

AMERICAN UNIVERSITY OF BEIRUT

PYROLYSIS OF PLASTIC WASTE INTO FUEL:AN
EXPERIMENTAL STUDY OF POLYETHYLENE
PYROLYSIS

by
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AN ABSTRACT OF THE THESIS OF

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Plastic waste is an increasing economic and environmental problem as such there is a great need to process this waste and reduce its environmental impact. In this research the pyrolysis of high density polyethylene (HDPE) waste products is investigated using both thermal and catalytic cracking techniques. The experimental work is carried out in a laboratory scale packed bed reactor operating under an inert atmosphere at a temperature of 450°C. Different reactor beds, including sand, cement and white clay are used in the reactor to enhance the thermal cracking of HDPE. In addition, the catalytic effect of sodium hydroxide, HUSY and HBeta zeolite catalysts on the degradation of HDPE waste is inspected; the liquid products obtained from the pyrolysis experiments were analyzed using GC/MS to identify composition and product distribution.

Varying the reactor bed material greatly altered the yield as well as the composition of the generated products. The highest yield of liquid (82%) was obtained over cement reactor bed with alkane composition of 57.6%. The carbon chain length was narrowed to C₁₀-C₂₈ when the zeolitic catalysts were employed, as well as a significant yield of aromatics was obtained mainly naphthalene and D-Limonene as an indication that products obtained are fuel-like products. Sand-HUSY and Cement HUSY produced the highest composition of alkanes of 80.8% and 60.8% respectively.

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CHAPTER I

INTRODUCTION

Plastics, yet indispensable, are a growing waste problem [1] necessitating drastic solutions to limit their damage. Plastics are inexpensive, durable and versatile. Their use is favored in manufacturing to meet various consumer needs. For instance, the total world production of plastics in 2010 was 265 million tons [2] of which China and Europe accounted for 23.5% (≈ 62 MT) and 21.5% (57 million ton) in that year, respectively. On the other hand, the United States of America accounted for 30.73 million ton in the year 2007 constituting 12.3% of MSW generated in that year [3]. Currently, plastic waste management in Europe is distributed towards 53% land filling, 29% energy recovery, 16% mechanical recycling and 2% feedstock recycling.

Land filling, or direct dumping of waste, is considered the cheapest in terms of operational and capital cost. However, a potential environmental impact of landfill gases (LFG), in conjunction with other problems as leachate contamination of ground water and incomplete decomposition makes this method non-sustainable. In fact, plastics are non-biodegradable in nature; hence, dumping them in landfills renders large land areas useless for tens or even hundreds of years. Besides, the environmental pollution from plastic waste (air, soil, underground water and sporadic fires) can severely affect surrounding communities.

Another approach is waste incineration. This method aims at reducing waste volume and landfill areas. The energy recovery from waste incineration is so intense it is used as an alternative to fuel sources in power plants and industrial furnaces (cement

industry). However incineration is a controversial issue due to the release of harmful gases (toxins etc.), which can cause severe harm to surrounding population and to the environment.

Mechanical recycling is another waste management approach and it involves a number of treatments and operations: separation of plastics by resin, washing to remove dirt and contaminants, grinding and crushing to reduce the plastic particle size, extrusion by heat and reprocessing into new plastic goods. However mechanical recycling recovers plastic waste into a product of low quality and strength that deteriorates further with subsequent recycling cycles.

Alternative technology known as feedstock recycling (resource recovery) is the conversion of plastic wastes into valuable and useful chemicals such as fuel or as raw materials (monomers etc.) for the petrochemical industry. Five main types of feedstock recycling processes have been investigated through scientific and academic research; chemical de-polymerization, gasification, thermal degradation (pyrolysis), catalytic degradation and hydrogenation. All these methods, however, suffer from a common drawback, which is the high operating cost. Despite this, feedstock recycling is a promising alternative for land filling, incineration and mechanical recycling as it preserves the raw materials contributed in the production of plastics and/or produces valuable products which are fuel (used as commercial diesel) and gas (which can be used for transportation and power generation).

A. Thesis Objectives

HDPE represents 70% of the heavy duty plastic products. HDPE plastic wastes are not mechanically recycled and the current employed strategies are directly or indirectly disposing this waste into the environment. The thermal degradation of HDPE usually takes place at high temperatures 400-800°C, therefore consuming large amounts of energy. Although the use of catalyst decreases the degradation temperature (e.g. by 100°C), it still doesn't make the process economically attractive. Hence, the purpose here is to be able to convert HDPE plastic waste into energy/fuel in an effective way while taking into consideration the economic and environmental constraints.

The objectives aimed to be achieved from this research are:

- 1- Design a lab-scale setup capable of converting HDPE plastic waste into liquid fuel.
- 2- Conduct experimental investigations to analyze process behavior and dynamics, and determine suitable operating conditions and catalysts.
- 3- Identify opportunities for process improvements, maximize conversion, improve product quality and ensure safe process operation.
- 4- Preliminary study the environmental emissions and energy usage and assess the economic feasibility.

B. Thesis Outline

The aim of this section is to briefly introduce each chapter and describe the methodology covering each topic.

Chapter I covers several sections. It highlights the problems entitled with municipal solid waste management and introduces pyrolysis as a proposed alternative to conventional treatment of plastic wastes. This chapter also covers a literature review and highlights several research conducted on thermal and catalytic pyrolysis of HDPE waste and the major findings.

Chapter II describes the laboratory scale setup built, at the American University of Beirut, and used for carrying out pyrolysis experiments on HDPE waste.

In Chapter III gas chromatography/ mass spectrometry (GC/MS) is used for the analysis of the products obtained from the thermal and catalytic experiments. The results of the analysis are presented in this section and a conclusion is drawn on the effect of using a catalyst on the yield and product selectivity.

Chapter IV investigates the economic feasibility of pyrolysis processes, which is expected to become more attractive as crude oil prices continue to increase. A number of worldwide applications proving the applicability of the pyrolysis process in dealing with various types of wastes were highlighted.

Chapter V concludes with the importance of pyrolysis as a relatively innovative, economical and environmentally friendly process as shown from the results obtained in the work.

C. Pyrolysis

Pyrolysis is the thermal decomposition of plastic wastes in an inert atmosphere (free of oxygen). The outcomes of this process are gases, liquids and residues; the hydrocarbons produced in the gas or liquid phase could have various usages depending on their carbon range and chemical compositions. Unfortunately research studies have proven that the hydrocarbons from thermal degradation are distributed over a wide range of carbon number therefore further treatment is required to improve product quality without maximizing the cost of plant. Over the years, several research studies investigated the use of different catalysts which proved to be efficient in minimizing energy consumption (reduce operating temperature), enhanced the product yields and improved their qualities. The generated products can be used as a substitute of commercial fuel or as a petrochemical feedstock.

During pyrolysis, the polymer undergoes bond breakage which is endothermic. The polymer molecules break down depending on the chain characteristics; polyethylene (PE) degradation occurs at 450°C, polypropylene (PP) at 380°C and polystyrene (PS) at 350°C; therefore different heat requirements are needed. In addition each polymer follows different decomposition mechanisms; PS breaks down via both end-chain scission and random chain scission because of its cyclic structure yielding mainly its monomer (styrene). PE and PP molecules decompose by random-chain scission, their large molecules break up randomly giving heavy hydrocarbon products. It is well known that by increasing the degradation temperature the heavy products are cracked further into valuable light hydrocarbons. The addition of a catalyst plays an effective role in facilitating molecules breakage into smaller ones and minimizing the process energy consumption.

In conclusion, the thermal degradation of plastic wastes occurs at high temperatures (500-700°C) and leads to the production of waxes and liquids (with long chain hydrocarbons) and very low gaseous yield; whereas catalytic degradation lowers the degradation temperature to 400-500°C; therefore reducing energy. Added value to the catalytic process is the higher selectivity of gases and condensates distributed over narrow range of carbon number. Also it minimizes the production of undesired products as chlorinated hydrocarbons especially when polyvinylchloride (PVC) is included in the process. For example, the thermal degradation of low density polyethylene (LDPE) in a fluidized bed reactor in the range of 500-700°C, can give oil (44%) and wax (45%) while gas can evolve at lower rates (10%); as the temperature is increased the gas yield increases at the expense of oil and wax. The research done over recent years focused on the products evolved from thermal and catalytic cracking in order to find an appropriate catalyst based on a desired outcome. For example, experiments on thermal and catalytic degradation of LDPE over HZSM-11 and Zn-ZSM-11 catalysts in a fixed bed reactor at 500°C, showed a significant decrease in the reaction temperature of about 145°C when the catalyst was employed. Solid residue (80%) was the main product from thermal pyrolysis; however catalytic degradation produced gases and condensate products with low solid contents (\approx 2-4%). The reactor temperature is an important factor which affects the initiation of polymer degradation, products yielded and their composition. However this temperature is not enough to completely convert polyolefins present in the reaction. As the temperature increases the distribution of the product yield changes to give more gaseous fraction over the waxy liquid component, also the content of the product is altered.

D. Literature Review

The pyrolysis of high density polyethylene (HDPE) and LDPE via thermal and catalytic cracking routes was heavily adopted in the research fields since they both have showed capabilities in transforming the plastic wastes into valuable products. A review of recent research in this field is highlighted next.

1. Thermal degradation of Polyethylene: HDPE and LDPE

Schirmer et al.[4]conducted the thermal decomposition of polyethylene using thermal gravimetric analysis (TGA) and a cyclod-sphere reactor. 4.5g of PE pellets were heated in the TGA to reaction temperature of 600°C under nitrogen. Non-catalytic degradation using TGA showed that complete degradation of polyethylene was achieved at 490°C. Some experiments were carried in the cyclod sphere reactor where 150g of PE (granule) were fed into the reactor. The process was batch mode and the reaction temperature was maintained at 440°C, the reaction time was 60min for the thermal process. The products obtained from PE pyrolysis were mainly waxes (65.76%) in the range of C₁₅-C_n, the yields of oil (C₅-C₁₅) and gas (C₁-C₄) were low compared with the yield of wax giving 21.88% and 11.6% respectively. Moreover the analysis of the oil yielded showed a wide spectrum of products.

Grieken et al.[5]employed a batch reactor for the thermal degradation in an inert atmosphere for both high and low density polyethylene. 50g of PE were fed into the reactor and different experiments were conducted by varying the temperature from 380°C, 400°C and 420°C. The resulted products were mainly solids, and the yield of liquid and gas products was negligible for the various temperatures tested. It was

noticed that HDPE thermal cracking occurs at higher temperature than LDPE leading as well to mainly wax. The analysis of the waxy products obtained from thermal degradation of LDPE showed their potential to be used in petrochemical application.

Ng et al.[6]thermally degraded polyethylene (HDPE and LDPE) in the temperature range of 450-500°C in a closed tubing bomb reactor, other few experiments were carried out in an open tubing reactor at 480°C. Reactions in both systems took place under a flow of nitrogen. HDPE thermal degradation in a closed system produced hard wax, distillates of 19.3% and low yield of gas at 450°C. The increase in temperature caused an increase in the yield of gas and naphtha at the expense of coke. At 500°C, distillates were at 56.4%, gas 23% and residue at 8.6%. The gas obtained contained mostly alkanes of 85% in the range of C₁-C₄, and olefins which decreased with the increase in temperature. Naphtha in the range of C₄-C₁₀ showed a decrease with the increase in temperature; α -olefin decreased from 27% to 3.3% with a corresponding increase in mono-aromatics from 1.1% to 25% at 450°C and 500°C respectively. HDPE thermal degradation in an open system promoted the production of gas oil over the expense of gas and naphtha. Naphtha and gas oil fraction composed of low aromatics (1%), less saturates (27%) but more olefins (40%) unlike those obtained from closed system. Distillates produced from the degradation of HDPE in an open and closed system do not meet the requirements of transportation fuels.

Sakata et al.[7]have studied the thermal degradation of high density polyethylene (HDPE) in a semi-batch glass reactor under the flow of nitrogen. 10g of HDPE were loaded into the reactor and the degradation temperature was maintained at 430°C in the furnace. The products evolved were 69% liquid and 21% residues with

only 9% gaseous products. The gaseous products obtained from thermal degradation were mainly C₃ (propane, propylene), C₂ (ethane, ethylene) and small amount of C₄ (butane, butane). The components of liquid products were distributed over a wide range of carbon number. The oil obtained contained paraffins and olefins but aromatics were not detected.

Miskolczi et al.[8] studied the thermal degradation of 200g of HDPE in a Pyrexbatch reactor for different temperatures (400°C, 420°C and 450°C) in a nitrogen atmosphere. The yield of gas (2.4% at 400°C) and liquid (3.1% at 400°C) increased with the increase in temperature yielding 5.8% gas and 74.5% liquid at 450°C. On the other hand the yield of residue decreased drastically with the increase in temperature; 93.5% at 400°C decreased to 19.7% at 450°C. A product analysis of the gaseous fraction showed that C₂ and C₄ are the dominating components. Concerning the liquid fraction, aliphatic hydrocarbons in the range of C₅-C₂₅ were dominant and the main types of fuels were gasoline, kerosene, diesel and heavy oil. Low sulfur content is favored for the advantage of both the environment and human health; therefore sulfur content was tested and was <20ppm for different degradation temperatures but it was noticed that the content decreased with the increase of temperature (14ppm at 450°C) which makes the liquid fraction favored for utilization as fuel-like product.

Hernandez et al.[9] carried out the thermal cracking of HDPE in a fluidized bed reactor under nitrogen flow and the reaction temperature was varied in the range of 400-800°C. At 400°C the yield of gas was almost negligible but started to increase with the increase of temperature yielding \approx 60g/100g of HDPE; however the gaseous fraction was obtained over a wide range of molecular weights. At 800°C, components

were mainly C_2 (16.5g ethene/100gHDPE), C_3 (10.5g propene/100g HDPE), C_4 (5.1g 1-butene/100g HDPE) and 2.2g benzene/100g HDPE. The same group[10] studied the thermal pyrolysis of HDPE and results were confounded with their previous findings; the products evolved from the thermal cracking of HDPE were (15% gases and 41% liquids) at 500°C and(58% gases and 24% liquids) at 700°C. The products in the liquid fraction were composed of wide range of carbon atoms (C_{10} - C_{40}) diolefins, olefins and paraffin were present while no aromatic compounds were identified.

Marcilla et al.[11]aimed to study the effect of the heating rates (flash and slow pyrolysis)on the degradation process of HDPE and the type of products obtained. Several experiments were carried out in a fluidized bed reactor under nitrogen as the fluidizing agent. In the flash experiments the reactor degradation temperature was in the range of 500-800°C, in the slow pyrolysis experiments the reactor was heated to 700°C with a rate of 5°C/min. It was obvious from both experiments (flash and slow pyrolysis) that higher percentages of liquid (heavy oil), wax and solid residues were obtained from thermal degradation. However in flash pyrolysis the increase in temperature caused a drastic increase in gas yield; 15.2% were released at 500°C which increased to 66.3% at 800°C.

Ng et al.[12]thermally cracked the blended HDPE with VGO (vacuum gas oil) under nitrogen in a fixed bed reactor; sand was also loaded to the reactor and the reaction temperature set at 510°C. Two concentrations of HDPE (5% and 10%) resulted in different conversions; thermal cracking of 5% HDPE resulted in 77% conversion of HDPE, producing 11.5% dry gas, 16% LPG, 33.5% gasoline and 15.3% coke;whereas lower conversion (52.4%) of HDPE was achieved when its concentration increased to

10% and the yield of product was lower giving 7%, 8.7%, 22% and 14.7% of dry gas, LPG, gasoline and coke respectively. In the gaseous fraction, olefins were mainly ethylene, propylene and 1-butene. Methane was produced in significant amount. Sand insured a better heat transfer which resulted in a better conversion.

Aguado et al.[13]observed that only 27% of LDPE was converted when thermally cracked in an inert atmosphere in a stirred batch reactor at 420°C. 20% of gases (C₁-C₅) mainly olefins and 6.6% heavy oil (C₁₃-C₃₅) mainly n-paraffins; while the yield of liquid (C₆-C₁₂) was negligible.

Marcilla et al.[14]employed LDPE in the thermal and catalytic cracking in a horizontal fixed bed reactor. The inert gas nitrogen was purged in to the reactor. The final temperature of the thermal experiments was 600°C. The main gaseous products evolved in the thermal degradation between 400-500°C were propane and propene of 13% yield and butane and butene of almost 11%. As the temperature increased the olefins C₂ and C₃ increased at the expense of alkanes.

