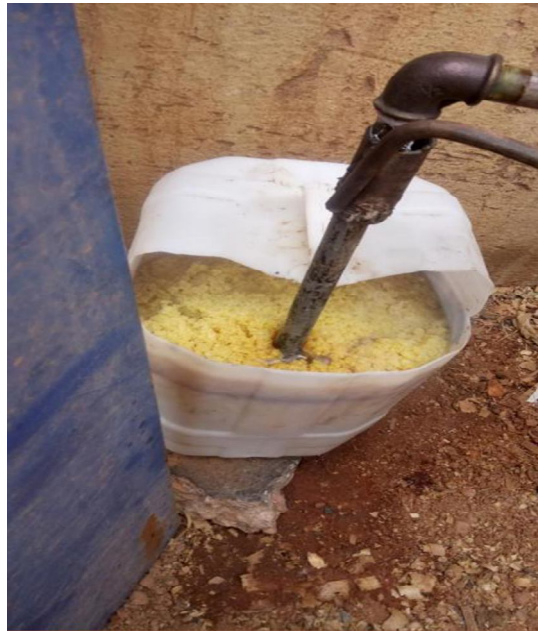
Figure (4.8): Wax outcome from LDPE

Figure (4.9): Wax from LDPE

Vertical reactor V5:

When 1 Kg mixture (1:1) of PP/HDPE was used, light yellow oil yielded as shown in figure (4.10) and the percentage of converting was 950 /1000 * 100 = 95%

Figure (4.10): Oil from (1:1) PP/HDPE

When 1 Kg mixture (1:1) of LDPE/HDPE was used, thick creamy oil yielded as shown in figure (4.11) and the percentage of converting was 960 /1000 * 100 = 96%

Figure (4.11): Wax from mixture (1:1) LDPE/HDPE

When 1.5 Kg mixture (1:1:1) of PP/HDPE/LDPE was used, light green oil due to the colour of PP was yielded as shown in figure (4.11) and the percentage of converting was 900 /1000 * 100 = 90%

Figure (4.12): Oil from mixture (1:1:1) of PP/HDPE/LDPE

4.3 SECOND STAGE RUNNING

Wax and heavy viscous oil reloaded to the unit and re-heated as second pyrolysis stage gives results as follows:

PP oil from previously processed in unit V4 yielded very light oil and the colour was also very light green as shown in figure (4.13). The amount of oil product was 950 ml from 1 Kg, and then Conversion percentage was 950 /1000*100 =95%

Figure (4.13): Oil from PP wax after second stage pyrolysis

The LDPE wax from previously processed in unit V4 yielded light oil.as shown in figure (4.14).

Figure (4.14): Oil from LDPE wax after second stage pyrolysis

4.4 PLASTIC OIL ANALYSIS

Tests For Oil Resulted From V1:

1. The gas chromatography mass spectrometry (GCMS):

The result of GCMS for PP oil sample done by university of medical science and technology shows the range of number of carbon in the

molecular structure was C7 to C13, which in the range of benzene and kerosene.

2. Sulfur and lead content test:

Table (4.1): Sulfur, lead content

Oil Sample	Sulfur content mg /l	Lead content mg /l
HDPE	Nil	< 0.375
PP	Nil	< 0.3650

Compared the sulfur test result of plastics oil by gasoline and diesel specification, the plastics oil were very excellent which no sulfur that's enables advanced emission control system and reduced air pollution, lead content effect.

3. Dioxin and Furan test:

Table (4.2): Dioxin and furan tests

Oil Sample	Dioxin and furan (gm)
HDPE	0.38
PP	-

This result was done in Egypt which was very difficult to be done again for other running experiment. For PCDD /PCDF the measurement uncertainty expressed as expanded uncertainty (at 95 % confidence level) is within the range $\pm$ 50%

4. Density:

Table (4.3): Density test

Oil Sample	Density @ 15°c g /cm3
HDPE	0.7884
PP	0.7781

Density of HDPE and PP oils when compared to Khartoum refinery Co. Ltd. Central Laboratory specification found both oil approximately similar to gasoline but a little higher. Higher densities having a greater volume of aromatics.[27]

5. FT-IR:

Table (4.4): FT-IR test

Oil Sample	FT-IR
HDPE	According to the scan, saturated (-C-H) stretching peaks were found, (C=C) were found, methyl group (-CH3) was found and methylene group (-CH2-) also was noticed.
PP	According to the scan, saturated (-C-H) stretching peaks were found, (C=C) were found, methyl group (-CH3) was found and methylene group (-CH2-) also was noticed.

