

1.Introduction

1.1 Background

The growing number of plastic wastes connected with growth of population and socio economic change of countries is becoming a serious global issue, thanks to extensive plastic usage all over the world; the treatment of waste plastic has gained the utmost importance. Scientists and experts all over the world are concerned over this major environmental problem.

World production of plastics in 1990 amounted to 100×10^6 t, and expected to grow 3-4% every year [2]

Plastics are being implemented in all branches of industry and everyday life and represent useful modern technical materials with versatile and to some extent, irreplaceable applications. Plastics have high resistance to physical and chemical attack; light weight is also characteristics of plastics.

Plastic produced will break down 20% in the first year, 15 % between the 1st and the 8th year and 65 % above 8 years. [2]

1.1.1 Fundamentals of Plastics

Early plastic resembled natural resins. These natural resins are organic solids that break with a conchoidal fracture in contrast to the planar surfaces created upon the fracture of crystalline materials or the drawn-out zones formed up on the breaking of gums and waxes. Natural resins refers mainly to oleoresins from tree sap but is also used for shellac, insect exudations, and mineral hydrocarbons. [2]

Plastics are classified under two groups thermosetting and thermoplastic based on their hardening process. [2]

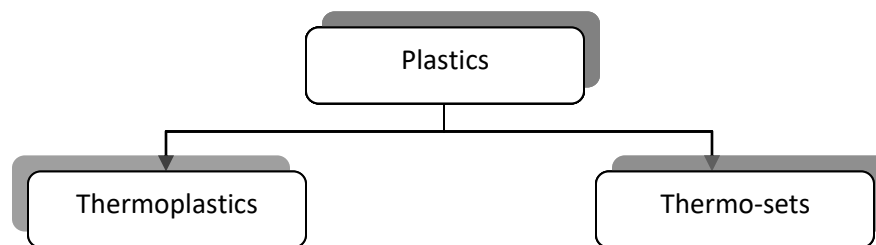


Fig.1.1 Classification of plastics based their hardening Process.

Thermoplastics are formed by simple cooling of polymer melt, and soften again if heated. They are normally composed of fairly high molar mass molecules because many physical properties effectively become molar mass independent only above certain molar mass, for instance melting temperature and the moduli of elasticity.

Thermosets are usually generated from fairly low molar mass polymer called oligomers (science) or prepolymers (industry).

Plastics are usually divided into four groups based on their application: Commodity plastics (standard plastics), Engineering plastics (technical plastics), High performance plastics and functional plastics. A commodity, engineering and high performance plastics have different applications, functional plastic only serve specific task. Commodity plastics are manufactured in great amounts and hence the terms bulk plastics or standard plastics. Engineering plastics possess improved mechanical properties compared to commodity plastics. Such improved properties may be higher moduli of elasticity, smaller cold flows, higher impact strengths etc. Engineering plastics are also often defined as those thermoplastics that maintain dimensional stability and most mechanical properties above 100 °C or below 0°C.

Table 1.1 Division group of plastics based on application and examples.[2]

Commodity Plastics	Poly vinyl chloride Polyethylene(High and low density) Isotactic polypropylene Standard polystyrene
Engineering plastics	Polyethylene teraphatalate Poly butylenesterephatalte Poly amides Poly Carbonates Polyoxymethylenes Poly methyl methacrylate Styrene-acrylonitrile (SAN) Acrylonitrile-butadiene-styrene(ABS)
High performance	Liquid crystalline polymers(LCP _s) Polyetherether ketone(PEEK) Poly sulfones Polyimides

1.1.2 Application of plastics

General applications of plastics include clothing, packaging, in manufacture of machinery, motor vehicle, in agriculture, electronics and communication technology. Now a day's high composite materials are used in Air space travel, construction, sports and recreation.

1.1.3 Advantages and Disadvantages of plastics

Lower energy cost per unit volume in processing plastics, durability, corrosion resistance, chemical resistance and low weight makes their application advantageous than other materials.

Disadvantages are those plastics that are manufactured for short term use are polluting and occupying large areas in the landfill. Most plastics are designed to survive on most unfavorable conditions, these made them non-degradable biologically and by Ultra Violet radiation. Currently researches have been done to make plastics biodegradable, the major disadvantage of this process is chemicals may be deposited to the soils and rivers which could be more hazardous.

An effort is required to minimize polymer wastes or to provide a suitable means for disposing and reuse.

Plastics that are disposed every year are becoming more and more hazardous to the environment. As mentioned above these plastics are derived from petroleum industries which is becoming scarce. What makes plastics more interesting is that some of them can be reprocessed to their original raw materials and others are used to produce oils, such oils can be further refined to produce fuels such as (Benzene, Diesel, methane ...etc). This technology of reusing plastics as energy source is an advantage for developing countries such as Ethiopia, to break the foreign oil dependency, meaning having non-fluctuating sustainable growth in the economy.

1.1.4 Methods of reusing and disposing plastic wastes.

1.1.4.1 Recycling

Clean regenerated materials command a price of up to 70% of that of a new material.[1] Recycling single grade waste process includes

Size reduction → washing → drying → Metal separation → sorting → Compounding → Destabilization → homogenization → granulation.[1]

Problems in recycling single grade wastes include degradation due to repetitive processing some include change in appearance, Chemical resistance alteration, process ability problems, failure in mechanical characterization, contamination of reprocessed plastic, handling scrap with a low bulk density.

Recycling of mixed wastes is more complex than single phase. Miscibility of different plastics is a major factor in recycling mixed plastic waste.

1.1.4.2 Chemical Products

Plastic wastes may contain so many varieties, be so badly contaminated and have such modified molecular structure due to degradation that direct recycling is not worthwhile. Such wastes include composite materials, filled plastics as well as thermo sets and elastomers, which cannot be re-melted. Most plastics contain 50 %wt fillers, stabilizers, plasticizers and other in alteration of density, transparency and flexibility.[2]

Hydrolysis

Leads to direct recovery of the original raw materials by targeted reaction of water molecules at the linkage points of the starting materials (thus reversing the polymerization process)

Alcoholysis

Chemical degradation of poly urethanes can be achieved by alcoholysis to give a polydioxy alcohol and small urethane fragment formed by transesterification.

Hydrogenation

In hydrogenation the C-C bonds of poly-olefins and polystyrene are broken by the addition of hydrogen. Alkanes are by far the largest group of products results from this mild decomposition process.

Pyrolysis

Pyrolysis is a thermal cleavage in complete or partial absence of air, accompanied by continuous generation of pyrolysis oils and gases suitable for chemical utilization or generation. Thermoplastics, thermosets, elastomers and composite materials can be recycled by pyrolysis. Major advantage of pyrolysis is 5 to 20 fold reduction in the volume of product gases which reduce gas purification.[2]

Upto 50% of the input material can be recovered in the liquid form mixture of gasoline and bituminous coal 95%.[2]

The product gases are high energy fuel gases with a calorific value of 50MJ/M³ at STP[1]. The main gaseous compounds are methane, ethane, ethylene and propylene. Oil mainly consists of Benzene, Toluene and Naphthalene.

In this paper pyrolysis is method selected and it is more elaborated in remaining parts of this paper.

1.1.4.3 Combustion

As mentioned earlier the calorific value of plastics is very high. All most 94% of oil products are used in heating purpose[2].

There would be no objective to this form of energy recycling since it allows the substitution of the oil and reduces the volume of garbage.

Major drawbacks with combustion of plastics wastes are with emissions. Halogen containing plastics such as poly vinyl chloride and polytetrafluoroethylene create problems as they release substantial

volumes of hydrogen chloride and fluoride on combustion. Furthermore, combustion releases metals, dyes, stabilizers, pigments and plasticizers.

1.1.4.4 Dumping and degradation

Because of highly visible litter problem by e.g. plastic bags, bottles and containers and the need to reduce space demands in dumping sites, it is often demanded that plastics should be bio- and UV-degradable.

Degradation products could penetrate into the ground water. In case of microbial degradation it would be difficult to ensure that long life products (e.g. drain pipes, plastic components used in construction).

1.2 Statement of the problem

To find an alternative way of producing energy fuels that could substitute or be used along with fossil fuels with high efficiency, economically feasible and environmentally friendly processes. Plastics are produced from petroleum being that, reversing the process by pyrolysis to produce good quality fuels such as benzene and Diesel oil.

1.3 Scope of study

The study is conducted by reviewing books and internet materials followed by laboratory experiment.

1.4 Significance of the study

This paper is intended to provide an insight on the production of Oil from plastic wastes by pyrolysis in an efficient and economical way by investigating different raw materials, equipments, catalysts and operational parameters.

1.5 Objective

1.5.1 General Objective

The objective of this project is to produce oil from plastic wastes by pyrolysis

1.5.2 Specific Objectives

Raw material preparation

The objective of raw material preparation is to reduce contamination of product and also to reduce size of raw material for increased interfacial area for mass transfer.

Reaction

Reaction objective is to thermally crack the plastic wastes to gas, oil and tar.

Refining

To refine the oil produced into different products such as benzene and diesel oil.

2. Literature Survey

Plastic waste is becoming a serious global issue, thanks to extensive plastic usage all over the world; the treatment of waste plastic has gained the utmost importance. Scientists and experts all over the world are concerned over this major environmental problem.

There are various methods for reutilizing the polymers, each one having its shortcomings or limitations. Yet, thermal and catalytic degradation of plastic into fuel is considered to be the most effective way of reusing polymers. Of late, experts have begun to pay attention to pyrolysis, especially thermal or catalytical degradation of plastics.