William et al.[15]degraded LDPE thermally in the fluidized bed reactor in the temperature range of 500-700°C. Nitrogen was the fluidizing gas and the bed material was silica sand. It was observed that gas yield increased from 10.8% to 71% as they temperature increased from 500°C to 700°C with a corresponding decrease in oil/wax fraction from 89% to 28.5% with the oil having the highest proportion. It can be concluded that wax decomposed to oil as the temperature continued to increase then to gas. The main gases evolved were ethene, propene and butene of yield 26.8%, 18.6% and 7.6% at 700°C respectively. Among the alkane gases methane was evolved significantly with yield of 11.8% at 700°C. Liquid products (oil and wax) were

distributed over a wide range of carbon number C_8 - C_{57} . As the pyrolysis temperature increased, aliphatics above C_{30} decreased with a significant increase in the single and poly-aromatic hydrocarbons (PAH) which comprised more than 25% in the oil produced. This raises environmental concerns due to the presence of PAH and requires a further treatment of the oil.

Renzini et al.[16]thermally cracked LDPE in a fixed bed reactor at 500°C for different reaction times (20 and 60 min). The non-catalytic degradation experiments yielded 81% solids mainly waxes with very negligible amounts (relative to solids) of liquids and gases of 6.4% and 12% respectively at reaction time of 20 min. On the other hand, the increase of reaction time to 60 min positively influenced the distribution of products yielding 24.4% and 18.7% of gas and liquid respectively.

Serrano et al.[17]carried out thermal degradation of low density polyethylene in a screw reactor altering two parameters, temperature and screw speed. The temperature was in the range of 400 - 550°C and the screw speed varied between 11 and 20r.p.m. Their investigations showed that to ensure an optimum performance of the system, the screw speed has to be lower than 15r.p.m. Experimental runs at 400 - 450°C showed a low conversion of plastic waste, and almost no gaseous or liquid products were obtained. However, the reactions that took place at 500°C showed a complete thermal degradation. The screw system gave a lower production of gaseous products and higher yields of heavy products when compared to the batch system; yielding gasoline (C_5 - C_{12}) and middle distillates (C_{13} - C_{33}) at 25% and 54%, respectively.

The pyrolysis of low density polyethylene in a batch autoclave reactor at 425°C and one hour residence time was tested by Insura et al.[18].The products yielded 90% oil, 10% gas and no coke detected. Gas composition was mainly alkanes of 69% (ethane and propane dominant gases) and 32% alkene. Long chain n-alkanes (46%) were the main component in the oil obtained from the thermal degradation of LDPE and 12.5 and 12% of n-alkene and aromatics (toluene, benzene and xylene) were obtained. These results were compatible with those obtained from thermal cracking of LDPE at 500°C investigated by Bagri et al.[19]in a fixed bed reactor; where high yield of oil (≈95%) and low gas (5%) was also achieved. The oil composition was mainly aliphatic in the range of C₉-C₅₀ whereas a very low amount of polycyclic aromatics (naphthalene and their methyl derivatives) was detected. Gases were composed of alkane (mainly ethane and propane) and alkene (mainly propene and butane).

The thermal degradation of LDPE was investigated by Aguado et al.[20]who employed a screw kiln reactor and investigated its screw speed effect on the conversion of LDPE and the selectivity of products yielded; the experiments were conducted in the temperature range of 450-550°C using nitrogen to insure an inert atmosphere. A total conversion of LDPE was observed at screw speed of 3r.p.m giving high selectivity toward heavy hydrocarbons; 35.5% heavy oil (C₁₃-C₂₃) and 26% wax (C₂₄-C₅₅) and low yield of gasoline (C₅-C₁₂) and gas (C₁-C₄) of 29 and 9% respectively. Therefore, the thermal degradation of LDPE led to a wide distribution of carbon number and heavy hydrocarbons were the major outcomes.

Table.1 summarizes all experiments -reported earlier- conducted on polyethylene varying the reactor, reaction temperature and residence time. On one

hand, fluidized bed technology enhances the yield of gas over liquid and wax yields, unlike other technologies. On the other hand, the reaction temperature significantly alters the yield of the products; increasing the temperature leads to lowering the yield of wax and increasing the yield of liquid.

Table 1 Thermal degradation of Polyethylene

Feedstock	Reactor type	T °C	Gas %	Liquid %	Wax %	Comment	Ref.
PE	TGA/ Cycled spheres reactor	440	11.68 (C1-C4)	21.88 (C5-C15)	65.76 (C15-Cn)	Low gas and oil yield 0.7 % of char was obtained	[5]
PE	Batch reactor	380-420	7.3	2.5	2.5	Thermal cracking led mainly to the production of wax	[6]
PE	Tubing-bomb reactor	450-500	23	56.4	8.6	High yield of naphtha, very little amount of gas and high residue.	[7]
HDPE	Semi-batch reactor	430	10	69	21	Gave high yield of heavy liquid and little amount of gas.	[8]
HDPE	Pyrex batch reactor	400-450	5.8	74.5	19.7	High liquid yield with heavy hydrocarbons, low yield of gas and significant yield of residue.	[9]
HDPE	Fluidized bed reactor	400-800	57.8	24	6.7	Products are distributed over a wide range of carbon number. A significant amount of char (11.5%) was yielded	[10] & [11]
HDPE	Fluidized bed reactor (flash pyrolysis)	500-800	57.8	24	6.7	Heavy hydrocarbons are produced over thermal experiment. A significant amount of char (11.5%) was yielded	[12]
HDPE	Fluidized bed reactor (slow pyrolysis)	700	26.1	42.5	6.6	Heavy hydrocarbons are produced over thermal experiment. A significant amount of char (17%) was yielded	
HDPE (blended)	Fixed bed reactor	450-500	27.6	33.5	15.3	Conversion of HDPE is not complete	

with VGO)						≈77%. Significant amount of coke (23.6%) was produced.	[13]
LDPE	Stirred batch reactor	420	20.6	0.7	6.6	Thermal cracking leads to 27.9% conversion of LDPE	[14]
LDPE	Fluidized bed reactor	500	10.8	43.9	45.3	The increase in temperature led to a significant increase in single and polycyclic aromatics in the derived oil which requires a further treatment. Wax contained aliphatics and no aromatics which gives it the potential to be used in petrochemical industry.	[16]
LDPE	Fluidized bed reactor	600	24.2	51	24.8		
LDPE	Fluidized bed reactor	700	71.4	24.6	4		
LDPE	Fixed bed reactor	500-20min	12	6.5	81.5	The increase in residence time influenced the increase in gas and liquid yield	[17]
LDPE	Fixed bed reactor	500-60min	24.4	18.7	57		
LDPE	Batch pressurized autoclave	425	10.2	89.8	0	No coke was formed.	[19]
LDPE	Fixed bed reactor	500	5	95	0	Low gas yield and negligible char	[20]
LDPE	Screw kiln reactor	450-500	9.4	28.9	35.7	Heavy hydrocarbons are produced over thermal experiment. 26% of char was produced	[21]

2. Catalytic degradation of Polyethylene: HDPE and LDPE

Schirmer et al.[4]catalytically decomposed polyethylene over HZSM-5 and Y-type zeolites in a cycled spheres reactor at 440°C. It was observed that the decomposition over zeolite catalysts caused a decrease in degradation temperature. In the catalytic degradation, H-ZSM-5 zeolites showed a higher activity due to its strong acidic sites and lower deactivation behavior because of its channel type surface which hinders accumulation of large coke molecules on its surface than Y-type zeolites. Both catalysts produced higher yield of light hydrocarbons, 67% oil (C₄–C₁₅) and 26% gases (C₁–C₄), 70% oil (C₄–C₁₅) and 21% gases (C₁–C₄) over H-ZSM-5 and HY 26 respectively. It is known that the increase in the amount of catalyst is accompanied with a decrease in the reaction temperature. However for HZSM-5 the increase in its amount doesn't cause further reduction in temperature due to its high acidity. Whereas Y-type zeolite which doesn't possess enough acidic sites to degrade heavy molecules an increase in its amount is needed to further reduce temperature. A 30:1 ratio of PE/HZSM-5 was chosen for the experiments conducted.

Lin et al.[21]prepared a mixture of 65% HDPE and 35% LDPE to be employed in the catalytic degradation in a fluidized bed reactor in the temperature range 290–430°C under an inertatmosphere. The acidic zeolite catalysts (HZSM-5, HMOR and HUSY) gave a higher yield of gaseous products than non-zeolite catalysts (MCM-41 and SAHA). HZSM-5 yielded 92.5% of volatiles with 35.2% in the range of C₁-C₄ and 54.2% in gasoline range C₅-C₉, with similar results obtained over HMOR which yielded 87.9% volatiles with ≈56% in the range of C₁-C₄ and 31% gasoline range. Whereas MCM-41 and SAHA produced 85.8% and 85.3% volatiles, with 26.7%

and 23.4% C₁-C₄, 58.2% and 61.6% gasoline range respectively. Therefore, MCM-41 and SAHA produced highly olefinic products with wide range of carbon number while HZSM-5 and HMOR produced about 60% in the range of C₃-C₅.

Grieken et al.[5]used low and high density polyethylene for catalytic cracking under mild conditions, n-HZSM-5, HY zeolite, amorphous silica alumina (SiO₂-Al₂O₃), MCM-41 and Pd-MCM-41, activated carbon and Pd charcoal powder were the catalysts used for carrying out the catalytic cracking experiments. These experiments were done in a batch reactor provided with a stirrer in 380-420°C temperature range under nitrogen atmosphere. The gas yield of 65% over n-HZSM-5 was highest among other catalysts at 380°C. Whereas the maximum yield of liquid of 50% was observed over MCM-41 of at 420°C. Significant yield of coke was observed over HY zeolite due to its high aluminum content. High stability of MCM-41 catalyst was observed which favored it to be employed in the catalytic degradation of both polyolefin. Cracking of LDPE over MCM-41 gave high paraffinic and aromatic fraction and waxy solid with low olefinic fractions compared with the cracking over other catalysts. MCM-41 was seen as the best catalyst for the degradation of HDPE to produce waxy solids with low olefinic content which is related to its BET surface area, meso-porosity and low acidity (compared to HZSM-5) which makes it suitable for commercial use.

Marcilla et al.[22]catalytically degraded HDPE and LDPE in a batch reactor system, having HZSM5 as a catalyst. The polyethylene and catalyst were fed to the system under nitrogen atmosphere and heated to 550°C. The structure of HDPE is different than that of LDPE which affected its behavior during pyrolysis and the composition of the products evolved from its thermal cracking. Therefore the

degradation of LDPE was observed at 380-435°C which is lower than that of HDPE 410-460°C. PE/HZSM-5 ratio was 10:1 and it was found that HZSM-5 enhanced the evolution of gases with yield of 70% for both polymers mainly olefins in the range of C₄-C₆. However the fraction of n-paraffin and iso-paraffin was higher for HDPE. The liquid obtained from the cracking of both polyolefin contained compounds of large carbon numbers C₇-C₁₃ and were mainly aromatics and olefins, while no diens were obtained from the degradation of LDPE, unlike HDPE.

Ng et al.[6]catalytically degraded the heavy products (wax A, B and C) obtained from thermal degradation of HDPE, over FCC catalyst KOB-627 in a fixed bed reactor. Wax A resulted from LDPE thermal degradation in a closed system at 460°C, Waxes B and C obtained from the degradation of HDPE in an open system were chosen to be upgraded catalytically to enhance their properties to meet the specifications of transportation fuel. Catalytic cracking of waxes (A, B and C) over KOB-627 yielded low coke, dry gas and low HCO but high yield of LPG and gasoline was obtained. At 510°C wax (A) catalytic degradation yielded 2.4% coke, 1.8% dry gas and 1.3% HCO, whereas it yielded 22.4% LPG (8%C₃ and 14.4%C₄) and 63% gasoline. Gasoline from A, B, and C contained 17.2, 20.3, and 21.7wt % n-paraffins, 6.9, 19.7, and 24.1 wt % n-olefins, and 17.3, 11.3, and 8.6wt % aromatics, respectively. Octane number of gasoline from waxes A, B and C was 78.4, 76.5, and 73.0, respectively, which is lower than commercial gasoline with RON of 87.

Sakata et al.[7]studied the catalytic degradation of polyethylene over several catalysts in a glass semi-batch reactor at 430°C. Silica Alumina catalysts (SA-1) and (SA-2) favored liquid production than ZSM-5; SA-2 with average acidity produced the

highest yield of liquid product $\approx 74\%$. While ZSM-5 with strong acidity yielded more gaseous 44% and less liquid product $\approx 50\%$. As for the non-acidic catalyst KFS-16B, favored the liquid production about 70% over the gaseous yield 11% and produced considerable amount of solids about 18% which is relatively high. The liquid products obtained from the catalytic degradation over SA-1, SA-2 and ZSM-5 contained light hydrocarbons (C_4-C_{10}). SA-1 enhanced the production of oil that contains more olefins but less aromatic than the catalytic degradation over ZSM-5. KFS-16B produced much lighter liquid products than the thermal degradation products but heavier than those produced over the acidic catalyst. The liquid products from degradation over KFS-16B contain mainly kerosene and diesel fraction oil.

Murata et al.[23] have employed HDPE for the catalytic cracking over silica-alumina (SA-1). The reaction took place in a stirred stainless steel reactor and PE was fed in to the reactor after being thermally treated. The reactor was heated up to 420°C under atmospheric pressure; SA-1 increased the evolution of gaseous products especially C_4 fractions and aromatic compounds were produced.

Miskolczi et al.[8] used HDPE for the catalytic cracking over an equilibrium fluid catalytic cracking catalyst (FCC) and clinoptilolite containing rhyolite tuff (NCM). The experiments took place in a pyrex batch reactor under an inert atmosphere in the range of $400-450^\circ\text{C}$. It was noticed that with the increase of temperature the yield of gas and liquid increased and results were similar for the three catalysts. At 450°C the degradation over FCC catalyst yielded 6.3% of gas and 82.5% liquid, for NCM the yield was 6.3% gas and 78.5% liquid and for HZSM-5 the yield was 15.1% and 81% respectively. C_3 and C_4 were dominating in the gas fractions over the different catalysts

employed. At 420°C, the yield of C₃ was 19% (over all the catalysts) and the yield of C₄ was 22%, 21% and 18.5% over FCC, NCM and HZSM-5, respectively. Major liquid components were C₅-C₂₈ aliphatic hydrocarbons, the main types of fuel found in the liquid produced from HDPE cracking were gasoline of high octane number C₈-C₁₃ and kerosene at low temperature, while at high temperature diesel oil and heavy oil were observed significantly. The sulfur content in liquid products was low supposedly adsorbed by the catalysts which increased their utility as fuels. Their low concentration of sulfur increases their advantage of usage being environmentally friendly.

Hernandez et al.[9] mixed HDPE with 20wt% of HZSM-5 and HUSY zeolite catalysts. The catalytic degradation took place in a fluidized bed reactor where sand was the fluidized bed and nitrogen was the fluidizing inert agent. The operating temperature was in the range of 400-800°C. It was noticed that the use of catalyst caused a reduction in the degradation temperature, also it favored the gas production; HZSM-5 produced gas 87.4% at 600°C, followed by HUSY 76% gas yield at 700°C. In addition the range of products was narrowed to C₃-C₅ hydrocarbons. In the catalytic pyrolysis using HZSM-5, the main volatile compounds are propene 21.3% at 700°C; using HUSY propene reached the highest yield 10.1% at 500°C. HZSM-5 favored mainly olefins, while HUSY favored olefins and some paraffin in the same range of carbon number.

Marcilla et al.[11] studied the influence of polymer/ catalyst (HDPE-HZSM-5) contact in a fluidized bed reactor under nitrogen atmosphere at 500°C; dry polymer-catalyst blend, and catalyst mixed with melted polymer. It was observed that the melted blend in the flash pyrolysis produced higher yields of gases and liquids than dry blend

HZSM-5; 90.9%, and 8.8% respectively at 700°C, these results were similar in the slow pyrolysis process where 87.6% and 7% are the gas and liquid products yielded respectively. The yield of lightest compounds as methane, ethane and ethene is more significant at high temperature in the melted blend than in the dry blend. In the melted blend C₃-C₅ hydrocarbons show higher yields, as well as aromatics are the major fraction analyzed in the liquid compound produced.