6. Flash point :

The test of the flash point of PP oil carried out by Sudan University of Science and Technology and the result was $< 40\,^0$c which was the same to the room temperature which means the sample cannot be tested with the flash point tester as shown in figure (4.15) below.
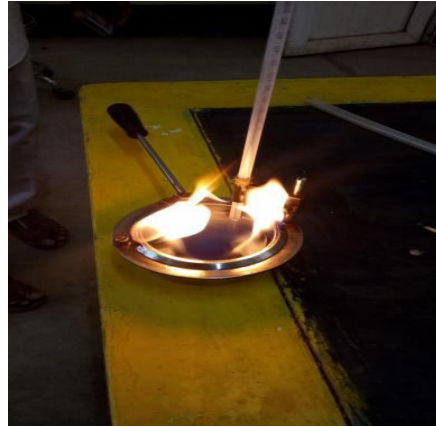

Figure (4.15): The PP oil flash point test

7. Kinematic viscosity:

The test of the kinematic viscosity carried out by Sudan University of science and technology for HDPE and PP oil, shown in figure (4.16). The result of test seen below in table (4.5).

Figure (4.16): The kinematic tester

Table (4.5): kinematic viscosity test

Material	Kinematic viscosity cm2/sec
HDPE oil	0.0137
PP oil	- 0.012

The result of test shown that the both plastic oil (HDPE and PP) similar to gasoline kinematic viscosity.

Tests For Oil Resulted From V5:

1. Density :

Table (4.6): Density test

Oil Sample	Density g/cm3
LDPE	0.7968
PP	0.7739
HDPE+ LDPE	0.7958
HDPE+ LDPE+ PP	0.7883

The fuel density affects engine calibration and power as the fuel mass injected/ stroke varies with fuel density. Density of PP similar to benzene density according to Sudan specification, but the HDPE and mixed oil density similar to diesel.

2. Viscosity @ 40c:

Table (4.7): Viscosity tests

Oil Sample	Viscosity cST
LDPE	3.173
PP	1.508
HDPE+ LDPE	2.826
HDPE+ LDPE+ PP	2.020

The viscosity of fuel is a measure of its internal resistance to flow. It influences the degree of preheat required for handling and storage. If the oil was too viscous, may become difficult to pump, hard to light the burner and tough to operate. According to Khartoum refinery Co. Ltd. Central Laboratory specification the PP oil was similar to benzene and the other oil (LDPE, HDPE+ LDPE, HDPE+ LDPE + PP) similar to diesel.

3. Calorific value gross:

Table (4.8): Calorific value tests

Oil Sample	Calorific value gross Mj/Kg
LDPE	44.838
PP	45.039
HDPE+ LDPE	44.847
HDPE+ LDPE+ PP	44.912

The calorific value of a fuel is the quantity of heat produced by its combustion at constant pressure and under normal conditions (I.e. 0°c and under a pressure of 1.013 m bar). So we have higher calorific value and lower calorific value. When compared plastic oil to fuel specification the (LDPE, HDPE + LDPE, HDPE+ LDPE + PP) having higher calorific value of diesel and PP oil have also higher calorific value of benzene.

4. Water content by distillation:

Table (4.9): Water content

Oil Sample	Water content V/V
LDPE	0.00
PP	0.00
HDPE+ LDPE	0.00
HDPE+ LDPE+ PP	0.00

All plastic oil having no water content which that's means very good where the water can cause spluttering of the flame at the burner and reducing the flame temperature.

5. Carbon residue MCR:

Table (4.10): Carbon residue

Oil Sample	MCR wt%
LDPE	0.4
PP	0.1
HDPE+ LDPE	*
HDPE + LDPE + PP	*

According to Khartoum refinery Co. Ltd. Central Laboratory specification below in table (4.13) we notice that the HDPE in the range of diesel and the LDPE oil in range of benzene. MCR did not carry out for mixed plastic oil due to technical reasons.

6. Flash point:

Table (4.11): Flash point

Oil Sample	Flash point ^{O}C
LDPE	*
PP	*
HDPE+ LDPE	60
HDPE+ LDPE+ PP	< 40

Flash point test for LDPE oil and PP oils did not carried out due to the nature of material which can flame at room temperature <40 also due to technical reasons.