2.1 Pyrolysis Definition

Pyrolysis is defined as a chemical degradation reaction that is caused by thermal energy in the absence of air (oxygen). It is supposed to be one of the most effective methods for preserving petroleum resources, in addition to preserving the environment by decreasing the volume of nondegradable waste. Degradation of plastic is achieved by heating at high temperature, with macromolecules breaking into smaller fragments, consisting valuable mixtures of hydrocarbons (gas, liquid and solid).[1]

The degradation of different types of waste plastics has been studied in the presence and absence of a catalyst. It is found that the properties of the products depend significantly on the characteristics of the applied catalyst. A catalyst also reduces the reaction temperature. The pyrolysis process, requiring high temperatures up to 1000°C can be carried out at much lower temperature (400–500°C) with the use of a proper catalyst. Recycling of waste plastic by pyrolysis can yield excellent results, even with heterogeneous waste plastic materials, where segregation is not economic

Plastics suitable for pyrolysis

Polymers are structurally made up of carbon atoms linked by single or double bonds. Hence, each polymer has a specific heat value. For example: Polyethylene and Polypropylene have calorific values of 18 720 BTU/lb and 18 434 BTU/lb, respectively. These organic molecules have a low decomposition temperature compared with inorganic matter. Nearly all conventional fuels are organic molecules. The heat content of an organic molecule depends upon number of carbon atoms in the molecular chain and the complexity of the molecular structure (linear, branched, cyclic, etc.). Thus, when any polymer decomposes or the polymer structure gets fragmented randomly, each fragment, depending upon number of carbon atoms, can be classified into various types of fuels. Hence, pyrolysis of polymers such as PE, PP and PS yield valuable hydrocarbons. A few polymers such as polyvinyl chloride, ABS, and PET are associated with heteroatoms such as Cl, N, and O apart from carbon and hydrogen. During pyrolysis these heteroatoms get converted into compounds such as HCl, N₂, and H₂O etc.[3]

2.2 Advantages and problems of Pyrolysis

The advantages of pyrolysis of waste plastics into liquid fuels include:

- it allows the recycling of waste mixed plastics that cannot be efficiently recycled by alternative means;
- it permits the recycling of unwashed and soiled plastics (e.g. agricultural plastics, mulch/silage/greenhouse films and dripper/irrigation tube);
- it enables recycling of plastic laminates, coextrusions and multilayer packaging films, particularly those with aluminium foil layers that are difficult to recycle using traditional reprocessing technologies.

Most commodity hydrocarbon plastics are suitable for pyrolysis. Generally the larger the substituent in the side chain, the easier the plastic can be degraded. The order of increasing side chain size is polyethylene<polypropylene<polyvinyl chloride<polystyrene.

Problems with many pre-existing plastic cracking technologies include:

- noncontinuous (batch) processes (not commercially viable);
- coking and carbon deposits on heat exchanging surfaces;
- stickiness of sand particles in fluidized-bed processes;
- unsatisfactory fuel quality;
- relatively high sulphur levels (100–700 ppm) in end product

2.3 Types of Pyrolysis

Pyrolysis and cracking of waste polyolefins (plastics) can be categorized as the tertiary mode of recycling. Application of this type of recycling is reasonable especially in case of polyolefins when their further using in primary recycling (conversion into products similar in nature to the original product) and secondary recycling (conversion into products of different shape for less demanding products) is impossible. Pyrolysis and cracking are considered as alternative methods of the final processing of waste plastics such as polyolefins. The tertiary mode of recycling is can be classified into two groups: thermal and catalytic cracking

2.3.1 Thermal Cracking

Thermal cracking often yields a low-value mixture of hydrocarbons with a very broad volatility range that can extend from hydrogen to coke. It is therefore important to determine the optimal pyrolysis conditions and/or the most advantageous catalyst to obtain marketable products (e.g. diesel fuel) from mixed plastic wastes.

The pyrolysis product yield and composition are controlled not only by the temperature, but also by the duration of the residence time. As a general rule of thumb the higher the pyrolysis temperature, the higher the yield of noncondensable gaseous products and the lower the yield of liquid fuels such as diesel. The optimum temperature range for the production of diesel products from waste plastics is 390 – 425°C. Studies in a tubular reactor have highlighted the importance of short residence time with high-temperature pyrolysis for obtaining a high yield of light olefins.

There is a dramatic increase in gas yield with increasing temperature of pyrolysis. While the hydrocarbon pyrolysis product yield increases with pyrolysis temperature, the yield of the oil fraction is higher at the lower pyrolysis temperatures. The composition of the pyrolysis oil also changes with pyrolysis temperature, generally containing larger quantities of aliphatic compounds at the lower temperatures than at higher temperatures where aromatics are the dominant compounds.

3.3.2 Catalytic Cracking

The poor selectivity of the thermal decomposition of polyolefins has promoted the development of catalytic cracking. Catalytic cracking lowers the pyrolysis process temperature and lowers the boiling temperature range of the resultant liquid products. The use of molecular sieves and amorphous silica–alumina catalysts for the cracking of waste polymers into a range of hydrocarbons has been widely studied Catalytic cracking has some distinct advantages over thermal cracking, such as, lowering the cracking temperature, increasing the reaction rate and increasing the production of iso-alkanes and aromatics which are desirable for diesel fuel. Suitable cracking catalysts have the ability to both substantially reduce the pyrolysis temperature and control the pyrolysis products.

Using catalysts does not only lower the activation energy, reduce the energy consumption and improve the process efficiency, but can also improve the selectivity and quality of the products produced.

Catalysts with acidic surface sites and hydrogen ion donating ability enhance the isomerization of products and thereby increase the yield of isomeric hydrocarbons that have a beneficial effect on the cetane rating and fuel quality. Catalysts having stronger acid sites of higher density are thus more effective in cracking polyolefins. However, strong acidity and large pore size both lead to faster deactivation of the catalyst. Pyrolyzing with catalysts having mild acidity and long life are preferred for the cracking of polyolefins.

A major problem with using catalysts in the pyrolysis of mixed plastics is that of coke formation deactivating the catalyst over time. The cost of these catalysts also influences their selection and commercial viability. The amount of the catalyst to be added to the waste plastic for catalytic cracking is at least 5 % by weight (typically 5 – 10 % by weight).

The problems associated with the use of a catalyst in the pyrolysis vessel are:

- the catalyst is a consumable and therefore adds to the running cost;
- the catalyst can have a short life-cycle due to poisoning/deactivation;
- the catalyst leads to increased levels of solid residue that requires disposal.

Compared with thermal degradation, the catalytic degradation showed an increase of liquid yield whereas that of residue was reduced, due to the decomposition of heavier residues into lighter oil product.

Table 1 Yields of gas, liquid and residue obtained from thermal and catalytic degradation of waste HDPE at 430°C

	Gas (%)	Liquid (%)	Residue (%)
Thermal degradation	20.0	75.5	4.5
Catalytic degradation	19.4	79.7	0.9

2.4 Feed stock options

The composition of the plastic feedstock for pyrolysis processes has a direct bearing on the quality of the resultant fuel products, especially flash point, cetane index, low-temperature properties and heteroatom content (e.g. sulphur, chlorine and nitrogen). While condensation polymers such as PET and polyamides can be broken down into their monomer units by thermal depolymerization processes, vinyl (addition) polymers such as polyethylene and polypropylene are very difficult to decompose to monomers. This is because of random scission of the carbon–carbon bonds of the polymer chains during thermal degradation, which produces a broad product range.

2.4.1 Polyethylene (PE)

There have been many reports on the thermal and catalytic degradation of high-density polyethylene (HDPE), as it is one of the main polymers in municipal solid wastes [1]. PE-derived fuel has a very low cetane rating and is very high in linear paraffins and 1-olefins. Paraffins are straight-chain hydrocarbons that are normally present in diesel. They are the first components to come out of solution as diesel cools. The tendency of paraffin crystals to aggregate up at low temperatures to form sheets can result in fuel-filter blockages, ultimately leading to interruption of the fuel flow. Paraffin crystals form in the fuel, making the gelled suspension appear cloudy. As these suspended flakes pass through the filter, they gum up its microporous surface. Due to the high concentration of linear n-paraffin hydrocarbons in fuel derived from PE, it is desirable to isomerize them in order to lower the cloud point and the freezing point of the fuel. The branched isomers do not exhibit the same tendency to crystallize as linear paraffins, so that wax crystals do not form until lower temperatures are reached.

2.4.2 Polypropylene (PP)

The liquid products of the pyrolysis of PP contain primarily olefins that resemble the molecular skeleton of PP (i.e. branched hydrocarbons). A distinguishing feature of PP pyrolysis is the predominant formation of a particular C₉ olefin in the pyrolysis product. The level of this C₉ compound identified as 2,4-dimethylhept-1-ene can be as high as 25 %. Also present are C₅ olefin, C₆ olefin, several C₁₅ olefins and some C₂₁ olefins [4].

The tertiary carbon sites in PP allows for the facile chain cleavage and rearrangements according to the Rice–Kossiakoff cracking mechanism. The noncondensable gas from PP pyrolysis contains elevated levels of propylene, isobutylene and n-pentane. Compared with PE, PP produces less coke residue and more liquid products, but with a higher content of ‘lights’. In the pyrolysis process of PP the intramolecular radical transfer is preferred to the intermolecular one, thus the low oligomer formation predominates, skewing the carbon number distribution towards the light end of the distillate spectrum. Consequently the pyrolysis oil of PP is much more volatile than that of PE, decomposing mainly through intermolecular radical transfer. The difference in the backbone structure of the products of these polymers is more important from the point of view of fuel properties. The isoalkanoic structure of PP is maintained in the thermal decomposition products, thus the octane number of the pyrolysis oil is typically high.

2.4.3 Polystyrene (PS)

Neat polystyrene feedstocks will depolymerize in a pyrolysis process to give predominantly styrene monomer—a liquid fuel with good energy content. The optimum pyrolysis temperature is 395°C to give a recovery ratio of 0.97 (i.e. 1000 kg polystyrene will yield 970 L liquid monomer) and 5 to 10% char residue. Fuel made from polystyrene feedstock will be high in aromatic character and have an energy content of 50 MJ/kg and a pour point of –67°C. However the flash point is only 26°C and the cetane rating only 12.6. The fuel needs to be blended with polyolefin-derived diesel or regular diesel in order to upgrade the flash point and cetane rating to within specification. Polystyrene has somewhat lower

thermal stability than the polyolefins and its pyrolysis can be undertaken between 380 and 420°C without producing gases or leaving significant amount of residue after total conversion. PS cracks to styrene, ethyl benzene, toluene, trimethylbenzene and some benzene. In spite of the fact that the majority of the carbon atoms are assembled into phenyl side groups in this polymer, a negligible amount of benzene is formed (1–3%) at these temperatures. This is because the aryl–alkyl bond connecting the phenyl group to the polymer chain is stronger than the bond of alkyl carbons along the chain. The pyrolysis of PS yields dominating components, styrene (bp 145°C) in the gasoline boiling range, styrene dimer in the diesel oil range, and styrene trimer boiling at 400°C. This pyrolysis product distribution suggests that the intermolecular radical transfer is negligible in PS. The pyrolysis of PS produces fuel with a high aromatic content and low storage stability. The high aromatic content of PS-derived oil helps to compensate for the low cetane number of PE oil.

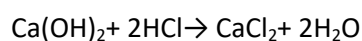
2.4.4 Polyethylene terephthalate (PET)

Pyrolysis of PET under mild conditions predominantly forms terephthalic acid (TPA). Since TPA easily sublimates it is often found in the condensing units of pyrolysis plants. Under high-severity conditions however, little TPA is observed. This is because at higher temperatures TPA is decomposed into benzene, carbon dioxide and benzoic acid [4].