Elordi et al.[24]investigated the degradation of HDPE in a conical spouted bed reactor at 500°C over the catalyst HY zeolite and under the flow of nitrogen to ensure an inert atmosphere. The main product is gasoline in the range of C₅-C₁₀ of 69% yield. It is noteworthy that the gasoline obtained fulfilled the EU requirements and its RON index is 96.5 similar to the commercial gasoline. The obtained gasoline contained almost no benzene which is the most undesired product in gasoline. Besides, the produced gasoline contained zero sulphur which made it environmentally favored over the commercial one which contained after treatment 50ppm of sulphur. This gasoline is mainly composed of iso-paraffin and aromatics which were mainly 7.5% xylene and 3.5% toluene. Gas yielded were about 25% having propylene and butane as main products.

Ng et al.[12]catalytically degraded the blended HDPE with VGO (vacuum gas oil) in the range of 450-500°C over FCC (KOB-627) which is an octane enhancing catalyst in a fixed bed reactor. The system was purged with nitrogen before and during the process. The use of the catalyst KOB-627 enhanced the conversion of polyethylene blended with VGO and promoted the yield of gasoline and LPG. The increase in the HDPE concentration also affected the yield of gasoline; only gas and coke were

produced when only 5% concentration HDPE was employed. However, a significant amount of gasoline was produced as HDPE concentration increased to 10%.

Olazar et al.[25] studied the influence of the commercial FCC catalyst on the degradation of HDPE in a conical spouted bed reactor under nitrogen atmosphere at 500°C. The pyrolysis was carried over fresh catalyst, mild and severe streaming treated catalysts. The fresh catalyst resulted in high gas yield, 52% in the range of C₁–C₄ with 13% C₅–C₉. As streaming was more severe, the acidity of the catalyst decreased and the yield of C₁–C₄ decreased to ≈22% and 8% over mild and severe streaming treated catalyst, respectively. While Diesel fraction was enhanced over the mild and severe streaming yielding 40% and 69% respectively. The main gaseous products obtained over severely treated catalysts were olefins mainly butene ≈3%, and 44% alkenes, 38% aromatics and 18% paraffin and iso-paraffin obtained in the light oil fractions. Such aromatics were 1.3% xylene, and 2.5% tri-methylbenzene. Diesel fraction contained 35% paraffin and iso-paraffin and 54% aromatics which were mainly naphthalene derivatives, 4.08% counting to methylnaphthalenes, 5.93% and 3.85% to di-methylnaphthalenes and tri-methylnaphthalenes respectively.

Aguado et al.[13] investigated the catalytic degradation of LDPE over mordenite zeolite catalyst MOR-0, MOR-8 and MOR-15 in a stirred batch reactor. The reactor was purged with nitrogen to ensure inert atmosphere, and experiments were carried out at 420°C. It was observed that the conversion of LDPE was enhanced to reach 57% over synthesized mordenite. About 26% of C₁–C₅, 21% gasoline (C₆–C₁₂) and 10.5% diesel (C₁₃–C₃₅) were yielded from the catalytic degradation over MOR-8 and these values were significantly higher from those obtained from the thermal

degradation. It was observed that olefins $\approx 80\%$ were the main components in the gaseous products yielded over both thermal and catalytic degradation. Propylene, 1-butene and isobutene contribute with 45-50% of those olefins and which are considered of high value in the petrochemical industry. The catalytic degradation over MOR-8 produced mainly olefins (45%) and n-paraffins (31%), with a lower fraction of aromatics (11%), isoparaffins (8%) and naphthenes (5%). While the catalytic decomposition over MOR-15, showed a decrease in olefins (28%) and paraffins (22%) with a corresponding increase in aromatics (25%), isoparaffins (15%) and naphthenes (10%). The use of mordenite with enhanced textural properties improved the evolved products and favored the production of light hydrocarbons in the gasoline range (C_6-C_{12}).

Marcilla et al.[14]employed LDPE to undergo catalytic cracking in a horizontal fixed bed reactor; the inert gas nitrogen was purged in to the reactor. During the catalytic degradation over H-Beta or HZSM-5 zeolites, the final temperature of the reactor was 500°C . At low catalyst concentrations, H-Beta had higher catalytic activity than HZSM-5. Over H-Beta, the gas obtained was rich in C_4 and C_5 compounds which constitute 60% of the gases evolved, while that evolved over HZSM-5 was richer in propane and propene since C_3 hydrocarbon was high.

Renzini et al.[16]carried out a catalytic degradation of low density polyethylene mixed with H-ZSM-11 or Zn-ZSM-11 in a fixed bed reactor. The reactor was purged with nitrogen and operated under atmospheric pressure at 500°C . The presence of the catalyst lowered the degradation temperature, thermal decomposition started at 473°C , while over Zn-ZSM-11 and H-ZSM-11 it started at 341°C and 327°C

respectively. H-ZSM-11 produced liquid of 30.5% but enhanced the production of gaseous hydrocarbons $\approx 63\%$, with 14.5% of liquefied petroleum gas (C_3-C_4). While, Zn-ZSM-11 catalyst produced liquid hydrocarbons of 81% with high yields of aromatic compounds about 53% of C_6-C_9 benzene, toluene, xylenes, tri-methylbenzenes, ethyl-toluene and ethyl-benzene. No polycyclic aromatics were obtained after 60 minutes of residence time over both catalysts Zn-ZSM-11 and H-ZSM-11.

Serrano et al.[17]mixed low density polyethylene with MCM-41 catalyst to undergo catalytic degradation in screw reactor in the temperature range 400-500°C. A complete degradation of LDPE was observed with compounds in the gasoline range C_5-C_{12} were the major product, about 75%, with high contribution of C_7 and C_8 and 13% in the range of C_1-C_4 . The yield of large carbon distribution compounds was low with 12% of $C_{13}-C_{33}$ and 1.3% $C_{34}-C_{55}$ which suggests that MCM-41 degrades these heavy fractions into lighter products. One of the drawbacks for using screw kiln is that it lowers the production of gases due to the lack of proper removal of volatile products evolved during cracking.

Uemichi et al.[26]conducted a catalytic degradation of low density polyethylene in fixed bed tubular flow reactor. HZSM-5 zeolite and commercial silica-alumina were the catalysts used because of their excellent activities and stabilities. The degradation of polyethylene was done under a helium atmosphere (0.11-0.15 MPa) in the temperature range of 375-425°C. The catalytic degradation over SA resulted with a high yield of gasoline range C_5-C_{12} hydrocarbons but with an octane number lower than that of the commercial gasoline. Furthermore, HZSM-5 resulted in a lower yield of liquid but with high concentration of aromatics which contributes to high octane

number. For the purpose of producing high quality, environmentally acceptable, gasoline of high octane number ≥ 90 a two-stage degradation took place where catalysts SA and HZSM-5 were loaded into the upper and lower layers of the reactor. Weight ratios of SA and HZSM-5 and temperature effect were tested after which 9:1 and at a temperature of 375°C were found the most effective in giving 58.8% of liquid in the range of $\text{C}_5\text{-C}_{12}$, with octane number of 94, 25.2% aromatics and 0.9% benzene.

Insura et al.[18] used low density polyethylene for the catalytic pyrolysis over $\text{Pt/Al}_2\text{O}_3$ and $\text{Rh/Al}_2\text{O}_3$ catalysts in a batch pressurized autoclave reactor. Reactions took place under nitrogen atmosphere at a temperature of 425°C . The presence of catalyst $\text{Pt/Al}_2\text{O}_3$ enhanced the formation of coke; 0.02g of Pt loaded into the reactor caused the yield of 5% of coke with a corresponding decrease in the yield of oil to 84.5% (oil yielded $\approx 90\%$ over non-catalytic degradation). The yield of gas $\approx 10\%$ from non-catalytic degradation was very similar to that obtained from Pt addition. Whereas the composition of gases formed was effected; the fraction of the alkanes ($\text{C}_2\text{-C}_3$ main components) increased from 69.6% to 90% at the expense of alkenes which decreased from 32% to 8.8% from no catalyst reaction and 4g fresh Pt addition. The composition of oil produced was also affected where the yield of cyclo-alkanes was reduced by 33% when 4g of Pt was loaded converting it to aromatic compounds as benzene, toluene and ethyl benzene. Also the alkane fraction was increased to 60% with a corresponding reduction in alkenes when 4g of Pt was added. 41% and 47% of gasoline in the range of $\text{C}_5\text{-C}_{12}$ was obtained from non-catalytic pyrolysis and over Pt respectively, without any further change in the yield as the catalyst loading increased. $\text{Rh/Al}_2\text{O}_3$, showed similar

activity as Pt/Al₂O₃ yielding high fraction of alkanes. However calcined Rh/Al₂O₃ and Pt/Al₂O₃ Promoted the yield of aromatics compared to that obtained from fresh catalyst.

Bagri et al.[19] carried out a two stage cracking of LDPE in a fixed bed reactor; initially it was thermally cracked at temperature of 500°C under nitrogen atmosphere then the evolved gases passed to the catalyst reactor where HZSM-5 and Y-zeolite were used as catalysts. The temperature of the catalytic degradation was in the range of 400-600°C. The product yielded from non-catalytic degradation was mainly oil of 95% with low yield of gas and no traces of char were detected. Whereas in the presence of zeolite, the oil yield decreased to 85% and it continued to decrease with a corresponding increase in gas yield as the temperature increased. Coke was found to form on the catalyst surface and a negligible decrease as temperature increased. Over Y-zeolite the gas yield consisted of a higher fraction of alkane (mainly methane and propane) than alkene gases (ethene and propene). Over HZSM-5 the yield of gas was higher with a dominating fraction of alkene (ethene and propene mainly) at high temperatures. Alkanes were mainly in the range of C₁-C₄ with the highest yield of propane. Pyrolytic oil constituted of mainly aliphatic in the range of C₉-C₅₀ with low concentration of aromatics (0.34%). However, aliphatic compounds decreased in the oil produced from catalytic degradation with lower carbon number, and higher concentrations of aromatics were observed over zeolites; 26% and 6% of aromatics over Y-zeolite and ZSM-5 respectively at 500°C. Y-zeolite with a lower silica: Alumina ratio than that of ZSM-5 favored the production of the higher yield of single and polycyclic aromatic hydrocarbons.

Puente et al.[27]catalytically degraded low density polyethylene dissolved in 2% of toluene in a fluidized bed reactor at 500°C. The catalysts employed were two equilibrium commercial FCC catalysts and an amorphous silica alumina referred to as E-cat A, E-cat B and cat C respectively. The main product yield over the three catalysts was gasoline with high aromatic content in the range of C₆-C₁₂ mainly benzene and xylene; gasoline yield over E-cat A was 43% with 26% aromatics, 64% gasoline of which 48% are aromatics were obtained over E-cat B and 77% gasoline of which 56% aromatics over cat C. Gas yield was low compared to liquid produced having the highest yield of 28% over E-cat A and 20% obtained over E-cat B and cat C. The most important gases were light olefins in the range of C₃-C₄ and iso-paraffins C₄-C₅ gases.

Aguado et al.[20]employed a screw kiln reactor to conduct a catalytic degradation of Low density polyethylene. The catalytic conversion of LDPE was carried over Al-MCM-41 at 400-450°C under a nitrogen atmosphere. The catalytic cracking resulted in only 52-69% of LDPE conversion (depending on screw speed) but it improved the selectivity of the products in the gasoline range of C₅-C₁₂ (66.5-77.7%) and produced gas of 20%. The research group did not only investigate the effect of the catalyst in the experiments but they have also studied the effect of the screw speed on the conversion of LDPE, the product yield and selectivity; it was noticed that the conversion of LDPE decreased with the increase of the screw speed, whereas gasoline selectivity increased which is in agreement with the previously reported research[17]. Gasoline contained about 50% olefins, 20% of iso-paraffins and aromatic content below 7% (with negligible amount of benzene<0.1%) which is advantageous to meet the requirements of commercial fuel.

Table 2 Catalytic degradation of Polyethylene

Feedstock	Reactor type	T °C	Catalyst	Gas %	Liquid %	Wax %	Comment	Ref.
PE	Cycled spheres	440	HZSM-5 (SM27)	32 (C1-C4)	62 (C5-C15)	5.8 (C15-Cn)	Both catalysts enhanced gas and oil production. 0.2 % and 0.5% of char was obtained with HZSM-5 and Y-zeolite respectively.	[5]
PE	Cycled spheres	440	Y-zeolite (HY26)	21 (C1-C4)	70 (C5-C15)	8.5 (C15-Cn)		
PE	Fluidized bed	290-430	HUSY	89.4	3.7	6.9	All catalysts were found to highly promote gas yield ≈90%. HZSM-5 and HMOR produced 60% in the range of C3-C5. While MCM-41 and SAHA promoted a wider range of carbon in the gasoline range.	[22]
PE	Fluidized bed	290-430	HZSM-5	92.5	3.2	4.3		
PE	Fluidized bed	290-430	HMOR	87.9	4.7	7.4		
PE	Fluidized bed	290-430	SAHA	85.3	4.9	9.7		
PE	Fluidized bed	290-430	MCM-41	85.8	6.4	7.8		
LDPE	Batch reactor	380	MCM-41	37.3	23.2	39.5	MCM-41 promotes the cracking of solids into lighter liquid and gaseous products. Paraffins and aromatic compounds are strongly promoted.	[6]
HDPE	Batch reactor	380	MCM-41	35.9	22.9	41.2		
LDPE	Batch reactor	550	HZSM-5	69	18.6	12.4	The catalyst favored the formation of gases in the light fraction C2-C4. Condensed product was mainly aromatics.	[23]
HDPE	Batch reactor	550	HZSM-5	71.4	15.5	13		
Wax A (LDPE)	Tubing-bomb	510	KOB-627	20	63	1.3	pyrolytic waxy product produced high yields of gasoline of good quality and LPG with little dry gas, and small amount of coke and heavy cycle oil.	[7]
Wax B (HDPE)	Tubing-bomb	470	KOB-627	18.3	67.7	1.9		
Wax C (HDPE)	Tubing-bomb	470	KOB-627	11	62.5	2.1		
HDPE	Semi-batch	430	KFS-16B	11	71	18	KFS-16B did not enhance gas production but gave lighter condensate products but it showed slower deactivation than other catalysts.	[8]
HDPE	Semi-batch	430	ZSM-5	44	50	6		
HDPE	Semi-batch	430	SA-1	23.7	67.8	8.5	SA-1 and SA-2 promoted liquid production with narrow range of carbon number.	[8]
HDPE	Semi-batch	430	SA-2	13.4	74.3	12.3		
HDPE	Stirred reactor	420	SA-1	nd	nd	nd	More gaseous products mainly C4 fraction and lighter oil was produced.	[24]
HDPE	Pyrex	400-450	NCM	6.3	78.5	15.2	NCM gave high yield of	

	batchreactor						liquid in gasoline range with low sulfur content and little amount of gas.	
HDPE	Pyrex batch	400-450	FCC	6.3	82.5	11.2	FCC gave the highest yield of liquid in the gasoline range of C8-C13 and low sulfur content.	[9]
HDPE	Pyrex batch	400-450	HZSM-5	15.1	81	3.9	HZSM-5 gave the highest yield of gas, and high yield of light liquid hydrocarbons.	
HDPE	Fluidized bed	400-800	HZSM-5	90.9	8.8	2.5	HZSM-5 highly promotes production of gas and products are distributed over a narrower range of carbon. 3.5% of coke was produced.	[10]
HDPE	Fluidized bed	400-800	HUSY	86.9	11.6	0.6	HUSY produces higher amount of aromatics&narrower distribution. 4.3%coke was produced.	
HDPE	Fluidized bed flash pyrolysis	500-800	HZSM-5 dry blend	78.4	3.7	3.5	Higher yield of gas than thermal with narrower distribution of products over carbon range. Significant amount of coke (14.4%) was produced.	
HDPE	Fluidized bed flash pyrolysis	500-800	HZSM-5 melted	90.9	8.8	2.5	Highest yield of gas and light condensate hydrocarbons. 3.1% of coke was obtained.	[12]
HDPE	Fluidized bed slow pyrolysis	700	HZSM-5 dry blend	61.5	21	6.2	Promote the yield of gas, and narrow carbon range. 13.8% of coke was obtained.	
HDPE	Fluidized bed slow pyrolysis	700	HZSM-5 melted	87.6	6.9	3.7	Promote the yield of gas, and narrow carbon range. 7.8% of coke was obtained.	
HDPE	Conical spouted bed	500	HY zeolite	25 (C1-C4)	69 (C5-C10)	0	Gasoline obtained meets the EU requirements where it contains no sulphur, negligible benzene content and with RON index 96.5. 6% of coke was obtained	[25]

