

RECOVERY OF LIQUID HYDROCARBON FUELS FROM WASTE PLASTICS

A THESIS SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF

Master of Technology
in
Chemical Engineering

By
A.RAMESH BABU



Department of Chemical Engineering
National Institute of Technology
Rourkela
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Under the Guidance of
Prof. R.K. Singh



Department of Chemical Engineering
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2007



**National Institute of Technology
Rourkela**

CERTIFICATE

This is to certify that the thesis entitled, “Recovery of Liquid Hydrocarbon Fuels from Waste Plastics” submitted by Sri A. Ramesh Babu in partial fulfillment of the requirements for the award of Master of Technology in Chemical Engineering with specialization in “Coal Chemical & Fertilizers” at the National Institute of Technology, Rourkela (Deemed University) is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University / Institute for the award of any Degree or Diploma.

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TABLE OF CONTENTS

S.No.	Title	Page No.
	ACKNOWLEDGEMENT	i
	ABSTRACT	iv
	LIST OF FIGURES	vii
	LIST OF TABLES	x
1	INTRODUCTION	01
2	LITERATURE REVIEW	06
2.1	Plastics	07
2.1.1	Types of waste Plastics & Their Recyclability	07
2.1.2	The composition of waste Plastics	08
2.1.3	Recycling – Effect of Contamination	09
2.1.4	Sources of waste Plastics	10
2.2	Recycling Techniques of Waste Plastics	11
2.2.1	Material Recycling of Waste Plastics	12
2.2.2	Energy Recovery Techniques	15
2.2.3	Chemical/Feedstock Recycling of Waste Plastics	16
2.2.3.1	Chemolysis	17
2.2.3.1.1	Hydrolysis	18
2.2.3.1.2	Alcoholysis	18
2.2.3.1.3	Glycolysis	18
2.2.3.2	Gasification/ Partial Oxidation	18
2.2.3.3	Pyrolysis	19
2.2.3.3.1	Hydro cracking of waste plastics	19
2.2.3.3.2	Thermal cracking of waste plastics	20
2.2.3.3.3	Catalytic Cracking of waste plastics	21

2.3	Catalytic Cracking of Polyolefins	21
2.3.1	Effect of Polymer type on Product Distribution	22
2.3.2	Effect of Particle/Crystallite size on Product Distribution	22
2.3.3	Process Design	23
2.3.3.1	Catalyst Contact Mode	23
2.3.3.2	Reactor Type	23
2.3.3.2.1	Batch and Semi-Batch Reactors	24
2.3.3.2.2	Fixed bed Semi-Batch Reactors	24
2.3.3.2.3	Fluidized bed Batch reactors	24
2.3.3.2.4	Continuous Flow Reactors (CFRs)	24
2.3.3.3	Effect of Feed Composition	25
2.3.3.4	Effect of Other Process Parameters	26
2.4	The Impact on Climate change and Human Health	27
3.	EXPERIMENTAL METHODS	29
3.1	Polymer Materials	30
3.1.1	Collection of Waste Plastic Materials	30
3.1.2	Preparation of HDPE & LDPE Pellets	30
3.2	Catalyst Materials	32
3.2.1	Silica Alumina	33
3.2.1.1	Structural Analysis of Si-Al by SEM	33
3.2.1.2	Composition Analysis of Si-Al by XRD	36
3.2.2	Mordenite	36
3.2.2.1	Composition Analysis of Mordenite by XRD	37
3.2.3	Activated Carbon	38
3.2.3.1	Structural Analysis of Activated Carbon by SEM	38
3.2.3.2	Composition Analysis of Activated Carbon by XRD	41
3.3	Pyrolysis	42

3.3.1	Thermal Pyrolysis	42
3.3.2	Catalytic Pyrolysis	42
4	RESULTS AND DISCUSSION	45
4.1	Thermal degradation of HDPE	46
4.2	Catalytic Degradation of HDPE	50
4.2.1	Catalytic Cracking of Waste HDPE by Silica Alumina	50
4.2.2	Catalytic Cracking of Waste HDPE by Mordenite	55
4.2.3	Catalytic Cracking of Waste HDPE by Activated Carbon	60
4.2.5	Isothermal catalytic and Non-catalytic degradation of Waste HDPE Plastics	65
4.3	Physical Analysis of Liquid Products	66
4.3.1	Solid residue	68
4.3.2	Liquid Hydrocarbon Products	68
4.3.2.1	Physical Properties of Liquid Fuels	68
4.3.2.1.1	Specific Gravity & Density	69
4.3.2.1.2	Pour Point	69
4.3.2.1.3	Flash Point	69
5	CONCLUSIONS AND RECOMMENDATIONS	71
	REFERENCES	74

ABSTRACT

Plastics are non-biodegradable polymers of mostly containing carbon, hydrogen, and few other elements such as chlorine, nitrogen etc. Due to its non-biodegradable nature, the plastic waste contributes significantly to the problem of Municipal Waste Management. The production of plastics is significantly growing. Nowadays the plastic production is more than 200MT worldwide annually. According to a nation wide survey, conducted in the year 2004, approximately 10,000 tones (ten thousand tones) of plastic waste were generated every day in our country (India), and only 60% of it was recycled, balanced 40% was not possible to dispose off. So gradually it goes on accumulating, thereby leading to serious disposal problems. Plastic is derived from petrochemical resources. In fact these plastics are essentially solidified oil. They therefore have inherently high calorific value.

Waste Plastics are mostly land filled or incinerated; however, these methods are facing great social resistance because of environmental problems such as air pollution and soil contamination, as well as economical resistance due to the increase of space and disposal costs. In a long term neither the land filling nor the incineration solve the problem of wastes, because the suitable and safe depots are expensive, and the incineration stimulates the growing emission of harmful and greenhouse gases e.g. NO_x, SO_x, CO_x etc. Accordingly, recycling has become an important issue worldwide. This method can be classified as energy recovery, material recycling and chemical recycling. Among them one of the prevalent alternative methods is the production of converted fuel and chemicals by means of the thermal or catalytic degradation of polymers.

The main objective of this study was to investigate the effect of catalyst amount, reaction temperature, plastic type (especially HDPE) and weight ratio of waste plastic to catalyst, with a semi-batch reactor, based on the results of yields and yield distributions of liquid product as a function of lapsed time. And to study the product yields and their distribution with different types of catalysts (Silica- Alumina, Activated Carbon, Mordenite) in the catalytic degradation of waste plastics with respect to time and temperature. And also for finding the effect of particle size and structure of the catalyst on product distribution and yield. One more objective is

quantitative analysis of gaseous, liquid and solid products from thermal and catalytic degradation of HDPE and the comparison of the physical properties of the liquid products and to suggest the best reactor design along with the economical factors effecting the commercialization of this technique.

We have studied extensively the catalytic nature of HDPE both under catalytic and non-catalytic methods with the application of some important suitable catalysts, and about the catalyst characterization by the application of SEM and XRD. The cracking temperature of HDPE was very when compare with other plastics as we have observed from the literature. It was minimum 460°C. we have reached better yield (76%) of liquid products with the application of Mordenite catalyst at this temperature. But, the time taken for the completion of the reaction was very high about one hr.

The yield and the composition of the liquid product vary along with feed to catalyst ratio and reaction temperature. And all the liquid products we got were analyzed for their physical properties. The specific gravities of all the samples were existed in the range of gasoline and diesel range of fuels. We have also tested pour point, flash point and fire point. These were varied along with their individual composition.

LIST OF FIGURES

Fig. No.	Title	Page. No.
Fig 3.1	Waste plastic materials collected for the process	30
Fig 3.2	Stirring during the melting process	31
Fig 3.3	Absorption of gases in water bath	32
Fig 3.4	SEM photographs of fresh Si-Al catalyst at 350 Magnification	34
Fig 3.5	SEM photographs of Used Si-Al catalyst at 350 Magnification	34
Fig 3.6	SEM photographs of fresh Si-Al catalyst at 6500 Magnification	35
Fig 3.7	SEM photographs of Used Si-Al catalyst at 6500 Magnification	35
Fig 3.8	Composition Analysis of Si-Al catalyst by XRD	36
Fig 3.9	Composition Analysis of Mordenite catalyst by XRD	37
Fig 3.10	SEM photographs of fresh activated Carbon catalyst at 350 Magnification	39
Fig 3.11	SEM photographs of used activated Carbon catalyst at 350 Magnification	39
Fig 3.12	SEM photographs of fresh activated Carbon catalyst at 6500 Magnification	40
Fig 3.13	SEM photographs of used activated Carbon catalyst at 6500 Magnification	40
Fig 3.14	Composition Analysis of Activated Carbon catalyst by XRD	41
Fig 3.15	Schematic representation of the current project (catalytic degradation of waste plastics for liquid fuel recovery)	43
Fig 3.16	Experimental set up of Pyrolysis	44
Fig 4.1	Reaction time vs Reaction temperature in thermal degradation of HDPE	47
Fig 4.2	The yields of liquid and gaseous products Vs Reaction Temperature	48
Fig 4.3	Solidified liquid product	48
Fig 4.4	Product distribution in thermal degradation of HDPE	49
Fig 4.5	Silica Alumina catalyst before (a) use and after (b) use	50
Fig 4.6	Product Distribution from catalytic degradation of HDPE using Si-	51

	Al catalyst	
Fig 4.7	Feed / catalyst vs time for the catalytic degradation of HDPE using Si-Al catalyst.	52
Fig 4.8	Feed / catalyst vs time for the catalytic degradation of HDPE using Si-Al catalyst	53
Fig 4.9	Time vs temperature for the catalytic degradation of HDPE using Silica-Al catalyst	53
Fig 4.10	Feed / catalyst vs liquid product yield for the catalytic degradation of HDPE using Si-Al catalyst	54
Fig 4.11	Temperature vs liquid product yield for the catalytic degradation of HDPE using Si-Al catalyst.	54
Fig 4.12	Modernite catalyst Before (1) use and After (2) use	55
Fig 4.13	Product Distribution from catalytic degradation of HDPE using Mordenite catalyst	56
Fig 4.14	Feed / catalyst vs time for the catalytic degradation of HDPE using Mordenite catalyst	57
Fig 4.15	Feed / catalyst vs time for the catalytic degradation of HDPE using Mordenite catalyst	58
Fig 4.16	Time vs temperature for the catalytic degradation of HDPE using Mordenite catalyst	58
Fig 4.17	Feed / catalyst vs liquid product yield for the catalytic degradation of HDPE using Mordenite catalyst	59
Fig 4.18	Temperature vs liquid product yield for the catalytic degradation of HDPE using Mordenite catalyst	59
Fig 4.19	Activated Carbon catalyst Before (a) use and After (b) use	60
Fig 4.20	Product Distribution from catalytic degradation of HDPE using A-C catalyst	61
Fig 4.21	Feed / catalyst vs temp for the catalytic degradation of HDPE using A-C catalyst	62
Fig 4.22	Feed / catalyst vs time for the catalytic degradation of HDPE using Act-C catalyst	63

Fig 4.23	Feed / catalyst vs %yield for the catalytic degradation of HDPE using A-C catalyst	63
Fig 4.24	Temperature vs liquid product yield for the catalytic degradation of HDPE using A-C catalyst	64
Fig 4.25	Time vs temperature for the catalytic degradation of HDPE using Act-C catalyst	64
Fig 4.26	Product Distribution of Isothermal degradation of Waste HDPE at 500°C& 4:1 of Feed/catalyst ratio	65
Fig 4.27	Different liquid products samples obtained during cracking	66
Fig 4.28	Solid carbon residue obtained after cracking	67

LIST OF TABLES

Table No.	Title	Page No.
Table 1.1	Per capita Consumption of Plastics in Some Selected Countries in the World	02
Table 1.2	Calorific Values of Some Plastic Materials	03
Table 2.1	Important physical properties of Plastics	07
Table 2.2	Types of waste plastics and their recyclables	09
Table 2.3	Common contaminants in recycled polymers	10
Table 2.4	Waste versus virgin pyrolysis of HDPE using ZSM-5 and under similar operating conditions	26
Table 2.5	Influence of certain process conditions in polyolefin pyrolysis	27
Table 3.1	Product distribution of LDPE & HDPE materials from melting	31
Table 4.1	Product distribution of thermal degradation of HDPE	46
Table 4.2	Product Distribution from catalytic degradation of HDPE using Si-Al catalyst	51
Table 4.3	Experimental Conditions for catalytic degradation of HDPE using Si-Al catalyst with liquid product yield	52
Table 4.4	Product Distribution from catalytic degradation of HDPE using Mordenite catalyst	55
Table 4.5	Experimental Conditions for catalytic degradation of HDPE using Mordenite catalyst with liquid product yield	56
Table 4.6	Product Distribution from catalytic degradation of HDPE using Mordenite catalyst	61
Table 4.7	Experimental Conditions for catalytic degradation of HDPE using A-C catalyst with liquid product yield	62
Table 4.8	Product distribution of Catalytic and non-catalytic degradation of waste HDPE plastics at F/C ratio 4:1	65
Table 4.9	Some of the physical properties of the liquid products	70

Chapter 1

INTRODUCTION

Background History

Objective

INTRODUCTION

Plastics have become an indispensable part in today's world. Due to their light-weight, durability, energy efficiency, coupled with a faster rate of production and design flexibility, these plastics are employed in entire gamut of industrial and domestic areas [1]. Plastic have moulded the modern world and transformed the quality of life. There is no human activity where plastics do not play a key role from clothing to shelter, from transportation to communication and from entertainment to health care [2].

Plastics are non-biodegradable polymers of mostly containing carbon, hydrogen, and few other elements such as chlorine, nitrogen etc. Due to its non-biodegradable nature, the plastic waste contributes significantly to the problem of Municipal Waste Management. The production of plastics is significantly growing. Nowadays the plastic production is more than 200MT worldwide annually. [3] The per capita consumption of plastics from a last few decades increasing rapidly, it is showed in the Table 1.1, the status of per capita consumption of plastics in some selected countries worldwide [7].

Table 1.1: Per capita Consumption of Plastics in Some Selected Countries in the World.

Country	Per Capita Consumption in Kg.
India (1998)	1.6
India (2000)	4.0
Vietnam	1.5
China	6.0
Indonesia	8.0
Mexico	13.0
Thailand	18.0
Malaysia	22.0
Western Europe	60.0
Japan	70.0
North America	78.0

According to a nation wide survey, conducted in the year 2004, approximately 10,000 tones (ten thousand tones) of plastic waste were generated every day in our country, and only 60% of it was recycled, balanced 40% was not possible to dispose off. So gradually it goes on accumulating, thereby leading to serious disposal problems. [1]. Plastic is derived from petrochemical resources. In fact these plastics are essentially solidified oil. They therefore have inherently high calorific value. The calorific values of some of the plastic materials along with coal and some of the petroleum products are shown in table2 [6].

Table 1.2: Calorific Values of Some Plastic Materials.[6,41]

Material	Btu per pound	Kilojoules per kilo
Coal	11,500	27,000
Diesel fuel	19,780	46,000
Gas oil	19,780	46,000
Heavy fuel oil	18,490	43,000
Kerosene	20,210	47,000
Light Distillate	20,640	48,000
Light Fuel oil	18,920	44,000
Medium Fuel Oil	18,490	43,000
Petrol	19,264-20,167	44,800-46,900
Plastics		
Polyethylene	20,000	46,500
Polypropylene	19,300	45,000
Polystyrene	17,900	41,600
PET	9,290	21,600
PVC	8,170	19,000

Theoretically this energy can be captured and transformed into other useful forms. It is a well-known fact that energy can neither be created nor destroyed but merely transformed. One of the most common methods of transforming energy from for example, a solid to another form is thermal treatment. Through the various methods of thermal treatment one may obtain heat, electricity or chemicals suitable for other applications [6].

Waste Plastics are mostly land filled or incinerated; however, these methods are facing great social resistance because of environmental problems such as air pollution and soil contamination, as well as economical resistance due to the increase of space and disposal costs [4]. In a long term neither the land filling nor the incineration solve the problem of wastes, because the suitable and safe depots are expensive, and the incineration stimulates the growing emission of harmful and greenhouse gases e.g. NO_x, SO_x, CO_x etc [3]. Accordingly, recycling has become an important issue worldwide. This method can be classified as energy recovery, material recycling and chemical recycling. Among them one of the prevalent alternative methods is the production of converted fuel and chemicals by means of the thermal or catalytic degradation of polymers [5].

Plastics pyrolysis, on the other hand, may provide an alternative means for disposal of plastic wastes with recovery of valuable liquid hydrocarbons. In pyrolysis or thermal cracking, the polymeric materials are heated to high temperatures, so their macromolecular structures are broken down into smaller molecules and a wide spectrum of hydrocarbons are formed. These pyrolytic products can be divided into a gas fraction, a liquid fraction consisting of paraffins, olefins, naphthenes and aromatics (PONA), and solid residues. In catalytic cracking, more aromatics and naphthenes are selectively formed in the presence of commercial fluid cracking catalysts (FCC) or reforming catalysts, so that the productivity and economics of pyrolysis processes are improved. [2] Cracking was realized both in the batch and continuous systems. It was also examined that the results obtained by batch cracking are useable to the continuous reactor planning. The goal of these experiments was the developing of a waste free so-called green technology [3].

The main objective of this study was to investigate the effect of catalyst amount, reaction temperature, plastic type (especially HDPE) and weight ratio of waste plastic to catalyst, with a

semi-batch reactor, based on the results of yields and yield distributions of liquid product as a function of lapsed time. And to study the product yields and their distribution with different types of catalysts (Silica- Alumina, Activated Carbon, Mordenite and a new catalyst) in the catalytic degradation of waste plastics with respect to time and temperature. And also for finding the effect of particle size and structure of the catalyst on product distribution and yield.

One more objective is quantitative analysis of gaseous, liquid and solid products from thermal and catalytic degradation of HDPE and the comparison of the physical properties of the liquid products and to suggest the best reactor design along with the economical factors effecting the commercialization of this technique.

Chapter 2

LITERATURE REVIEW

Plastics

Recycling Techniques of the Waste Plastics

Catalytic Cracking of Polyolefins

The Impact on Climate Change and Human Health

LITERATURE REVIEW

2.1 Plastics:

Plastics are macromolecules, formed by Polymerization and having the ability to be shaped by the application of reasonable amount of heat and pressure or some other form of force [8].

Polymerization is the process by which individual units of similar or different molecules ("mers") combine together by chemical reactions to form large or macromolecules in the form of long chain structures, having altogether different properties than those of starting molecules ("mers"). Several hundreds, and even thousands of "mers" combine together to form the macromolecules, or what we call, Polymers.

2.1.1 Physical Properties of Plastics:

Plastics have physical characteristics, which need to be considered when processing any product. The following table contains physical data for several commercially available plastics.

Table 2.1: Important physical properties of Plastics [8]

Plastic No.	Plastic	Thermal Properties			Strength		Density g/cc	Float?
		Tm	Tg	Td	Tensile	Compressive		
		°C	°C	°C	Psi	Psi		
1	PET (polyethyleneterep hthalate)	245 265	73 80	21 38	7000 10500	11000 15000	1.29 1.40	Compl etely sinks
2	HDPE (high density polyethylene)	130 137		79 91	3200 4500	2700 3600	0.952 0.965	Floats
3	V/PVC (polyvinyl chloride)		75 105	57 82	5900 7500	8000 13000	1.30 1.58	Compl etely sinks
4	LDPE (low density polyethylene)	98 115	-25	40 44	1200 4550		0.917 0.932	floats
5	PP (polypropylene)	168 175	-20	107 121	4500 6000	5500 8000	0.900 0.910	floats
6	PS (polystyrene) Styron		74 105	68 96	5200 7500	12000 13000	1.04 1.05	Compl etely sinks

2.1.2 Types of Waste Plastics & Their Recyclability [8]

The following table shows different types waste plastics and their recyclability with standard mark for recycling to identify easily with many examples.

Depending upon their nature and properties, the polymers are classified as Plastics, Rubbers or Elastomers and Fibres.

There are mainly two types of Plastics: Thermoplastics and Thermosetting Plastics

Thermoplastics are those, which once shaped or formed, can be softened by the application of heat and can be reshaped repeatedly, till it loses its property.

Example: Polyethylene, Polypropylene, Nylon, Polycarbonate etc.








Applications are: Polyethylene Buckets, Polystyrene Cups, Nylon ropes etc.

Thermosetting Plastics are those, which once shaped or formed, cannot be softened by the application of heat. Excess heat will char the material.

Example: Phenol formaldehyde, Urea Formaldehyde, Melamine Formaldehyde, Thermosetting Polyester etc.

Applications are: Bakelite Electrical switches, Formica / sermica table tops, melamine Cutlery etc.