The pyrolysis of PET has been found surprisingly to yield no liquid products. [5] It is widely known that compounds that undergo sublimation, such as terephthalic acid and benzoic acid, are produced by the thermal decomposition of PET and this causes problems in plastic pyrolysis plants. Interestingly It has been found that the addition of calcium hydroxide (slaked lime) gives high selectivity for benzene formation without producing sublimation compounds such as terephthalic acid. The yield of benzene is around 35 wt% at 700°C and a 10.0 calcium hydroxide/PET molar ratio. [6]

2.4.5 Poly vinyl chloride (PVC)

PVC is not recommended as a feedstock material for pyrolysis. The reasons for this being that it contains about 57 % chlorine by weight which will affect diesel quality and can produce chlorinated hydrocarbons, and also because it thermally decomposes to hydrochloric acid that is very corrosive and toxic. The presence of 1 – 3 % PVC in the feedstock stream results in the product fuel oil having a total chlorides level of 5000–10 000 ppm. However at the same PVC levels the total chloride concentration in the diesel can be reduced to less than 10 ppm by the addition of lime hydrate according to the following reaction:



PVC in the feedstock stream in limited amounts can thus be tolerated if a HCl removal process based on calcium hydroxide (slaked lime) injection is used. This is essentially form of in situ scrubbing in the pyrolysis reactor itself. This method is used by a number of pyrolysis processes since the fuel oil end products need to be low in chlorine to minimize engine corrosion problems. In the pyrolysis of commingled plastics, lime can be added to the input material and the PVC content reduced down to 2 – 3 % in order to avoid deposits of CaCl_2 in pipework. The chlorine content of the final diesel should not exceed 10 ppm. It has been demonstrated that oil recovered from PVC-containing plastic feedstock can be used as a fuel. Cost is the main obstacle since it requires a large amount of slaked lime to neutralize the HCl gas that is produced by the thermal cracking.

2.5 Influence of main operational parameters

Both the activity and selectivity of the catalysts heavily depend on the following reaction variables:

- temperature;
- catalyst amount;
- time;
- Plastic composition.
- Type of reactor

Henceforth, their respective effect over the catalytic cracking of plastics is described:

2.5.1 Temperature

Temperature is likely the most important variable affecting the catalytic cracking of plastics. Reaction temperatures are usually in the range 300 –450 °C. In general, a temperature increase leads towards a parallel activity enhancement of the catalysts. Nevertheless, it must be taken into account that at high temperatures the simultaneous occurrence of thermal cracking reactions is favoured, which may modify the product selectivity. Additionally, the temperature affects in a different way the reactions involved in the carbocationic chain pathway (initiation, propagation, termination) as they can be either mono or bimolecular, also changing the selectivity attained.

Several studies have been performed reporting the effect of temperature in the catalytic cracking of plastics. Among this

- In the catalytic cracking experiments of high-density polyethylene (HDPE) over HZSM-5 zeolite in a fluidized bed within the 290–430°C range, that as temperature rises, the yield of lighter hydrocarbons increases as well as that of BTX and coke. In addition, it is observed that a decrease of the olefin/paraffin ratio in the gaseous fraction from 5.4 to 3.6. [7]
- In another study performed in a semi-batch reactor, the influence of the temperature on the catalytic cracking of a model plastic mixture (46.5% LDPE, 25% HDPE and 28.5% PP) over both

nanocrystalline HZSM-5 and Al-MCM-41 was also studied in the range 375–450°C. The conversion increased with temperature leading to total conversion at 450°C for a plastic/catalyst mass ratio of 100. However, the share of heavier hydrocarbons augmented with temperature for the products obtained over Al-MCM-41, which was ascribed to the larger extent of thermal cracking reactions and also to the vaporization of these heavier compounds at the highest reacting temperature, leaving subsequently the reaction medium. [8]

2.5.2 Catalyst Amount

It was investigated that the catalytic cracking of HDPE over HZSM-5 zeolite varying the polymer-catalyst mass ratio from 1:10 to 1:1 at 360°C in a fluidized-bed reactor. The obtained conversions were always above 90%. However, some differences were appreciated regarding the product distribution. The increase in polymer/catalyst mass ratio led towards higher yields of gaseous C₁–C₄ hydrocarbons (61–69%) and coke. This is an expected result since primary cracking reactions leading towards the formation of C₃–C₄ are favoured as the amount of catalyst is increased, whereas the secondary reactions involving these olefinic gases occur in a minor extension, due to the really short residence time in the fluidized-bed reactor. [7]

On the other hand, the catalytic cracking of a model plastic mixture (46.5% LDPE, 25% HDPE and 28.5% PP) at 400°C in a semi-batch reactor was carried out varying the plastic/catalyst mass ratio (P/C) from 200 to 4 [8]. When nanocrystalline HZSM-5 zeolite was employed as catalyst, the selectivity towards gases (C₁–C₄) and gasoline (C₅–C₁₂) was always within 45–50%, irrespective of the P/C ratio used. However, the composition of both gaseous and gasoline fractions changed significantly. The paraffin/olefin proportion in gaseous hydrocarbons increased on diminishing the plastic/catalyst mass ratio. The same trend was observed for the aromatic content in the gasoline fraction, as shown in Table 2. These results suggest that secondary reactions involving the olefins produced directly from the plastic cracking take place in a growing extent as the amount of catalyst is increased. [7]

Table 2. Aromatic hydrocarbon content in the gasoline fraction resulting from the cracking of a polyolefin mixture at 400°C over *n*-HZSM-5 zeolite at different P/C ratios [9]

P/C ratio (w/w)	Benzene (%)	Toluene (%)	Ethylbenzene (%)	Xylenes (%)	Trimethylbenzenes (%)
200	0.33	0.41	0.25	0.91	0.64
100	0.6	0.34	0.28	0.99	0.44
50	0.81	0.87	0.54	3.39	0.23
10	0.98	3.46	1.28	6.90	0.81
4	1.03	5.32	1.74	9.19	2.28

Both examples illustrate clearly the influence of the catalyst amount in the product selectivity. Therefore, an adequate tuning of both primary/secondary reactions is required to achieve the desired product distribution.

2.5.3 Time

Changes in the performance of catalysts with time are directly related to their deactivation kinetics. The deactivation of USY zeolite in the catalytic cracking of HDPE using thermo gravimetric analyses (TG) has been investigated. It has been observed that USY zeolite was deactivated by coke deposition and established an exponential relationship between the activity decay and the measured coke content. [10]

In another study of the deactivation of several zeolites (HZSM-5, HY, H-mordenite) and silica–alumina in the cracking of LDPE in a fixed bed has been analyzed. The plastic, previously melted at 310°C, was fed into the catalytic bed by capillary pressure. Catalyst deactivation was studied within the temperature range 375–526°C using a space time (W/F) of 7–23 g catalyst min g⁻¹ of polyethylene. HZSM-5 was observed to be the most effective catalyst for degrading the plastic into gasoline range hydrocarbons rich in isoparaffins and aromatics with very low deactivation by coke deposition during the time on stream. [11]

In addition to this the catalyst Deactivation in polystyrene degradation is also studied. In this case, a strong deactivation was appreciated over all the catalysts because of the formation of unsaturated and polyaromatic compounds (indane and naphthalene derivatives) that were converted to coke, in keeping with previous observations [12].

2.5.4 Heating rate

The heat is supplied by indirect heating such as the combustion of the gases or oil or directly by hot gas transfer. Very slow heating rates coupled with a low final maximum temperature maximizes the yield of char, for example, the production of char from wood in the form of charcoal involves a very slow heating rate to moderate temperatures. The process of carbonization of waste results in reduced concentrations of oil/tar and gas product and are regarded as by-products of the main charcoal forming process. Moderate heating rates in the range of about 20–100°C/min and maximum temperatures of 600°C give an approximate equal distribution of oils, char and gases. This is referred to as conventional pyrolysis or slow pyrolysis. Because of the slow heating rates and generally slow removal of the products of pyrolysis from the hot pyrolysis reactor, secondary reactions of the products can take place. Generally, a more complex product slate is found. Very high heating rates of about 100–1000°C/s at temperatures below 650°C and with rapid quenching lead to the formation of a mainly liquid product, referred to as fast or flash pyrolysis. In addition, the carbonaceous char and gas production are minimized. The primary liquid products of pyrolysis are rapidly quenched and this prevents breakdown of the products to gases in the hot reactor. The high reaction rates also cause char-forming reactions from the oil products to be minimized [13,14].

2.5.5 Plastic waste composition

The composition of the raw plastic wastes may have a huge influence on the performance of the catalysts. Hence, catalysts leading to high conversions for the cracking of pure polymers have often been observed to lose their activity to a large extent when cracking a real mixture of plastic wastes. In addition, plastic wastes makeup varies largely, depending on the origin of the waste, making difficult to foresee in a general way the performance of the different catalysts.

It was proven that the presence of a 4 wt % of EVA copolymer in LDPE decreases the activity of mesoporous catalysts (Al-MCM-41, Al-SBA-15) to values close to those of thermal cracking. [15]

2.5.6 Types of reactors

The low thermal conductivity of the molten polymers and their extremely high viscosity are the major problems for the catalytic cracking reactor design. The most widely used reactor systems have been:

- fixed bed
- fluidized bed

2.5.6.1 FIXED-BED REACTORS

The fixed bed is likely the most classical catalytic reactor. However, its usage with plastics as feed is not straightforward since the high viscosity and low thermal conductivity of plastics pose serious problems for being loaded into the reactor. In some systems, the molten polymer is introduced into the reactor through a capillary tube from a pressurized tank [16]. The most usual technical solution is to carry out a previous thermal cracking of the plastic. Then, the liquid or gaseous compounds resulting from the thermal process can be fed easily into the fixed bed [17].

2.5.6.2 FLUIDIZED-BED REACTORS

Fluidized-bed reactors are featured by presenting both temperature and composition homogeneity. This is a remarkable advantage for the cracking of polymers due to their low thermal conductivity and high viscosity that usually lead to the appearance of temperature gradients in other reaction systems wherein heat is not as properly transferred.

2.6 Theory of plastic pyrolysis

The decomposition of plastics can be considered as de-polymerization of polymer into low-molecular product. The general reaction mechanism for the thermal degradation is described with the following steps

- Initiation may occur at random or end-chain positions.
- Depropagation is the release of olefinic monomeric fragments from primary radicals.