7. Sulfur Content %:

Table (4.12): Sulfur content

Oil Sample	Sulfur content %
LDPE	*
PP	*
HDPE+ LDPE	0.122
HDPE+ LDPE+ PP	0.071

Sulfur content test for LDPE oil and PP oil did not carried out due to technical reasons. And the result of mixed oil compared to our fuel specification found both similar to diesel.

4.5 COMPARATIVE ANALYSIS OF THE RESULT

Generally, the performance of the five types reactors designed and applied in this work can be shortened to only two feasible reactors viz. V1 and V5. That is because of the low performance of the domestic pressure cooker as well as V2 and V3 reactors.

Therefore, Vertical reactors gives better performance of pyrolysis as far as the results of this work is concerned. The results of conversion percentage of V1 and V5 are displayed in table (4.13) below

Table (4.13): Percentage of Oil Conversion

Material	Reactor type	Conversion %
HDPE	Vertical reactor V1	81.7
HDPE	Vertical reactor V1	95
PP	V1	82.2
PP	V5	95
PP / HDPE	V5	95
HDPE/LDPE	V5	96
HDPE/ LDPE/PP	V5	90

Table (4.13) shows clearly that all percentages for V5 are more than 90% except the PP case which is a little less therefore, design of vertical

reactor V5 is best among the six designs used which conversion % more the 90 to waste types.

Table (4.14): Properties results summary from reactor V1 compared to traditional fuels

Test	HDPE oil from V1	PP oil from V1	Benzene	Diesel
Flash point	43	< 40	< 40	55 – 60
Density @ 15 ºc	0.7884	0.7781	0.710 - 0.770	0.81 - 0.870
Calorific value gross	*	*	44 - 47	42 – 44
Viscosity @ 40 ºc	*	*	< 1.00	2.0 - 5.0
Water content by distillation	*	*	0.00	< 0.05
Carbon residue MCR	*	*	0.1 - 0.2	0.1 - 0.3
Sulfur content	Nil	Nil	< 0.03	0.05

Table (4.15): Properties results summary from plastic oil pyrolysis twice compared to traditional fuels

Test	LDPE oil	PP oil	HDPE + LDPE oil	HDPE+ LDPE+ PP oil	Benzene	Diesel
Flash point	< 40	< 40	60	< 40	< 40	55 - 60
Density @ 15 °c	0.7968	0.7739	0.7966	0.7883	0.710 - 0.770	0.81 - 0.870
Calorific value gross	44.838	45.039	44.847	44.912	44 – 47	42 - 44
Viscosity @ 40 °c	3.173	1.508	2.826	2.826	< 1.00	2.0 - 5.0
Water content by distillation	0.00	0.00	0.00	0.00	0.00	< 0.05
Carbon residue MCR	0.4	0.1	*	*	0.1 - 0.2	0.1 - 0.3
Sulfur content	*	*	0.122	0.071	< 0.03	0.05

From The Above Table We The Following Can Be Deduced:

- The PP oil which pyrolysed twice was very clear oil and similar in characteristics to benzene, which when added to the traditional TukTuk travelled same distance as traditional fuel without adding the domestic oil, when adding to PP oil the result was better than the traditional fuel where the difference in the distance was 5 Km.

Figure (4.17): The traditional TukTuk

Figure (4.18): The plastic oil used in TukTuk

- The HDPE oil and PP oil from reactor V1 also has similar properties to gasoline. So when added HDPE oil to the traditional TukTuk travelled distance more than the distance by traditional fuel.

- When added LDPE oil pyrolysed twice has an intermediate properties between gasoline and diesel, so when added to the TukTuk there was difference from the traditional fuel without adding domestic oil which the density and viscosity higher than benzene specification that's mean the flow is lower oil in consumption and less wear.

- The (HDPE + LDPE) oil similar to diesel in properties. That was confirmed when adding as a fuel to the TukTuk the engine deactivated and didn't work.

- The mixed oil (HDPE + LDPE + PP) was similar to diesel in properties when adding small amount of PP oil to the traditional cresset lighting for long time. As shown in figure (4.19) below.

Figure (4.19): Traditional cresset lighted by PP oil

4.6 CALCULATION

In comparison between the PP oil with domestic oil, PP oil only and the traditional fuel (benzene).

According to this work 600 ml of PP oil only enables TukTuk to travel 11 Km.