Table 2.2: Types of waste plastics and their recyclables: [9]

Mark	TYPE	RECYCLABLE	ABBREVIATION	DESCRIPTION
	Type 1	Yes	PET	Polyethylene Terephthalate Beverages.
	Type 2	Yes	HDPE	High-Density Polyethylene Milk, detergent & oil bottles, toys, containers used outside, parts and plastic bags.
	Type 3	Yes, but not common	V/PVC	Vinyl/Polyvinyl Chloride Food wrap, vegetable oil bottles, blister packages or automotive parts.
	Type 4	Yes	LDPE	Low Density Polyethylene, Many plastic bags, shrink-wraps, garment bags or containers.
	Type 5	Yes	PP	Poly Propylene. Refrigerated containers, some bags, most bottle tops, some carpets, and some food wrap.
	Type 6	Yes, but not common	PS	Polystyrenes. Through away utensils, meatpacking, protective packing.
	Type 7	Some	_____	OTHER. Usually layered or mixed plastic.

2.1.3 Recycling – Effect of Contamination:

In polymers used for recycling, contamination is omnipresent, resulting in reduction of the quality of recycling. It can be in the form of dirt, printing inks, paper, metals, foil, additives, pesticides, partially oxidized polymers; contamination by foreign bodies can be noticed even in PET and HDPE bottles collected from roadsides. In very old scraps of building products, electrical and electronic system, vehicles, furniture etc., which now come for recycling may contain very high concentration of additives in particular, fire retardants, which are now banned. Contamination can be reduced if consumers can be organized to segregate polymer products

before disposal. However accidental or unintentional mixtures, multi-component products etc do pose problems.

Table 2.3: Common contaminants in recycled polymers:[8]

Polymer	Recycle source	Contamination
PET	Beverage bottles	PVC, green PET, Al, water, glue, oligomers
HDPE	Milk/water bottles	PP, milk residue, pigments, paper, EPS, cork
LDPE	Greenhouse films	Insecticides, soil, Ni, oxidation products
LDPE	Shopping bags	Paper receipts, printing ink, food scraps
PP	Battery cases	Pb, Cu, acid, grease, dirt
HDPE	Detergent bottles	Paper, glue, surfactants, bleach, white spirit
PET	Photographic film	Silver halides, gelatin, caustic residues
Phenolic	Circuit boards	Cu, tetrabromobisphenol A
LDPE	Multi layer film	Ethylene vinyl alcohol, polyamide, ionomer
PVC	Beverage bottles	PET, PE, paper, Al foil, PP
ABS	Appliance housings	Polybrominated flame retardants
SBR	Automobile tires	Steel wire, fiber, oil extender
LDPE	Mulch film	Soil (up to 30%), iron (up to 3% in soil)

The simple and widely used process for separation is by using differences in density, e.g. HDPE Cups and PET bottles. Separation and purification by chemical reaction process will give better results. Mixtures of solvents allowing selective dissolution can be used for multi component plastic products.

2.1.4 Sources of Waste Plastics

Plastic wastes can be classified as industrial and municipal plastic wastes according to their origins; these groups have different qualities and properties and are subjected to different management strategies [4].

Industrial plastic wastes:

Industrial plastic wastes are those arising from the plastics manufacturing and processing industry. Usually they are homogeneous or heterogeneous plastic resins, relatively free of contamination and available in fairly large quantities. For industrial plastic wastes, repelletization and remolding seem to be a simple and effective means of recycling. But when plastic wastes are heterogeneous or consist of mixed resins, they are unsuitable for reclamation. In this case thermal cracking into hydrocarbons may provide a suitable means of recycling, which is termed chemical recycling.

Municipal plastic wastes:

Municipal plastic wastes normally remain a part of municipal solid wastes as they are discarded and collected as household wastes. Plastics usually account for about 7% of the total MSW by weight and much more by volume. In order to recycle municipal plastic wastes, separation of plastics from other household wastes is required. Although MSW separation technologies have been studied extensively, it is still not possible to classify MSW mechanically and obtain marketable fractions. So waste separation at the household is required with regard to recycling of municipal plastic wastes.

If household wastes are separately disposed into three parts:

- (1) Combustibles such as paper, kitchen waste, textiles, and wood,
- (2) Incombustibles such as metals, glass, ceramics, and
- (3) Plastics, then the collected plastics will be mixed plastic wastes with major components of PE, PP, PS, PVC, etc.

2.2 Recycling techniques of waste plastics: [9]

Basically there are 4 different ways of recycling of plastics: [2]

1. **Primary Recycling** – Conversion of waste plastics into products having performance level comparable to that of original products made from virgin plastics. These methods are undergone in to material recycling methods.

2. **Secondary Recycling** – Conversion of waste plastics into products having less demanding performance requirements than the original material. These are also a part of material recycling methods.
3. **Tertiary Recycling** – The process of producing chemicals / fuels / similar products from waste plastics. These methods are known as chemical recycling or feedstock recycling methods.
4. **Quaternary Recycling** – The process of recovering energy from waste plastics by incineration.

Plastics recycling will cover a wide range of different methods. The main areas are given below.

- a) Material recycling
- b) Chemical recycling
- c) Energy Recycling

Combinations of these are well known and in use to some extent. In all these methods is common that the yield of organic material is not more than the input of plastic waste material. The recycling routes of plastics discussed here below.

2.2.1 Material recycling of waste Plastics [10]

Initial upgrading: Once the plastic has been collected, it will have to be cleaned and sorted. The techniques used will depend on the scale of the operation and the type of waste collected, sorting of plastics can be by polymer type (thermo set or thermoplastic for example), by product (bottles, plastic sheeting, etc.), by color, etc

Size reduction techniques: Size reduction is required for several reasons; to reduce larger plastic waste to a size manageable for small machines, to make the material denser for storage and transportation, or to produce a product, which is suitable for further processing. There are several techniques commonly used for size reduction of plastics.

Cutting: is usually carried out for initial size reduction of large objects. It can be carried out with scissors, shears, saw, etc.

Shredding: is suitable for smaller pieces. A typical shredder has a series of rotating blades driven by an electric motor, some form of grid for size grading and a collection bin. Materials are fed into the shredder via a hopper, which is sited above the blade rotor. The product of shredding is a pile of coarse irregularly shaped plastic flakes, which can then be further processed.

Agglomeration: is the process of pre-politicizing soft plastic by heating, rapid cooling to solidify the material and finally cutting into small pieces. This is usually carried out in a single machine. The product is coarse, irregular grain, often called crumbs.

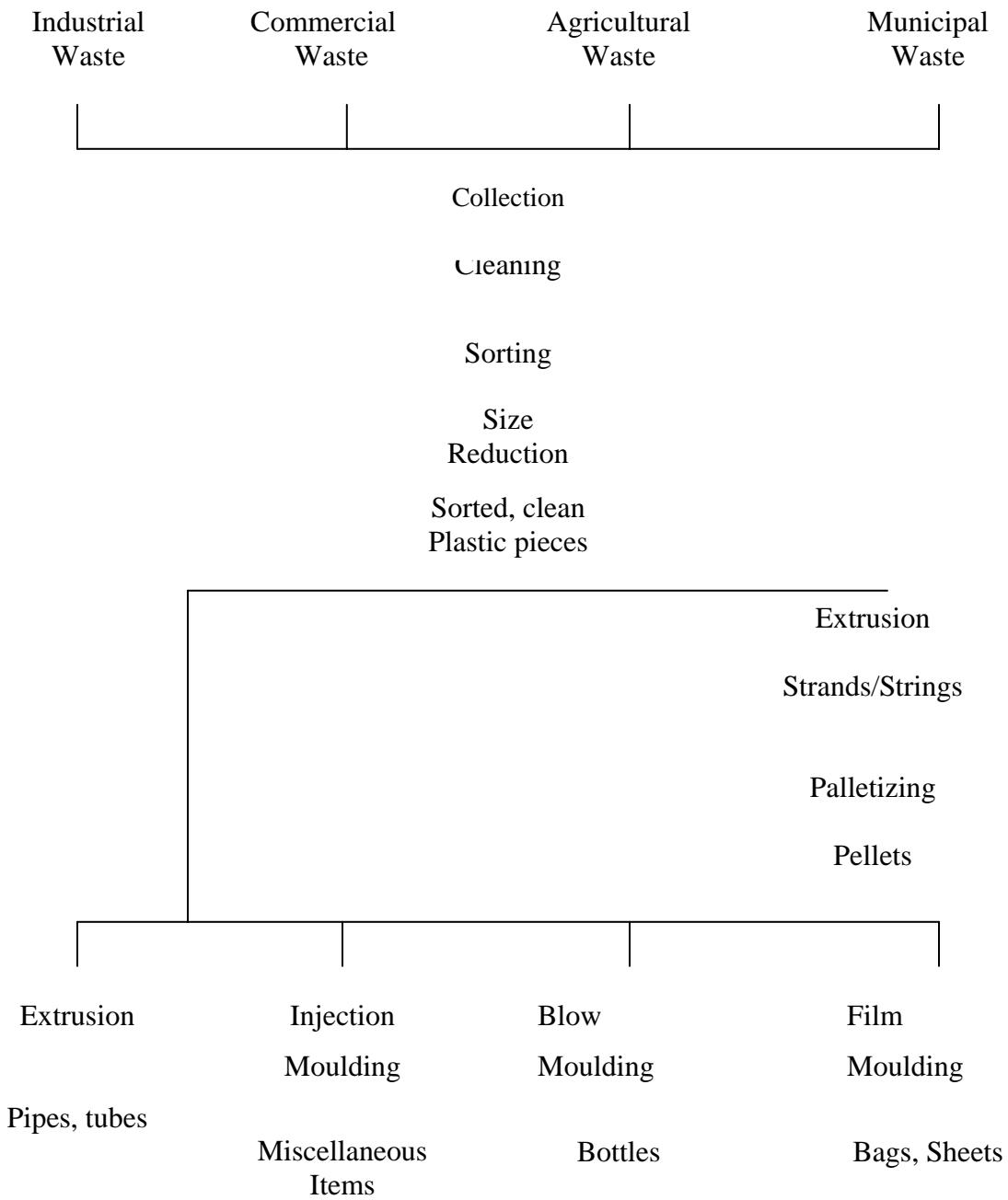
Further processing techniques:

Extrusion and palletizing: The process of extrusion is employed to homogenize the reclaimed polymer and produce a material that is subsequently easy to work. The reclaimed polymer pieces are fed into the extruder, are heated to induce plastic behavior and then forced through a die (see the following section on manufacturing techniques) to form plastic spaghetti, which can then be cooled in a water bath before being palletized.

Manufacturing techniques:

Extrusion: The extrusion process used for manufacturing new products is similar to that outlined above for the process preceding pelletisation, except that the product is usually in the form of a continuous 'tube' of plastic such as piping or hose.

Injection moulding: The first stage of this manufacturing process is identical to that of extrusion, but then the plastic polymer emerges through a nozzle into a split mould. This type of production technique is used to produce moulded products such as plates, bowls, buckets, etc.



Blow moulding: Again the spiral screw forces the plasticized polymer through a die. This manufacturing technique is used for manufacturing closed vessels such as bottles and other containers.

Film blowing: Film blowing is a process used to manufacture such items as garbage bags. It is a technically more complex process than the others described in this brief and requires high quality raw material input. The process involves blowing compressed air into a thin tube of polymer to expand it to the point where it becomes a thin film tube. One end can then be sealed and the bag or sack is formed.

2.2.2 Energy Recovery System:

The two main alternatives for treating municipal and industrial polymer wastes are energy recycling, where wastes are incinerated with some energy recovery and mechanical recycling. The incineration of polymer waste meets with strong societal opposition. Here one incineration method is described for energy recovery from waste plastics including PVC.

Municipal Solid waste Incinerators: [11]

Municipal solid waste incinerators are a proven, robust technology for dealing with very different mixed waste types of different origin. The typical MSWI is built for dealing with waste of a caloric value between 9 and 13 MJ/kg. MSWI's are currently a default technology for the treatment of integral household waste in countries such as Denmark, Sweden, the Netherlands and Germany. In Europe, on average some 7% of this integral household waste consists of plastics.

Description of the process:

Municipal Solid Waste Incinerators (MSWIs) are in principle built for the treatment of municipal or similar industrial wastes. In such a kiln the waste, after it is tipped into storage and has been made more homogeneous, is transferred to a grid-type kiln. This rolling grid is placed under a certain slope, so that the waste is slowly transported with such a speed, that full incineration takes place. At the end of the grid slags remain. The slags are treated in order to recover the ferrous and non-ferrous fraction. Just like in the case of a rotary kiln, the flue gases pass through cleaning equipment such as an electro filter, an acid scrubber, a caustic scrubber, an active carbon scrubber. In modern MSWIs, the energy is also recovered as much as possible. The flue gas cleaning process leads to fly ash and flue gas cleaning residue, which has to be land filled. A large fraction of the

chlorine input into the MSWI ends up in the flue gas-cleaning residue. A process has been developed for the neutralization of flue gases with sodium bicarbonate. As such, this has no significant influence on the amount of flue gas cleaning residue generated. However, this residue can be treated at a separate plant recovering soda and salt. In that case, much lower residual amounts of hazardous waste have to be disposed of.

Resource needs and Emissions:

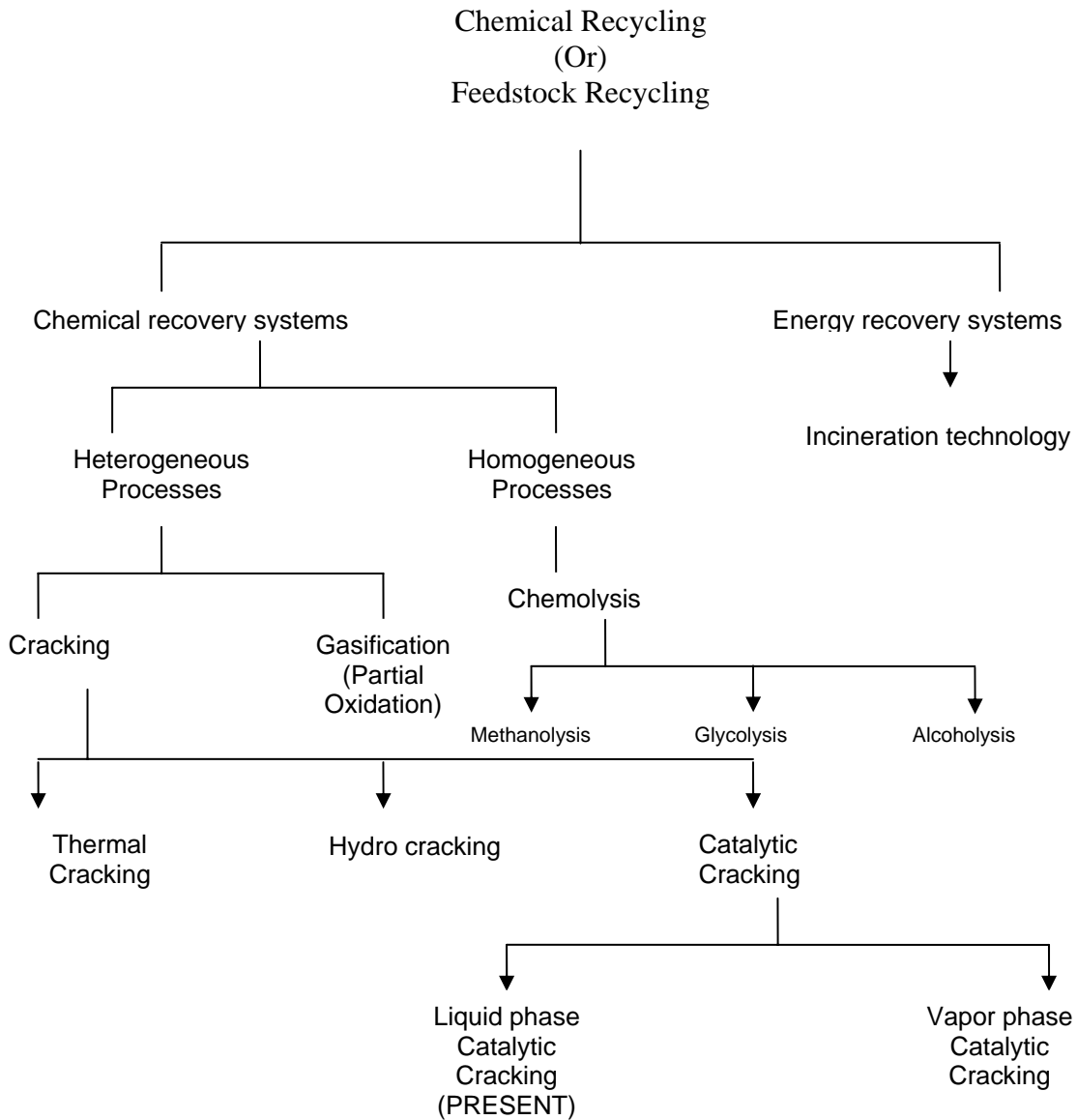
The most decisive is the influence of the type of flue gas cleaning equipment on the amount of flue gas cleaning residue. Wet scrubbers result in residues whose salt fractions can be discharged. Other scrubbers result in a flue gas cleaning residue that has to be land filled 100%.

- As a function of the composition of the waste: the component-related emissions to air, water and waste residues on the basis of the mass balances;
- As a function of the caloric value of the waste: the process-related emissions to air and water;
- As a function of the ash content of the waste: the amount of slags and fly ash.

2.2.3 Chemical Recycling:

Feedstock recycling also known as chemical recycling or tertiary recycling, aims to convert waste polymers into original monomers or other valuable chemicals. These products are useful as feedstock for a variety of downstream industrial processes or as transportation fuels. The different routes of chemical recycling are showed below.

Chemical recycling techniques are spread into the following ways.



2.2.3.1 Chemolysis/ Solvolysis:

Individual plastics are chemically treated or depolymerized and turned back into monomers. Chemolysis uses chemical agents as catalysts for complete depolymerisation of plastic resins. Chemolysis includes a range of processes such as glycolysis, hydrolysis, methanolysis, alcoholysis, saponification dialysis etc.

2.2.3.1.1 Hydrolysis: [12]

Hydrolysis leads to direct recovery of the original raw materials by targeted reaction of water molecules at the linkage points of the starting materials. All hydrolysable plastics such as polyamides, polyesters, polycarbonates, polyureas, and polyurethanes are resistant to hydrolysis under normal conditions of use.

Hydrolysis of polyurethane foams is particularly interesting since they have a very low density (30 kg/m^3) and thus take up considerable storage space. Product yields are outstanding. Almost 100% of the polyether and ca. 90% of the amine can be recovered. The regenerated materials can be reused directly, together with fresh starting material, for the same foam material. Raw material in the waste can thus be fed back again to the same production process and the environment is thus not burdened by that quantity of waste material.

2.2.3.1.2 Alcoholysis: [12]

Chemical degradation polyurethanes can also be achieved by alcoholysis to give a polyhydroxy alcohol and small urethane fragments formed by transesterification. Carbon dioxide is not formed in this reaction. If a diol is used as the alcohol, then the urethane fragments also contain terminal hydroxyl groups. These polyhydroxy alcohols can be converted directly to polyurethane foam following the addition isocyanates and varying proportions of new polyhydroxy alcohols.

2.2.3.1.3 Glycolysis:

The degradation of polymers in the presence of glycol such as ethylene glycol or diethylene glycol is known as glycolysis. And in the presence of methanol it is known as Methanolysis.

2.2.3.2 Gasification or Partial oxidation: [13]

The direct combustion of polymer waste, which has a good calorific value, may be detrimental to the environment because of the production of noxious substances such as light hydrocarbons, NO_x, sulfur oxides and dioxins. Partial oxidation (using oxygen and/or steam), however, could generate a mixture of hydrocarbons and synthesis gas (CO and H₂), the quantity and quality being dependent on the type of polymer used. A new type of waste gasification and smelting system using iron-making and steel-making technologies has been described by Yamamoto et al.,

reportedly to produce a dioxin-free and high-calorie purified gas. Hydrogen production efficiency of 60–70% from polymer waste has been reported for a two-stage pyrolysis and partial oxidation process. Co-gasification of biomass with polymer waste has also been shown to increase the amount of hydrogen produced while the CO content reduced. The production of bulk chemicals, such as acetic acid, from polyolefins via oxidation using NO and/or O₂, is also possible.

2.2.3.3 Pyrolysis: [13]

Cracking processes break down polymer chains into useful lower molecular weight compounds. This can be achieved by reaction with hydrogen, known as hydrocracking or by reaction in an inert atmosphere (pyrolytic methods), which can be either thermal or catalytic cracking.