- Hydrogen chain transfer reaction, which may occur as intermolecular or intramolecular processes, leads to the formation of olefinic species and polymeric fragments. Moreover, secondary radicals can also be formed from hydrogen abstraction through an intermolecular transfer reaction between a primary radical and a polymeric fragment.
- β -cleavage of secondary radicals leads to an end-chain olefinic group and a primary radical.
- Termination takes place either in a bimolecular mode with the coupling of two primary radicals or by disproportion of the primary macroradicals.

The decomposition of plastics depends on the plastic type, with different reaction mechanisms of plastics proposed with four types [18].

- End-chain scission; the polymer is broken up from the end groups successively yielding the corresponding monomers. When this polymer degrades by depolymerization, the molecules undergo scission to produce unsaturated small molecules (monomers) and another terminal free radicals. (Polymethylmethacrylate, polytetrafluorethylene, polymethacrylonitrile, polyethylstyrene, polystyrene, polyisobutene)
- Random-chain scission; the polymer is broken up randomly into smaller molecules of varying chain lengths, producing a volatile with or without a double bonds. (Polystyrene, polyisobutene, polyethylene, polypropylene, polybutadiene)
- Chain-stripping; the reactive substituents or side groups on the polymer chain are eliminated, leaving an unsaturated chain. This polyene then undergoes further reaction, including β -scission, aromatization and coke formation. (Polyvinylchloride, polyvinyl fluoride, polyacrylonitrile)
- Cross-linking; the formation of a chain networks occur from thermosetting polymers, when heated at high temperature. This is pyrolytic condensation and rearrangement of carbon networks to form high-strength materials. (Thermosetting plastics)

2.7 Process Flow diagram

In order to obtain an oil product in the pyrolysis of waste plastics, the major steps for waste plastics that are derived from the household, industry, etc. are basically shown in Figure 1.0

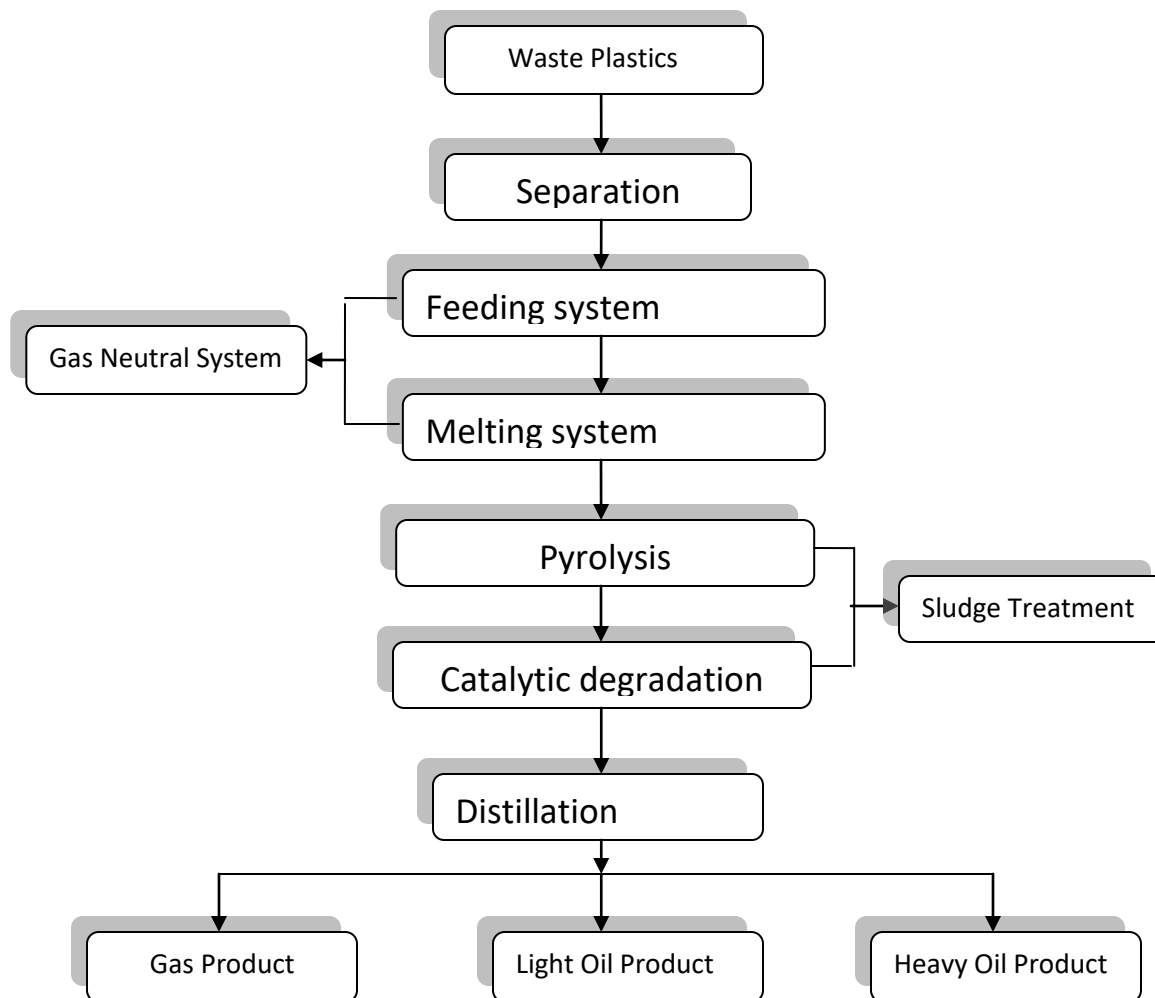


Figure 1.2Continuous process flow diagrams for waste plastics into oil recovery

Waste plastics as a reactant for obtaining the valuable products are invariably contaminated with materials such as soil, iron and wood etc. and also consist of various types of plastics. This material cannot be directly used in the pyrolysis process. Therefore, in the next step separation treatments must be applied to obtain waste plastic with a homogeneous composition. If it contains a lot of various contaminative materials in waste plastics, it leads to poor economics by increasing the recycling procedure cost. Thus, the important point for the pyrolysis process is the purification of waste thermoplastics, especially excluding PVC and PET in the reactant. Here, PVC and PET in the plastic feedstock can cause unfavourable emission due to the presence of Cl as well as high char/coke yields since they are not well degraded in the general pyrolysis process, respectively. The waste material must be separated into individual components, such as thermoplastic, PVC, PET, thermosetting, iron, aluminum and paper, etc.

In the third step, the separated plastics are delivered by the feeding system such as the conveyor, hopper and extruder, etc. to the melting reactor, after cutting to a small size. The feeding system is continuously controlled with a constant reactant amount and classified as heated or non heated case of the extruder. By preheating the plastic feedstock the melting time in the melting reactor can be shortened thus improving production rates. Moreover, the film type reactant is very bulky and voluminous, which makes it difficult to ensure continuous feeding, is easily dosed at the melting system after melting in the feeding system. In the unheated case, a hard reactant of several millimeter size is adequately controlled by a continuous feeding system. Thus, the feeding system will be determined by the profile of waste plastics that are exited from industry, agriculture and household, etc. Other important point is that if there is trouble in a continuous automatic feeding system, it can be quickly transferred to a manual system.

The next step is the melting system, where the solid plastic is changed to a low viscosity melt. If there is sufficient time to melt the polymer in the melting reactor, the pyrolysis and/or catalytic degradation process as the next step of melting system will be well controlled without trouble in a continuous system. The residence time of plastics in the reactor depends on the plastic type and the desired viscosity extent. Thus, in order to reduce the melting time of reactant in the melting system, it needs be heated in the feeding system prior to the melting system. Moreover, as the system is scaled up to a big plant, this is a very important parameter for heating the feeding system.

In the pyrolysis and catalytic degradation of polymer at temperature 300–450 °C the melted reactant is degraded into a smaller molecule and also upgraded to oil product with a high quality. Several processes of pyrolysis and catalytic degradation are available, such as pyrolysis process only, liquid-phase catalytic degradation after the melting process and catalytic degradation after the pyrolysis process, according to the characteristics of the oil produced.

For the processes of different reactor types, kiln and retort pyrolysis processes are characterized by a relatively low capital investment. However, they suffer from unfavorable economics, due to the high processing costs compared with the value of the oil product obtained. Also, the characteristics of this process are relatively long residence times of waste in the reactor, poor temperature control due to

large temperature gradients across their internal dimensions, fouling walls of the reactor by carbon residue and low liquid product quality due to the production of a diverse number of pyrolysis products.

Fixed-bed pyrolysis–catalytic cracking process for oil recovery of waste plastic is in use at several commercial processes. The reactor type in the pyrolysis or/and catalytic cracking process is generally constant stirred tank reactor (CSTR) and plug flow reactor. The problem is the fact that carbon residues tend to foul the walls of the reactor and thus give poor heat transfer from the external wall to the center of the reactor. Furthermore, CSTR type can deal with a relatively high viscosity reactant, but the problem of heat transfer by a big reactor diameter can be more important, compared with that of plug flow reactor. Basically, waste plastics are melted to materials of low viscosity and then the liquefied reactant is thermally decomposed to low-molecular-weight hydrocarbons in the pyrolysis reactor. These reactants are cracked in a fixed-bed reactor using solid catalyst to yield the oil and gas products. The characteristics of this process are the quality of the oil product, very similar to that of conventional gasoline, kerosene and diesel oils, but the drawback of the catalyst is high cost and short life-cycle due to poisoning/deactivation.

The fluidized-bed process yields a uniform product and a high conversion during a short reaction time. In addition, the problem of low thermal conductivity of polymers is overcome by a fluidized system and thus heat transfer gradients are eliminated. Some advantages are high-quality product, low energy requirement supplied by combustion of a portion of the gas by-product, good temperature control, the efficient removal of impurities present in the waste plastic, application on a relatively small scale, and also a robust and relatively inexpensive process to establish. On the contrary, this process has problems with toleration in the chlorine produced, the removal of solid sludge from the fluidized bed and also its long-term durability.

In the pyrolysis process, one of the most important decision items is the degradation temperature in the reactor. The degradation temperature must be decided by the type and composition of plastics contained in mixed thermoplastics, because of their different degradation temperatures. For a reactor with a big diameter in a large-scale plant the temperature gradient must also be taken into consideration in determining the degradation temperature, because of heat transfer limitations for viscous fluids with low thermal conductivity in the large reactor. Moreover, the coke accumulated on the internal surface of reactor during a long reaction time hinders heat transfer between heat source and viscous fluid in the reactor. Thus, the heat supply of the plant is gradually increased with the progress of reaction time. Optimization process control for hindering the coke formation is an important key in a large-scale plant.