- 600 ml gives 11 Km
- 1000 ml gives X
- X = 11* 1000 / 600 = 18.33 Km. thus 1 litter gives 18.33 Km
- Gallon equal 4.5 litter, so : 18.33 * 4.5 = **82.48 Km**

According to this work 600 ml of PP + oil enables TukTuk to travel 12 Km

- gives 12 Km
- 1000 ml gives X
- X = 12 * 1000 / 600 = 20 Km so1 litter gives 20 Km
- Gallon equal 4.5 litter, so :   20 * 4.5 = **90 Km**

It is noticed that the difference between PP oil and PP oil plus domestic oil was 7.5 Km.

According to this work 600 ml of Traditional fuel (benzene) enables TukTuk to travel 9Km. Km

- 600 gives 9 Km
- 1000 ml gives X
- X= 9 * 1000 / 600 = 15 Km so 1 litter gives 15 Km
- Gallon equal 4.5 litter, so :   15 * 4.5 = **67.5 Km**

It is noticed that the difference between (PP oil and domestic oil) and benzene was 22.5 Km.

This mean using PP plastic oil will allow increase distance to travel 25% per litter of fuel and in the same time will lower fuel consumption by 25%.

According to this work 500 ml of HDPE oil only enables TukTuk to travel 13 Km.

- 500 ml gives 13 Km
- 1000 ml gives X
- X = 11* 1000 / 500 = 26 Km. thus 1 litter gives 26 Km
- Gallon equal 4.5 litter, so : 26 * 4.5 = **117 Km**

According to this work 500 ml traditional fuel enables TukTuk to travel 10 Km

- 500 gives 10 Km
- 1000 ml gives X
- X = 10 * 1000 / 500 = 20 Km so1 litter gives 20 Km
- Gallon equal 4.5 litter, so :   20 * 4.5 = **90 Km**

It is noticed that the difference between (HDPE oil and benzene was 27 Km.

This mean using HDPE plastic oil will allow increase distance to travel 30% per litter of fuel and in the same time will lower fuel consumption by 30%.

According to this work 500 ml of LDPE oil only enables TukTuk to travel 11 Km.

- 600 gives 11 Km

- 1000 ml gives X

- X= 11 * 1000/ 500 = 22 Km so 1 litter gives 22 Km

- Gallon equal 4.5 litter, so : 22 * 4.5 = **99 Km**

According to this work 500 ml traditional fuel enables TukTuk to travel 10 Km

- 500 gives 10 Km
- 1000 ml gives X
- X = 10 * 1000 / 500 = 20 Km so1 litter gives 20 Km
- Gallon equal 4.5 litter, so :   20 * 4.5 = **90 Km**

It is noticed that the difference between (LDPE oil and benzene was 9 Km.

This mean using LDPE plastic oil will allow increase distance to travel 10% per litter of fuel and in the same time will lower fuel consumption by 10%.

4.7 CONCLUSION

- The oil product from vertical reactor V1 was very good and clear but the temperature at which the gases begin was not know because there was no temperature control. So the reactor V5 (vertical reactor without condenser) being the best one for pyrolysis process and give us high percentage of conversion.

- Plastic oil produced from all samples was comparable to properties of the traditional fuel (Benzene and Diesel) as the results of density, flash point, calorific value, NMR and FTIR were in the same ranges for these tests.

- The oil product from reactor V1 similar specification to benzene in density and flash point but did not carried the other tested.

- All the result of plastic oil after comparable confirm that the LDPE oil from reactor V5 where pyrolysis twice similar to benzene.

- Also the (HDPE + LDPE) oil and (HDPE + LDPE + PP) oil similar to diesel.

- PP plastic oil will increases distance travelled by TukTuk 25% per litter compared to traditional fuel, while HDPE plastic oil will increases distance travelled by TukTuk 30% per litter compared to traditional fuel and the LDPE oil will increases distance travelled by TukTuk 10% per litter compared to traditional fuel.

- The wax product from horizontal reactor when but in the sun light for time the product will be some viscous but did not convert to oil completely. So can called as intermediate product or if tested and know the feature can be a single product.

4.8 RECOMMENDATION

1) Improve the reactor efficiency by adding more tools to control the temperature of gases outcome.

2) Used a suitable and more than one condenser to detected a specific product outcome.

3) More test to ensure the final product either gasoline or diesel like octane number and TPN tests.

4) More tested like gas analysis CO,CO_2 and NO_X concentration in the plastic oil.

5) Used a catalyst in pyrolysis to improve the properties of oil product and motivated the process.

6) Poly ethylene terephthalate (PET) and tires should be used in future work studies.

7) Other application must use according to the nature of oil product to know the effective of it.

8) Provided laboratories for dioxin and furan tests.

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