2.2.3.3.1 Hydro cracking: [13]

Hydro cracking of polymer waste typically involves reaction with hydrogen over a catalyst in a stirred batch autoclave at moderate temperatures and pressures (typically 423–673 K and 3–10 MPa hydrogen). The work reported, mainly focuses on obtaining a high quality gasoline starting from a wide range of feeds. Typical feeds include polyolefins, PET, polystyrene (PS), polyvinyl chloride (PVC) and mixed polymers, polymer waste from municipal solid waste and other sources, co-mixing of polymers with coal co-mixing of polymers with different refinery oils such as vacuum gas–oil and scrap tyres alone or co-processed with coal. To aid mixing and reaction, solvents such as 1-methyl naphthalene, tetralin and decalin have been used with some success. Several catalysts, classically used in refinery hydrocracking reactions, have been evaluated and include transition metals (e.g., Pt, Ni, Mo, Fe) supported on acid solids (such as alumina, amorphous silica–alumina, zeolites and sulphated zirconia). These catalysts incorporate both cracking and hydrogenation activities and although gasoline product range streams have been obtained, little information on metal and catalyst surface areas, Si/Al ratio or sensitivity to deactivation is quoted.

2.2.3.3.2 Thermal cracking: [4]

Thermal cracking, or pyrolysis, involves the degradation of the polymeric materials by heating in the absence of oxygen. The process is usually conducted at temperatures between 500- 800°C and results in the formation of a carbonized char and a volatile fraction that may be separated into condensable hydrocarbon oil and a non-condensable high calorific value gas [1]. The proportion of each fraction and their precise composition depends primarily on the nature of the plastic waste but also on process conditions.

In the case of polyolefins like polyethylene or polypropylene, thermal cracking has been reported to proceed through a random scission mechanism that generates a mixture of linear olefins and paraffins over a wide range of molecular weights [1]. In other cases, like polystyrene and polymethylmetacrylate, thermal degradation occurs by a so-called unzipping mechanism that yields a high proportion of their constituent monomers [1].

In pyrolytic processes, a proportion of the species generated directly from the initial degradation reaction are transformed into secondary products due to the occurrence of inter and intramolecular reactions. The extent and the nature of these reactions depend both on the reaction temperature and also on the residence of the products in the reaction zone, an aspect that is primarily affected by the reactor design.

In addition, reactor design also plays a fundamental role, as it has to overcome problems related to the low thermal conductivity and high viscosity of the molten polymers. Several types of reactors have been reported in the literature, the most frequent being fluidized bed reactors, batch reactors and screw kiln reactors [1].

Pyrolysis and gasification of plastics and other carbonaceous fuels have been studied extensively in the past. Recent progress in converting plastic wastes into petrochemicals by means of pyrolysis in the absence of a catalyst has been reviewed by Kaminsky. Four types of mechanisms of plastics pyrolysis have been proposed:

- (a) End-chain scission or depolymerization: The polymer is broken up from the end groups successively yielding the corresponding monomers.
- (b) Random-chain scission: The polymer chain is broken up randomly into fragments of uneven length.
- (c) Chain-stripping; Elimination of reactive substitutes or side groups on the polymer chain, leading to the evolution of a cracking product on one hand, and a charring polymer chain on the other.
- (d) Cross-linking: Formation of a chain network, which often occurs for thermosetting polymers when heated.

These different mechanisms and product distributions are to some extent related to bond dissociation energies, the chain defects of the polymers, and the aromaticity degrees, as well as the presence of halogen and other hetero-atoms in the polymer chains. For common plastics the decomposition mechanisms and associated monomer yield are listed in Table 2. The pyrolysis of PS occurs by both end-chain and random chain scission and the monomer recovery is only some 45%. For PE and PP, the main components of municipal plastic wastes, the pyrolysis occurs through the random-chain scission mechanism and a whole spectrum of hydrocarbon products is obtained. The gas and oil yields from polyolefin pyrolysis are about 50 and 40% wt. of the feed at 750°C, respectively, and the oil fraction consists mainly of higher boiling point hydrocarbons (tar).

2.3 Catalytic cracking of Polyolefin: [4]

A number of experimental studies have been carried out by various researchers with the objective of improving liquid hydrocarbons yield from plastics pyrolysis by introducing suitable catalysts, Common plastics such as PE and PP have already been tested extensively; the catalysts tested are mainly those used in the petrochemical refinery industry. The laboratory experimental set-up in these studies is a mostly flow reactor; it may be useful to distinguish between two modes of catalyst usage: ‘liquid phase contact’ and ‘vapor phase contact’. In ‘liquid phase contact’, the catalyst is contacted with melted plastics and acts mainly on the partially degraded oligomers from the polymer chains; in ‘vapor phase contact’, the polymer is thermally degraded into hydrocarbon vapors which are then contacted with the catalyst. The current project is developing for the production of liquid hydrocarbon fuel by the application of liquid phase contact catalytic cracking.

2.3.1 Effect of Polymer Type on Product distribution

PONA distributions of catalyzed decompositions show that the olefin yield far exceeds the yield of paraffins, naphthenes, or aromatics (PNAs) in the pyrolysis of PP and HDPE [14,15]. Lee *et. al.* also showed that the catalytic degradation of waste LDPE produced more paraffins and aromatics than those of waste HDPE and PP [15]. Marcilla *et. al.* investigated the pyrolysis of different PE grades (LLDPE, HDPE, LDPE) by thermogravimetry. They observed slight differences in their decomposition behaviors but only in the presence of the catalyst (MCM-41) [16]. Conversely, PS pyrolysis exhibits high yields of aromatics, as high as 97wt% of liquid product, far exceeding those obtained with PE or PP (< 20 wt % of liquid yield) [15, 17]. Consequently, very low yields in PNAs are observed. This is attributed to the polycyclic nature of PS and the thermodynamic challenge posed in converting cyclic compounds to aliphatic chains or alkene compounds. A closer look at the aromatic yield in many of these catalyzed reactions reveals that, the product selectivity is higher for benzene, toluene and ethyl benzene unlike in thermal pyrolysis, where the main product is styrene [17, 18]. This clearly indicates the similarity and variance in the cracking mechanisms among these three polyolefins.

2.3.2 Effect of Particle/Crystallite Size on Product Distribution

The effect of catalyst particle size has only been sparsely studied in literature. You *et. al.* investigated the effect of particle size of MFI zeolites on the catalytic degradation of polyethylene wax and found that whereas conversion decreased with particle size, product quality increased [25]. Furthermore, particle sizes in the nano-range have been investigated. Serrano *et. al.* reported conversions as high as 90%, temperatures less than 350°C for the cracking of PP, LDPE and HDPE using nano-crystalline ZSM-5 [19]. Aguado *et. al.* observed similar results in the batch pyrolysis of PP and LDPE mixtures using nano-HZSM5 [26]. Based on these results, it can also be deduced that nano-ZSM-5 catalyzed reactions result in very high gas yields in the range of C₃-C₆ products, and apparently in much higher concentrations than is observed with micron-sized ZSM-5. These nano-sized particles are this effective because of their increased surface area. Conversely, high surface area combined with a very small pore system poses great difficulty in achieving decent amounts of gasoline range products in the C₅-C₁₂ range. Moreover, the nano-catalyst selectivity to liquid products is also very limited [26, 19]. This could be resolved by investigating

the particle size effect with catalysts that are selective to gasoline range liquid products such as FCC catalysts.

Costa *et. al.* found that a submicron base Y-zeolite for their FCC catalyst formulation showed a reduction in cracking of gas oil but showed a low selectivity for coke [27]. On the other hand, Tonetto *et. al.* observed that the effect of zeolite crystallite size on conversion and product distribution depended on the size of the decomposed hydrocarbon molecules [20]. The processes used in both studies, including the synthesis and embedment of sub-micron into an FCC catalyst seem both labor intensive and costly procedures. Subsequently, one may infer that an easier and economical approach might be to consider varying already formulated FCC catalysts with particle sizes ranging in the sub-microns. The effect of FCC catalyst fines on PP and HDPE pyrolysis will be discussed in this thesis.

2.3.3 Process Design

Thus far, the effects of catalyst and polymer type on the resulting product distribution in polyolefin pyrolysis have been discussed. Literature shows that the distribution can also be affected by other process parameters such as the means of polymer and catalyst contact during degradation, reactor type, feed composition (virgin/waste plastic) and degradation process conditions. To avoid a lengthy bibliography, only the most recent (after 1999) and relevant works will be discussed in this review.

2.3.3.1 Catalyst Contact Mode

One may be able to investigate the catalytic steps involved in polymer degradation by considering different modes of catalyst introduction to the polymer feed. Sakata *et. al.* investigated two modes of contact in the batch pyrolysis of PP using various solid acids: “liquid phase contact” and “vapor phase contact” [28]. For the catalytic degradation in the liquid phase contact, both catalyst and polymer are placed in the reactor and heated to the operating temperature. Whereas, with the vapor phase contact mode, the polymer is first thermally degraded into HC vapors and then contacted with the catalyst. It was observed the HC vapors underwent further cracking in the vapor phase whereas the product yield in the liquid or melt phase contact did not differ significantly from that obtained by purely thermal degradation of PP [28]. In this study, the liquid phase contact mode was used along with different types of catalyst to produce liquid hydrocarbons from waste HDPE.

2.3.3.2 Reactor Type

A wide range of reactors has been used on a lab-scale in polyolefin pyrolysis. The reactor set-ups investigated thus far falls under one of the following categories: Batch, Continuous flow (CFR), modifications or combinations of either of the aforementioned.

2.3.3.2.1 Batch and Semi-Batch Reactors [30]

A common variable in batch and semi-batch operations is nitrogen, which is used for the continuous removal of volatiles from the reactor vessel. The products are then collected by passing the vapors through a condensation system. Most are made out of pyrex or stainless steel. A key disadvantage with this is the high reaction times observed. Furthermore, under batch operation, it seems that the potential of a catalyst is minimized with similar product yields to thermal at similar conditions. From an industrial viewpoint, continuous reaction systems are preferred to batch set-ups for operational reasons.

2.3.3.2.2 Fixed Bed Semi-Batch reactor [30, 21]

Polymer and catalysts samples are heated separately and reacted by vapor phase contact. Degraded polymer fragments are carried to the catalyst bed/mesh by a carrier gas, in most cases N_2 . Typically the catalyst bed is heated to a higher temperature than the polymer bed.

2.3.3.2.3 Fluidized bed batch reactors [22-23]

Riser simulator reactors are fluidized batch reactors, specifically designed to simulate similar conditions found in a catalytic riser reactor used in the FCC process. It is adapted for liquid phase catalytic reaction, in which heat from the catalysts could vaporize the melt polymer feed while simultaneously cracking the resulting hydrocarbons.

2.3.3.2.4 Continuous Flow Reactors (CFRs) [24]

More recently, researchers have moved focus towards reactors with greater feasibility in the industrial arena such as fluidized bed reactors, which mimic the FCC unit in the petroleum industry. Generally, CFRs are characterized by much shorter residence time (less than a few seconds to a few minutes), improved uniformity and dispersion. Most of the more recent works in polyolefin pyrolysis are on fluidized bed reactors. The use of continuous flow reactors in polyolefin pyrolysis prior to 1998 has been discussed [24].

The University of Hamburg, in particular, has done a lot of research in feedstock recycling from waste plastics using FCCs, and has subsequently developed the ‘Hamburg process’ which makes use of an indirectly heated fluidized bed [17]. During catalytic cracking, quartz sand is replaced by the respective FCC catalyst as packing material. Amongst the various catalysts investigated, FCCs produced the most decent liquid yields in PE pyrolysis.

Unlike a batch reactor, a fluidized bed reactor is suited for pyrolysis because it provides very good heat and material transfer rates hence generating largely uniform products. However, the disadvantages are many and include:

- Broad residence time distribution of solids due to intense mixing.
- Attrition of bed internals and catalyst particles.
- Difficulty in scale-up.
- Defluidization problems [26].
- Requires large amounts of catalysts.
- Low liquid yields due to ‘over cracking’.

On the other hand, other continuous systems, such as the three-step continuous flow pyrolysis process involving a pre-heat, cracking reactor and separation zones, have been investigated by a few. In this method the polymer is first pre-heated to a molten state in a CFR such as an extruder and driven into the ‘reactor’ where it is further ‘cracked’ at elevated temperatures..

2.2.7.3 Effect of Feed Composition

Many have demonstrated that plastics waste can indeed be converted to useful chemical feedstock by both non-catalytic [29, 14, 15] and catalytic pyrolysis [23]. The present issues are the necessary scale up, minimization of waste handling costs and optimization of gasoline range products for a wide range of plastic mixtures or waste. In addition, controlling the product distribution is still an issue with waste and mixtures. Waste contents like PVC and biomass do have an influence on the pyrolysis products.

In general, the decomposition of polyolefin mixtures occurs roughly in the same range as their virgin counterparts (350 -500°C). However, waste polyolefins may degrade at slightly lower temperatures and achieve higher conversions than the respective virgin polyolefins [29,]. As with virgin plastics, the addition of catalysts in waste pyrolysis greatly influence product yields and conversion rates; however, the disparities between waste and virgin polyolefin pyrolysis lie mainly in the resulting product composition [14]. It is clear that during pyrolysis, interactions between the different materials in a waste feed have a significant effect on the selectivity of specific liquid and gaseous product components as shown in Table 2.3.

Typically, PE pyrolysis favors mostly the formation of paraffins; however, upon increasing its PS or PP content, the yield of aromatic and alkenic products is greatly enhanced, thus improving its

octane value [14]. Due to the radicals formed during PS decomposition, the conversions of PP and PE are improved by PS addition. Conversely, PS decomposition seems to be immune to effects by either of the other polyolefins.

Table 2.4: Waste versus virgin pyrolysis of HDPE using ZSM-5 and under similar operating conditions.

Yield (wt% of feed)	Virgin HDPE	Waste HDPE ([34]) *
Gas	87.1	90.65
Liquid	0	3.71
Coke	1.5	3.43
Residue	11.4	1.69
Gaseous product breakdown		
C1-C4	72.6	56.37
C5-C8	24.6	34.22
BTX	2.7	1.66

Approximate waste composition: 38 wt% HDPE, 24wt% LDPE, 30wt% PP, 7wt% PS, 1wt% PVC.

2.2.7.4 Effect of other Process Parameters

The effect of other process parameters such as reaction temperature, pressure, reaction time and catalyst loading has been investigated in literature. These are summarized in Table2.4.

Table 2.5: Influence of certain process conditions in polyolefin pyrolysis

Process Parameter	Results
Temperature	<ul style="list-style-type: none"> • Conversion increases with temperature resulting in decrease of aliphatic content. • Dermibas <i>et. al.</i> observed that gaseous products (C2-C4) and liquid products (C5-C9) increased and decreased with temperature respectively [31]. • Effect of the catalysts on the yields and structure of products

	becomes less significant with increasing temperature.
Pressure	<ul style="list-style-type: none"> • Murata <i>et. al.</i> demonstrates the inverse relation of pressure to temperature in the pyrolysis of polyethylene [33].
Residence time [32]	<ul style="list-style-type: none"> • Key parameter in fluidized bed reactors. Generally conversion increases with residence time. • Miskolczi <i>et. al</i> observed that the catalyst activity of HZSM-5 and an FCC catalyst decreased with increasing cracking time in the pyrolysis of HDPE waste. • Effect of residence time on product yield is more pronounced at lower than higher temperatures
Catalyst loading [26, 32]	<ul style="list-style-type: none"> • Conversion increases with catalyst loading.

2.4 The impact on climate change and human health:

Recent research for the Community Recycling Network casts doubt on whether pyrolysis and gasification are the right processes for dealing with our residual municipal waste. The research modeled impacts from different treatment methods using data on the chemical and physical characteristics of residual waste once a recycling rate of 60 per cent had been achieved. The researchers used life-cycle analysis to examine the impacts of treatment methods on climate change and human toxicity [10].

Climate change

Waste disposal contributes towards climate change, for example through the release of methane from landfill sites or the burning of fossil fuel based plastics. Sending untreated waste to landfill and incineration are the worst options for climate change. Pyrolysis and gasification are likely to replace renewable energy such as wind and solar because they are included in the Renewables Obligation, which requires energy companies to buy and sell 10 per cent renewable energy. Pyrolysis and gasification are therefore poor options in climate change terms. This could obviously change if the Government was to take pyrolysis out of the Renewables Obligation.

Human toxicity

Human toxicity is a measure of the potential risk to health from a plant. Like incineration, pyrolysis and gasification produce emissions:

- Air emissions include acid gases, dioxins and furans, nitrogen oxides, sulphur dioxide, particulates, cadmium, mercury, lead and hydrogen sulphide;
- Solid residues include inert mineral ash, inorganic compounds, and any remaining unreformed carbon (which is also inert) – these can be between 8 and 15 per cent of the original volume of waste;
- Other emissions include treated water – used to wash the waste in the pre-treatment stage, and clean the gas.

The research for the Community Recycling Network again suggested that untreated waste going to landfill was by far the worst option for human toxicity, followed by standard incineration. Pyrolysis performed well. However, there are two important warnings attached to these conclusions.

First, the researchers did not evaluate the toxic impacts of ash residues. These impacts could be significant, especially over a long time period (100 – 1000 years) as they leach from landfills. If ash had been included, it is likely that the thermal treatments would be amongst the worst performers in terms of human toxicity.

Second, firm conclusions about human toxicity are difficult to draw, because even the best emissions data is incomplete and the true impact of most chemicals and the impacts of mixtures of chemicals are poorly understood.

Chapter 3

EXPERIMENTAL METHODS

Polymer Materials

Catalyst Materials

Pyrolysis

Thermal Pyrolysis

Catalytic Pyrolysis

EXPERIMENTAL METHODS

3.1 Polymer Materials

3.1.1 Collection of the waste plastic materials

The waste plastics used by me for the process consisted mainly of HDPE products in the form of used plastic disposable glasses. A person was allotted for collecting the material. He collected the glasses that were used by students during the time of semester examination and the various functions taking place in our college. Payment was made to him on a daily basis for his labor. The LDPE packaging bags used for the packaging of new computers was also used as raw materials.



Fig 3.1: waste plastic materials collected for the process.

3.1.2 Preparation of HDPE & LDPE pellets:

The material that was collected was subjected to cutting by using scissors manually. This was done to increase the surface area of contact of the material during melting process. The material was then directly taken into the melting process. For this purpose a cylindrical stainless steel vessel of 27.2 cm diameter and 30 cm height was used. The weight of the vessel was 1395g. The vessel was put on an electrical domestic heater and a temperature of around 150°C was maintained for melting. Total time taken for single batch of reaction was around 15 minutes. The following table shows the composition of the final products of melting of a single batch.

Table 3.1: Product distribution of LDPE & HDPE materials from melting.

Material Used	Wt. of the material	Wt. of final pellets	Wt. of gases evolved	%age loss
HDPE	200g	195g	5g	2.5
LDPE	300g	286g	14g	4.67



Fig 3.2: Stirring during the melting process.

Continuous stirring was done during the process to avoid sticking of the plastic materials to the bottom of the vessel and for better distribution of heat. As the table above shows, the gases coming from the process are directed into the water bath. Here the gases are completely absorbed.



Fig 3.3: Absorption of gases in water bath

According to literature the gases coming from the process are in the range of LPG and HCl gases [1]. But we were unable to collect the gases. During the stirring process, the lid of the vessel was opened intermittently. Then some of the gases escaped to the atmosphere. The molten plastic in liquid form was cooled to room temperature to obtain the solid form. Then the material was broken into small sizes in the range of 10mm-30mm. These pellets were ready for the pyrolysis process.

3.2 Catalyst Materials

The waste plastics are thermally or catalytically degraded into gases and oils, which can be utilized as resources of either fuels or chemicals over solid acid catalysts, relatively sharp distribution curves with peak tops at the lighter hydrocarbons. It is well known that the oils produced by catalytic degradation over solid acids contain less olefinic compounds and are rich in the aromatics compared to the oils obtained by thermal degradation. Although the catalysts used in these works

were solid acids such as silica-alumina and zeolite, the relationship between the acid amounts and strength of the catalysts and the compositions of the resulting oils is not yet well defined.[35] The catalysts employed in this work were purchased from outside through the consultancy SS Enterprises, Rourkela. They didn't mention any composition. Hence, we have analyzed those samples for their structural analysis and their composition by using Scanning Electro Microscopy (SEM) and for finding composition we have used X Ray Diffraction (XRD).

3.2.1 Silica Alumina:

Silica Alumina is white amorphous powdery catalyst. It consists of 87% SiO₂, 13% Al₂O₃ from the literature and the matching composition of some identified elements has been showed by XRD in the fig.