Also, the impact on the environment in the pyrolysis of waste plastics must be taken into consideration. If a PVC material is contained in the reactant, the hydrochloric acid is evolved during decomposition of PVC which causes air pollution. Thus, a system is needed in order to remove the chlorine components in gas products. The rest of the gas products consisting of light hydrocarbons can be used as fuel gas in the heating system. Also the nonvolatile material generated in the melting and pyrolysis process, which includes a small amount of volatile hydrocarbon components, is discharged to a sludge treatment

system. After being sufficiently heated in the sludge system, the product obtained is used as valuable oil, but the solid char/coke retained is landfilled or incinerated.

Finally, the product obtained is separated from the distillation tower, such as gas product, light oil product and heavy oil product. Our target is light oil product and/or heavy oil product, which is generally obtained by control of reactor temperature and distillation system such as temperature gradient, reflux ratio and reboiler temperature, etc. The distribution of the oil product must be decided by market circumstances.

2.8. Product Yield

In thermal or catalytic cracking the main products of processing are gas, naphtha, both light and heavy gas oil fractions, and solid residue similar to coke. The main product of high-temperature pyrolysis process, 600–800 °C, is C₂–C₄ olefins containing the gaseous fraction.

2.8.1 Product Yield from the Feedstock Recycling of Single and mixed plastics

The detailed analysis of the derived oil/wax and gas products from the pyrolysis of plastics in relation to process conditions and different types of plastic is essential in providing data for the assessment of the feedstock recycling process. In addition, the yields and composition of gases and oils from the pyrolysis of mixed plastic waste are important in assessment of the process and to determine the possibility of any interactions between the plastics during pyrolysis.

Table 3 shows the yield of gas, oil/wax and char from the fixed bed pyrolysis of the main polyalkene plastics, polyethylene and polypropylene, found in municipal solid waste [19 – 20].

Table 3 Product yield from the pyrolysis of polyalkene plastics

Feedstock	Reactor type	Temperature (°C)	Gas (wt%)	Oil/wax (wt%)	Char (wt%)
PE	Fluidized-bed	760	55.8	42.4	1.8
PE	Fluidized-bed	530	7.6	92.3	0.1
LDPE	Fluidized-bed	700	71.4	28.6	0
LDPE	Fluidized-bed	600	24.2	75.8	0
LDPE	Fluidized-bed	500	10.8	89.2	0

LDPE	Fixed-bed (batch)	700	15.1	84.3	0
HDPE	Fixed-bed (batch)	700	18.0	79.7	0
LDPE	Fixed-bed (batch)	500	37	63	0
LDPE	Ultra-fast pyrolysis	825	92.9	5	2
HDPE	Fixed-bed (batch)	450	13	84	3
HDPE	Fixed-bed (batch)	430	9.6	69.3	21.1
HDPE	Vacuum	500	0.9	97.7	0.8
LDPE	Vacuum	500	2.7	96	1
LLDPE	Fluidized-bed	730	58.4	31.2	2.1
LLDPE	Fluidized-bed	515	0	89.8	5.9
PP	Fixed-bed (batch)	380	24.7	64.9	10.4
PP	Fixed-bed (batch)	700	15.3	84.4	0.2
PP	Fluidized-bed	740	49.6	48.8	1.6
PP	Vacuum	500	3.5	95	< 0.1
PP	Fixed-bed (batch)	500	55	45	0.0

Table 4 shows the gas, oil/wax and char from the pyrolysis of other plastics [19 - 20]. All of the plastics produced an oil/wax and gas and in some cases a char. The product yield related directly to the type of plastic, the reactor type and the process conditions, particularly pyrolysis temperature. The product oil produced from pyrolysis varies considerably in colour. For example, it has been reported that at temperatures of approximately 500 °C, the polyalkene plastics, PE, HDPE, LDPE and PP produce a light-coloured waxy product [19].

Table 4 Product yield from the pyrolysis of other plastics

Feedstock	Reactor type	Temperature (°C)	Gas (wt%)	Oil/wax (wt%)	Char (wt%)
PS	Vacuum	500	<0.1	99.3	0.4
PS	Fixed-bed (batch)	700	3.4	83.8	3.5
PS	Fluidized-bed	500	0.2	99.7	<0.1
PS	Fluidized-bed	580	9.9	89.5	0.6
PS	Fluidized-bed	600	0.7	98.7	<0.2
PS	Fluidized-bed	532	11.5	88.5	
PS	Fluidized-bed	708	15.2	83.3	
PVC	Vacuum	520	58.5	32.4	8.5
PVC	Fixed-bed (batch)	700	55.8	31.7	13.8
PVC	Fluidized-bed	740	63.1	28.1	8.8
PVC	Fluidized-bed	520	84.6	6.3	9.1
PET	Fixed-bed (batch)	500	73.4	9.1	18.5
PET	Fixed-bed (batch)	700	38.7	41.3	15.6
Thermoset plastics					
Polyurethane	Fluidized-bed	760	37.9	56.3	0.3
Polyester	Fluidized-bed	768	50.8	40	7.1
Polyamide	Fluidized-bed	760	39.2	56.8	0.6
Polycarbonate	Fluidized-bed	710	26.5	46.4	24.6

2.8.2 Product Yield from the Feedstock Recycling of Single and mixed plastics

Table 5 shows the gas, oil/wax and char from the pyrolysis of mixed plastics.

Table 5 Product yield from the pyrolysis of mixed plastic

Feedstock	Reactor type	Temperature (⁰ C)	Gas (wt %)	Oil/wax (wt %)	Char (wt %)
Plastic mixture	Vacuum	520	6.3	91.8	1.3
Plastic mixture	Fixed-bed	700	9.6	75.1	2.9
Plastic mixture	Fluidized-bed	600	44.7	43.2	7.6
Plastic mixture	Fixed-bed	500	85.2	12.5	3.0
MSW plastic	Fluidized-bed	787	43.6	26.4	25.4
MSW plastic	Fixed-bed	430	25	59	16

2.8.3 Gas Composition from the Feedstock Recycling of Single and mixed plastics

The table below shows the composition of gases derived from the pyrolysis of individual single plastics from various researchers [19,20] and pyrolysis of mixed plastic waste representative of the plastics found in municipal solid waste. The three polyalkene plastics, HDPE, LDPE and PP, behave quite similarly in that the main gases to be formed are alkene gases derived from the thermal degradation of their similar polyalkene chemical structure. **Table 6** Gas composition from the pyrolysis of single plastics.

	Reactor type	H ₂ wt%	CH ₄ wt%	C ₂ H ₆ wt%	C ₂ H ₄ wt%	C ₃ H ₈ wt%	C ₃ H ₆ wt%	C ₄ H ₁₀ wt%	C ₄ H ₈ wt%	CO ₂ wt%	CO wt%	HCl wt%
HDPE	Fixed-bed	0.12	1.9	2.21	6.08	1.31	4.56	0.22	0.36			
PE	Fluidized bed	0.8	23.8	6.7	20	0.08	5.6		0.6			

LDPE	Fixed-bed	0.05	1.14	1.67	4	1.33	4	0.32	2.00			
LDPE	Fluidized bed		22		28		18					
LLDPE	Fluidized bed		4.6	22	19.4	0.8	12	13.1				
PP	Fixed-bed	0.05	0.93	1.45	3.5	1.0	3.53	0.23	1.29			
PP	Fluidized bed	0.7	28.2	4.0	13.9	0.09	3.7		0.4			
PS	Fixed-bed	0.04	0.53	0.08	0.2	0.02	0.05	0.00	0.06			
PS	Fluidized bed		0.06		0.04							
PVC	Fixed-bed	0.12	0.77	0.47	0.15	0.24	0.19	0.11	0.15			52.93
PET	Fixed-bed	0.31	0.71	0.03	1.41	0.13	0.09	0.00	0.00	22.7	13.29	0.00
Polyester	Fluidized bed	0.3	3.8	0.2		0.05	0.1				17.4	
Polyurethane	Fluidized bed	0.7	16.1	1.8	7.2	0.2	1.3		0.1	1.8	34	
Mixed plastic	Fixed-bed	0.08	0.97	1.01	1.67	0.7	0.83	0.14	2.20	2.06		2.31
Mixed plastic	Fluidized bed	0.22	2.87	2.39	5.6	1.26	5.53	0.24	6.3			1.4

3. Materials and Methods

3.1 Study area description

The study is conducted in the laboratory with set up of different equipments

3.2 Sampling Techniques

Sample is taken from each raw material randomly with size distribution lower than 2mm.

3.3 Physical and chemical properties measured

Physical properties measured are mass and Volume

No chemical properties were measured since the equipments for testing were out of service

3.4 Laboratory procedure

Table 1.6 Materials Used for the experiment

Material	Capacity
Round bottom Flask	50 ml
Glass connecting Tube with three Outlets	-
2 round bottom flask	100 ml
Electrical Stove	400 w(power)
Vacuum pump	-
Glass fiber insulating material	-
Digital Balance	-
Measuring Beaker	
Erlenmeyer flask	
Laboratory cutting mill	
Glass tube condenser	

Chemicals Used

Polyethylene terephthalate (PET)

Poly styrene foam

Polyethylene (HD & LD)

Zeolite

Zeolite (Hydrogen cation)

Diatomite

By thermally cracking plastics without presence of air to produce an oil that contain different hydrocarbons including benzene and Diesel oil.

3.4.1 Experiment on Polyethylene terephthalate(PET) pyrolysis

Procedure(1) (Without catalyst)

-A set up was created having round bottom flask, condenser and collecting flask heated by stove

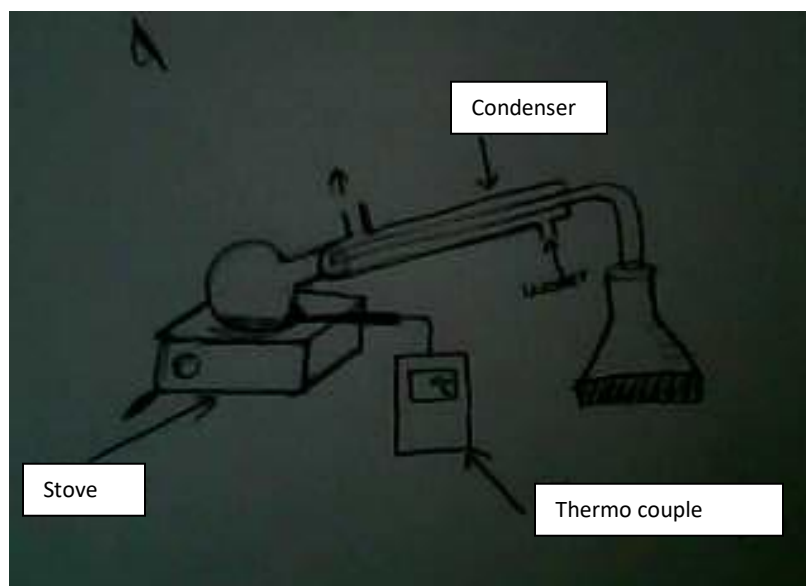


Fig 1.3 Laboratory setup for PET pyrolyser

-A Polyethylene terephthalate(plastic bottle) is crushed in a laboratory cuttermill to size below 2 mm.