HDPE (blended with VGO)	Fixed bed reactor	450-500	KOB-627	36	54	10	The presence of the catalyst increased the conversion of HDPE ≈100% with significant amount of gasoline.	[13]
HDPE	Conical spouted bed	500	FCC fresh	52	35	13	13% diesel fraction	[26]
HDPE	Conical	500	FCC mild streaming	22	38	38	40% diesel fraction	
HDPE	Conical	500	FCC severe streaming	8	91	1	69% diesel fraction	
LDPE	Stirred batch	420	Mordinite MOR-0	22.1	2.3	14.1	38.5% conversion with traditional MOR-0.	[14]
LDPE	Stirred batch	420	Mordinite MOR-8	25.6	21.2	9.8	56.6% conversion with MOR-8	
LDPE	Stirred batch	420	Mordinite MOR-15	25.8	21	10.3	57.1% conversion with MOR-15	
LDPE	Horizontal fixed bed	500	H-Beta	Nd	Nd	12	H-beta catalyst decreases degradation temperature and exhibit higher catalytic activity than HZSM-5 at low concentrations but it shows a higher production of coke. Gas is richer in C4 and C5.	[15]
LDPE	Horizontal fixed bed	500	HZSM-5	nd	nd	4	C3 main compound and low coke deposite on its surface	[17]
LDPE	Fixed bed	500- 20min	HZSM-11	39	57	4	Degradation temperature was decreased by 145 °C when catalyst was employed. 3.22 and 2.22% of polycyclic aromatics over Zn-ZSM- 11 and H-ZSM-11 respectively.	
LDPE	Fixed bed	500- 20min	ZnZSM11	17	81.5	1.5		
LDPE	Fixed bed	500- 60min	HZSM-11	62.5	30.5	7	As residence time increased the yield of gaseous fraction increased. No polycyclic aromatics at 60 min residence time over both catalysts.	
LDPE	Fixed bed	500- 60min	ZnZSM11	40	55	4.8		
LDPE	Screw reactor	400-500	MCM-41	12.7	86	1.3	Major product of 80% gasoline	[18]

LDPE	Fixed bed tubular flow	375-425	SA : HZSM-5 (9:1)	39	59	2	59% gasoline fraction (C1-C12), Octane number 94. Aromatic and benzene content was 25.2 and 0.9% respectively. PE was converted to environmentally accepted gasoline.	[27]
LDPE	Fixed bed tubular flow	375-425	HZSM-5	51	48	1	Low gasoline yield and high aromatic content	
LDPE	Fixed bed tubular flow	375-425	SA	nd	nd	nd	Low quality gasoline range liquid	
LDPE	Batch pressurized autoclave	425	Pt/Al ₂ O ₄	9.8	88.1	2.1	Increased the yield of alkanes over the expense of alkene in the gas fraction. Ethane and propane dominated the gaseous compounds. Coke formed on the catalyst surface. Gasoline yield was 47%, the yield of cycloalkanes decreased.	[19]
LDPE	Batch pressurized autoclave	425	Rh/Al ₂ O ₄	11	85.4	3.5	Increased the yield of alkanes over the expense of alkene in the gas fraction. Methane was the dominating gas of 46%. Coke formed on the catalyst surface.	
LDPE	Fixed bed	400-600	HZSM-5	10-29	88-70	2-4	Methane, ethane and propane dominating gases in alkanes fraction. Higher polycyclic aromatics than thermal process.	[20]
LDPE	Fixed bed	400-600	Y-Zeolite	13-26	85-70	2-4	Propane and methane dominating gases in alkanes. Significant yield of aromatics and higher PAH than obtained in thermal process	
LDPE + 2%toluene	Fluidized bed	500	E-Cat A (FCC)	28	62	10	High aromatics in the gasoline were obtained ≈30%	
LDPE + 2%toluene	Fluidized bed	500	E-Cat B (FCC)	20	73	7	High aromatics in the gasoline were obtained ≈50%	[28]
LDPE + 2%toluene	Fluidized bed	500	E-Cat C (FCC)	20	70	10	High aromatics(≈60%) in gasoline were obtained	

LDPE	Screw kiln	400-450	Al- MCM41	18	78	2	High yield of gasoline with aromatics <7% and negligible amount of benzene	[21]
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CHAPTER II

EXPERIMENTAL SETUP

A. Material

Waste HDPE was obtained from collected waste shampoo bottles (found in the Lebanese market), cut and grinded into small particle of 3-5mm diameter. Different beds were selected and tested for the purpose of investigating their effect on the decomposition process and the product yield. Sand with particle size of 250 μ m and bed depth of 4cm was used along with cement and white clay. The compositions of the different bed materials were determined using X-Ray Diffraction (XRD) as shown in Fig.1-3. Sand was found to be mainly composed of Silica Oxide (SiO_2), cement was composed of a mixture of several compounds; of which are Hatrurite, (Ca_3SiO_5) and Chromium (Cr); whereas white clay was composed of Bassanite ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$). Another type of experiments was carried out using Sodium hydroxide pellets (NaOH) obtained from Sigma Aldrich. Sodium hydroxide was used as a basic catalyst to study its effect on the degradation process, product yield, product distribution as well as to differentiate its effect from the acidic catalysts tested HBeta and HUSY obtained from Zeolyst International.

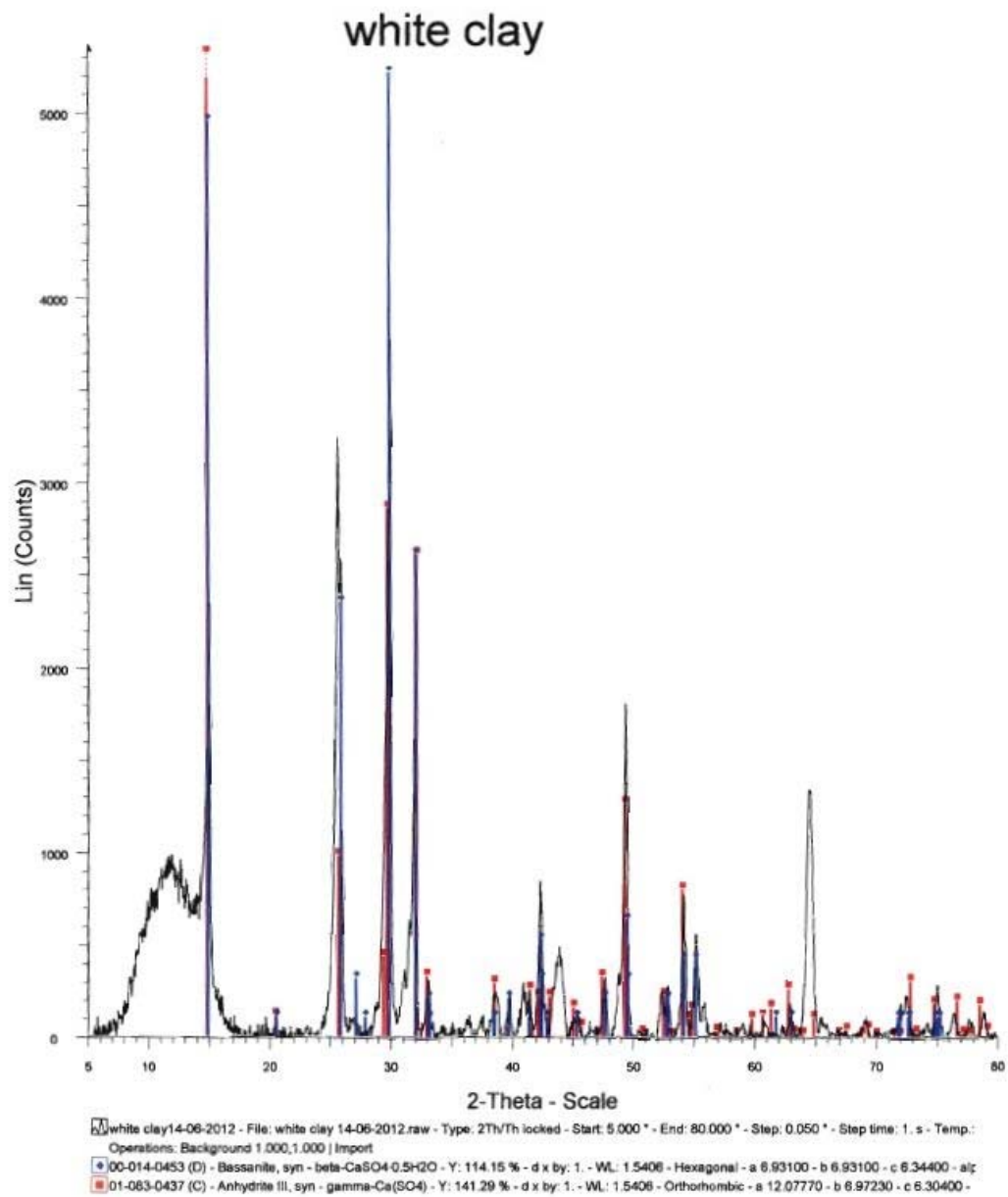


Figure 1 White Clay XRD

Cement

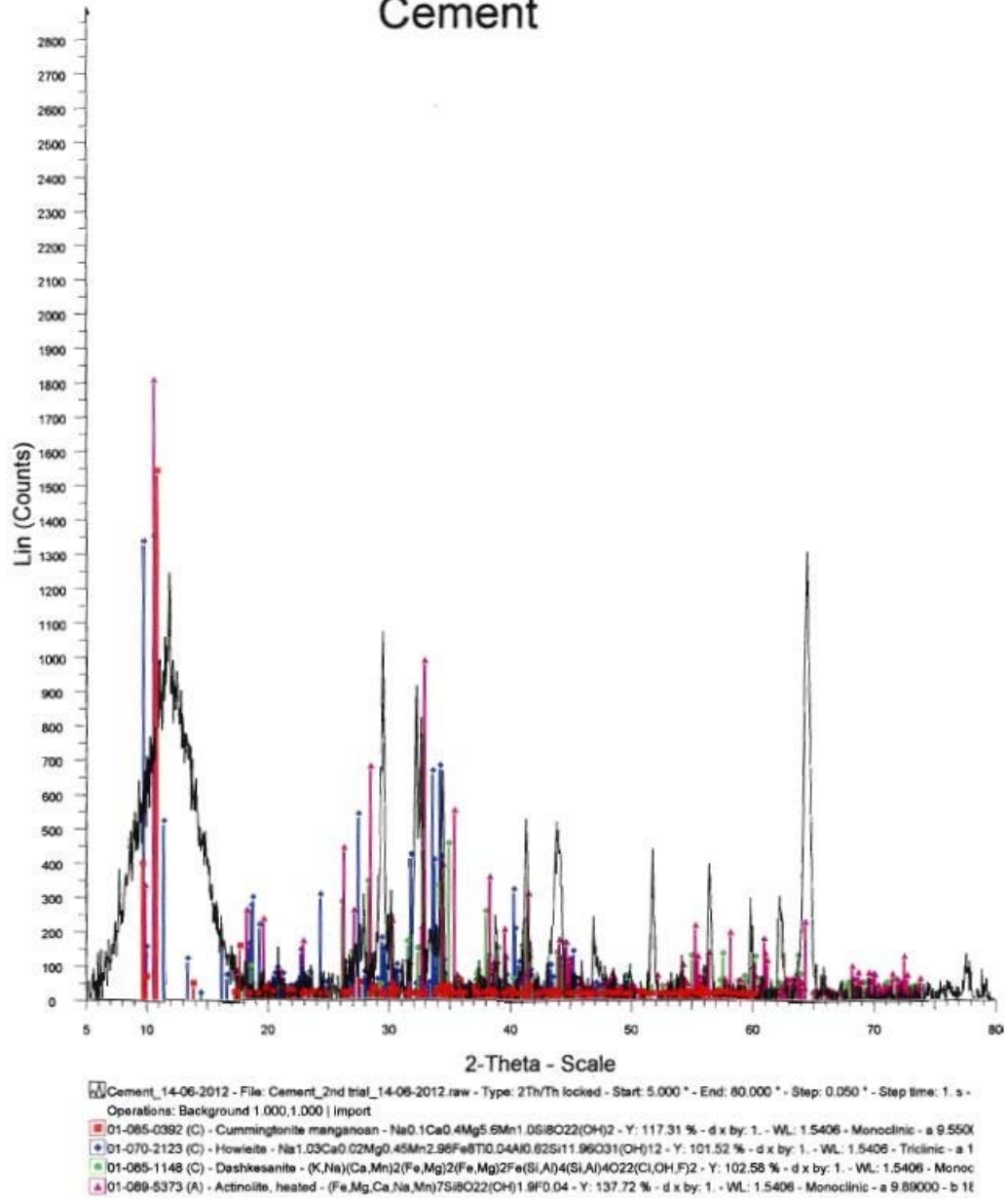
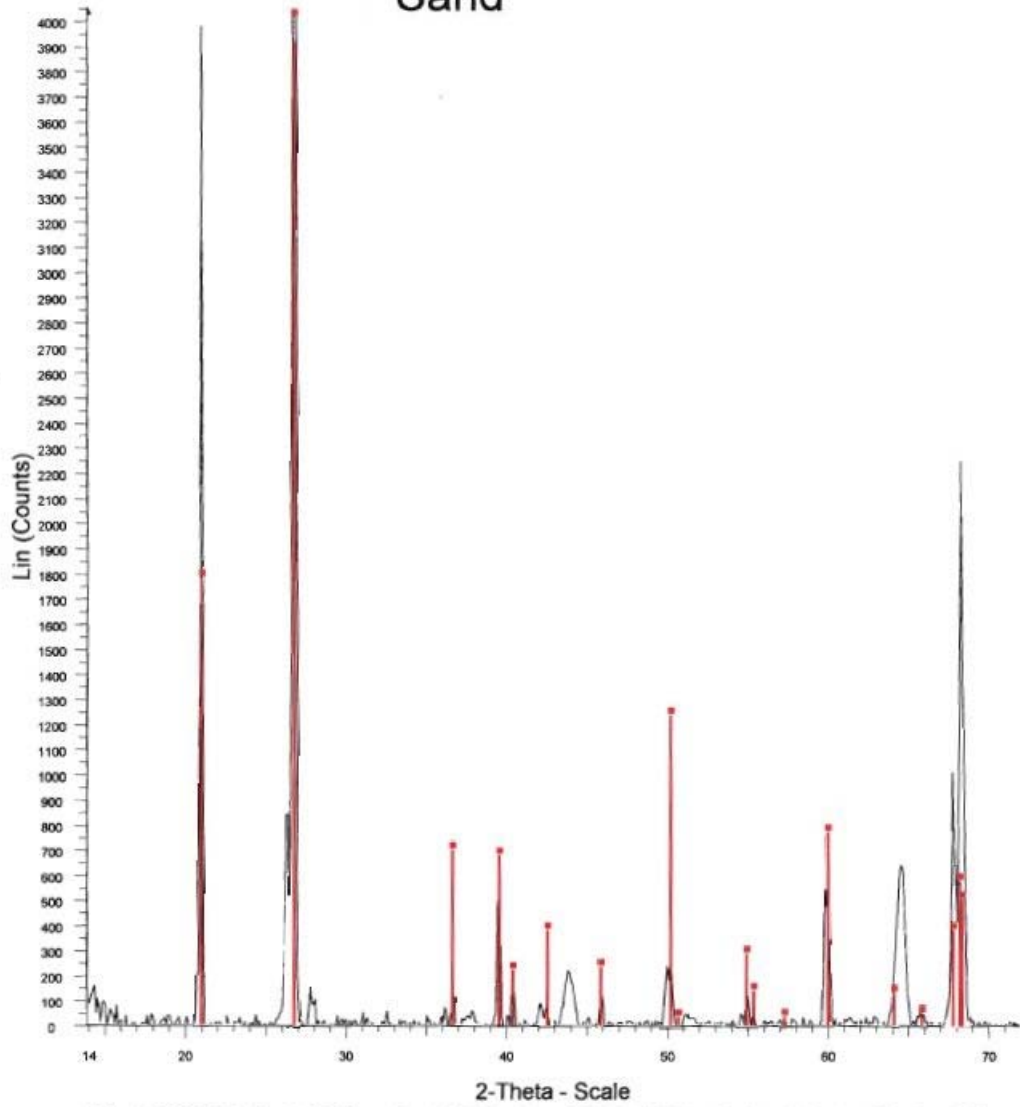


Figure 2 Cement XRD

Sand



Sand 14-06-2012 - File: Sand 14-06-2012.raw - Type: 2Th/Th locked - Start: 5.000 ° - End: 75.000 ° - Step: 0.100 ° - Step time: 0.5 s - Temp.: 25 °C (Operations: Background 1.000,1.000) Import
01-065-0794 (A) - Quartz - SiO₂ - Y: 79.19 % - d x by: 1. - WL: 1.5406 - Hexagonal - a 4.91000 - b 4.91000 - c 5.40000 - alpha 90.000 - beta 90.000 -

B. Remarks on Catalysts

Zeolite catalysts especially HZSM-5 which has high external surface area and possesses strong acidity, promotes the production of light hydrocarbons in the range of C3-C6. The module (Si/Al ratio) of the catalyst affects the distribution of product yield; a higher module gives higher gasoline yield than gases. HZSM-5 (Si/Al=1000) is expected to produce 42% gasoline and 33% gases while HZSM-5 (Si/Al=65) will give 69% gases and 20% gasoline. A decrease in polymer to catalyst ratio decreases the degradation temperature and alters product distribution toward light gaseous products[4]; several polymer to catalyst combinations were tested to find the appropriate ratio; PE: HZSM-5 of 30:1 reduced degradation temperature by 13% and 10:1 reduced the temperature by 19%. Worth noted is that a further decrease in polymer: catalyst ratio did not show a further reduction in degradation temperature. Although HZSM-5 is considered as the most active cracking catalyst for LDPE and HDPE, low conversion (did not exceed 10%) was observed when this catalyst was employed with a mixture of polyethylene and polypropylene. This fact is related to the large cross section of PP which blocks zeolite micropores and prevents other polymer molecules to have access to the acidic sites of the catalyst.

n-HZSM-5 (nanometer size HZSM-5) has a larger surface area (81m²/g) than HZSM-5 (7m²/g) therefore the former possesses higher number of acidic sites than HZSM-5. Consequently n-HZSM-5 was able to convert pure polypropylene by 67%.