3.2.1.1 Structural Analysis of Si-Al Catalyst by SEM:

JEOL, JSM-6480LV Scanning Electro Microscope was used to analyze the structure of the Si-Al catalyst. The photographs were as showed below. From the SEM test of catalyst it can be seen that the catalyst has large number of pores in its structure, therefore its surface area for catalysis reaction is more. But again the pores are very large in size, which reduces its activity a bit when compare with the some of the other catalysts. It can be seen that clearly at 350 magnification the large pore sizes. Here, we have compared the catalyst's structures before and after use of it. We may observe that the residue remained from the reaction was formed on the surface of catalyst and the pores were filled by it.

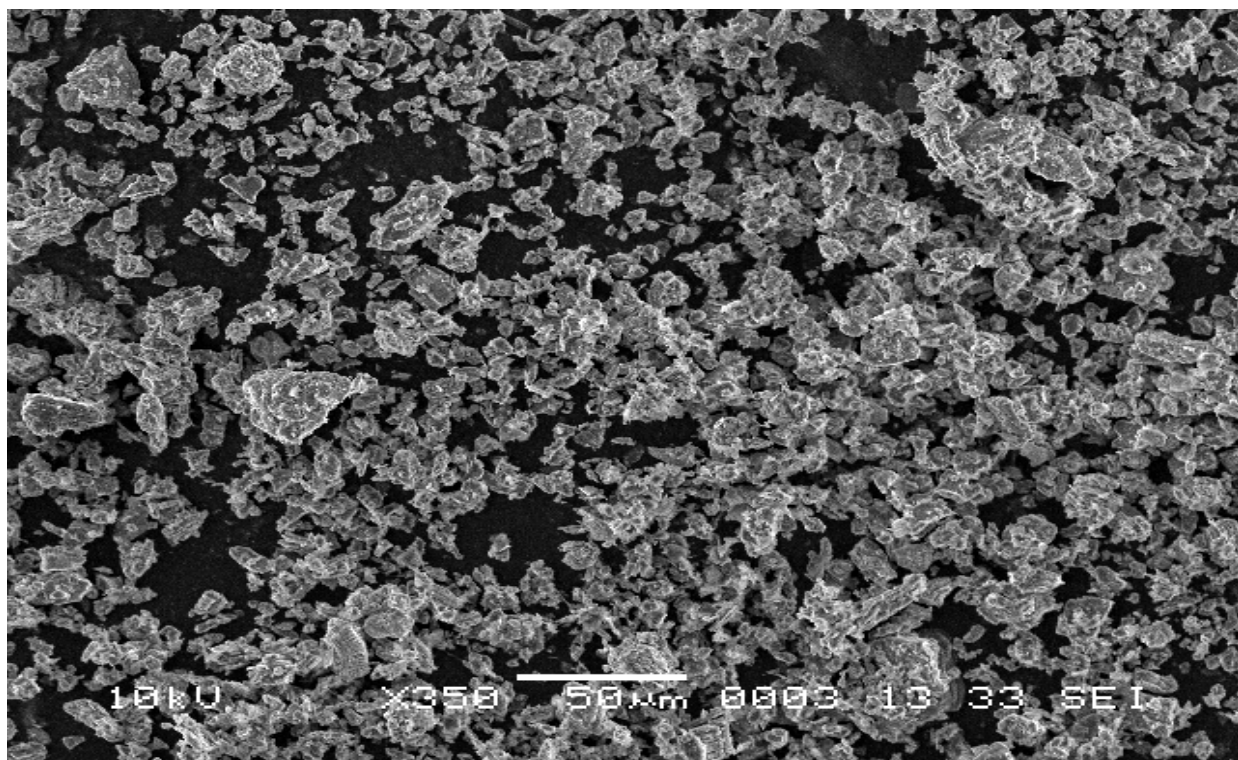


Fig 3.4: SEM photographs of fresh Si-Al catalyst at 350 Magnification.

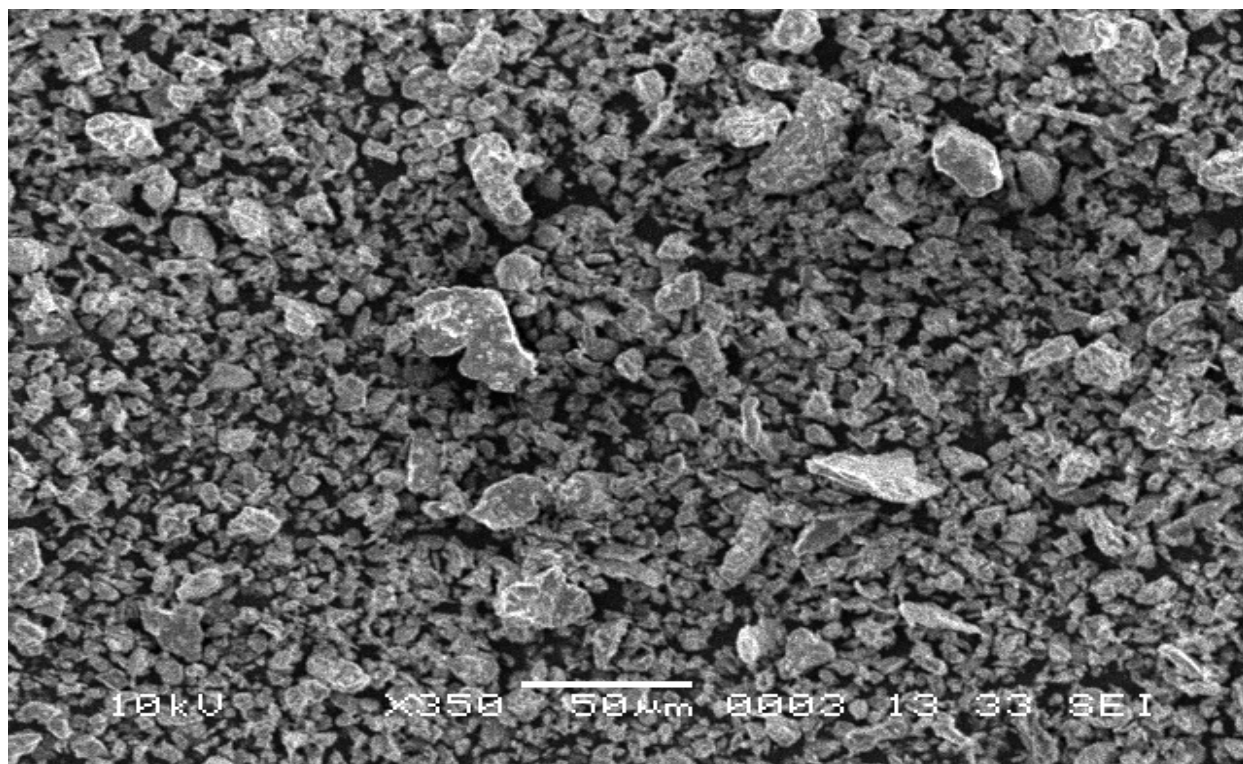


Fig 3.5: SEM photographs of Used Si-Al catalyst at 350 Magnification.

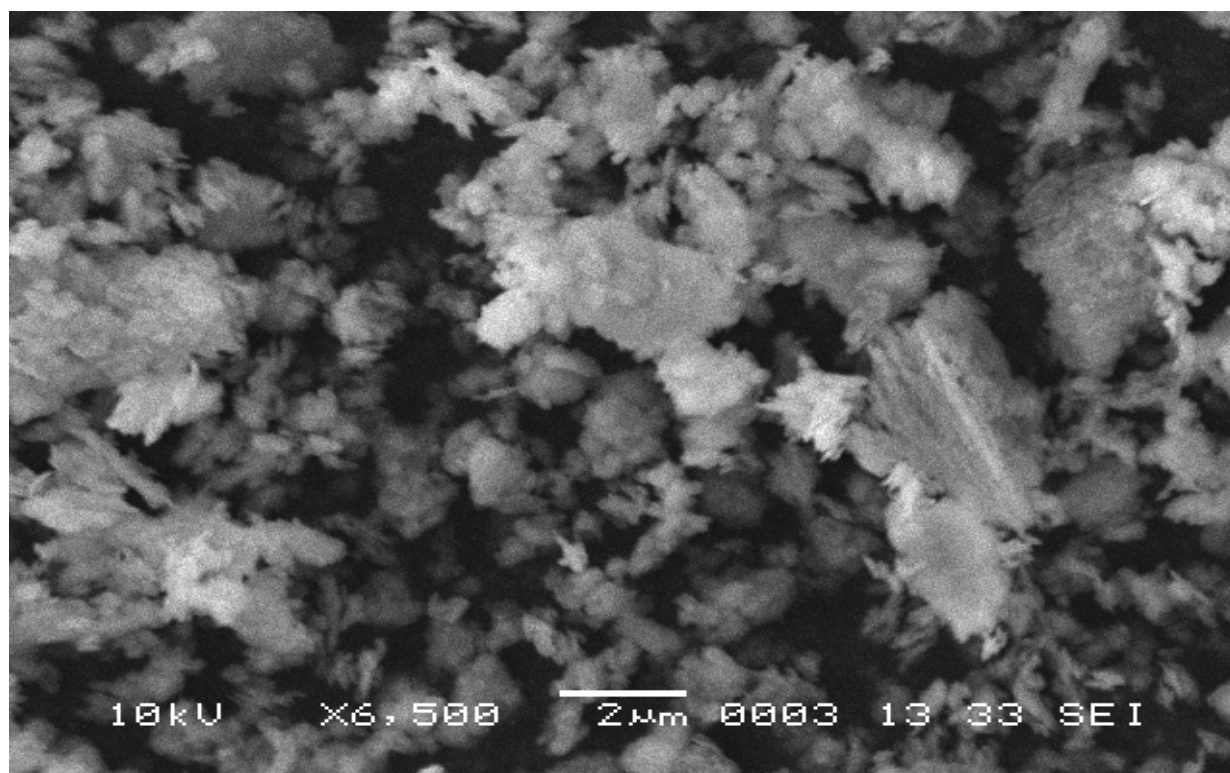


Fig 3.6: SEM photographs of fresh Si-Al catalyst at 6500 Magnification.

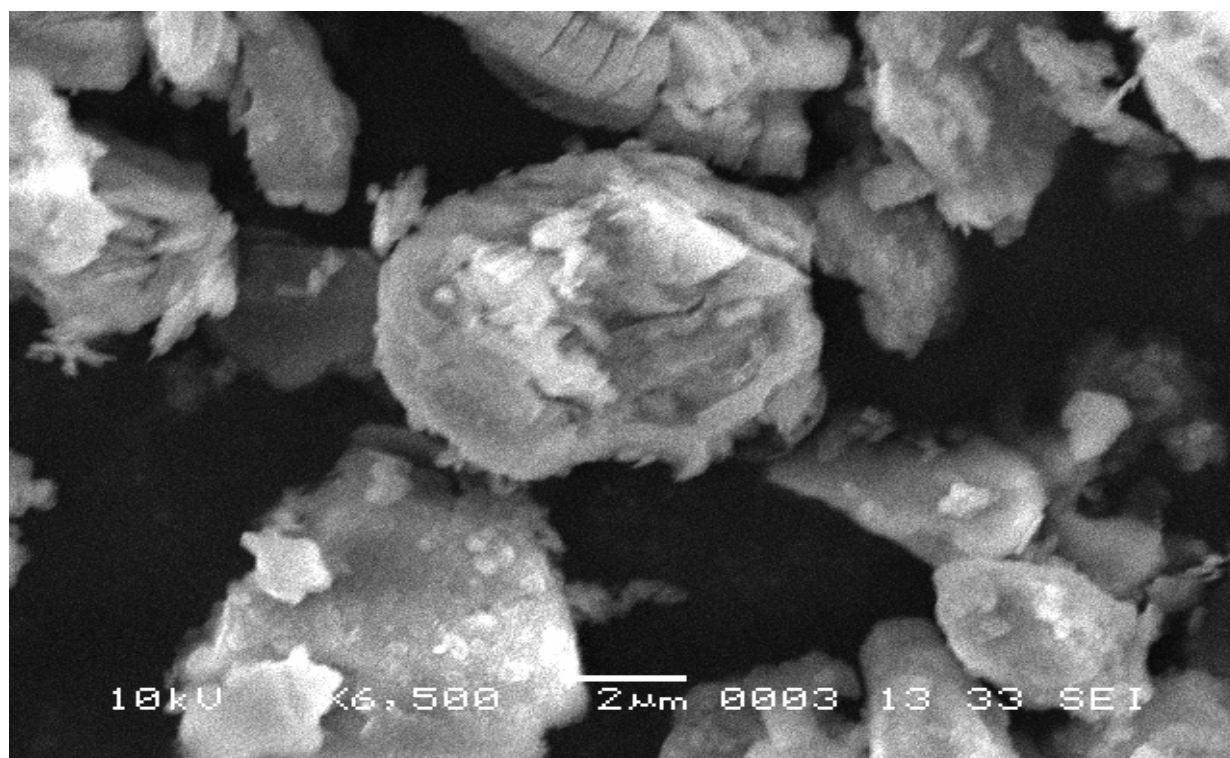


Fig 3.7: SEM photographs of Used Si-Al catalyst at 6500 Magnification.

3.2.1.2 Composition Analysis of Si-Al Catalyst By XRD:

X'Pert, the Philips analytical X-Ray diffractor was used for our work. It can be seen that from the fig. the presence of silica and alumina in the combination of Kaolinite, Quartz. These were matched about 95 % of the existing composition.

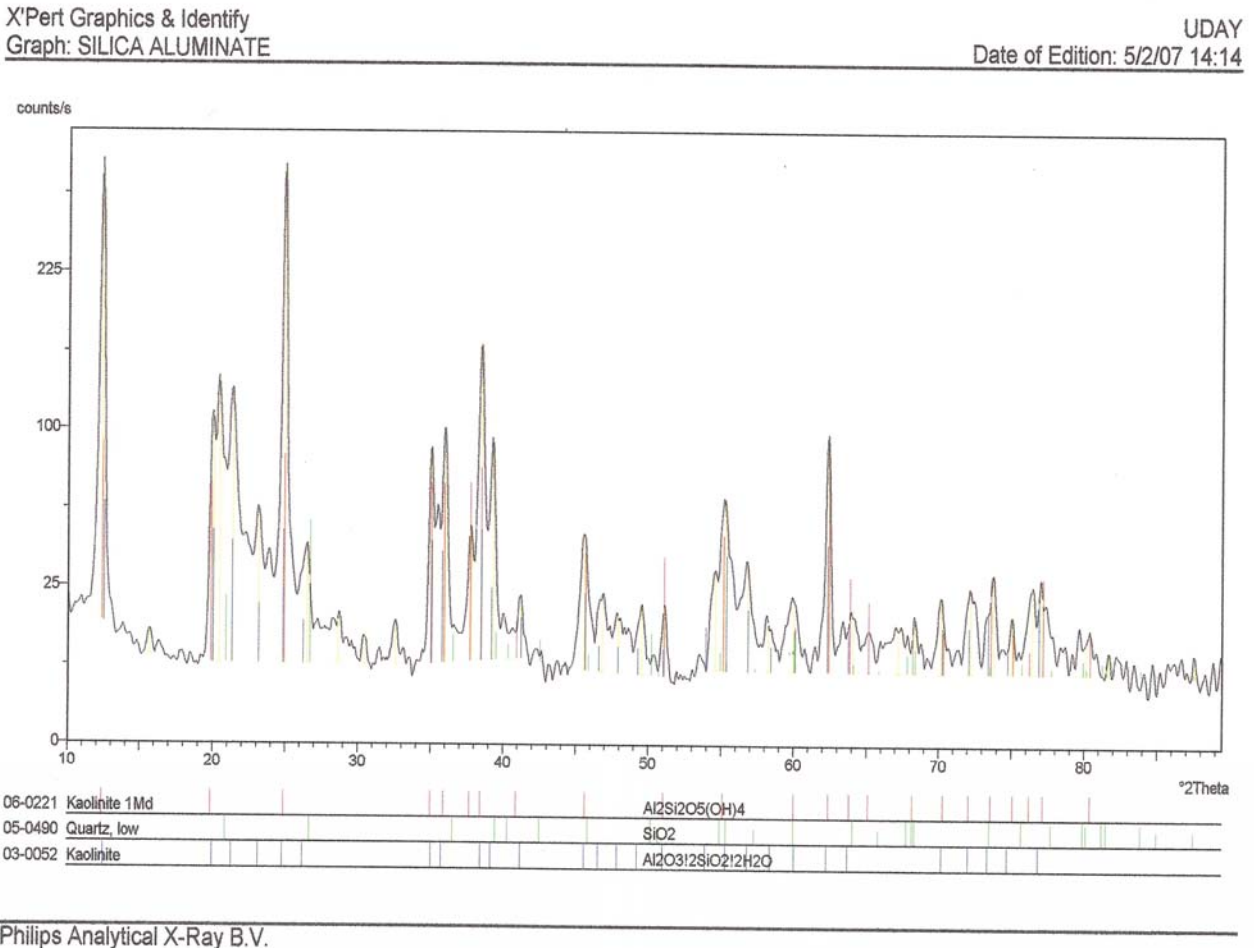


Fig 3.8: Composition Analysis of Si-Al catalyst by XRD.

3.2.2 Mordenite:

Mordenite is a rare zeolite mineral with the chemical formula, $(Ca,Na_2,K_2)Al_2Si_{10}O_{24} \cdot 7(H_2O)$. It is a zeolite. It was first described in 1864 by Henry How. He named it after the small community of Morden, Nova Scotia, Canada, along the Bay of Fundy, where it was first found.

Mordenite is orthorhombic. It crystallizes in the form of fibrous aggregates, masses, and vertically striated prismatic crystals. It may be colorless, white, or faintly yellow or pink. It has

Mohs hardness of 5 and a density of 2.1. When it forms well developed crystals they are hairlike; very long, thin, and delicate. The mineral is found in volcanic rock such as rhyolite, andesite, and basalt. It is associated with other zeolites such as stilbite and heulandite. Good examples have been found in Iceland, India, Italy, Oregon, Washington, and Idaho.

Because of its wetting nature when exposed to air SEM test was not done. We have tested only on XRD for its composition analysis.

3.2.2.1 Composition Analysis of Mordenite by XRD:

From this analysis we have observed that the presence of Sodium aluminum oxide Hydrate and Gibbsite mineral in maximum quantity.

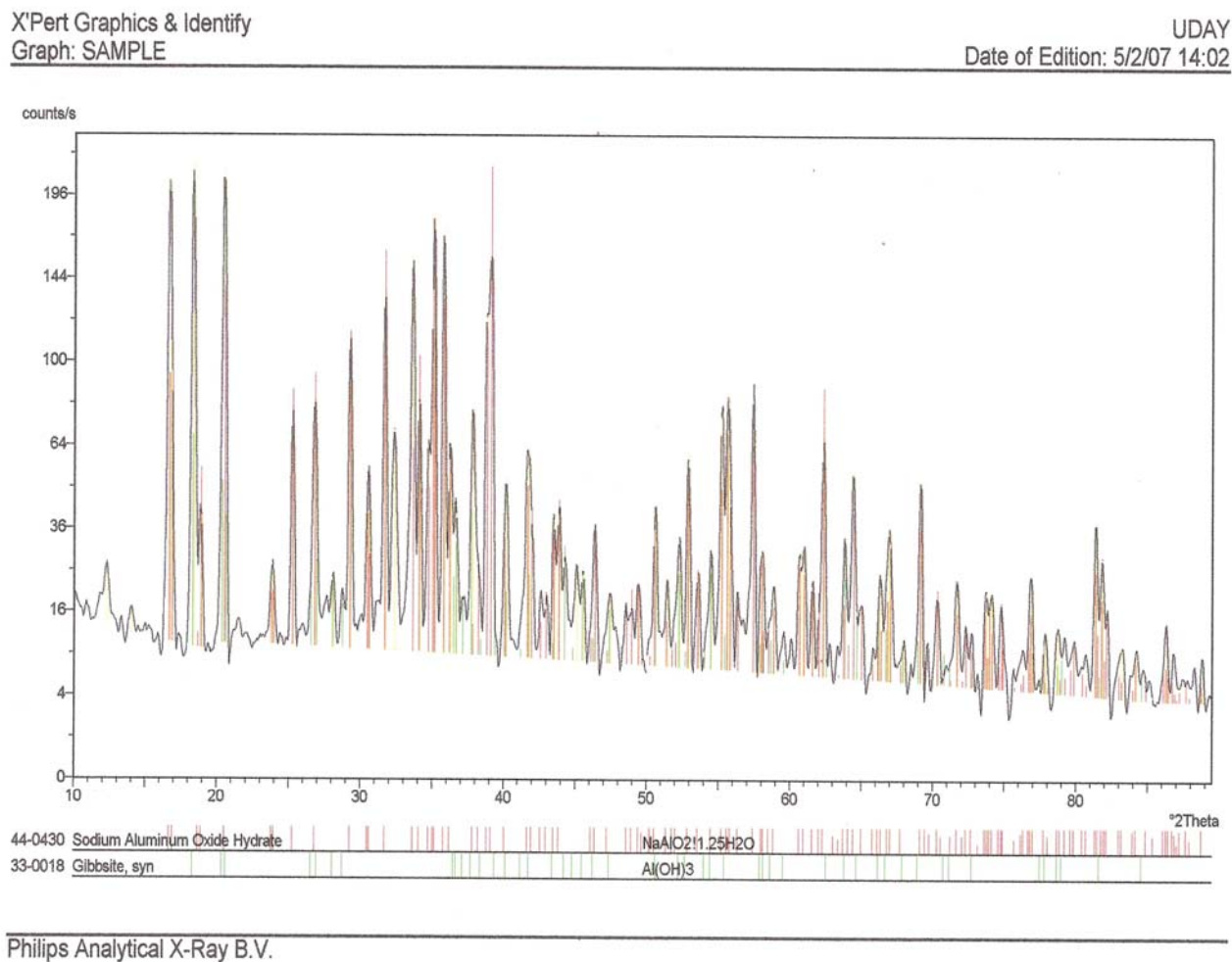


Fig 3.9: Composition Analysis of Mordenite catalyst by XRD.