-A sample of 25g crushed PET is weighed and added to the round bottom flask.

-The stove is set to a maximum point and the process began. A time measurement is taken for two hours at temperature of 500 °C.

-A solid product is collected at the flask and in the condenser tube.

Procedure (2) (With vacuum and without catalyst)

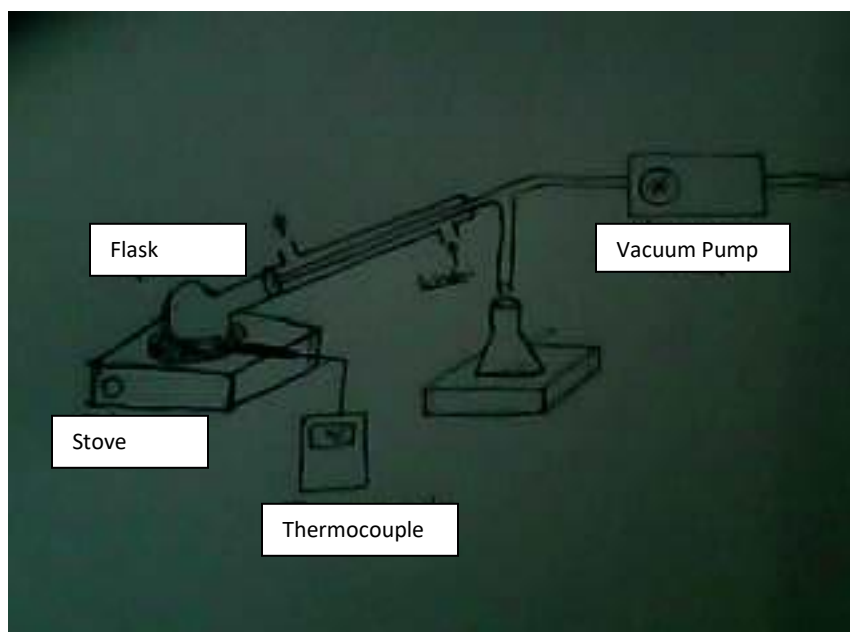


Fig 1.5 Laboratory setup for PET pyrolysis under vacuum

- A new setup is created having vacuum pump connected to the condenser.
- A new sample of 25 g PET is weighed on Balance and added to round bottom flask
- The stove is set to maximum point and the process began. A time measurement for two hours at temperature of 500°C
- A solid product is collected at the flask and in the condenser tube.

N.B. Since the amount of solid collected was very small it was difficult to take any measurement of the product both quantitatively and qualitatively.

Data

Experiment No.	Sample	Weight	Temperature	Time	Product type	Product weight
(1)	PET	25 g	500 °C	2hr	Solid	-
(2)(with vacuum)	PET	25 g	500 °C	2hr	Solid	-

Results

Pyrolysis of the PET results a formation of solid products which are difficult to measure and to determine.

From literature, the pyrolysis temperature above 700 °C is required to thermally crack PET into Oil. In the lab experiment we have been able to attain maximum temperature of 560 °C by the stove. This made pyrolysis of PET impossible.

The equipment we have set and the equipment in the lab do not comply to conduct the experiment.

Energy utilized for one experiment

$$= 0.4 \text{ kw} \times 2 \text{ hr}$$

$$= 0.8 \text{ kwh}$$

$$= 0.8 \text{ kwh to produce 0g of oil}$$

3.4.2 Experiment on Polystyrene

Procedure (1) (with catalyst zeolite)

A setup is created having round bottom flask 50ml, glass connecting tube, collecting round bottom flask, stove electrical, vacuum pump, insulating fiber glass.

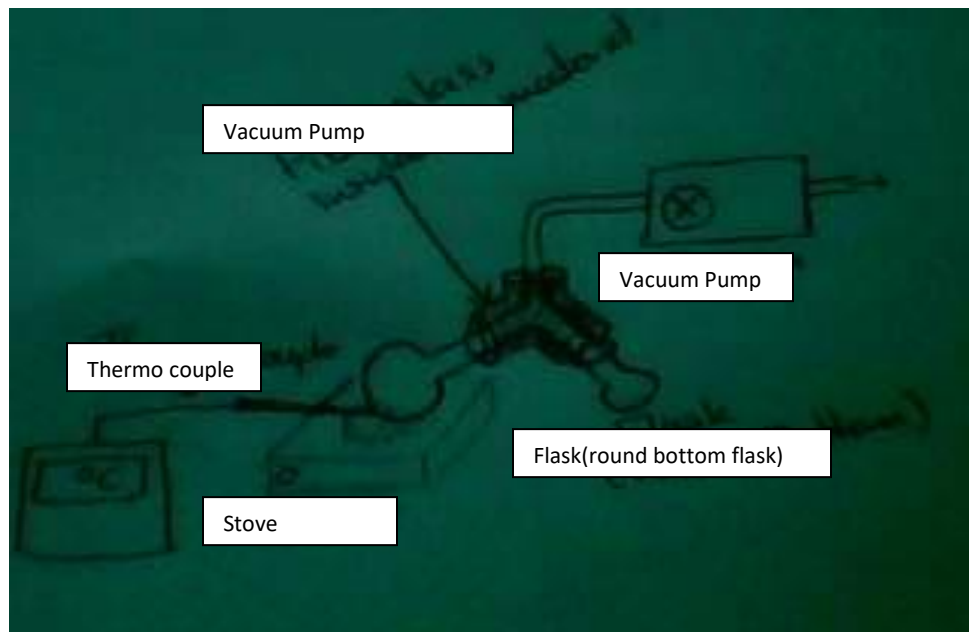


Fig 1.6 laboratory setup for polystyrene foam pyrolysis

- Polystyrene foam s size reduced by a laboratory cutting mill and a 2mm below sized polystyrene is collected.
- A sample of 4 g Polystyrene weighed and added to 25 ml round bottom flask.
- A zeolite catalyst of 1 g is weighed and added to the flask
- A vaccum is started to remove the oxygen in the flask

- The stove is switched on, heating the flask gradually to the melting point of the polystyrene
- After the melting point has reached the stove is set to maximum temperature.
- When the material in the flask is depleted the time and temperature data are recorded.

The Above procedure is repeated 3 times and then the product is weighed.

Data

Experiment No.	Sample	Weight	Catalyst type	Catalyst weight	Temp	Average time individually	Product type	Total product weighted
1	Polystyrene foam	4 g	Zeolite	1g	<500 °C	15 min	Oil	10 g
2	"	4 g	zeolite	1g	<500 °C		Oil	
3	"	4 g	zeolite	1g	<500 °C		Oil	
4	"	4 g	zeolite	1g	<500 °C		Oil	

Result

In the presence of zeolites as catalysts the result show that from 4 different experiments a total of 16 g polystyrene is converted to 10 g of oil.

$$\text{The yield calculated} = \frac{\text{Product collected}}{\text{Raw material fed}} = \frac{10 \text{ g}}{16 \text{ g}} * 100\% = 62.5\%$$

From literature the yield is about 50-75% [1] therefore, the experiment with the current catalyst ratio is feasible. Polymer to catalyst ration taken is.

$$4\text{g (polymer)}/1 \text{ g (catalyst)} = 4$$

Total energy consumption

The stove power is 400w in which the 4 experiments lasted an average of 15 minute individually

$$E = P * t$$

E= Energy

P= Power

T=time

Energy utilized for one experiment

$$=0.4\text{KW} * 0.25 \text{ hr}$$

$$=0.1 \text{ kwh}$$

$$0.1 \text{ Kwh} * 4 = 0.4 \text{ kwh to produce 10 g of oil}$$

Procedure (2) on polystyrene with (diatomite catalyst)

The previous setup shown in fig 1.6 was used except with different catalyst diatomite.

- A sample of 4 g polystyrene is weighed polystyrene is added to a 25 ml round bottom flask.
- A diatomaceous earth catalyst of 1g is weighed and added to the flask.
- The vacuum is started to remove the oxygen in the flask
- The stove is switched on, heating the flask gradually to the melting point of polystyrene.
- After melting point is attained the stove is set to its maximum point.
- When the material in the flask depleted the time and temperature data are recorded
- The above procedure is repeated 2 times and the following data are recorded.

Data

Experiment No.	Sample	Weight	Catalyst type	Catalyst weight	Temp	Average time individually	Product type	Total product weighted
1	Polystyrene foam	4 g	Diatomite	1g	<560 °C	19 min	Oil	2g
2	"	4 g	Diatomite	1g	<560 °C		Oil	

Result

A Polymer to catalyst ratio of 4 was taken

An 8 g sample was pyrolysed to produce 2g of oil with time of 28 minutes.

$$\text{The yield} = \frac{2 \text{ g}}{8 \text{ g}} * 100 = 25\%$$

Diatomite catalyzed reaction yield is very much lower compared to zeolite catalyzed reaction but the diatomite catalyzed oil has more purity than zeolites.

Energy utilized for one experiment

$$=0.4 \text{ kw} * 0.31 \text{ hr}$$

$$= 0.124 \text{ kwh}$$

$$0.124 * 2 = 0.248 \text{ kwh to produce 2g of oil}$$

3.4.3 Experiment on polyethylene bag

Procedure(1) (with zeolite catalysts)

- The same setup is used as with polystyrene
- The poly ethylene bag is manually cut by scissors.
- 10 g polyethylene is weighed and added to the flask
- Zeolite catalyst of 1 g is weighed added to the flask
- Vacuum is switched on to remove the oxygen.
- The stove is then switched on and gradually heated to melting point of polyethylene
- The stove is set to maximum point
- When the material in the flask is depleted the time and temperature data recorded.