The Hbeta zeolite catalyst type has a good combination of several factors which affects its catalytic influence; it has acid sites of high strength, large pore

diameter (0.64nm) and small crystal size (0.2 μ m). This catalyst gives selectivity of gaseous products (C1-C4) of 35%, and 60% in the gasoline range (C5-C12).

HY/HUSY zeolites possess large pores, cage-type structure and medium acid sites strength. They are subject to rapid deactivation from coke accumulation on its large pores; whereas MCM-41 and silica-alumina possess weak acid sites thus are of better resistance to coke deactivation. HZSM-5 has the highest activity amongst all catalysts.

MCM-41, HMCM-41, and Al-MCM-41 shifts the selectivity of products evolved in the catalytic pyrolysis of polyolefins toward hydrocarbons in the gasoline range (C5-C11) of 60-80% because of its large pores and medium acidity.

Silica-alumina (SA) which is cheaper than zeolites or mesoporous catalysts gives high yield of gasoline but with low RON in addition to its low activity. Increasing polymer to catalyst ratio lowers the possibility of catalyst deactivation. A combination of SA and HZSM-5 usually gives a high yield of gasoline with improved quality.

C. Laboratory Scale Reactor

The fixed bed reactor was made of stainless steel as shown in Fig.5, used for the purpose of conducting pyrolysis experiments. HDPE was fed into the reactor, over which a material bed of silica sand was added. HDPE Pyrolysis experiments were run in the temperature range of 450-500°C, the reactor was heated and maintained at the desired temperature by using external burners. The temperature was measured using a thermocouple placed in the middle of the reactor. The fluidizing agent was nitrogen (N₂) flow of 8l/min, purged initially in the reactor to ensure a medium free of oxygen.

Two types of experiments were carried out; thermal, using waste HDPE and varying the fluidizing bed; sand, cement and white clay and catalytic employing NaOH, HBeta or HUSY as catalyst with different beds; sand, cement and white clay.

During thermal pyrolysis reactions, 10grams of HDPE were placed in the reactor; a material bed was added, and the reactor was then closed, pressured with air to ensure no leakage. The reactor was pre-purged with nitrogen for 10 min then heated externally, plastic wastes were first converted to their molten state ~130-135°C under pressure. The melting point of HDPE was predetermined using Differential Scanning Calorimeter (DSC Q 2000) which showed one peak at 131.7°C Fig.4.

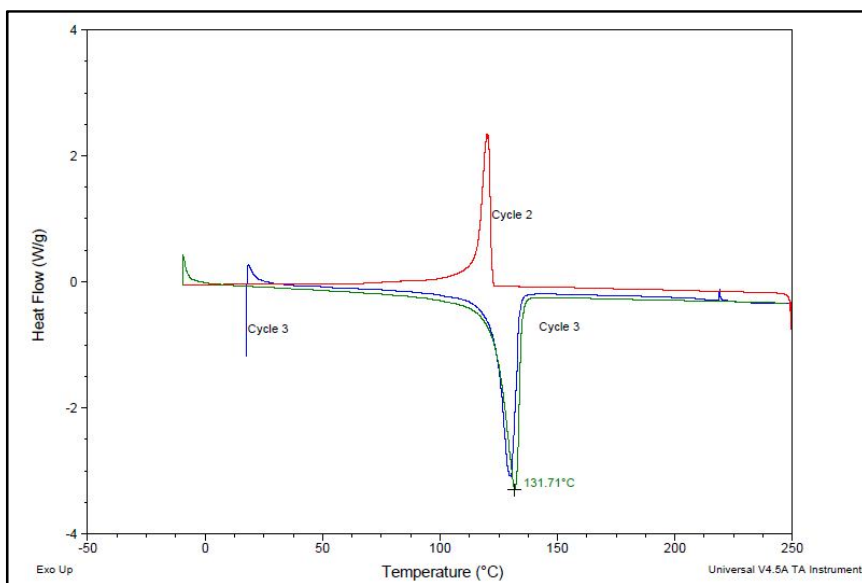


Figure 4 HDPE DSC

When the temperature reaches 130°C, the relief valve is opened to release any water vapor or light gases. The cracking of HDPE occurs in the temperature range of 400-450°C. The external burners were regulated to maintain the reaction temperature is achieved the external heaters were regulated at 450°C. The evolved gases from the pyrolysis reaction then pass through a cooling coil before entering the condenser where they condensate as liquid and wax.

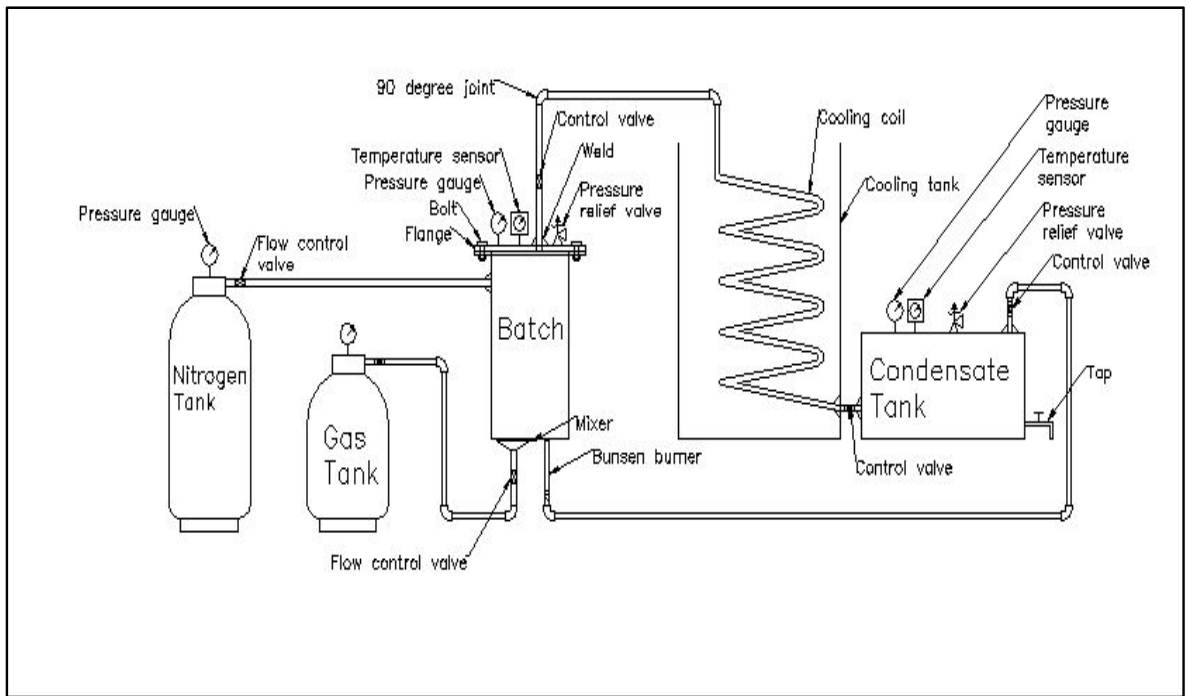


Figure 5 Experimental Setup Sketch



Figure 6 Laboratory Scale Experimental Setup

CHAPTER III

RESULTS AND DISCUSSIONS

Two types of experiments were carried out, thermal and catalytic. The thermal pyrolysis was conducted at 450°C while varying the fluidizing bed; sand, cement and white clay. On the other hand, the catalytic experiments were done in the presence of one of these catalysts, NaOH, HUSY and Hbeta under different reactor beds: sand, cement or white clay.

A. Products analysis:

At the end of each experiment, liquid and wax products were collected, weighed and dissolved in Dichloromethane (DCM) GC grade. These compounds were identified and quantified by a Thermo GC-MS provided with an HP-5MS column (30 m x 0.25 mm x 0.1 μm). The column program is: injector temperature, 280°C; initial column temperature, 40°C; initial time, 5 min; heating rate, 12°C/min; final temperature, 305°C; final time, 25 min; run time, 53.33 min; carrier gas, Helium, 1 ml/min; average velocity, 38 cm/s; solvent delay, 6 min. The ion trap detector had a mass range from 50 to 650 amu and is linked to a computer provided with the NIST library.

The following figures show the chromatograms obtained from GC/MS and their corresponding readings NIST library; noting that readings were based on a similarity index (SI) greater than 800, which is a very good match between our compound and that matching with the library.

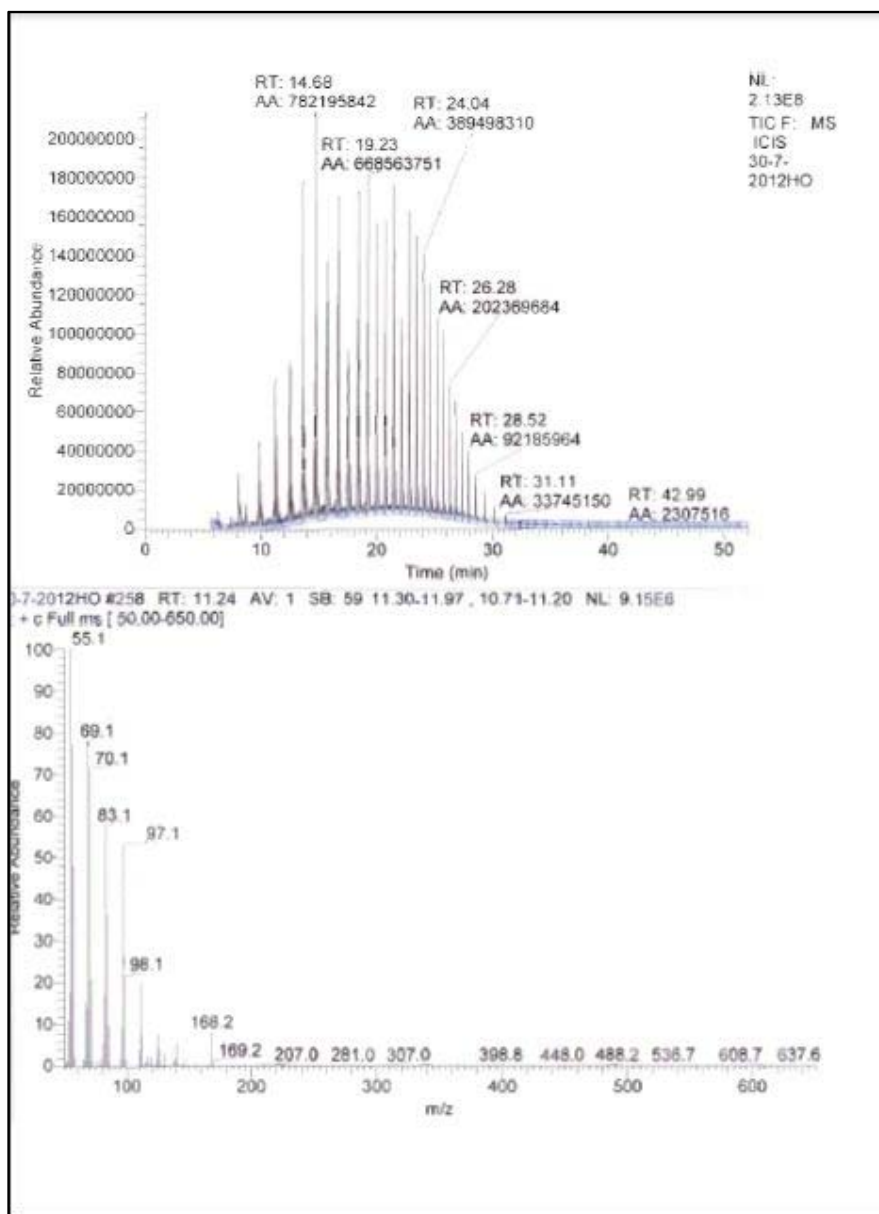


Figure 7 GC/MS chromatograms

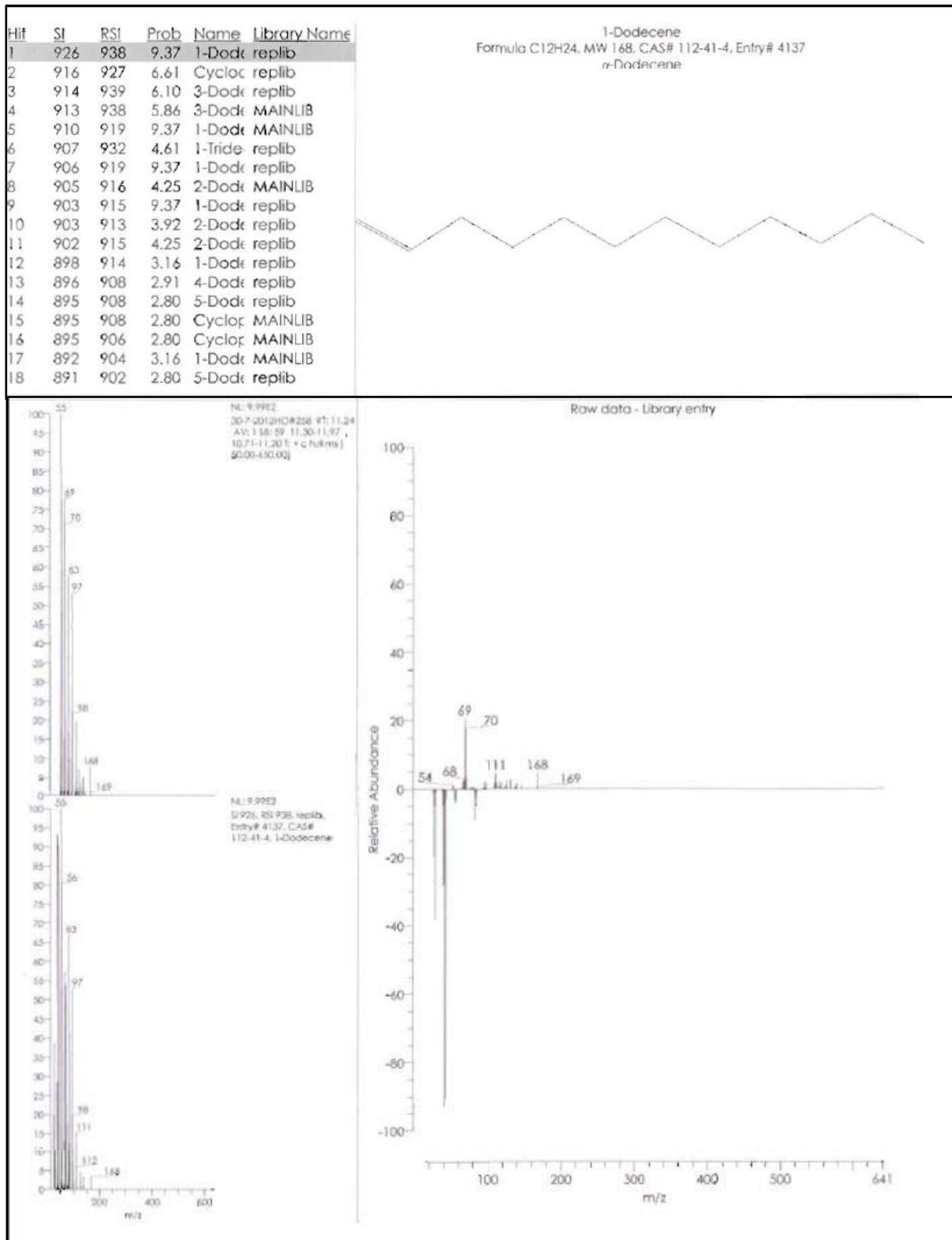


Figure 8 Compound detected using NIST library

1. Thermal degradation of waste HDPE under the effect of different reactor beds

In order to validate the results obtained from each pyrolysis run, all batches were repeated a number of times. The product yields from the thermal degradation of HDPE waste carried out at 450°C are shown in Table 3. The wax obtained was of very low viscosity and yellow color, whereas the light green liquid was mixed with dark brown heavy oil. It is worth mentioning that when the same experiment was carried out without any bed material in the reactor, the product yield gave 100% wax of high viscosity and dark yellow color.