3.2.3 Activated Carbon:

Activated carbon, also called activated charcoal or activated coal, is a general term which covers carbon material mostly derived from charcoal. For all three variations of the name, "activated" is sometimes substituted with "active". By any name, it is a material with an exceptionally high surface area. Just one gram of activated carbon has the surface area of approximately 500 m², typically determined by nitrogen gas adsorption, and includes a large amount of microporosity. Sufficient activation for useful applications may come solely from the high surface area, though often further chemical treatment is used to enhance the absorbing properties of the material [37]. We have used granulated activated carbon as catalyst for our process. Granulated activated carbon has a relatively larger particle size compared to powdered activated carbon and consequently, presents a smaller external surface. Diffusion of the adsorbate is thus an important factor. These carbons are therefore preferred for all adsorption of gases and vapours as their rate of diffusion are faster [37].

3.2.3.1 Structural Analysis of Activated Carbon Catalyst by SEM:

From the SEM test of catalyst it can be seen that the catalyst has large number of pores in its structure, therefore its surface area for catalysis reaction is more. The reaction was very fast because of its large surface area. It can be seen that the pores were filled by the residue in the used catalyst.

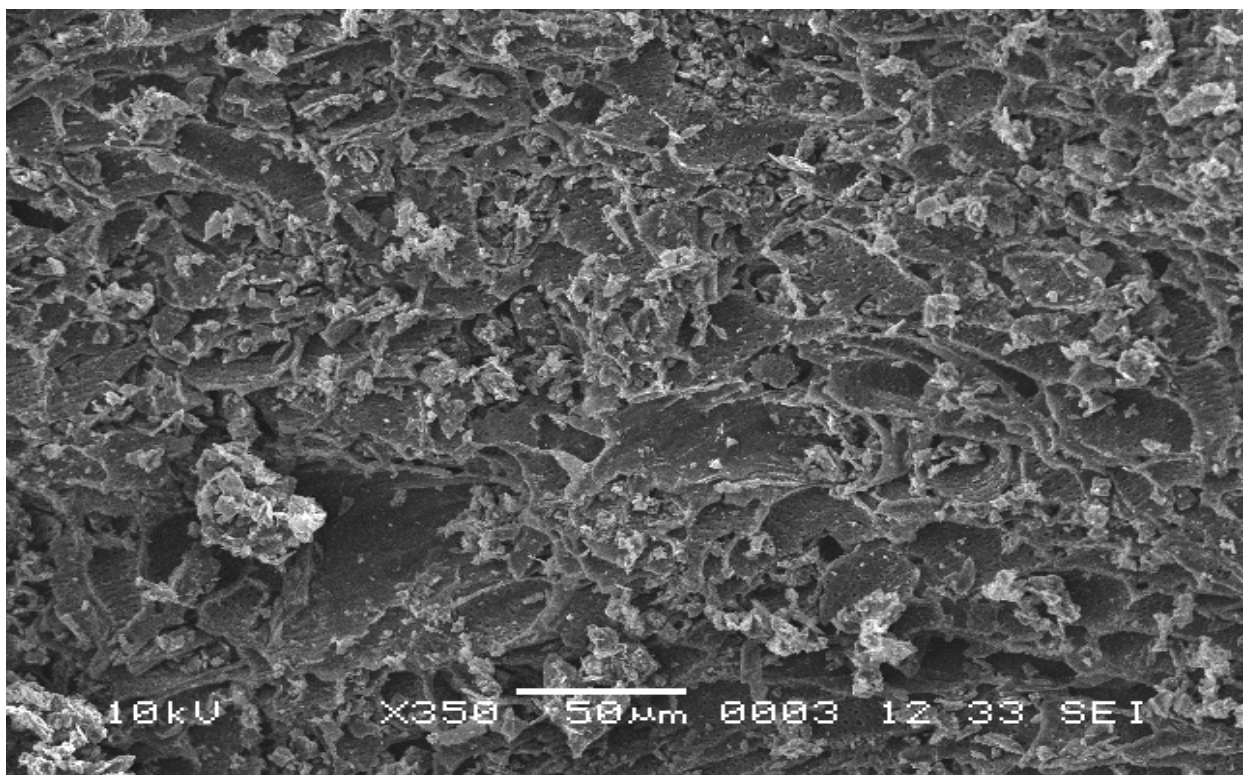


Fig 3.10: SEM photographs of fresh activated Carbon catalyst at 350 Magnification.

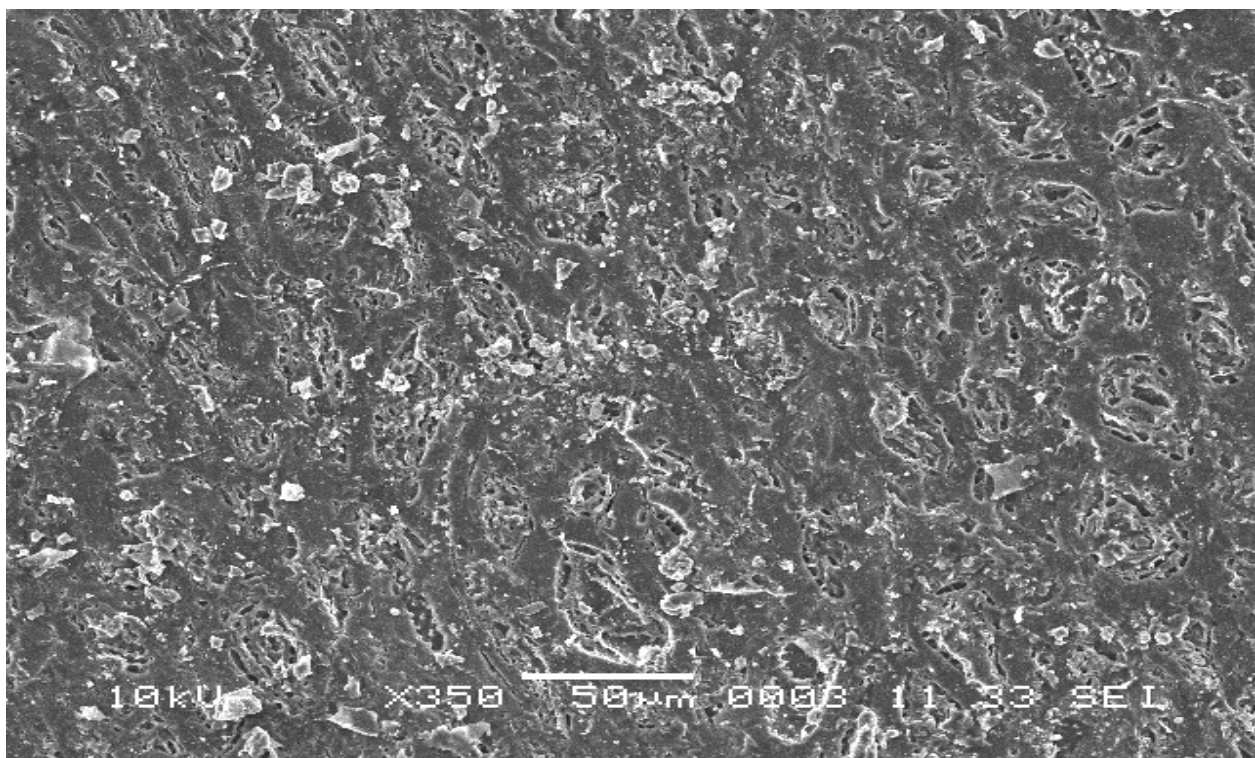


Fig 3.11: SEM photographs of used activated Carbon catalyst at 350 Magnification.

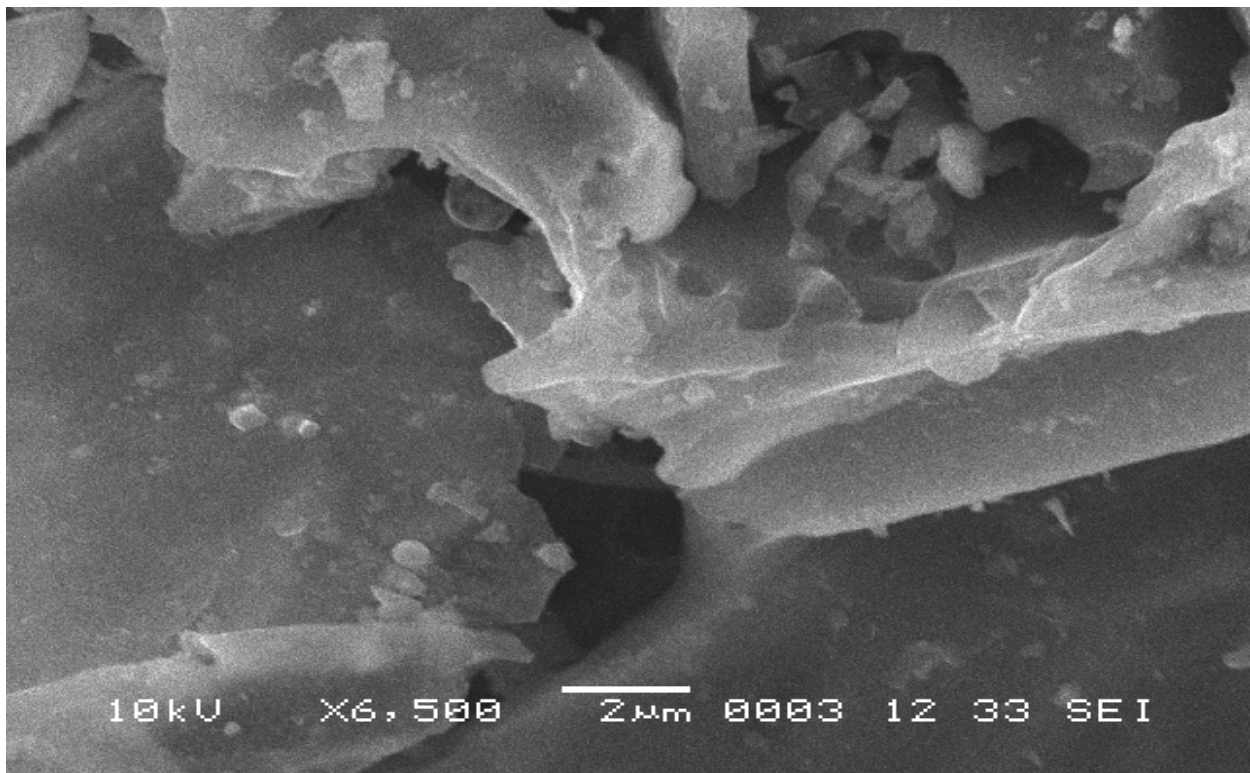


Fig 3.12: SEM photographs of fresh activated Carbon catalyst at 6500 Magnification.

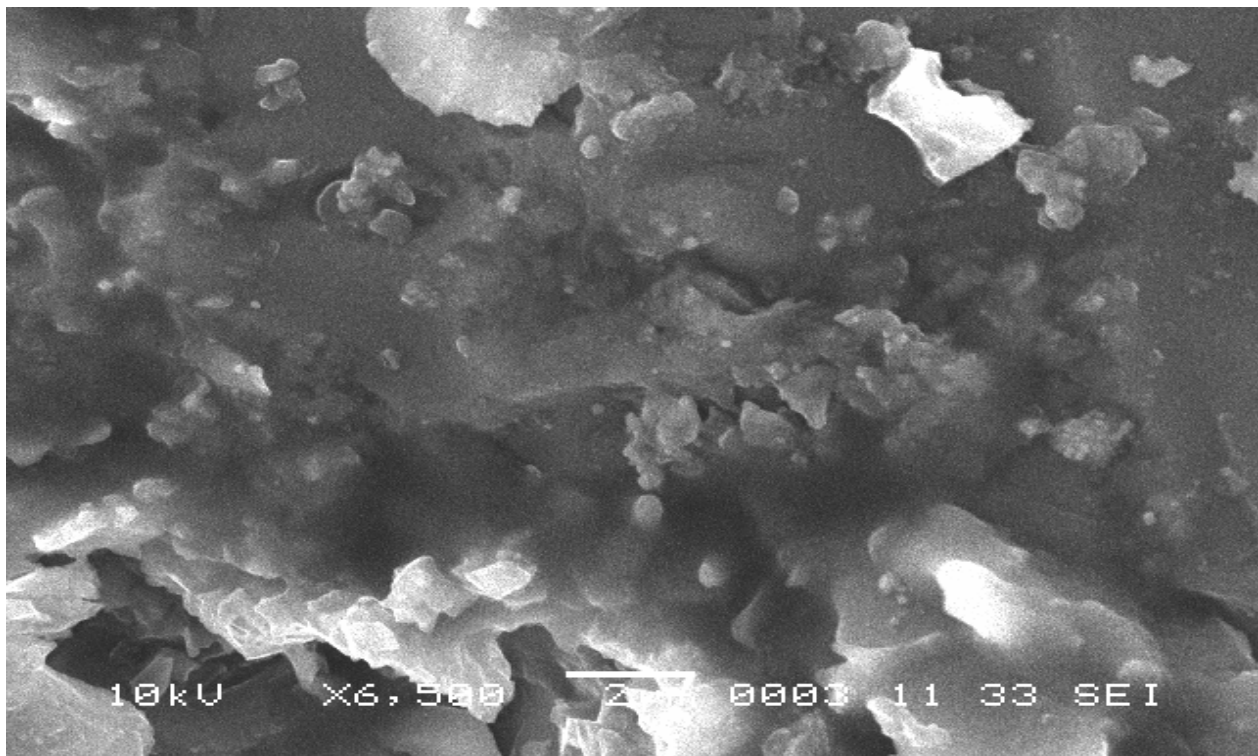
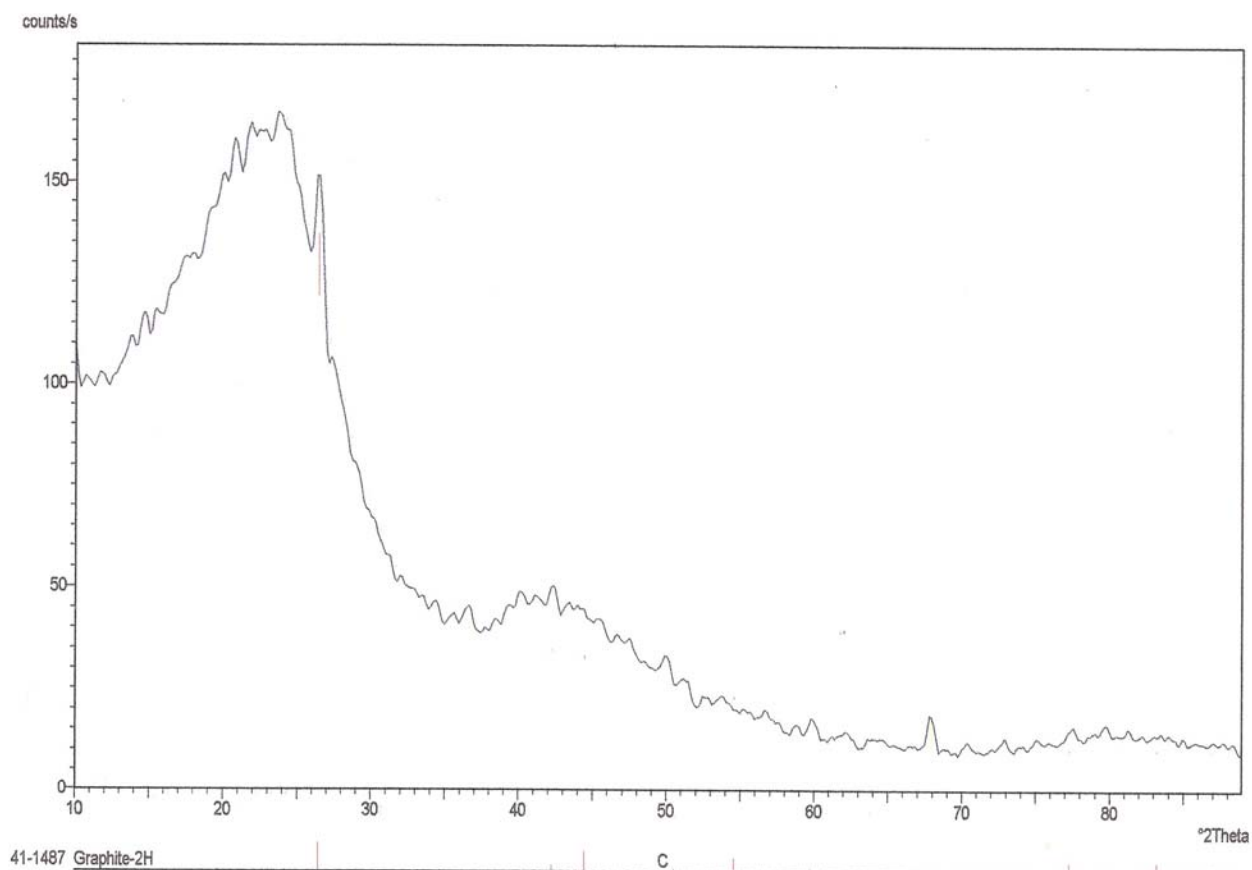


Fig 3.13: SEM photographs of used activated Carbon catalyst at 6500 Magnification.

3.2.3.2 Composition Analysis of Activated Carbon by XRD:

X'Pert Graphics & Identify
Graph: ACTIVATED CARBON

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Philips Analytical X-Ray B.V.

Fig 3.14: Composition Analysis of Activated Carbon catalyst by XRD.

To find the composition of activated carbon we have used XRD analysis. The peaks were as shown in fig. The highest peak indicated the presence of graphite in maximum quantity. And the small peaks were might be the presence of some acids used to activate this carbon.

3.3 Pyrolysis

Pyrolysis or cracking processes break down polymer chains into useful lower molecular weight compounds. This can be achieved by the application of heat at atmospheric pressure in the absence of oxygen, which can be either thermal or catalytic cracking.

3.3.1 Thermal Pyrolysis

The molten waste plastic pellets were taken into a cylindrical cast iron reactor of volume 0.3 lit (300 ml). The reactor was completely packed with the material. The reactor was perfectly sealed with M-Seal for the prevention of leakage of vapors. Then the reactor was put inside a furnace with the support of a stand. The furnace used was muffle furnace made by SHIMADEN CO. LTD, Japan coupled with SR1 and SR3 series digital controller. With the help of controller we set the process at different temperatures for different experiments. The rate of increase of temperature is 25°C/min. The vapors that are coming from the reactor were passed through the pipeline connected to the top of the reactor. The vapors were allowed in to a glass condenser as show in the fig. Then the condensed liquids were collected. The non-condensable gases were very less and probably negligible in quantity.

3.3.2 Catalytic Pyrolysis

The schematic representation of the method has been showed in the fig. As shown in the schematic representation of the process the waste plastic is sorted based on physical properties such as, hard, soft, films etc. Size reduction of the sorted feed is carried out using crusher, cutter and shredder and graded into uniform size The graded feed is mixed and fed to Melting Vessel through pre heater feeder.