The above procedure is repeated once and the data is collected

Data

Experiment No.	Sample	Weight	Catalyst type	Catalyst weight	Temp	Average time individually	Product type	Total product weighted
1	Polyethylene bag	10 g	zeolite	1g	<544°C	1:20 hr	Oil	7.4 g
2	"	10 g	zeolite	1g	<544°C		Oil	

Result

A polymer to catalyst ration of 10 was taken

From 20 g of total raw material 7.4 g of oil was produced

$$\text{The yield} = \frac{\text{Product collected}}{\text{Raw material fed}} = \frac{7.4 \text{ g}}{20 \text{ g}} * 100 = 37 \%$$

The total energy consumption is

Energy utilized for one experiment

$$= 0.4 \text{ kw} * 1.25 \text{ hr}$$

$$= 0.5 \text{ kwh}$$

$0.5 \times 2 = 1$ kwh is required to produce 7.4 g of oil

Procedure(2)(with zeolite(hydrogen bonded))

The same setup and procedure as above is used with hydrogen bonded zeolite catalyst.

Data

Experiment No.	Sample	Weight	Catalyst type	Catalyst weight	Temp	Average time individually	Product type	Total product weighted
1	Polyethylene bag	10 g	zeolite	1g	<530 °C	45 minute	Oil	1.9 g

Result

A polymer catalyst ratio of 10 was taken

$$\text{The yield} = \frac{\text{Product collected}}{\text{Raw material fed}} = \frac{1.9 \text{ g}}{10 \text{ g}} * 100 = 19 \%$$

Total energy consumption

Energy utilized for one experiment

$$= 0.4 \text{ kw} * 2 \text{ hr}$$

$$= 0.8 \text{ kwh}$$

0.8 kwh to produce 1.9 g of oil

Experiment on mixed plastics

- The same setup is used as in polyethylene and Polystyrene experiments.
- A mixture of plastics wastes of Polyethylene and polystyrene with 71wt% and 29 wt% of polystyrene is weighed with total mass of 3.5 g is added to the flask.
- A mixture of catalysts both zeolite and diatomite with equal proportion and total mass of 1g is weighed and added to the flask.
- A vacuum is created in the flask.
- The stove is set to maximum point and the experiment is conducted.

After the material in the flask is fully depleted total time, temperature are measured.

Data

Experiment No.	Sample	Weight	Catalyst type	Catalyst weight	Temp	time	Product type	Total product weighted
1	71 wt% PE 29 wt% PS	3.5 g	Zeolite 0.5 wt%.diatomite 0.5 wt%	1g	<550 °C	20 minute	Oil	0.7 g

Result

A polymer catalyst ration of 3.5 was taken

$$\text{The yield} = \frac{\text{Product collected}}{\text{Raw material fed}} = \frac{0.7 \text{ g}}{3.5 \text{ g}} * 100 = 20 \%$$

Total energy consumption

Energy utilized for one experiment

$$= 0.4 \text{ kw} * 0.33 \text{ hr}$$

$$= 0.132 \text{ kwh}$$

0.132 kwh to produce 0.7 g of oil

4. Results and Discussions

Summary results

Tabel1.7 Summarized results of Laboratory experiment

Material	Catalyst	Yield	Energy consumption	Temprature
Polyethylene teraphthalate	-	0%	0.8kwh	500 °C
Polystyrene(PS)	Zeolite	62.5%	0.04 kwh/g	560 °C
	Diatomite	25%	0.124 kwh/g	560 °C
Polyetylene(PE)	Zeolite	37 %	0.135 kwh/g	544 °C
	H+ bonded zeolite	19 %	0.421 kwh/g	530 °C
Mix of PE&PS	Zeolite&diatomite	20 %	0.185 kwh/g	550 °C

As seen from the table above polystyrene with zeolite catalysts have higher yield with low energy consumption making it preferable in pyrolysis. It is very much difficult in industrial scale production since most plastics are contaminated by either other plastics or other materials.

Recycling of polyethylene bags under zeolite is also preferable if the pure waste can be accessed .Polyethylene bags are more easier to handle than polystyrens which reduce the cost of material handling in large scale operations.

Mixture of different plastics can only be economical in large scale production.Major draw backs of this plastics are in the sorting,cleaning and transporting mechanisms.If this problems are solved it would be an asset for developing nations such as ours to have a alternate fuel source beside imported oil.

6. Large Scale Production

6.1 Process Flow Diagram

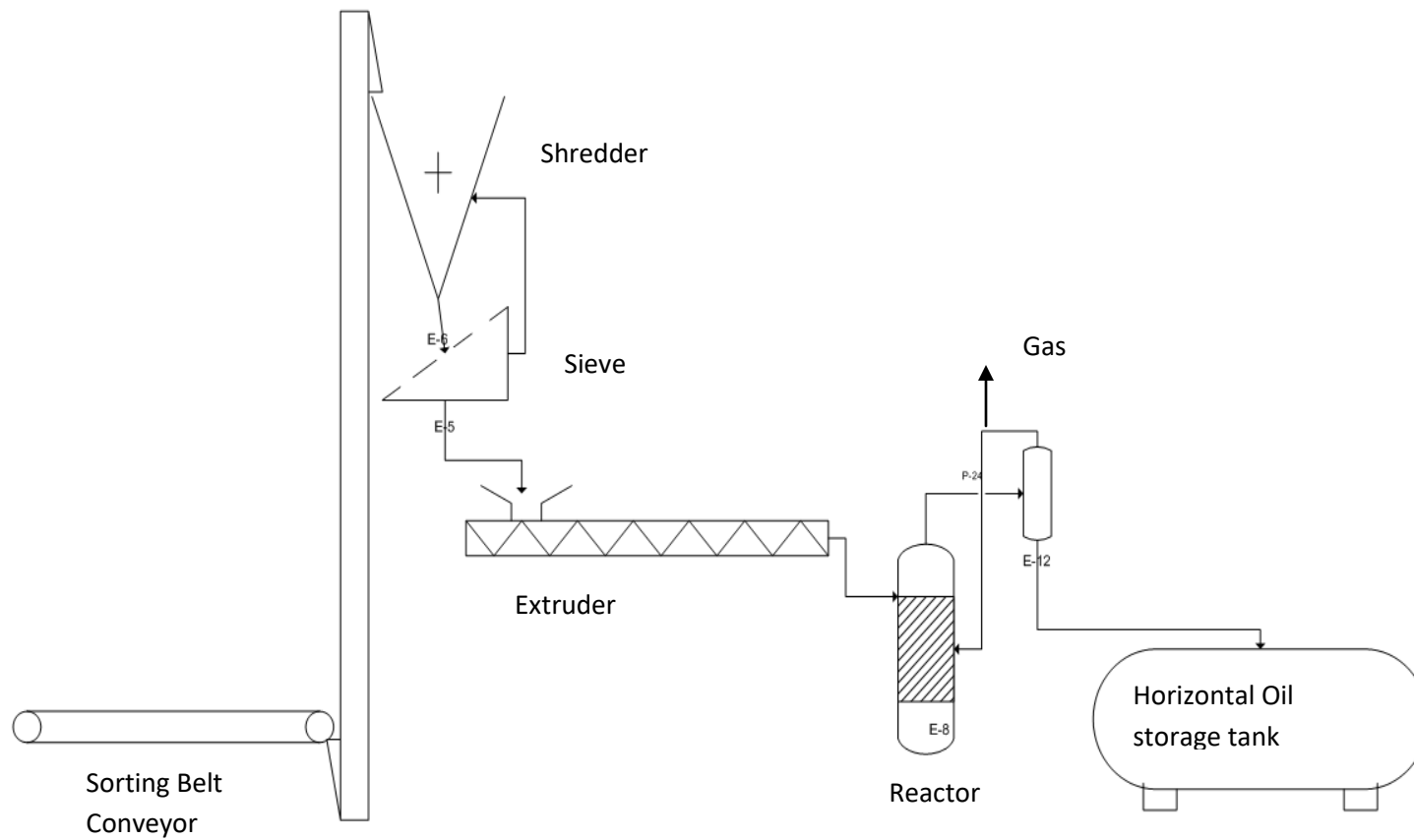


Fig Process flow diagram large scale production

6.2 Process description

First the waste plastic is collected from different areas of Addis Ababa by using various mechanisms. After the collection process, using belt conveyor as a conveying mechanism, the plastics are sorted manually. Here impurities like metals and soil are removed. Next the plastics are dried using natural methods, sunlight. After this using a bucket elevator the dried plastics are fed into a shredding machine, in which the size of the plastic is reduced to 1 cm. Those plastics which have oversized are separated using mechanical sieve and return to the shredder. The undersized plastic then goes to the extruder. Here the plastic are transported and heated to certain temperature. Now the heated plastic are fed to a reactor which has a temperature of 350-700⁰c. In order to enhance the product yield and due to other reasons catalyst is added to the reactor. The products solid and liquid are recovered from the reactor and conveyed to their storage tanks and the gas is used to heat the reactor.

6.3 Market Study

In order to estimate the capacity of the plant we use overview of Addis Ababa city solid waste management system as a main source. [21]

Solid waste generation

- ❖ City of Addis Ababa generates a solid waste of 0.4kg/c/day
- ❖ More than 200,000t are collected each year
- ❖ about 550t/day, 80% of the total waste collected
- ❖ the municipality increased the collection rate from 60% to 80%
- ❖ Sources of Waste Generated
 - 76% households,
 - 18% institutions ,commercial, factories, hotels,
 - 6% is street sweeping.

Physical composition

Organic 60%, Recyclables 15 % , Others 25%

- Vegetable 4.2 %,
- Paper 2.5%,
- rubber/plastics 2.9%,
- Wood 2.3%,
- Bone 1.1%,
- Textiles 2.4 %,
- Metals 0.9%,
- Glass 0.5%,
- combustible leaves 15.1%,
- Non-combustible stone 2.5%,
- All fine 65

Solid Waste Management

Collection of solid waste

- The Municipality Spends large proportion of its budget on collection, transport, and disposal of solid waste
- Solid waste collection services divided in to two sub-systems: primary and secondary collection
- Primary collection is done by micro and small enterprises
- Payment is Volume based rate (30 birr perm³)

From the above data the waste plastic which is generated per day is around 3% of 550ton.

$$\text{Capacity of the plant} = \frac{2.9 * 550 \text{ ton/day}}{100} = 15.9 \text{ ton/day}$$

By giving some allowance we approximate the capacity to 10 t/day.

From literature the oil price which is generated by applying pyrolysis process is about \$30–50/barrel. [22]

According to Ethiopian Oil Enterprise, annual consumption of our country is 2,176,188 tones fuel worth 1.42 billion. In which our total production of oil take 0.09% of the market share.