The silica sand bed produced the largest amount of gases at 51%, while the liquid yield reached 40% and that of wax was at 9%. The cement bed produced the largest amount of liquids at 82% with a gas yield of 18%. The white clay bed produced the largest amount of wax with a yield of 13% and the least amount of gas (10%).

Table 3 Lumped product yield from the pyrolysis of HDPE waste at 450°C

Reactor Bed	Gas (%)	Liquid (%)	Wax (%)
No bed	0	0	100
Silica sand	51	40	9
Cement	18	82	0
White clay	10	77	13

The GC-MS analysis (Tables 5-8) showed, with all reactor beds, that the carbon chain number in the obtained alkanes was ranging from C₁₀ to C₄₄. When a silica sand bed was used, the alkenes were distributed between C₁₀ and C₂₂. On the other hand, the cement bed produced the narrowest alkenes distribution over a range from C₁₀-C₁₅. The white clay bed gave a slightly broader distribution over a C₁₀-C₁₉ range.

Heneicosane (C₂₁H₄₄) was the dominant component among all alkanes, while Tridecene (C₁₃H₂₆) and Nonadecene (C₁₉H₃₈) were dominant in the alkenes. D-Limonene (C₁₀H₁₆) was present in almost all samples as the most abundant aromatic compound. Alcohols such as Hexadecanol (C₁₆H₃₄O) and Heptadecanol (C₁₇H₃₆O) were obtained with all beds except with Silica Sand.

Table 4 Group species yield from HDPE waste pyrolysis at 450°C

Reactor Bed	Alkane (%)	Alkene (%)	Aromatics (%)	Alcohols (%)
No bed	38	49	13	0
Silica Sand	43.3	47.5	9.2	0
Cement	57.6	25.1	6.3	11
White clay	47.7	39.9	4.5	7.9

Aromatics containing, D-Limonene (C₁₀H₁₆) and Cyclotetradecane (C₁₄H₂₈) were produced at the highest combined yield of 9.2% when a silica sand bed was utilized. Cyclotetradecane (C₁₄H₂₈) disappeared with the use of the other reactor beds, and the overall aromatics contents was decreasing in the following order,

Silica Sand > Cement > White clay

Note that, the cement bed produced the highest yield of D-Limonene (C₁₀H₁₆) of 6.3%. The yield of single-bonded (alkanes) and double-bonded (alkenes) followed separate paths, and were found to increase in the following order,

For the alkanes: Cement > White clay > Silica Sand

While for the alkenes it was in the expected reverse order:

Silica Sand > White clay > Cement

It is obvious from the above that varying the reactor bed material is greatly influencing the product selectivity and yield.

Table 5 GC-MS Wax product composition from the pyrolysis of HDPE waste at 450°C

Alkanes	formula	%
decane	C10H22	0.7331315
undecane	C11H24	1.082574873
dodecane	C12H26	1.787227514
tridecane	C13H28	1.623239394
tetradecane	C14H30	2.576173719
pentadecane	C15H32	3.338624606
hexadecane	C16H34	2.757327358
octadecane	C18H38	3.602535836
nonadecane	C19H40	2.990667663
heneicosane	C21H44	4.447284708
docosane	C22H46	2.753187857
tetracosane	C24H50	2.310591346
heptacosane	C27H56	1.949866505
octacosane	C28H58	1.94530645
tetratetracontane	C44H90	4.118987671
		38.016727

Alkynes	formula	%
1,10-undecadiene	C11H20	0.604617844
1,11-dodecadiene	C12H22	0.868561094
1,13,tetradecadiene	C14H26	5.860799448
1,19-eicosadiene	C20H38	5.448249109
		12.7822275

Alkenes	formula	%
1-decene	C10H20	3.258939788
1-undecene	C11H22	3.640380477
1-dodecene	C12H24	3.647408712
1-tridecene	C13H26	3.804068403
1-pentadecene	C15H30	4.468485104
1-hexadecene	C16H32	0.36840321
3-heptadecene	C17H34	3.510915941
1-nonadecene	C19H38	14.28087642
1-docosene	C22H44	7.456530783
9-hexacosene	C26H52	3.858878429
17,pentatriacontene	C35H70	0.906158241
		49.2010455

Table 6 GC-MS liquid product composition from the pyrolysis of HDPE waste in a silica sand bed, reactor at 450°C

Alkane	formula	%
Decane	C10H22	1.63037189
Undecane	C11H24	2.294500358
Dodecane	C12H26	2.556696675
Tridecane	C13H28	3.177672939
Tetradecane	C14H30	3.373761606
Pentadecane	C15H32	2.678912716
Hexadecane	C16H34	3.09638205
Heptadecane	C17H36	2.807981503
Nonadecane	C19H40	6.079152068
Heneicosane	C21H44	13.23839093
Octacosane	C28H58	1.539537993
Tetratetracontane	C44H90	0.838923982
		43.31228471

Alkene	formula	%
1-Decene	C10H20	4.725972
1-Tridecene	C13H26	19.87524
5-Undecene	C11H22	0.436245
1-Dodecene	C12H24	5.933535
1,Hexadecene	C16H32	3.233266
1,Nonadecene	C19H38	10.22966
1-Docosene	C22H44	3.234699
		47.66862

Aromatics	Formula	%
Cyclohexene,1-methyl 5,1,methylethenyl	C10H16	1.636193907
Cyclotetradecane	C14H28	7.38290546
		9.019099367

Table 7 GC-MS liquid product composition from the pyrolysis of HDPE waste in a cement bed reactor at 450°C

Alkane	formula	%
Decane	C10H22	2.193545733
Undecane	C11H24	3.123780852
Tridecane	C13H28	2.423829175
Pentadecane	C15H32	4.801055397
Hexadecane	C16H34	3.398129955
Heptadecane	C17H36	3.257739902
Octadecane	C18H38	3.562295565
Nonadecane	C19H40	7.3286062
Eicosane	C20H42	3.833018202
Heneicosane	C21H44	9.383411091
Tetracosane	C24H50	2.90938963
Octacosane	C28H58	8.243992629
Tetratetracontane	C44H90	3.144699474
		57.6034938

Alkene	formula	%
1-Decene	C10H20	4.639628858
1-Tridecene	C13H26	10.86793185
1-Dodecene	C12H24	4.82195046
1,Pentadecene	C15H30	4.805712946
		25.13522411

aromatics	formula	%
D-Limonene	C10H16	6.333100933

Alcohol	formula	%
1-Hexadecanol	C16H34O	8.157040398
1,Heptadecanol	C17H36O	2.771140752
		10.92818115

Table 8 GC-MS liquid product composition from the pyrolysis of HDPE waste in a white-clay bed reactor at 450°C

Alkane	formula	%
Undecane	C11H24	3.005243522
Tridecane	C13H28	3.42654967
Tetradecane	C14H30	4.188709027
Pentadecane	C15H32	4.956630549
Octadecane	C18H38	4.606491966
Eicosane	C20H42	3.456229976
Heneicosane	C21H44	11.20409718
Octacosane	C28H58	7.284960194
Tetratetracontane	C44H90	5.585616104
		47.71452819

Aromatics	formula	composition
D-Limonene	C10H16	4.52909614

Alkene	formula	%
1-Decene	C10H20	5.610630762
1-Undecene	C11H22	5.198585938
1-Dodecene	C12H24	4.797218389
1-Tridecene	C13H26	7.097678306
1,Hexadecene	C16H32	6.505893438
1,Pentadecene	C15H30	4.529771915
1-Nonadecene	C19H38	6.131187666
		39.87096641

Alcohol	formula	composition
1-Hexadecanol	C16H34O	4.663406071
1,Heptadecanol	C17H36O	3.222003183
		7.885409254

2. Catalytic degradation of waste HDPE over HUSY, HBeta and NaOH while altering the reactor beds

In the catalytic reaction, the reactor was first fed with HDPE waste, fluidizing bed and on top the catalysts was added. This method of preparing for the catalytic experiment was followed to force the evolved gases to pass through the pores of the catalyst after passing through the fluidizing bed. Each catalyst, NaOH, HUSY and HBeta were tested with the different reactor beds. The product yield from the catalytic degradation of HDPE waste carried out at 450°C is shown in Table 9.

Table 9 Group species yield from HDPE waste catalytic degradation at 450°C

Reactor Bed	Catalyst	Gas %	Liquid %	Wax %
Silica sand	NaOH	19	81	0
Silica sand	HUSY	73	23	4
Silica sand	HBeta	81	15	4
Cement	HUSY	54	40	6
Cement	HBeta	30	67	3
White clay	HUSY	45	40	15
White clay	HBeta	60	35	5

The silica sand bed with NaOH produced the largest amount of liquid at 81%, while the gas yield reached 19% and no wax was obtained. Both catalysts, HUSY and HBeta gave the highest yield of gas with Silica Sand, 73% and 81% respectively. The yield of products obtained when employing either HUSY or HBeta as a catalyst changed significantly when altering the reactor bed.

Hbeta gave the highest yield of liquid at 67% when the reactor was packed with cement; however the case was different when employing Hbeta catalyst with silica sand and white clay yielding; gas (81%), liquid (15%) and wax (4%) and gas (60%), liquid (35%) and wax (5%). The catalyst HUSY gave slightly higher yield of gas (54%,

45%) than liquid (40%, 40%) when employed with cement and white clay beds, respectively. The yield of wax (15%) was the highest with white clay.

The GC-MS analysis (Tables 11-17) showed when a silica sand-NaOH reactor bed is used the carbon chain number of the obtained alkanes was ranging from C₁₀ to C₄₄. When silica sand was used with either HUSY or HBeta, the carbon chain number of alkanes was narrowed to (C₁₀-C₂₈). Similar result was obtained with cement and white clay beds where the carbon chain number in the alkanes ranged from C₁₀-C₂₉ and from C₁₀-C₃₅ with HUSY, and from C₁₁-C₂₉ and C₁₀-C₃₆ with HBeta. Alkenes were distributed between C₁₀ and C₂₃ in silica sand-NaOH, cement-HBeta, white clay-HUSY and white clay-HBeta. On the other hand, alkenes obtained in the cement-HUSY and silica sand-Hbeta were the narrowest ranging from C₁₁-C₁₈ and from C₁₅-C₁₉, respectively. However, no alkenes were obtained in the silica sand-HUSY bed reactor.

Octacosane (C₂₈H₅₈) was the dominant component among all alkanes in silica sand-HUSY (17.7%), white clay-HBeta (11%), cement-HUSY (8.5%) and silica sand-NaOH (7%), while Nonadecane (C₁₉H₄₀), Heneicosane (C₂₁H₄₄) and Heptadecane (C₁₇H₃₆) were the dominant component in the alkanes obtained in the silica sand-Hbeta, cement-Hbeta and white clay-HUSY bed reactors respectively. Nonadecene (C₁₉H₃₈) was the dominant product in the alkenes for all bed reactors except for silica sand-HBeta and cement-HUSY where Hexadecene (C₁₆H₃₂) and Dodecene (C₁₂H₂₄) were the dominant alkenes obtained, respectively. D-Limonene (C₁₀H₁₆) was present in almost all samples as the most abundant aromatic compound; however cyclotetradecane (C₁₄H₂₈) was the dominant aromatic compound for cement-HBeta and white clay-Hbetabed reactors and Naphthalene 1,7-dimethyl (C₁₂H₁₂) was the dominant aromatic obtained with the reactor bed silica sand-HBeta. Alcohols such as Hexadecanol

(C₁₆H₃₄O) and Heptadecanol (C₁₇H₃₆O) were obtained with silica-NaOH, cement-HUSY and cement-Hbeta. Heptacosanol (C₂₇H₄₂O) and Eicosanol (C₂₀H₄₂O) were obtained in the white clay-HUSY and white clay-HBeta bed reactors respectively. On the other hand, no alcohol compounds were detected neither in silica sand-HUSY nor silica sand-HBeta bed reactors.

Table 10 Group species yield from HDPE waste catalytic degradation at 450°C

Reactor Bed	Catalyst	Alkane %	Alkene %	Aromatics %	Alcohols %
Silica sand	NaOH	41.3	46.8	1.9	10
Silica sand	HUSY	80.8	0	19.2	0
Silica sand	HBeta	60.9	12.3	26.8	0
Cement	HUSY	60.8	12.2	24.5	2.5
Cement	HBeta	59.9	19.4	9.4	11.3
White clay	HUSY	50.2	34.4	10.8	4.6
White clay	HBeta	61	25.7	4.6	8.7

Table 11 GC-MS liquid product composition from the pyrolysis of HDPE waste in a silica sand bed with NaOH reactor at 450°C

Alkane	formula	%
Decane	C10H22	1.30574045
Undecane	C11H24	2.016638755
Dodecane	C12H26	2.262920955
Tridecane	C13H28	2.591158797
Tetradecane	C14H30	2.536409747
Pentadecane	C15H32	3.87897074
Octadecane	C18H38	2.777039188
Nonadecane	C19H40	3.430689314
Eicosane	C20H42	3.117863726
Heneicosane	C21H44	5.94787961
Octacosane	C28H58	6.987505177
Tetratetracontane	C44H90	4.496490879
		41.34930734
Aromatics	formula	%
D-Limonene	C10H16	1.874647794

Alkene	formula	%
1-Decene	C10H20	4.697014599
1-Tridecene	C13H26	5.045249048
1-Dodecene	C12H24	0.433207893
1-Tridecene	C13H26	7.139152732
1-Hexadecene	C16H32	6.413743414
1-Pentadecene	C15H30	5.61085969
1-Nonadecene	C19H38	12.17320141
1-Docosene	C22H44	5.282224571
		46.79465336

Alcohol	formula	%
1,Hexadecanol	C16H34O	6.187960523
1,Heptadecanol	C17H36O	3.793430989
		9.981391513

Table 12 GC-MS liquid product composition from the pyrolysis of HDPE waste in a silica sand bed with HUSY reactor at 450°C

Alkane	formula	%
Decane	C10H22	2.350302497
Undecane	C11H24	2.269588931
Dodecane	C12H26	3.018805881
Tridecane	C13H28	3.521130536
Tetradecane	C14H30	4.210689456
Pentadecane	C15H32	5.700168818
Hexadecane	C16H34	4.624523536
Heptadecane	C17H36	4.689455916
Octadecane	C18H38	6.187361156
Nonadecane	C19H40	12.95901911
Eicosane	C20H42	4.423995161
Heneicosane	C21H44	9.139325127
Octacosane	C28H58	17.75310516
		80.84747128

Aromatics	formula	%
Benzene, 1-ethyl-3-methyl	C9H12	2.487217682
Benzene, 1,2,4-trimethyl	C9H12	4.485521243
D-Limonene	C10H16	5.714025549
Benzene,1,2,3,4,tetramethyl	C10H14	1.535805754
Naphthalene, 1-methyl	C11H10	4.929958496
		19.15252872

Table 13 GC-MS liquid product composition from the pyrolysis of HDPE waste in a silica sand bed with HBeta reactor at 450°C

Alkanes	formula	%
decane	C10H22	1.987032121
undecane	C11H24	2.664170246
dodecane	C12H26	2.945580184
tridecane	C13H28	6.714912485
tetradecane	C14H30	3.921331651
pentadecane	C15H32	3.490691815
heptadecane	C17H36	1.935194727
octadecane	C18H38	3.752676425
nonadecane	C19H40	18.26265448
Eicosane	C20H42	2.903104213
heneicosane	C21H44	9.453315791
octacosane	C28H58	2.89723977
		60.9279039