The molten waste plastic pellets were taken into a cylindrical cast iron reactor of volume 0.3 lit (300 ml). The reactor was completely packed with the material along with catalyst. We have used different types of catalysts with various feed/catalyst ratios (1:1, 1:2, 1:3, 1:4, 1:5) at different reaction temperatures. We have taken the raw material in the form of irregular shape along with the solid catalysts into the reactor the reaction was taken in liquid phase then the

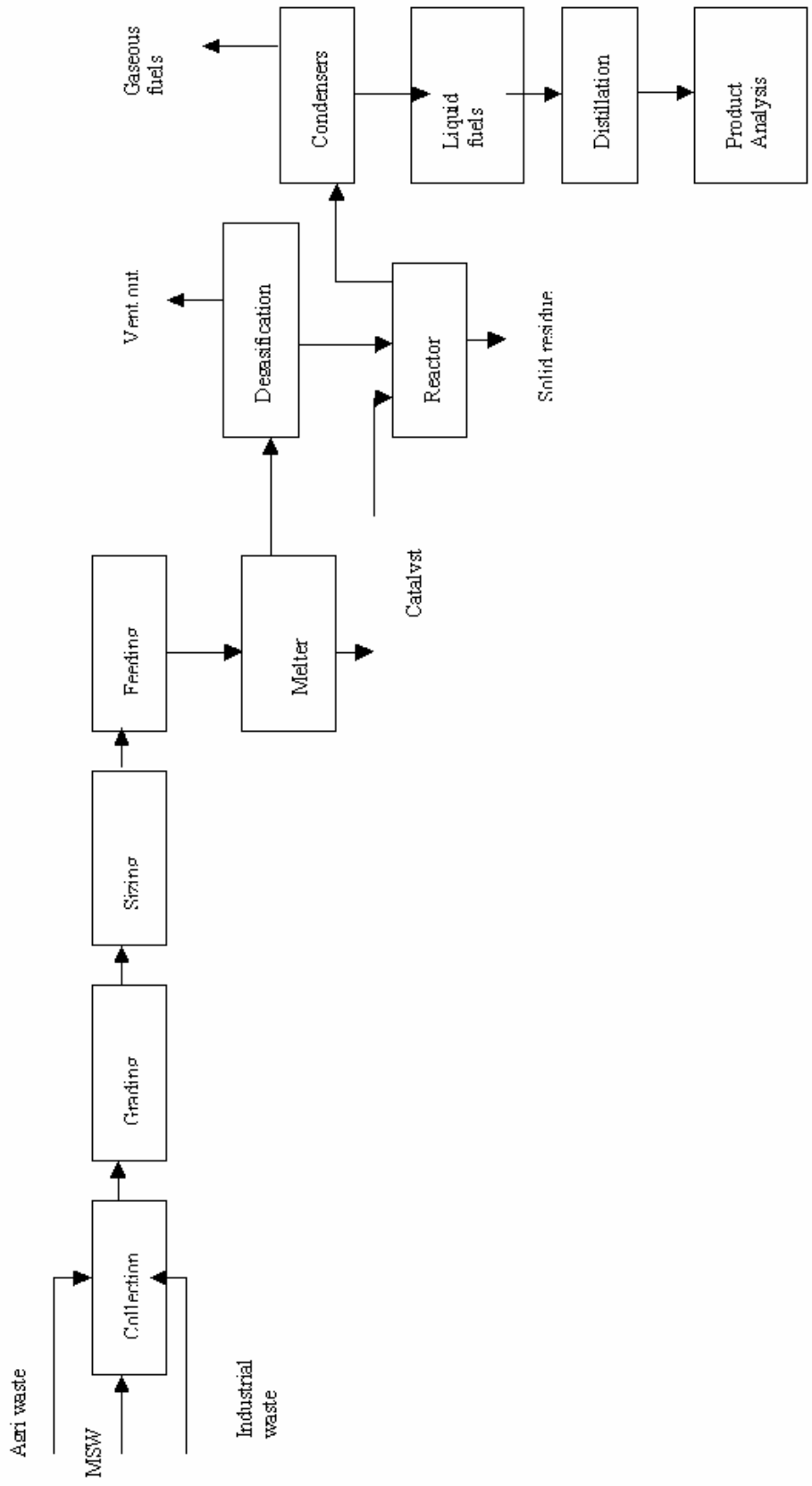


Fig 3.15. Schematic representation of the current project (catalytic degradation of waste plastics for liquid fuel recovery)

vapors which were evolved from the reactor were condensed with a small capacity laboratory glass condenser at the end we collected the liquid fuels and the gases which were non-condensable were allowed in to a water bath just to absorb them. But we were unable to collect them and analyze them. But the literature says the non-condensable gases which are coming from this process are exists in the range of LPG.



Fig 3.16: Experimental set up of Pyrolysis.

The chlorine content might be in negligible quantity because we have taken only HDPE material. The rate of heat supplied was $25^{\circ}\text{C}/\text{min}$. we have conducted around 35 experiments by changing various process parameters like reaction temperature, feed/catalyst ratio, and with different types of catalysts. The results are showed in the next chapter results and discussion.

Chapter 4

RESULTS AND DISCUSSION

Thermal Degradation of HDPE

Catalytic Degradation of HDPE

Physical Analysis of Liquid Products

RESULTS AND DISCUSSION

The experiments on pyrolysis were conducted by using HDPE as the raw material. Both catalytic and non-catalytic processes were done. The range of temperatures applied was 470-650°C. And the heat supplied at the rate of 15°C/min. We have observed that the thermal sensitivity of waste plastics (HDPE) along with different catalysts and without any catalysts. The effects of various process parameters on liquid product yield have been observed. Some of the important physical properties of the liquid products were measured and compared with standards of gasoline and diesel range of products.

4.1 Thermal Degradation of HDPE:

We have conducted the experiments using HDPE as the raw material by the application of various range of temperatures and noted the product distribution along with reaction time taken for the complete degradation of the material. Thermal degradations of all plastics occur between 350 and 500°C. One of the degradation characteristics in the type of plastic is the level of temperature at which the degradation takes place. The temperature levels of thermal degradation of the reactants were in the following order: waste PS < waste PP < waste LDPE, HDPE [38]. Thermal degradation of HDPE occurs around 500°C, that's why we started our experiments starting with 500°C and observed the products distribution as shown in the table 4.1.

Table 4.1: Product distribution of thermal degradation of HDPE

Temperature in °C	%Solid	%Liquid	%Gases	Rn time min	Nature of liquid product
500	2.80	76	21.20	30	Stable liquid fuel
575	2.75	78	19.25	10	Solidified liquid fuel
600	2.85	68.2	28.95	8	Solidified liquid fuel
625	2.85	51.4	45.79	6	Solidified liquid fuel
650	2.83	36.11	61.06	6	Solidified liquid fuel

The figure below shows the solidified liquid fuel obtained during thermal cracking. The degradation starts at 570°C for every process but the time taken for the complete degradation of material was alters as shown in the fig. The cracking of HDPE was started at 500°C but time taken for the completion of the reaction was very high i.e., about 30 min. But for the other processes at very high temperatures the time taken was very less, and the liquid product yield was going to be decrease further simultaneously the gaseous products yield was increases. But one more important notification was the liquid products produced at these high temperatures were unstable in liquid form, they turned into solid form as shown in fig 4.3. But the liquid produced at 500°C was very stable in liquid form itself as shown in fig.

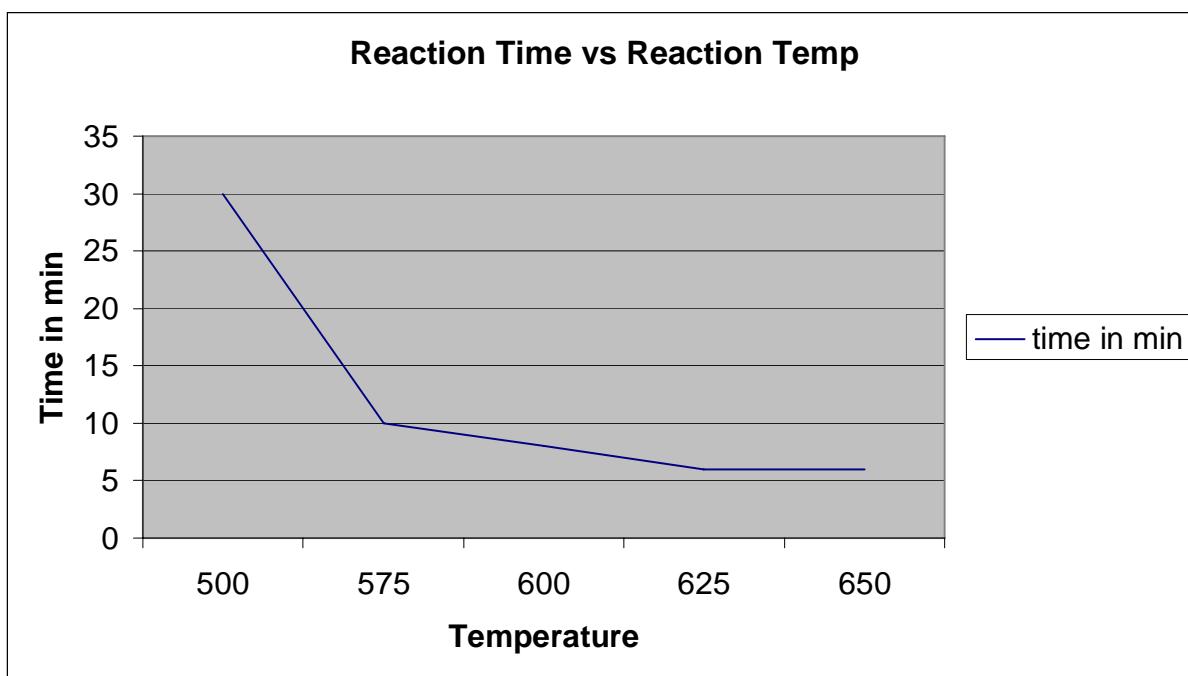


Fig 4.1: Reaction time vs Reaction temperature in thermal degradation of HDPE

The liquid product yield at 575°C is more than the others but it was solidified one. The liquid product at 500°C is very much stable in liquid state but the time taken for the completion of the reaction was about 30 min simultaneously the energy consumption was more. If our aim is to produce liquid fuels then this option is best one. The specific gravities of the liquid products were tabulated below. We may observe that the increase in temperature supports the increase in gaseous product's yield and at the same time it shows the decrease in liquid

product's yield as shown in the fig.4.1, below but residue is quite common from all the experiments as shown in fig 4.2.

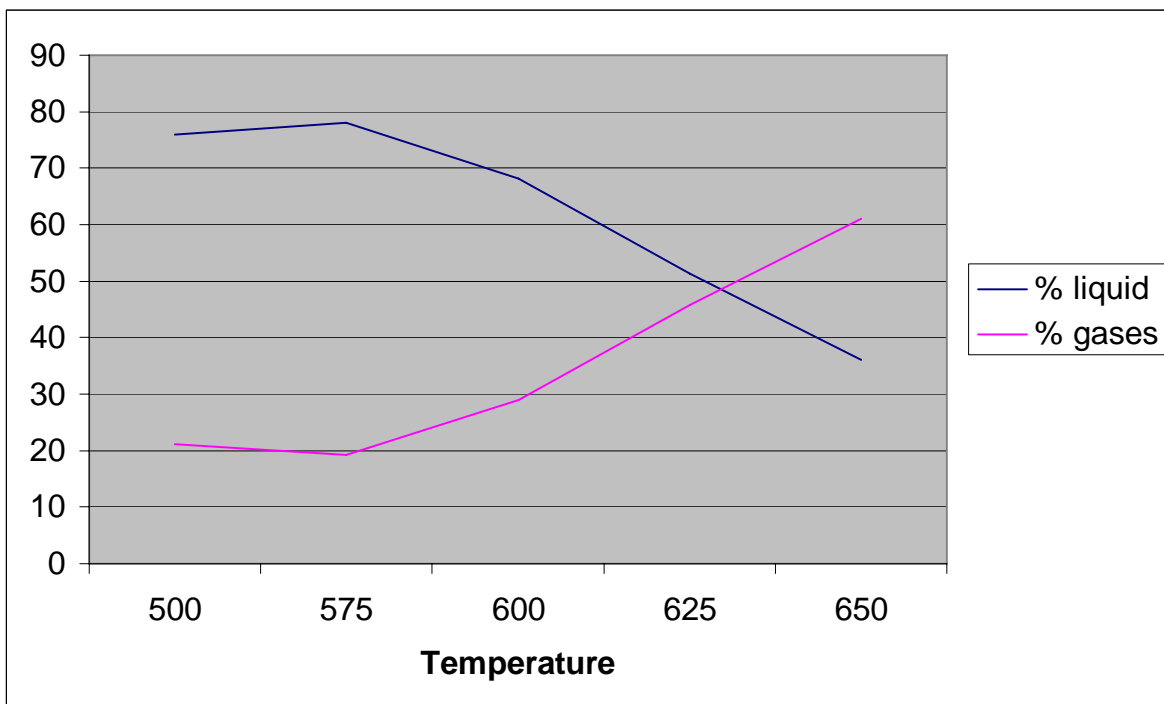


Fig 4.2: The yields of liquid and gaseous products Vs Reaction Temperature.

According to literature the solidified liquid contain mostly the paraffines. Therefore at high temperatures we are getting wax type paraffine products.



Fig 4.3: Solidified liquid product

The product distribution varies very much in thermal degradation of HDPE. The main products were both liquid and gaseous. The further increment in temperature supports the increment in gaseous fuels. But we were unable to collect these gases.

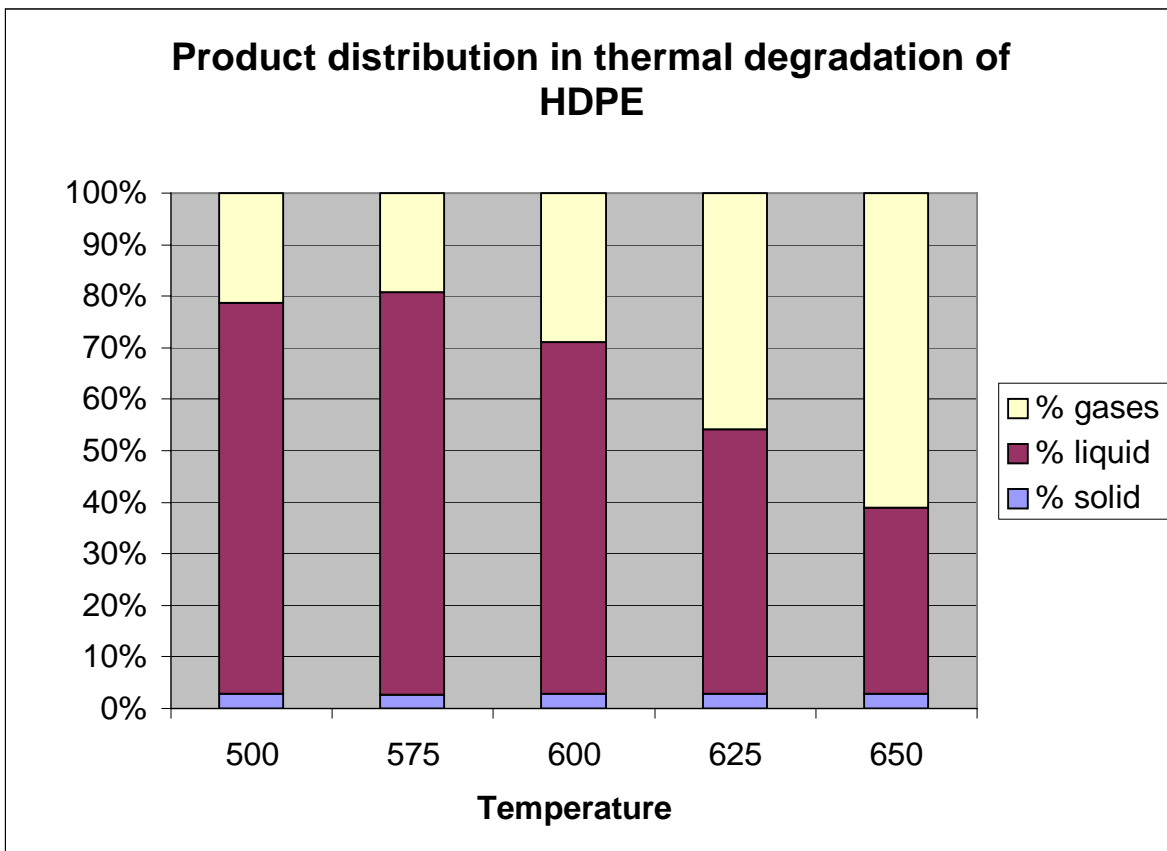


Fig 4.4: Product distribution in thermal degradation of HDPE

4.2 Catalytic Degradation of HDPE:

Liquid-phase catalytic degradation of waste polyolefinic polymers (HDPE) over fluid cracking (FCC) catalysts like Silica Alumina, Aluminum Silicates, Mordenite and Activated carbon were carried out at atmospheric pressure with a semi-batch operation. The effect of experimental variables, such as catalyst amount and its physical structure, reaction temperature, plastic types on the yield and accumulative amount distribution of liquid product for catalytic degradation was investigated. Let us see in every case how the product distribution varies with reaction temperature and with feed to catalyst ratio and with the structure of catalysts.

4.2.1 Catalytic Cracking of Waste HDPE by Silica Alumina:

Silica Alumina is white amorphous powdery catalyst. It consists of 87% SiO_2 , 13% Al_2O_3 from the literature and the matching composition of some identified elements has been showed by XRD in the fig. From the SEM test of catalyst it can be seen that the catalyst has large number of pores in its structure, therefore its surface area for catalysis reaction is more. But again the pores are very large in size, which reduces its activity a bit when compare with the some of the other catalysts.

The figure below shows Silica Alumina before use and after use. The black color indicates the residue mixed with the catalyst and we have observed that this solid residue deactivates the catalyst as shown in its SEM structural photograph. But it has been observed that the residue retained was contains almost the carbon, which acts as a catalyst. Hence, we can use it further directly to some far.



Fig 4.5: Silica Alumina catalyst before (a) use and after (b) use

The product distribution from the catalytic degradation of HDPE using Si-Al as catalyst was as shown in the table. We got maximum yield of liquid product at 550°C and for the feed to catalyst ratio of 1:3 with the specific gravity of 0.77, which exists, in the range of gasoline products. The other liquid products using Si-Al were somewhat high in density as shown in table. they may exists in the range of diesel.

Table 4.2: Product Distribution from catalytic degradation of HDPE using Si-Al catalyst.

Catalyst	Ratio	Temperature °C	%Solid	%Liquid	%Gases
Silica Alumina	1	500	3.167	58.33	38.503
Silica Alumina	2	520	3.167	66.67	30.163
Silica Alumina	3	550	3	78.57	18.43
Silica Alumina	4	570	3.27	54.54	42.19

The feed to catalyst ratio, time required for conversion, temperature needed and the percentage yield of liquid products is given in the table. It clearly shows the trail with 1:3 feed to catalyst ratio is optimum when compared with the others with reaction time of 15 min and the reaction temperature of 550°C with the maximum liquid products yield of 78.57 % and which are exists in the range of gasoline.

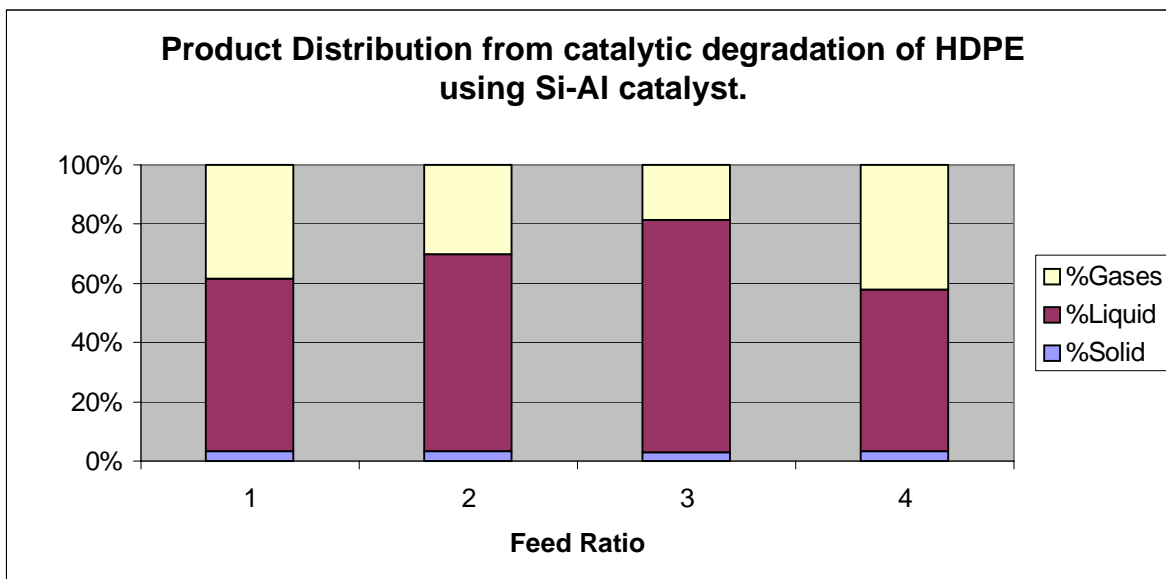


Fig 4.6 : Product Distribution from catalytic degradation of HDPE using Si-Al catalyst

Table 4.3: Experimental Conditions for catalytic degradation of HDPE using Si-Al catalyst with liquid product yield.