6.4 Material Balance

From literature pyrolysis of mixed plastic @ 750⁰c (PE 60%, PP 5%, PS 25%, PET 2.8% Other 7.2%) yields the following products [23-24]

Gas 35% by weight

Liquid 51%by weight

Solid residue 13%by weight

Total Products

For our capacity 10t/day, the products will be

$$\text{Gas} = (35/100) * 10 \text{ t/day} = 3.5 \text{ t/day}$$

$$\text{Liquid} = (51/100) * 10 \text{ t/day} = 5.1 \text{ t/day}$$

$$\text{Solid} = (13/100) * 10 \text{ t/day} = 1.3 \text{ t/day}$$

Catalyst consumption

From literature taking plastic to catalyst ratio 50 by weight

Total catalyst required will be $(10/50) \text{ t/day} = 0.2 \text{ t/day}$

Solvent consumption for cleaning

In order to clean the reactor we use a solvent which is isoamyl alcohol which has a reasonable cost with good cleaning ability.

The reactors are cleaned at the end of each shift.

An amount of 5 lit of isoamyl alcohol per 5 batch.

6.5 Energy Balance

From the experiment, the maximum energy requirement for two hour pyrolysis is 0.8kwh/g.

$0.8 \text{ kwh/g} * 1,000,000 \text{ g/batch} = 8,000,000 \text{ kwh required per day.}$

$$= 8\text{GJ/day}$$

The product gas calhorific value is 50 MJ/M^3

Total gas production per day = $10\text{t/day} * 0.35 = 3.5 \text{ ton/day} = 3500 \text{ Kg/day}$

Density of the gas = 1.170 Kg/m^3

Total energy per day = $(3500 \text{ Kg/day} / 1.170 \text{ Kg/m}^3) * 50 \text{ MJ/M}^3$

$= 148.556 \text{ GJ/day}$

$$= 148.556 \text{ GJ/day} / 20\text{hrs/day}$$

$$= 7.42 \text{ GJ/hr} = 2.06 \text{ MW}$$

Comparing the two requirements product gas can be used to fire up the reactor.

6.6 Equipment selection

The main equipment for plastic pyrolysis are single shaft plastic shredder, mechanical sieve, plastic extruder and heater, reactor, liquid oil storage tank and material handling equipments like bucket elevator belt conveyor screw conveyor.

6.7 Economics

6.7.1 Purchased equipment cost

The Purchased equipment cost can be calculated as follows

	Equipment	price (dolar)
1	single shaft plastic shredder	7500
2	mechanical sieve	1000
3	bucket elevator	1500
4	belt conveyor	2000
5	plastic extruder and heater	10000
6	reactor	12946.3
7	liquid oil storage tank	540000
8	screw conveyor	1500
	Purchased equipment cost	576446.3

6.7.2 Total capital investment

Total capital investment calculated based on the purchased equipment cost.

Direct cost	Solid-Liquid processing	
Purchased equipment cost	100	576446.3
Purchased equipment installation	39	224814.057
Instrumentation and controls	13	74938.019
Piping	31	178698.353
Electrical	10	57644.63
Buildings	29	167169.427
Yard improvements	10	57644.63
Service facilities	55	317045.465
Land	6	34586.778
Total Direct Plant Cost	293	1688987.659
Indirect Cost		0
Engineering and supervision	32	184462.816
Construction expenses	34	195991.742
Total Direct and Indirect Plant Cost	359	2069442.217
Contractors fee	18	103760.334
Contingency	36	207520.668
Fixed Capital Investment	413	2380723.219
Working Capital	74	426570.262
Total Capital Investment	487	2807293.481

6.7.3 Total production cost

Raw Material cost

1.Waste plastic

From literature 30 birr perm³ of plastic is invested [21]

Assuming 50kg of plastic per m³ volume

For 10 t/day the money invested will be = $(10/50) \times 1000 \times 30 = 1500$ dollar/day

1500 dollar/day * 300 day = 450000 dollar/year

2. Catalyst

Taking zeolite as a catalyst

112 llar per ton, Cost of zeolite = $0.2 \times 400 = 112$ dollar/day

112 dollar/day * 300 days = 33600 dollar/year

3.Solvent

Amount of money invested on solvent (iso amyl alcohol) will be 1liter = 0.847dollar

10 liter/day consumption * 0.847dollar = 8.47 dollar/day

8.47 dollar/day * 300 days = 2541 dollar/year

Raw material cost annually = $(450000 + 33600 + 2541)$

Raw material cost= 486141 dollar/year

Operating labor

The factory works 24 a day, 2 shift per day and 2 hr cleaning time

Process	Personnel requirement	Per shift	Unit Personnel wage birr /month	wage birr/month
Sorting and drying	36	18	500	18000
Shredder	4	2	1000	4000

Sieving	4	2	1000	4000
Extrusion	4	2	1000	4000
Reactor	4	2	1000	4000
Material handling	4	2	1000	4000
Total wage/month				38000

38000 birr/month/17.3 dollar = 2196.53 dollar/month

Total operation labor cost annually= 2196.53 dollar/month*12 months

Total labor cost = 26,358.38 dollar/year

Total production cost without depreciation

$$TPC = 1.24(C_{RM} + C_{WT}) + 2.74C_{OL} + 0.233*FCI + 1.24C_{UT}$$

Taking $C_{UT} = 0.15$ TPC, $C_{WT}=0$

Rearranging and calculating f for TPC

$$TPC = 1.24(C_{RM}) + 2.74C_{OL} + 0.233FCI + 1.24*0.15 TPC$$

$$TPC = (1.24/0.814)C_{RM} + (2.74/0.814) C_{OL} + (0.233/0.814)FCI$$

$$= (1.523*486141) + (3.366*26358.38) +(0.286*2380723.219)$$

Total Production cost/annum= 1,510,001.891 dollar

6.7.4 Unit cost

Liquid production per annum = 8400 liters/day * 300days = 2,520,000 liter

Unit cost = Total Production cost/ annul production capacity

Unit cost = 1,510,001.891 dollar /2,520,000 litter= 0.599 dollar per liter of oil

Taking a profit margin of 50% the selling price = 0.89 dollar/ liter

6.7.5 Gross profit

From literature oil which is produced from pyrolysis of plastic which is further purified by fractional distillation is around 15 – 30 dollar per barrel

Annual Sales = Total rate of production * Unit selling cost

$$= 2,520,000 \text{ liter/year} * 0.89 \text{ dollar/liter} = 2,242,800 \text{ dollar}$$

Gross profit = sales – TPC = 2,242,800 - 1,510,001.891 = 732,798.1 dollar

Gross Profit = 732,798.1

Depreciation = FCI / 10years

$$= 2380723.219 / 10$$

Depreciation = 238,072.3219 dollar

Assuming income tax = 30%

Income tax = Tax rate * (Gross profit- Depreciation)

$$\text{Income tax} = 0.3(732,798.100 - 238,072.3219) = 148,417.73 \text{ dollar}$$

Net profit = gross profit – income tax – depreciation

$$= 732,798.100 \text{ dollar} - 148,417.73 - 238,072.3219$$

$$= 346,307.94 \text{ dollar/year}$$

Net profit = 346,307.94 dollar/year

Return on investment (ROI)

I) Before income tax

$$ROI_{\text{overall}} = \frac{\text{Total gross profit} - \text{Total depreciation}}{\text{Total capital investment}} * 100$$

$$ROI_{\text{overall}} = \frac{(10 * 732,798.1) - (10 * 238072.3219)}{10 * 2807293.481} * 100\% = 17.6 \%$$

II) After income tax

$$ROI_{\text{overall}} = \frac{\text{Total net profit}}{\text{Total capital investment}} * 100\%$$

Total capital investment

$$ROI_{\text{overall}} = \frac{10 * 346,307.94}{10 * 2807293.481}$$

$$\text{Pay back period} = \frac{\text{Total Capital Investment}}{\text{Net profit/year} + \text{Depreciation/year}}$$

$$= \frac{2807293.481}{346,307.94 + 238072.3219}$$

$$= 4.8 = 5 \text{ yr}$$

Cash flow

Year of operation	-2	-1	0	1	2	3	4	5	6	7	8	9	10
Fixed capital	- 714.22	- 1666.5											
Working capital			-426.57										
Sales				2,243	2,243	2,243	2,243	2,243	2,243	2,243	2,243	2,243	2,243
Operating and direct costs				-1,510	-1,510	-1,510	-1,510	-1,510	-1,510	-1,510	-1,510	-1,510	-1,510
Gross profit				732.7	732.7	732.7	732.7	732.7	732.7	732.7	732.7	732.7	732.7
Cumulative gross profit				732.7	1465.4	2198.1	2930.8	3663.5	4396.2	5129	5861.6	6594.3	7327
Depreciation				-238.07	-238.07	- 238.07	-238.07	- 238.07	- 238.07	- 238.07	- 238.07	-238.07	-238.07
Gross profit - Depreciation				494.6	494.6	494.6	494.6	494.6	494.6	494.63	494.63	494.63	494.63
Income tax			714.215	-148.4	-148.4	-148.4	-148.4	-148.4	-148.4	-148.4	-148.4	-148.39	-148.39
Net profit			714.215	346.2	346.2	346.2	346.2	346.2	346.2	346.2	346.2	346.24	346.24
Cumulative net profit			714.215	1060.5	1406.7	1752.9	2099.2	2445.4	2791.7	3137.9	3484.1	3830.37	4176.61
Cash flow	- 714.22	- 1666.5	287.64	584.3	584.3	584.3	584.3	584.3	584.3	584.3	584.3	584.3	584.31
Cumulative cash flow	- 714.22	- 2380.7	-2093.1	- 1508.76	-924.4	-340.1	244.2	828.5	1412.8	1997.1	2581.4	3165.7	3750.04
Net present value	- 944.55	- 1916.5	287.64	508.10	441.8	384.2	334.1	290.5	252.6	219.7	191.01	166.1	144.43
Cumulative NPV	- 944.55	-2861	-2573.4	-2065.3	-1623.5	- 1239.3	-905.2	-614.7	-362.1	-142.4	48.61	214.7	359.14

5. Conclusion and Recommendation

5.1 Conclusion

Pyrolysis of plastic into oil has many advantages besides subsidizing energy of non oil producing countries one if it is that it can reduce considerable area that plastics occupy in the land fill.

The process requires quite a lot human resources both professionals and labours that would open employment opportunity for many, most of collection, sorting are done manually since there is no efficient way of collected and sorting plastics on machine basis.

Further research in pyrolysis process can increase efficiency, high yield and affordability of the oil produced which in turn could give a break to people who are burdened with sky rocketing energy prices.

5.2 Recommendation

Most of literatures include condenser after the reactor, in fact we have been able to understand that product condenses at ambient temperature without condenser which reduces the cost of equipment.

Careful selection of reactors and catalysts is required to have better yield in both quantity and quality, extended time.

Sorting is the basic problem plastics recycling, it needs training for personnel's to reduce contamination in reactors.

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