Aromatics	formula	%
benzene, 1-ethyl-3-methyl-	C9H12	2.616036238
benzene, 1,2,4-trimethyl-	C9H12	4.075810132
benzene, 1-methyl, 3(1-methylethyl)-	C10H14	1.429467753
D-limonene	C10H16	2.257639209
benzene, 1-methyl-3-propyl-	C10H14	1.290674748
benzene, 2-ethyl-1,4-dimethyl-	C10H14	1.487467051
benzene, 1-methyl, 4(1-methylethyl)-	C10H14	1.923097126
Naphthalene	C10H8	1.758621072
naphthalene, 1-methyl-	C11H10	2.405042356
naphthalene, 1,7-dimethyl-	C12H12	6.170948768
naphthalene, 1,6,7,-trimethyl-	C13H14	1.371970427
		26.78677488

Alkenes	formula	%
1,pentadecene	C15H30	2.701433991
1-hexadecene	C16H32	5.953189296
1-nonadecene	C19H38	2.15640925
9-nonadecene	C19H38	1.474288678
		12.28532122

Table 14 GC-MS liquid product composition from the pyrolysis of HDPE waste in a cement bed with HUSY reactor at 450°C

Alkane	formula	%
Decane	C10H22	1.407043785
Undecane	C11H24	3.679209245
Dodecane	C12H26	3.867077551
Tridecane	C13H28	3.087789372
Tetradecane	C14H30	4.680946344
Pentadecane	C15H32	4.032347653
Hexadecane	C16H34	3.750110206
Heptadecane	C17H36	3.752464934
Octadecane	C18H38	3.763655802
Nonadecane	C19H40	0.292334459
Eicosane	C20H42	3.242597894
Heneicosane	C21H44	3.131885313
Docosane	C22H46	2.598848665
Tricosane	C23H48	2.772743832
Tetracosane	C24H50	3.397844275
Pentacosane	C25H52	2.975555764
Octacosane	C28H58	8.488066023
Nonacosane	C29H60	1.85866924
		60.77919036

Alkene	formula	%
1-Undecene	C11H22	2.78757098
3-Dodecene	C12H24	2.805231725
1-Pentadecene	C15H30	2.390649304
1-Hexadecene	C16H32	2.372173302
3-Octadecene	C18H36	1.863730031
		12.21935534

Aromatics	formula	%
Benzene, 1-ethyl-4-methyl	C9H12	0.555930622
D-limonene	C10H16	6.492434678
Benzene, 1,2,4,5-tetramethyl	C10H14	1.262314364
Naphthalene, 1-methyl	C11H10	5.184150749
Cyclotetradecane	C14H28	3.231817561
Naphthalene, 1,7-dimethyl	C12H12	3.202442871
Naphthalene, 1,3-dimethyl	C12H12	4.57640257
		24.50549342

Alcohol	formula	%
1-Heptadecanol	C17H36O	2.495960887

Table 15 GC-MS liquid product composition from the pyrolysis of HDPE waste in a cement bed with HBetareactor at 450°C

Alkane	Formula	%
Undecane	C11H24	1.420833103
Dodecane	C12H26	1.987229772
Tridecane	C13H28	2.304440958
Tetradecane	C14H30	3.21030286
pentadecane	C15H32	3.546272783
hexadecane	C16H34	3.304450959
heptadecane	C17H36	3.355493137
Octadecane	C18H38	3.53464453
nonadecane	C19H40	3.13765154
eicosane	C20H42	3.71857197
heneicosane	C21H44	6.865512587
docosane	C22H46	3.439855666
tetracosane	C24H50	6.565698684
hexacosane	C26H54	2.697128988
heptacosane	C27H56	2.90770252
octacosane	C28H58	5.709662132
nonacosane	C29H60	2.174985252
		59.88043744

Alkene	formula	%
3-undecene	C11H22	1.170171473
5-undecene	C11H22	0.535432599
3-dodecene	C12H24	2.572874885
1-nonadecene	C19H38	9.584260501
1-docosene	C22H44	2.706461053
9-tricosene	C23H46	2.781860682
		19.35106119

Aromatics	formula	%
D-limonene	C10H16	1.775164754
2,4-dimethylstyrene	C10H12	1.036826172
naphthalene	C10H8	0.529341438
cyclotetradecane	C14H28	3.039053399
naphthalene, 2,6-dimethyl-	C12H12	1.493878442
naphthalene, 1,6,7,trimethyl-	C13H14	1.536229852
		9.410494056

Alcohol	formula	%
1-heptadecanol	C17H36O	6.30144193
2-hexadecanol	C16H34O	3.071687884
1-pentacosanol	C25H52O	1.984877493
		11.35800731

Table 16 GC-MS liquid product composition from the pyrolysis of HDPE waste in white clay with HUSY reactor at 450°C

Alkane	formula	%
Decane	C10H22	1.379642844
Undecane	C11H24	1.304625545
Dodecane	C12H26	2.04013653
Tridecane	C13H28	2.023476364
Tetradecane	C14H30	2.580558865
Pentadecane	C15H32	2.494401918
Hexadecane	C16H34	1.384729558
Heptadecane	C17H36	3.926007374
Octadecane	C18H38	2.703111742
Eicosane	C20H42	2.648887594
Heneicosane	C21H44	2.624690639
Docosane	C22H46	3.046302003
Tricosane	C23H48	3.050413114
Tetracosane	C24H50	2.765545826
Pentacosane	C25H52	1.480911904
Hexacosane	C26H54	2.782924361
Tetratriacontane	C34H70	2.992496057
Octacosane	C28H58	3.072163644
Nonacosane	C29H60	2.687958212
Pentatriacontane	C35H72	3.181352493
		50.17033659

Alkene	formula	%
1-Undecene	C11H22	2.56808639
1-Dodecene	C12H24	2.91021926
1-Tridecene	C13H26	1.661331797
1-Tetradecene	C14H28	4.279032304
1-Pentadecene	C15H30	2.885695901
8-Heptadecene	C17H34	2.974009633
1-Octadecene	C18H36	3.183544528
1-Nonadecene	C19H38	6.52257964
1-Docosene	C22H44	4.228808831
1-Tricosene	C23H46	3.175946965
		34.38925525

Aromatics	formula	%
Benzene,1-ethyl-3-methyl	C9H12	0.851449337
Cyclodecane	C10H20	2.520468855
D-Limonene	C10H16	4.438499277
Benzene,1,2,3,5,tetramethyl	C10H14	0.541055871
Cyclohexadecane	C16H32	1.563043909
Cyclotetracosane	C24H48	0.883127307
		10.79764456

Alcohol	formula	%
1-Heneicosanol	C21H44O	1.678382965
1-Heptacosanol	C27H56O	2.964380641
		4.642763606

Table 17 GC-MS liquid product composition from the pyrolysis of HDPE waste in white clay with HBeta reactor at 450°C

Alkanes	formula	%
Decane	C10H22	0.239600136
Undecane	C11H24	1.01379387
Dodecane	C12H26	1.722987036
Tridecane	C13H28	2.126187041
Tetradecane	C14H30	3.236019989
Pentadecane	C15H32	2.904519255
Hexadecane	C16H34	3.632393668
Heptadecane	C17H36	3.551690388
Octadecane	C18H38	3.52620554
Nonadecane	C19H40	3.450550781
Eicosane	C20H42	3.889897555
Heneicosane	C21H44	7.216157801
Docosane	C22H46	3.382901806
Tetracosane	C24H50	3.276276596
Octacosane	C28H58	11.63951762
Nonacosane	C29H60	2.304462764
Pentatriacontane	C35H72	1.998848535
Hexatriacontane	C36H74	1.925367155
		61.03737753

Alkenes	formula	%
1-decene	C10H20	0.57898904
1-undecene	C11H22	1.433713427
3-dodecene	C12H24	2.766106534
1-tridecene	C13H26	1.980449674
1-hexadecene	C16H32	3.51175384
3-heptadecene	C17H34	3.555423679
1-nonadecene	C19H38	5.916674043
1-docosene	C22H44	3.200035556
9-tricosene	C23H46	2.762142
		25.70528779

Alcohols	formula	%
1-eicosanol	C20H42O	3.512729931
1-tetracosanol	C24H50O	2.788971143
1-pentacosanol	C25H52O	2.379039131
		8.680740205

Aromatics	formula	%
D-limonen	C10H16	0.633016682
naphthalene	C10H8	0.532824432
Cyclotetradecane	C14H28	2.111096161
Naphthalene,1,3,dimethyl-	C12H12	1.299657195
		4.57659447

Major improvements were achieved when using catalysts; products obtained from the catalytic degradation of HDPE waste were lighter than products evolved from the thermal cracking; for instance the carbon chain ranged between C10-C28 over the various acidic catalysts used; however the carbon chain was longer C10-C44 in the thermal degradation of HDPE and when NaOH was employed as a basic catalyst. In addition, certain aromatic products as limonene and naphthalene were produced significantly over the catalysts while aromatic compounds were not detected in the thermal degradation process. This is an important indication that the products obtained

from the catalytic cracking of HDPE waste are fuel-like products. Silica sand-HUSY and Cement-HUSY reactor beds gave the highest alkane composition of 80.8% and 60.8% respectively.

CHAPTER IV

ECONOMIC EVALUATION

A. Economic Assessment of Waste Thermal Degradation Process

An economic assessment, also known as a feasibility study aims to evaluate the effectiveness of the feedstock recycling process in terms of cost versus revenue.

Islam et al. [28] studied the techno-economic feasibility of the waste tire pyrolysis process. The study was carried for three plant sizes: medium commercial scale (144 tons/day), small commercial scale (36 tons/day), pilot scale (3.6 tons/day). A fixed bed fire-tube pyrolysis reactor converted bicycle tire waste into 9 % (gas), 46%(pyrolysis oil), 35%(carbon) and 10% (steel). Tables 17-18 present a value estimate of the costs of different variables needed for the study.

Table 18 Summary of production cost for three different scale solid tire waste pyrolysis plants (US\$)

Plant capacity	144, 36 and 3.6 tons/day of tire waste
Location, time, currency	Bangladesh, 2010, US\$
Annual operating time	7512 h @ 24 h/day
Maintenance	2.5% of FCI
Overheads	2% of FCI
Taxes and insurance	1.5% of FCI
Other fixed operating costs	1% of FCI
Feedstock cost	20 US\$/ton
Labor rate	1.00 US\$/h (regular duty @ 8 h/day)
Total labors (in equivalent of shift operators)	76, 44 and 7 for three respective plant
General overheads	60% of total salaries
Electricity price	0.10 US\$/kWh (600, 180 and 30 kW for three respective plant)
Interest rate	10%
Plant life	20 years

Table 19 Parameters used in cost estimation

Plant capacity	144 tons/ day	36 tons/ day	3.6 tons/ day
Base equipment cost	2.5×10^6	1×10^6	0.20×10^6
Fixed capital investment (FCI)	5.69×10^6	2.27×10^6	0.45×10^6
Total capital required	6.54×10^6	2.62×10^6	0.52×10^6
Annualized capital cost/Capital charges	768123	307249	61455
<i>Fixed operating cost:</i>			
Salary for employee	190304	110176	17528
Maintenance + overheads + taxes and insurance + other fixed operating costs	398125	159250	31850
<i>Variable operating cost:</i>			
Feedstock	901440	225360	22536
Electricity	450720	135216	22536
General overheads	114182	66105	10516
Total operating cost	2054771	696107	104966
Total production cost of pyrolysis oil	2822894	1003356	166421
Unit production cost of pyrolysis oil (US\$/ton)	136	193	321

The capital and operation cost for the process of collecting and shredding tire waste, as well for the process of separating steel from carbon black and the processing of controlling plant emissions to abide environmental constraints were estimated.

$$\text{Total Plant Cost} = \text{Direct Cost} + \text{Indirect Cost}$$

Direct Cost: installed equipment;

Indirect Cost: engineering, design, supervision, management, commissioning, & contractor's fees;

Base equipment cost, indirect and direct cost factors were determined from previous published research[29], [30] and [31].

$$\text{Direct Plant Cost(DPC)} = \text{TEC} (1 + \sum F)$$

TEC: Total Equipment Cost;

F: direct cost factor;

Piping and instrumentation factor= 15%, a structure and building factor (25%), a site improvement factor (15%), and a utilities factor (20%).

$$\text{Indirect Cost (IDC)} = \text{DPC} \times \text{ICF}$$

ICF: Indirect Cost Factor; accounts for the engineering, design, supervision, commissioning, management costs and contractor's fees=30%

$$\text{FCI} = \text{DPC} + \text{IDC}$$

FCI: Fixed Capital Investment;

$$\text{TCR} = \text{FCI} + 10\%(\text{FCI}) + 5\%(\text{FCI})$$

TCR: Total Capital Requirement;

Startup cost = 10% (FCI)

Working capital = 5% (FCI)

The Annual capital charges were determined using the following equation:

$$\text{ACC} = \frac{\text{TCR} \times I}{\{1 - (1 + I)^{-N}\}}$$

I: interest rate; N: Plant life time;

$$\text{Operating Cost} = \text{Fixed Operating Cost (FOP)} + \text{Variable Operating Cost (VOC)}$$

FOP = Labor cost + Maintenance (2.5%FCI) + overheads (2%FCI) + taxes and insurance (1.5%FCI) + other fixed operating costs

VOC= Feedstock + Electricity + General Overheads

Total Production Cost=ACC+ Operating Cost (FC +VC)

In conclusion, the study showed that medium commercial scale plant (144tons/day) was economically feasible giving the lowest production price of crude pyrolysis oil.

Fels et al[32]carried out a techno-economic and environmental assessment of a tire waste pyrolysis plant based on previous experience of the two operating tire plants in Shanghai and Taiwan.

The technical assessment of the tire pyrolysis plant showed that valuable products were obtained; 10% gas, 45% oil, 35% and 10% of carbon and steel respectively. The HHV of gas was 32MJ/kg with a composition CH₄ (24.3%), H₂ (17.6%), C₄ (14.2%), C₂H₆ (13.3%), C₂H₄ (9.4%), CO₂ (11.0%), N₂ (6.2%) and CO (4%). Oil obtained (mostly heavy distillate) was composed of alkenes, alkenes and aromatics having HHV of 39.6%. Carbon obtained could either recycled and given back to the tire manufacturer or processed to be used as activated carbon.

On the other hand, the environmental assessment has showed that waste water (150tonnes/month) resulted from the cleaning of tires could be treated, and the oil obtained (390l/month) could be used for the combustion in the burner. Gaseous emissions as CO, NO_x and SO₂ were at least 100 times less than Canadian standards. The major metallic emissions were in “class 1” roughly 0.16 µg/m³; However

Canadian standard being 50. Estimated Dioxins/Furan (PCDD/F) emissions were 0.005 µg/m³ considered as an insignificant amount.

Economic assessment was done on a base case tire pyrolysis plant with capacity of 10,000 ton/year. The table below shows that the total capital investment would be \$504/t/year.

Table 20 Capital Costs (\$ millions) for Tire Pyrolysis Plant; 10,000 t/year tires

ITEM	BASIS	REFERENCE	VALUE, \$10 ⁶
Equipment (E)	given	Yeung-Chen (2008)	3.00
Other Direct costs	given	Yeung-Chen (2008)	1.13
Working Capital	0.1 (capital)	Peters <i>et al.</i> (2003)	0.50
Contingency	0.08 (capital)	Peters <i>et al.</i> (2003)	0.40
Total Capital	—		5.04 (504/t/year)

Table 21 Operating Revenue and Costs for 10,000 t/year Tire Pyrolysis Plant

OPERATING REVENUE				OPERATING EXPENSES			
ITEM	VALUE	UNIT \$	\$10 ⁶ /y	ITEM	VALUE	UNIT \$	\$10 ⁶ /y
Oil sales	4500 t/year	\$ 400/t	1.80	Power	2000 MWh/y	\$0.05/kWh	0.10
Carbon sales	3500 t/year	\$ 300/t	1.05	Labour	45 people	\$45,000/y	2.03
Steel sales	1000 t/year	\$ 150/t	0.15	Maintenan	—	—	0.05
Tipping fee	10,000 t/year	\$ 80/t	0.80	Other	—	—	0.35
	Total Revenue		3.80		Total Expenses		2.53

The table above shows the operating revenue vs. the operating cost. Revenue is collected from pyrolysis oil sales, carbon and steel sales and the tipping fees which the payments are taken for tire disposal.