Feed	Catalyst	Feed/catalyst	Temp	Time	Liquid product	% Yield
55	14	4	570	10	30	54.54545
70	23.5	3	550	15	55	78.57143
60	30	2	520	30	40	66.66667
60	60	1	500	45	35	58.33333

The different trends of the products obtained and its relation with time, temperature, amount of catalyst used is shown below. We have observed that the reaction time increases with the decrease in the reaction temperature and the initial rate of degradation was decreased with feed to catalyst ratio.

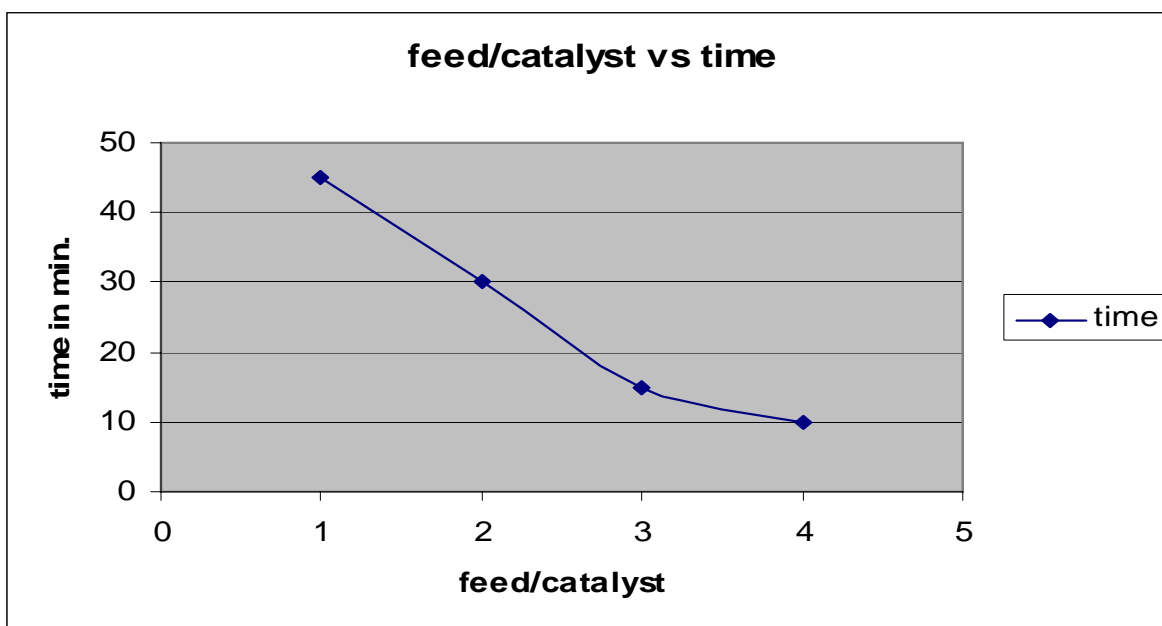


Fig 4.7: Feed / catalyst vs time for the catalytic degradation of HDPE using Si-Al catalyst.

Catalyst acts to decrease the initial cracking temperature and for the better range of liquid fuels as shown in fig.4.7 with maximum yield and without any solidification. The liquid products produced were much stable in liquid form for longer time when compared with the products from the thermal degradation.

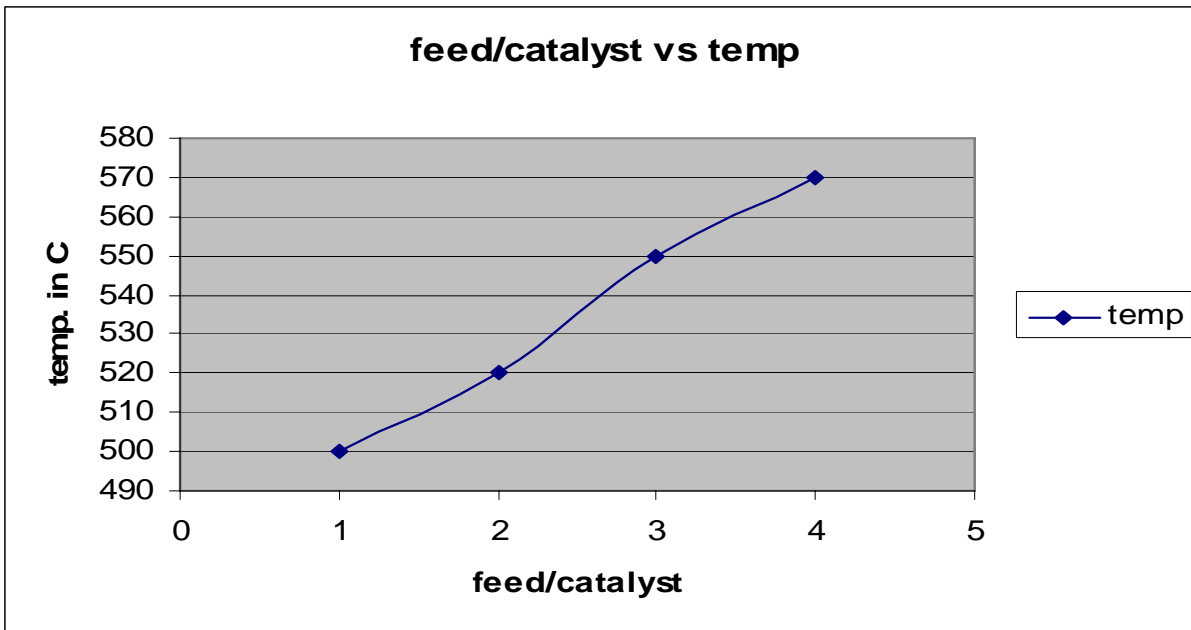


Fig 4.8:Feed / catalyst vs time for the catalytic degradation of HDPE using Si-Al catalyst.

As in the case of thermal degradation if the reaction temperature increases then the required time to complete the reaction will decrease as shown in fig below.

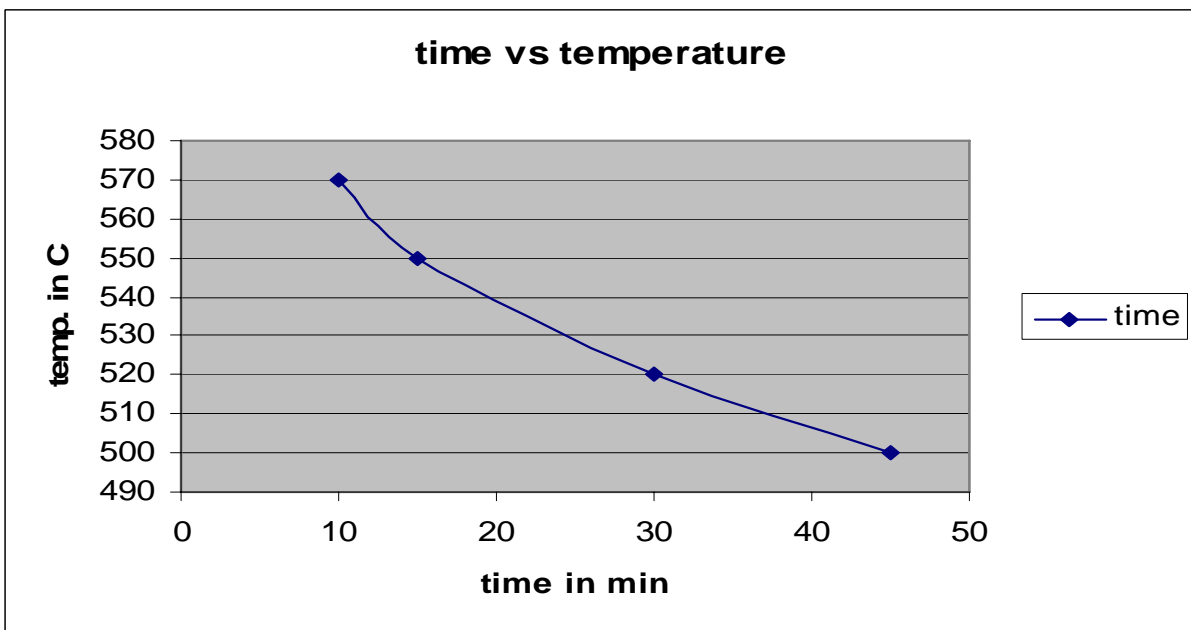


Fig 4.9: Time vs temperature for the catalytic degradation of HDPE using Si-Al catalyst.

The liquid product yield was maximum for the feed to catalyst ratio of 1:3 as shown in the fig.4.10 where we got about 78.57 % of liquid fuel and it was stable for longer time.

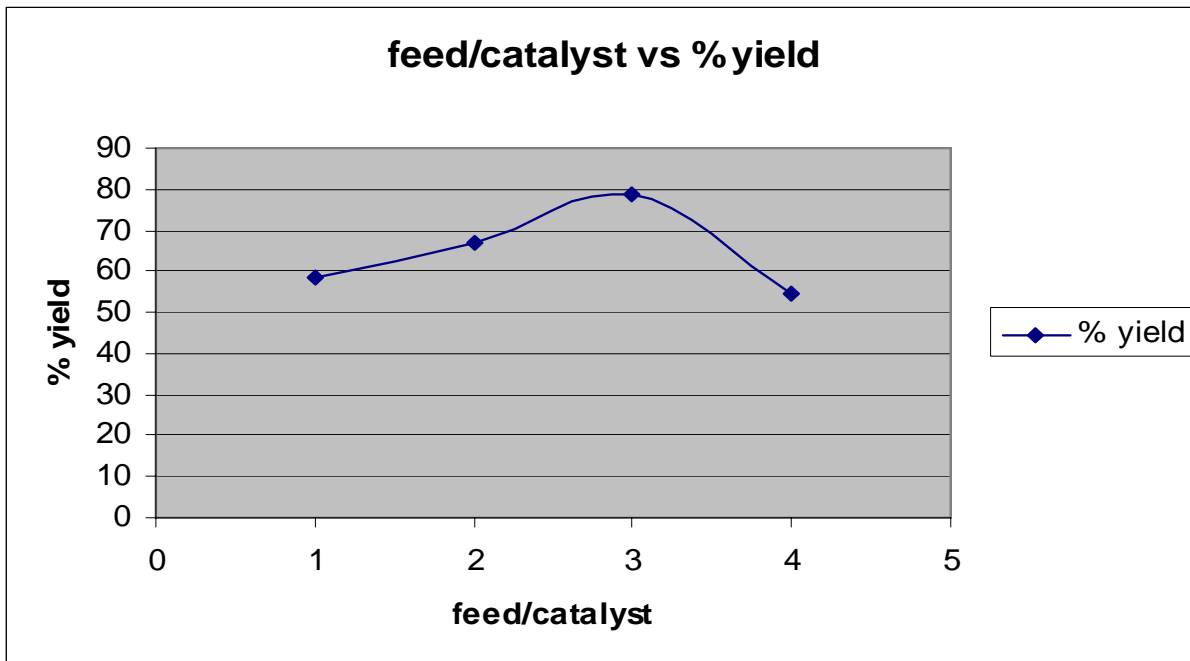


Fig 4.10: Feed / catalyst vs liquid product yield for the catalytic degradation of HDPE using Si-Al catalyst.

Si-Al catalyst supports the process at 550°C to give better liquid product yield and with minimum reaction time as show in fig 4.11.

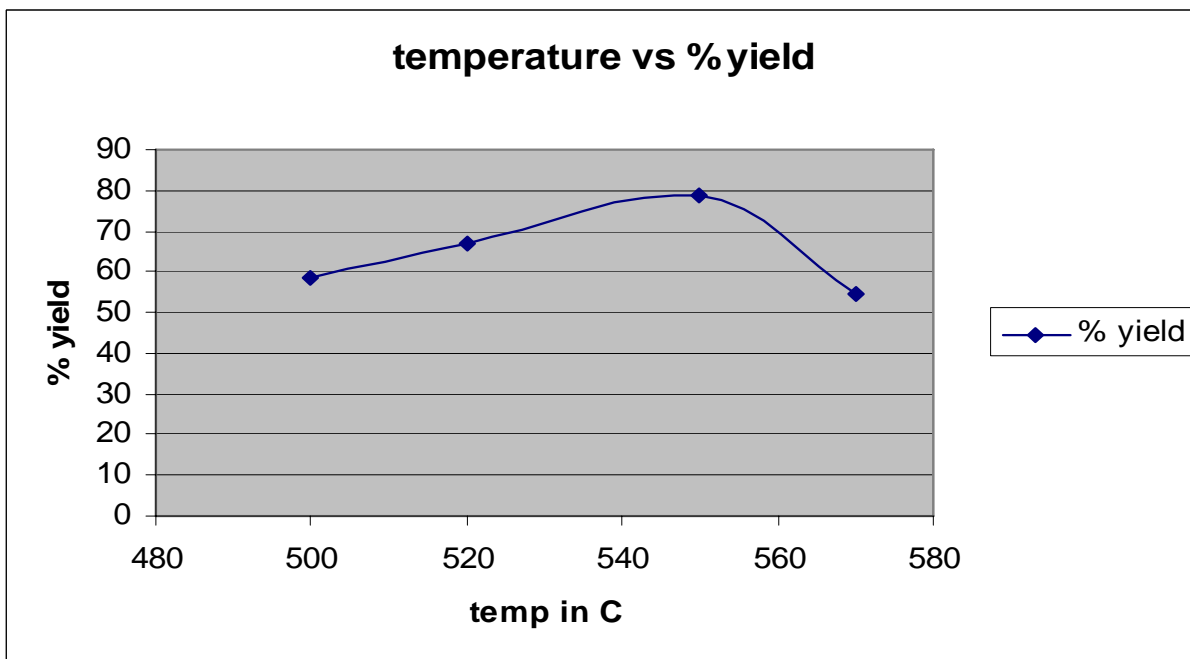


Fig 4.11: temperature vs liquid product yield for the catalytic degradation of HDPE using Si-Al catalyst.

4.2.2 Catalytic Cracking of Waste HDPE by Mordenite

Mordenite is white colored lumpy catalyst, which becomes wet when exposed to air. It consists of 91.7% SiO₂, 8.23% Al₂O₃ and 0.03% Na₂O₃. Some of the components were identified from XRD as shown in fig. Because of its wetting nature with air we were unable to find it's structure by using SEM. The figure below shows Mordenite before use and after use.

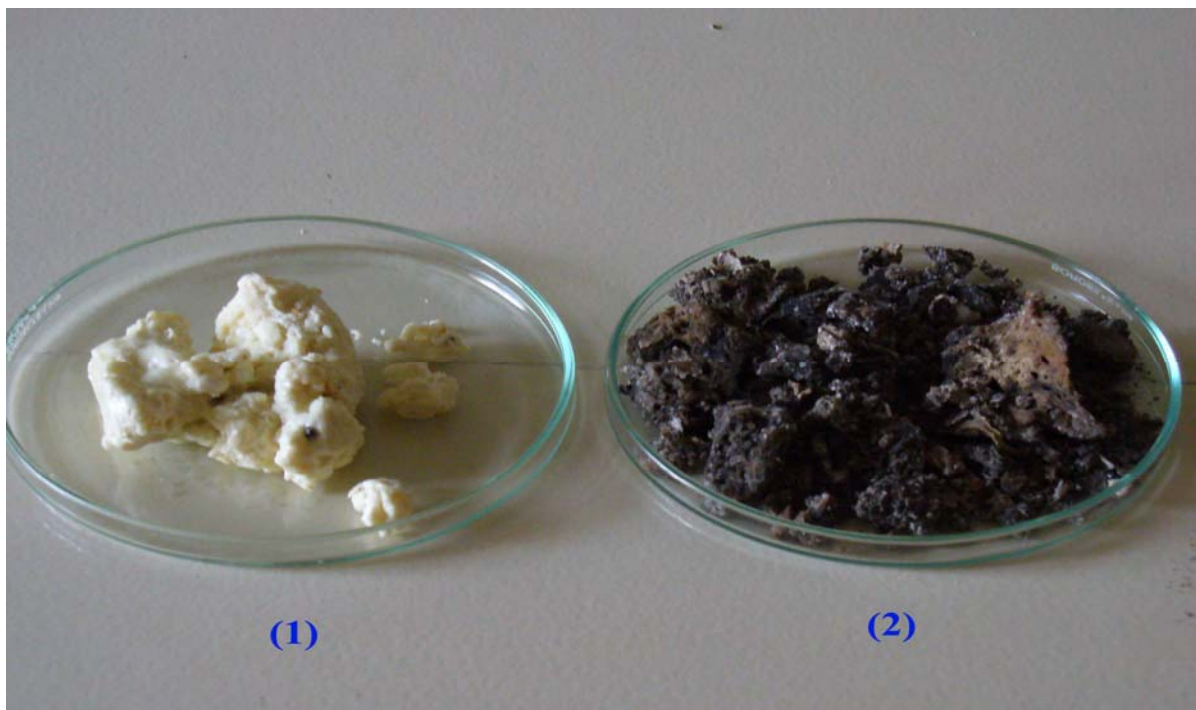


Fig 4.12: Mordenite catalyst Before (1) use and After (2) use

The black color appears because of the residue layer formed on the surface of the catalyst used but the deactivation was very less it again we could use. The product distribution from the catalytic degradation of waste HDPE using mordenite as catalyst was as shown in the table.

Table 4.4: Product Distribution from catalytic degradation of HDPE using Mordenite catalyst.

Catalyst	Ratio	Temperature°C	%Solid	%Liquid	%Gases
Modernite	1	460	3.2	76	20.8
Modernite	2	480	3.167	56.67	40.163
Modernite	3	500	3.2	60	36.8
Modernite	4	520	3.2	80	16.8

We got maximum yield of liquid product at 520°C and for the feed to catalyst ratio of 1:4 with the specific gravity of 0.75, which exists, in the range of gasoline products. The other liquid products using mordenite were somewhat high in density as shown in table 4.4 they may exist in the range of diesel.

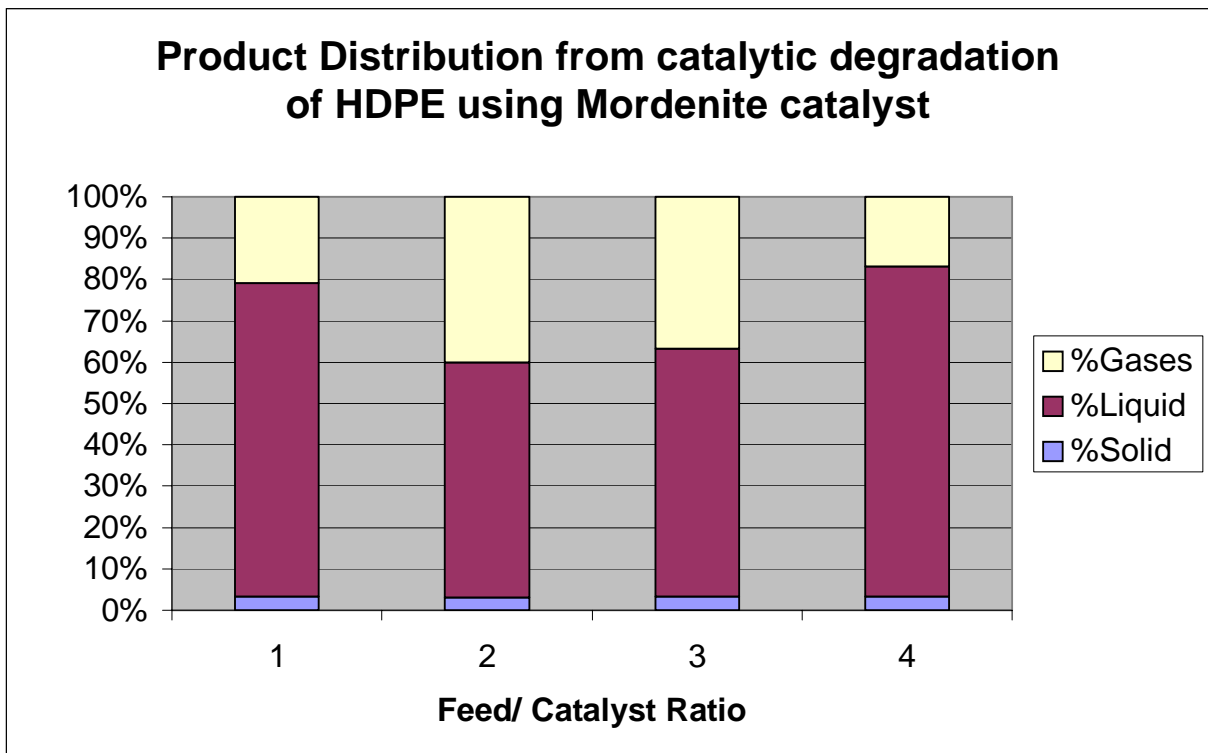


Fig 4.13: Product Distribution from catalytic degradation of HDPE using Mordenite catalyst

The feed to catalyst ratio, time required for conversion, temperature needed and the percentage yield of liquid products is given in the table underneath.