In conclusion, the assessment showed that the tire pyrolysis plant could be operating in a safe and non-polluting environment and can produce pyrolysis oil and carbon black with a capability to recover steel. The capital cost was at \$504/year

for each ton of tires processed and the operating costs were at \$250/t. A 15% rate of return would result if the oil could be sold at \$450/t (\$80/bbl) at 0 carbon value (i.e. if carbon wasn't sold) or \$180/t at \$500/t carbon.

On the other hand, the economic feasibility of pyrolysis plants depend on the price of crude oil, therefore, several pyrolysis plants were found economically unprofitable. For instance, Ebenhausen is a pyrolysis plant built according to Hamburg University pyrolysis plant was seen economically unviable. BASF, Ludwigshafen is an industrial plant with capacity of 300,000ton/y that was shut off in 1996 due to economic barriers related to waste supply and gate fees. Therefore, when assessing the economic feasibility of plastic cracking pyrolysis plants, it's necessary to correlate the prices with crude oil prices. Several processes were seen unfeasible when the price of crude oil was at \$30 per barrel but these could see the light today after the price has peaked above \$100 per barrel.

B. Life Cycle Assessment (LCA)

Life cycle assessment is considered one of the best methodology to compare between the different waste management scenarios[33]. This methodology is referred to as “from the cradle to grave approach” as it assesses the performance of waste management technologies in terms of energy and material consumption, direct and indirect emissions and waste generation. The following table shows an evaluation of the principal environmental impact categories for the five scenarios for plastic waste management.

Table 22 Indicators of principal environmental impact categories, as evaluated for the five scenarios for plastic waste management[33]

Impact category	Landfill	Combustion	Mechanical recycling	MR + L-T pyrolysis	MR + hydrocracking
Energy consumption, MJ/kg _{recycled or virgin PET}	<i>51.59</i>	6.45	-5.41	12.14	-11.40
Crude oil consumption, g/kg _{recycled or virgin PET}	<i>1462</i>	995	-74.76	-145.86	-210.65
Water consumption, kg/kg _{recycled or virgin PET}	<i>47.11</i>	45.92	3.48	14.06	25.26
CO ₂ -equivalent, kg/kg _{recycled or virgin PET}	5.3	7.3	1.4	1.7	2.02
Air emissions of organic compounds, g/kg _{recycled or virgin PET}	<i>26.8</i>	14.3	-0.05	1.42	4.78
Waste production, kg/kg _{recycled or virgin PET}	<i>2.49</i>	0.19	0.09	0.20	0.26

*Values in boldface type indicate the best environmental performance, whereas values in italic type indicate the worst.

Mechanical recycling dominates the good environmental performance of the plastic waste management technology. However feedstock recycling (pyrolysis and hydrocracking) schemes show remarkable savings in terms of crude oil consumption, an added value is the notable decrease in emissions when compared to landfilling and combustion scenarios of plastic waste.

C. EXAMPLE APPLICATION

The following table summarizes different pyrolysis processes for plastic wastes, auto shredded residues and tires along with other wastes. Many plants are still in operation; however some ceased operation mainly because their economic viability and profitability were unsatisfactory. For instance, the BASF pyrolysis plant was shut down because a long-term waste supply was not sustained and fees were relatively high. Another plant, Hamburg University plant, was shut down after two years of its operation due to its unprofitability.

Table 23 Pyrolysis processes for plastic wastes, auto shredded residues and tires along with other wastes[34]

Process	Actors involved	Technology	Process description	Input/output	Technical status
Akzo	Akzo Nobel (NL)	Two circulating fluidized beds	Fast pyrolysis in a CFB reactor (700-900°C), where waste is converted with steam into fuel gas, HCl and residual tar, and combustion in the second CFB. The process is based on the Battelle process for biomass gasification	I: shredded MPW with high percentage of PVC, PCV cable, pipe scrap O: HCl, CO, H ₂ , CH ₄ , other hydrocarbons, fly ash	Pilot (30kg/h) since 1994. Some tests on a large scale (200-400 kg/h)
Amoco	Amoco Chem. Corp.		Catalytic cracking at 490-580°C	I: PE, PP, PS, plastic wastes mixed with vacuum gas oil O: naphtha, light mineral oil gases	Pilot since 1991
AMRA	Center of Competence on Env. Risks (I), Univ. of Napels II (I)	Bubbling fluidized bed	Gasification in a BFB of sand, fluidized by air, steam and nitrogen at a temperature between 750 and 900°C	I: polyolefins and RDF shredded at a size <2.5 cm O: syngas, energy	Pilot (20-50kg/h) in Caserta (I)
Battelle	Battelle memorial Inst. (USA)	Two circulating fluidized beds	Gasification in a SFB of sand, fluidized by steam and nitrogen at a temperature between	I: PE, PS, PVC and MPW shredded at a size <2.5 cm O: ethylene, H ₂ , CH ₄	Pilot (9kg/h) in Vermont (USA) since 1992

			800 and 1000°C		
BP polymer cracking	BP Chemicals, Elf Atochem, DSM, Enichem, Fina	Bubbling fluidized bed	Low-temperature pyrolysis (500°C) in a BFB of sand. The product is cleaned from HCl and fine particles and then fractionated	I: clean plastic wastes (<2% PVC) O: mainly waxy hydrocarbon products to be used in existing petrochemical plants and refineries	Pilot (50kg/h) in Grangemouth (UK)
BASF cracking	BASF AG	Melting vessel, indirectly heated	Liquid phase pyrolysis in a 3-stage process: liquefaction at 300°C in a stirred kettle; cracking in a gas fired tubular furnace at 350-480°C; separation of products, oils (60-70%) and gases (20-30%), in a distillation column	I: plastic wastes (max. 8% PVC) O: petrochemical gaseous and liquid feedstocks (naphtha, aromatic compounds, high-boiling oils)	Demonstration (15.000t/y) in Ludwigshafen (D) started in 1994 and shut-down in 1996
Compact Power	Compact Power Ltd (UK)	Tubular reactor + fixed bed	High-temperature pyrolysis (800°C) of the shredded waste conveyed by a screw feeder. Fixed-bed gasification of the char residue. Combustion of gas from pyrolysis and gasification units at 1250°C in a high temperature furnace	I: MSW, sewage sludges, scrap tire crumb O: energy	Pilot (360 kg/h) Demonstration (8000t/y) in Avonmouth (UK) Operational: 60,000t/y in Dargavel (UK)
DBA	Deutsche Babcock-Anlagen	Rotary kiln, indirectly heated	Low-temperature pyrolysis (450-500°C) in an indirectly heated rotary kiln	I: plastic wastes O: energy	Operational: 6t/h, Burgau (D)
Eddith	Thide Environment S.A. (F) and Institut Francais du Petrol (F)	Rotary kiln, externally heated	Drying to reduce moisture until 10%. Low-temperature pyrolysis (450-550°C) in an externally heated rotating tubular reactor. Combustion at 1000°C of produced gas with air coming from the dryer	I: MSW, sewage sludges O: energy, CARBOR® (coke-like product)	Pilot (500kg/h) in Vernouillet (F). Demonstration (1250 kg/h) in Nakaminato (J). Operational: 20,000 t/y, Hoigawa (J) 50,000 t/y, Arras (F)

Ebara	Tsukishima (J)	Two internally revolving fluidized beds	Pyrolysis in a fluidized bed and combustion of the products (mostly oil) in the second fluidized bed reactor	I: plastic wastes O: energy	Operational: 4t/h, Yokohama (J) 3x6.25 t/h, Funabashi (J)
Ebara TwinRec	Ebara Corp. (J), Alstom Power until 2002	Internally revolving fluidized bed + ash-melting system	Gasification of the shredded waste material in a revolving fluidized bed, operated at 500-600°C, which separates combustible part from inert and metallic ones. Combustion of syngas and char in a cyclone combustor (1350-1450°C) at a low excess air ratio	I: ASR, plastic and electronic wastes, sewage sludge, MSW O: energy, ferrous and non-ferrous metals, glass granulate	Pilot (0.3t/h) in Sodeguara (J) and (1 t/h) in Fujisawa (J) since 1997. Operational: 19t/h in Aomori (J), 18t/h in Kawaguchi (J), etc. and 60t/h in Selangor (Malaysia, under construction)
Fuji	Fuji Recycle Ind., Mobil Oil, Nippon Steel Corp., Shinagawa Fuel Corp.	Extruder + fixed bed	Extrusion at 300°C; mixing with liquid product recycled from the pyrolysis reactor; Thermal decomposition in the reactor; catalytic cracking in a fixed bed reactor using a zeolite-based ZSM-5 catalyst at 400°C	I: polyolefines industrial wastes O: gasoline, kerosene, diesel	Pilot (400t/y) in Okegawa City (J) for general plastic waste Demonstration (5000t/y) in Aioi City (J) for industrial plastic waste
Hamburg -ABB	University of Hamburg (D), Asea Brown Boveri	Bubbling fluidized bed	High-temperature pyrolysis (600-800°C) in a BFB, fluidized with liquid-free pyrolysis gas or inert (steam +N ₂) gas	I: shredded plastic wastes (having as low as possible Cl content) O: high yield of olefins, BTX-rich oil	Pilot (40kg/h) at the Univ. of Hamburg. Demonstration (5000t/y) operated in Ebenhausen(D) 1986-1989

Mazda	Mazda Motor Corp.	Fixed bed	Catalytic cracking in a fixed bed reactor that uses $AlCl_3+HCl$ catalyst at 250-450°C	I: ASR O: 60% oil (petrol, kerosene)	Pilot (400t/y)
Mitsui R21	Mitsui Eng. And Shipbuilding (J), Mitsui Babock Energy Ltd (J)	Rotary kiln, indirectly heated	Two stage process that starts with a low-temperature pyrolysis (<450°C) in a rotary kiln and is followed by a high-temperature combustion (1300°C) of the gaseous and solids products in an ash-melting furnace. The process derives from Siemens Schwel-Brenn Process (D)	I: MSW and municipal commercial waste, plastic waste, sludge O: energy, ferrous and non-ferrous metals, glass granulate	Operational: 2x110 t/d, Yame Seibu (J) 2x200 t/d, Toyohashi City (J) 2x70 t/d, Ebetsu City (J) 2x130 t/d, Koga Seibu (J) 2x105 t/d, Nishi Iburi (J) 2x105 t/d, Kyohoku (J)
Nikon	Nikon Rikagaku		Catalytic cracking at 200-250°C and 1bar with metal catalyst	I: plastic wastes of 10mm particle size O: 80% oil	Pilot
Noelle-KRC	Noelle-KRC Energie und Umwelttechnik GmbH (D)	Externally heated rotary kiln + entrained flow reactor	Low-temperature pyrolysis (550°C) in a rotating kiln. Subsequent gasification with pure oxygen (at flame temperature of 1400-2000°C and at a pressure of 2-50bar) of dedusted gas, cooled condensates and water-quenched, screened and pulverized coke-like residues. Recovery of obtained syngas or its combustion in a boiler, gas turbine or engine	I: MSW, industrial waste slurries, dried sewage sludges O: syngas, energy	Pilot (0.5 t/h) in Freiberg (D) Demonstration (116,000t/y) in Northeim (D) for MSW and dewatered sludges

NKT	NKT Res. Center (DN), Danish EPA		Low-temperature pyrolysis (375°C) with subsequent metal extraction. Light plastics are sorted out in the pretreatment section together with sand and metals	I: PVC wastes (cables, flooring, etc.) or MPW to be treated to obtain almost pure PVC O: Metal concentrate (up to 60% lead) for recycling; calcium chloride; coke and organic condensate to be used as fuel	Pilot (200 t/y) since 1998
PKA	PKA Umwelttechnik GmbH&Co. KG (D); PEC-Product en EnergieCentrale (NL)	Rotary kiln, indirectly heated	Drying followed by low-temperature pyrolysis (500-550°C) in a rotary kiln for about 1 h. Gasification of produced at 1000°C to obtain CO/H ₂ -rich gas; char fines are separately gasified by oxygen at 1500°C.	I: MSW, ASR, industrial plastic wastes, spent tires, contaminated soil O: energy	Pilot (24,000t/y) in Aalen-Goldshöfen (D) Operational: 3x4t/h, Delfzijl (NL)
Pyropleq	Mannesmann, Technip (F), WasteGen (UK)	Rotary kiln, indirectly heated	Low-temperature pyrolysis (450-470°C) in a rotary kiln, with internal blades, indirectly heated by hot gases at 550°C. Combustion of the product gas at 1200°C after a high-temperature particulate collection	I: MSW O: energy	Operational: 2x3 t/h, Burgau (D) 2x6.7 t/h Dortmund (D) under construction

VebaOel	VebaOel AG in Gelsenkirchen (VebaPyrolyse anlagen)	Rotary kiln, indirectly heated	High-temperature pyrolysis (650-800°C) of plastic waste, fed into the rotary kiln via a screw feeder. Solid cokes and pyrolytic vapours are sent to further treatments in gasification or hydrogenation plant	I: ASR + vulcanized elastomers O: coke (~80%), oil, gas	Operational: 0.5t/h, Gelsenkirchen (D) 12.5 t/h, Ruhr area (D)
Takuma SBV	Takuma Corp. (J)	Indirectly heated rotary kiln + ash-melting system	Drying of crushed waste followed by low-temperature pyrolysis (500-550°C) in a rotary kiln for about 1 h. Combustion of the pyrolysis gas in a high temperature combustion chamber. The process derives from Siemens Schwel-Brenn Process (D)	I: MSW, ASR, sewage sludge O: energy, iron, aluminum	Demonstration (7000t/y) in Fukuoka (J) Operational: 90t/d, Kanemura (J) ASR 2x81 t/d, Kokubu (J) MSW 2x63 t/d, Oshima (J) MSW
Toshiba	Toshiba (J), Yamanaka		Pyrolysis + gasification + gas cracking	I: ASR	Operational: 20,000 t/y (J)
Von Roll RCP	Von Roll Umwelttechnik AG (CH)	Reciprocating grate + circulating fluidized bed	Pyrolysis in a Von Roll forwards reciprocating grate. Gas and solids residue are sent to a smelting reactor and then to a CFB furnace operated at less than 1000°C	I: ASR, plastic wastes, MSW O: energy	Operational: 6t/h, Bremerhaven (D)

CHAPTER V

CONCLUSION

The pyrolysis of plastic wastes is a promising alternative to landfill and incineration. On one hand, the pyrolysis process is environmentally friendly where life cycle assessments have showed that the emissions of these plants are lower than the Canadian standard. On the other hand, with the rapid increase in world crude oil prices, pyrolysis plants will become economically feasible; where fuel like products could be produced at a lower price.

In this research, different reactor bed materials: silica sand (with and without NaOH), cement and white clay were used to thermally degrade HDPE waste in a pyrolysis batch reactor. These beds altered the lumped product yield as well as the composition of the products. C₁₀-C₄₄ alkanes and C₁₀-C₂₂ alkenes were obtained along with aromatics and alcohols at varying compositions.

The use of catalysts narrowed the carbon chain length of alkanes to C₁₀-C₂₈, as it altered the composition of the products, and decreased the reaction's energy consumption through increasing the rate of polymer decomposition. It is expected that selecting an appropriate bed material with added catalytic refining could upgrade the pyrolysis generated liquids into valuable fuel compounds. We have concluded that cement reactor bed is the most appropriate bed for the production of high liquid yield and low aromatic compounds content, as for the catalytic degradation the combination of cement reactor bed with HBeta catalyst will give the highest yield of liquid with the smallest carbon chain ranging between C₁₁-C₂₉.

During our research we have encountered few difficulties related to the accessibility of certain equipment which led to limiting the accuracy of our work.

Therefore a number of recommendations are suggested for future research in this field:

- Use/acquisition of a thermal gravimetric analysis (TGA) instrument for the purpose of determining the degradation of plastic waste.

- The use of the tube furnace which would help in minimizing the operational limitations encountered with the batch reactor. This includes leakage from the reactor pipings, and the accuracy in monitoring the reactor pressure and temperature. In addition, the collection of products evolved from the pyrolysis experiments would be much easier.

- Study the effect of residence time on the product yield.

- Investigate the use of NaOH with different reactor beds including cement and white clay.

- Analyze the gas product composition with GC/MS.

- Pyrolysis can handle various types of waste; waste tires are a growing environmental problem which should acquire a greater attention. Future research should be driven towards investigating the pyrolysis of waste tires.

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