Table 4.5: Experimental Conditions for catalytic degradation of HDPE using Mordenite catalyst with liquid product yield.

Feed	Catalyst	Feed/catalyst	Temp	Time	Liquid product	% Yield
50	12.5	4	520	20	40	80
50	16.66	3	500	30	30	60
60	30	2	480	60	34	56.66667
50	50	1	460	60	38	76

The feed to catalyst ratio, time required for conversion, temperature needed and the percentage yield of liquid products is given in the table. It clearly shows the trail with 1:4 feed to catalyst ratio is optimum when compared with the others with reaction time of 40 min and the reaction temperature of 520°C with the maximum liquid products yield of 76% and which are exists in the range of gasoline. This liquid was very light fuel when compared with the products produced from he thermal degradation and the catalytic degradation using the catalysts Si-Al, Activated Carbon.

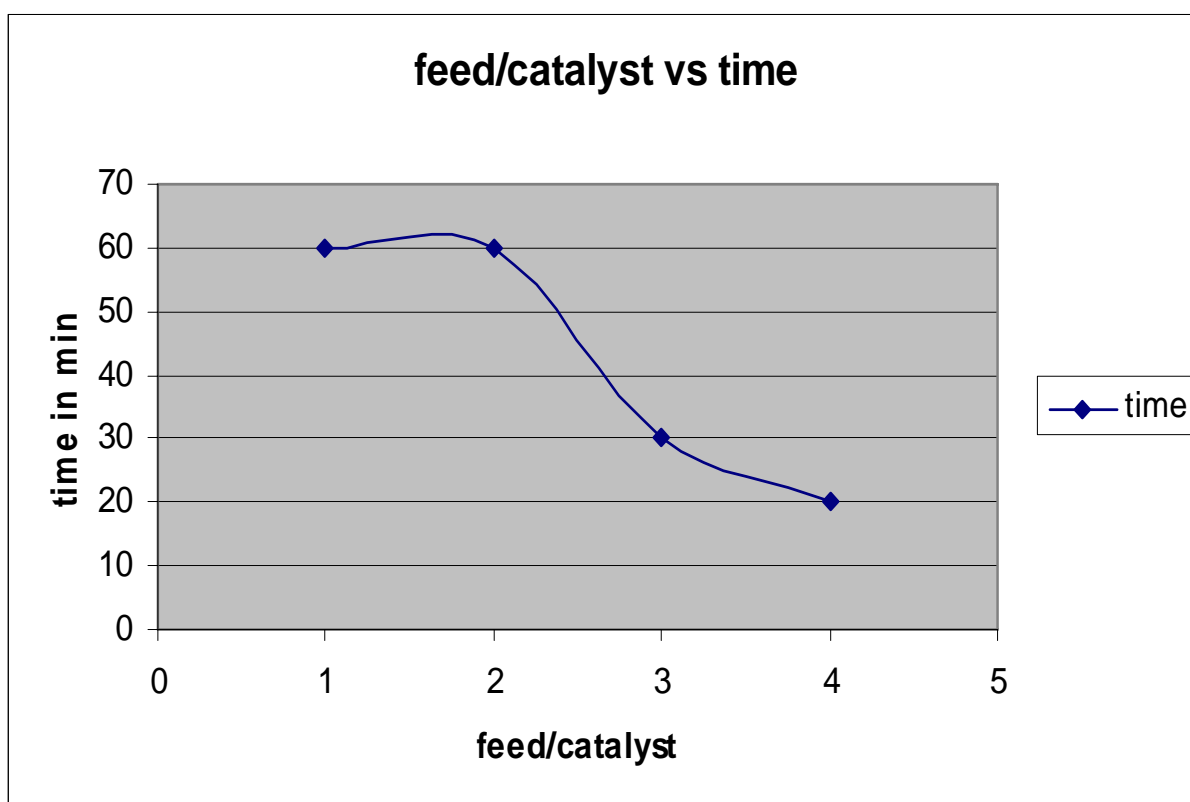


Fig 4.14: Feed / catalyst vs time for the catalytic degradation of HDPE using Mordenite catalyst.

The different trends of the products obtained and its relation with time, temperature, amount of catalyst used is shown below. We have observed that the reaction time increases with the decrease in the reaction temperature and the initial rate of degradation was decreased with feed to catalyst ratio.

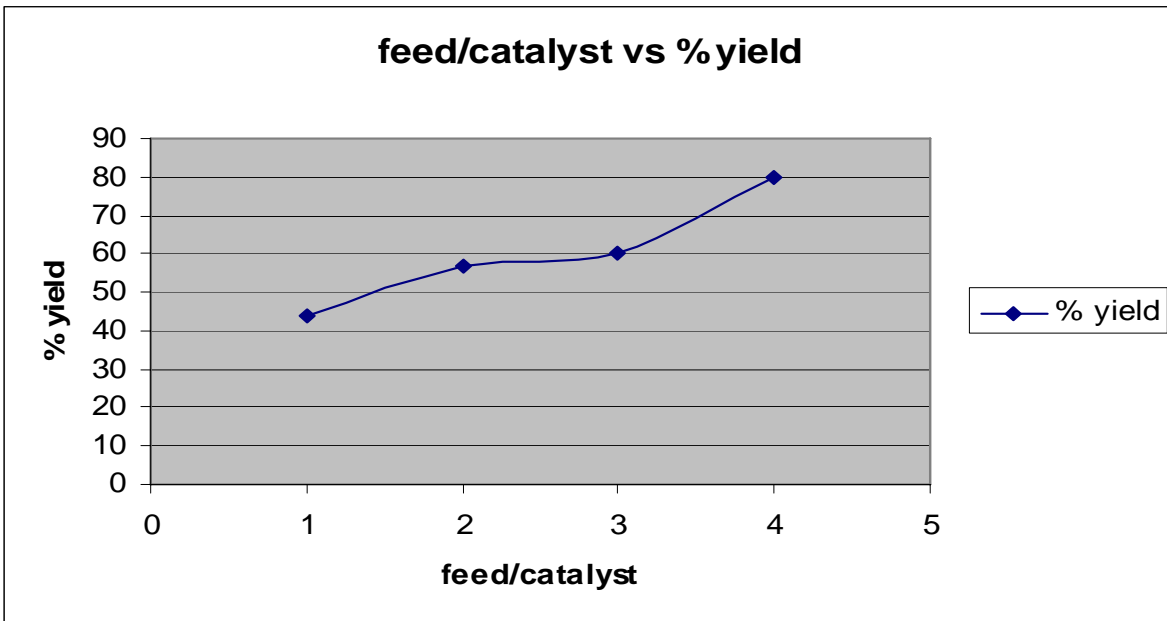


Fig 4.15: Feed / catalyst vs time for the catalytic degradation of HDPE using Mordenite catalyst.

The reaction temperature was very much less when compared with all other catalysts. We could find that 460°C as the minimum degradation temperature in this case by using mordenite catalyst.

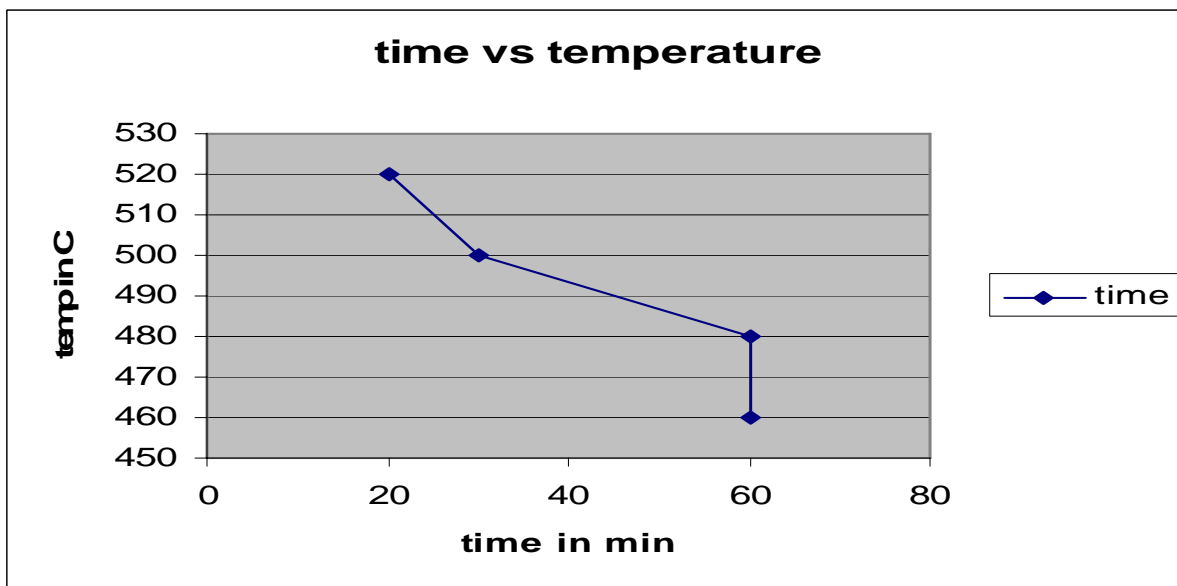


Fig 4.16: Time vs temperature for the catalytic degradation of HDPE using Mordenite catalyst.

At minimum reaction temperature the time required for the completion of the reaction was very high i.e., about one hr. But the products coming were very light fuels.

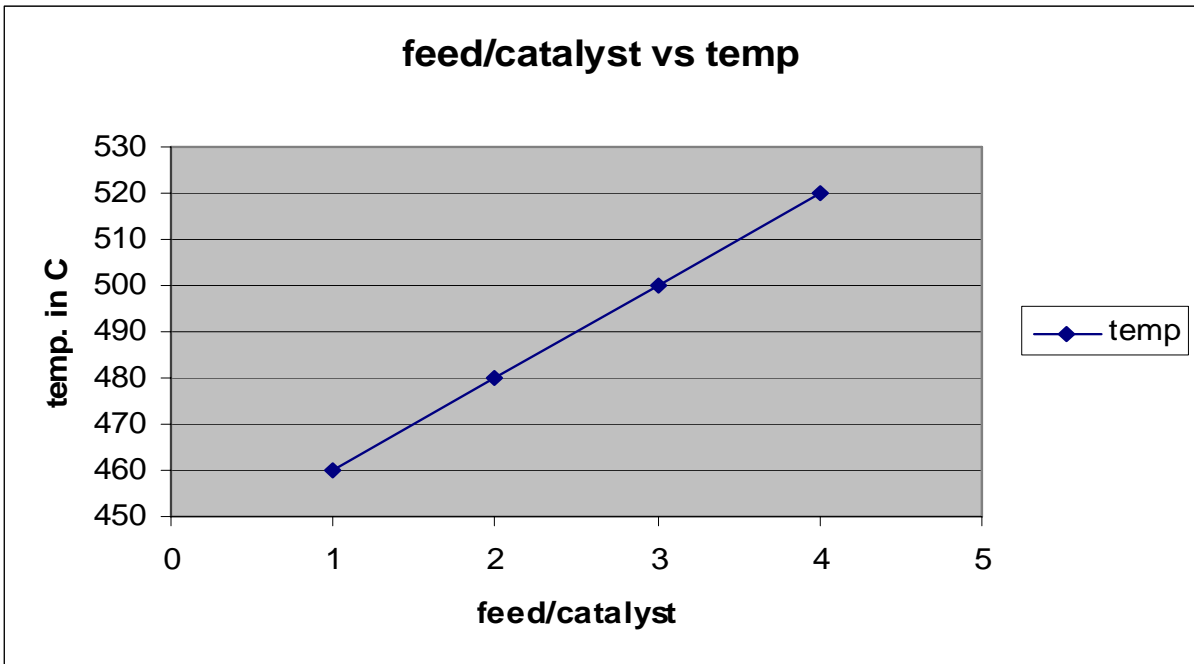


Fig 4.17: Feed / catalyst vs liquid product yield for the catalytic degradation of HDPE using Mordenite catalyst.

The liquid product yield was maximum for the feed to catalyst ratio of 1:4 as shown in the fig.4.18 where we got about 80 % of liquid fuel and it was stable for longer time.

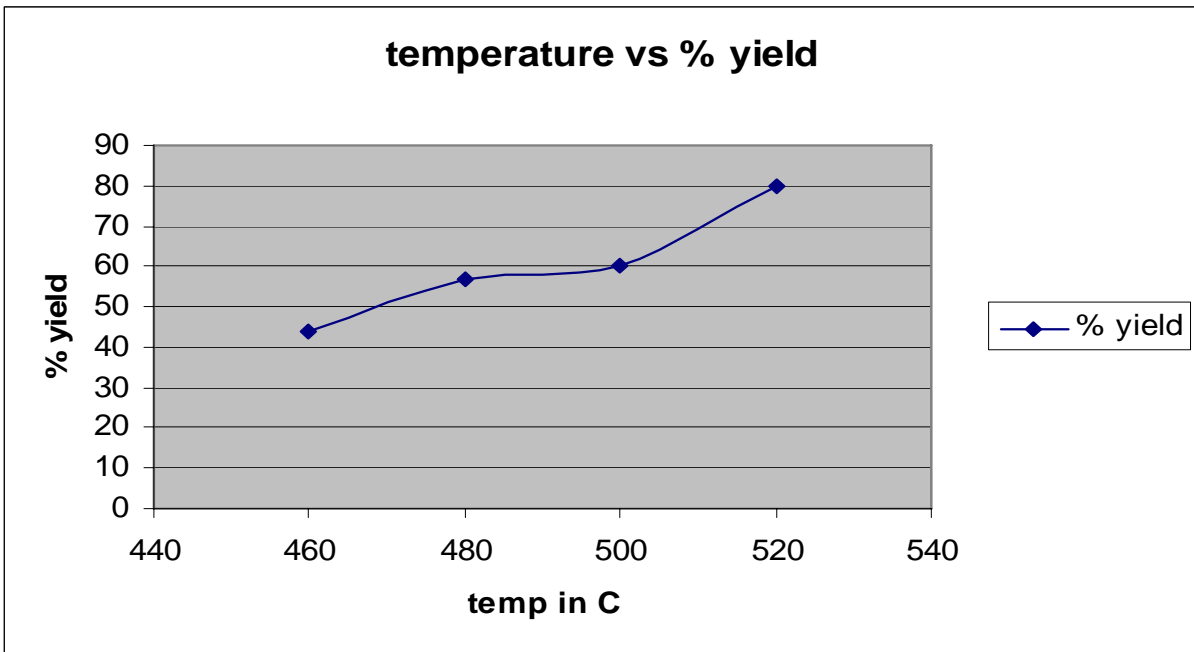


Fig 4.18: Temperature vs liquid product yield for the catalytic degradation of HDPE using Mordenite catalyst

Mordenite catalyst supports the process at 520°C to give better liquid product yield and with minimum reaction time as show in fig.

4.2.3 Catalytic cracking of Waste HDPE by Activated Carbon:

Activated carbon acts as a very good catalyst by providing sufficient surface area and excellent porosity. The reaction was very fast like thermal degradation but the products were almost having the nature like the products from thermal degradation. Those were easily solidified. The structural photographs from SEM were showed in fig.3.10 and the composition analysis was done by XRD as shown in fig.3.14 Its almost shows the presence of pure graphite. The figure below shows Activated Carbon before use and after use.



Fig 4.19: Activated Carbon catalyst Before (a) use and After (b) use

Here one more advantage we may observe that the carbon residue formed on the surface of the used catalyst will act as the catalyst, the composition also almost same. But the porosity is somewhat less.

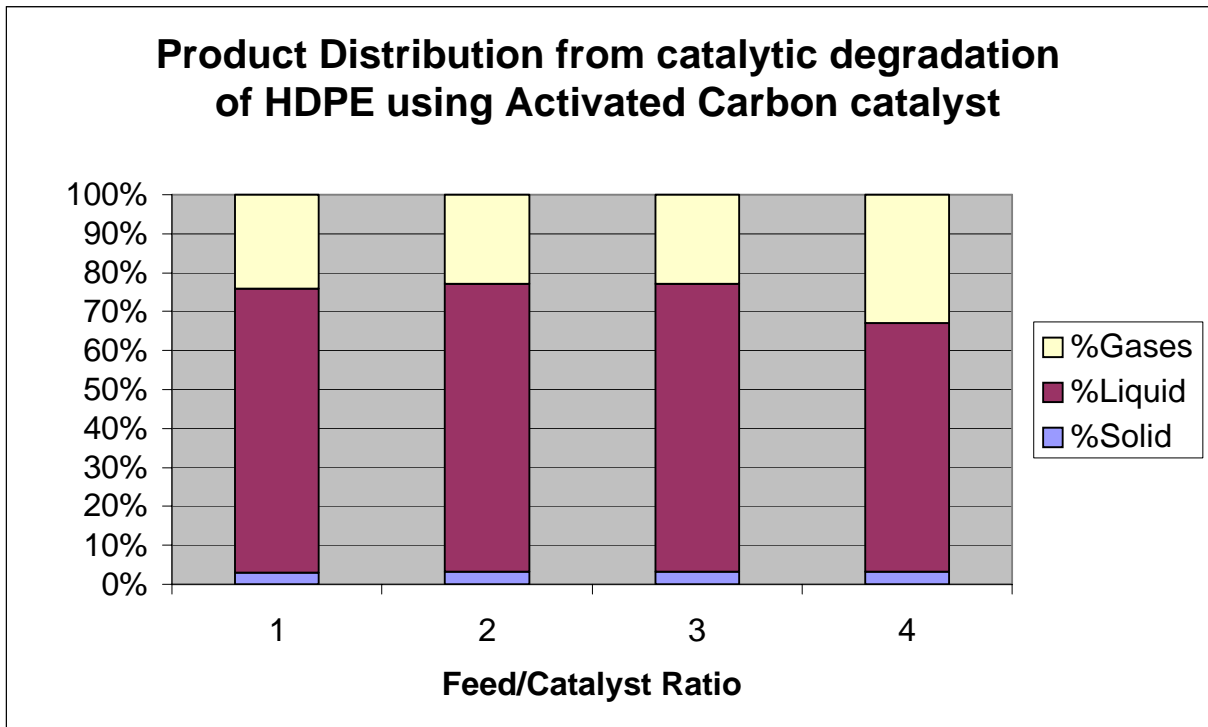


Fig 4.20: Product Distribution from catalytic degradation of HDPE using A-C catalyst

The feed to catalyst ratio, time required for conversion, temperature needed and the percentage yield of liquid products is given in the table underneath.

Table 4.6: Product Distribution from catalytic degradation of HDPE using Mordenite catalyst.

Catalyst	Ratio	Temperature	%Solid	%Liquid	%Gases
Activated Carbon	1	470	3.09	72.72	24.19
Activated Carbon	2	490	3.2	74	22.8
Activated Carbon	3	510	3.2	74	22.8
Activated Carbon	4	530	3.2	64	32.8

We got maximum yield of liquid product at 490°C and at 510°C for the feed to catalyst ratio of 1:2 and 1:3 with the specific gravity of 0.855, which exists, in the range of diesel products. The liquid products using activated carbon were somewhat high in density.

Table 4.7: Experimental Conditions for catalytic degradation of HDPE using A-C catalyst with liquid product yield.

Feed	Catalyst	Feed/catalyst	Temp	Time	Liquid product	% Yield
50	12.5	4	530	20	32	64
50	16.66	3	510	30	37	74
50	25	2	490	40	37	74
55	50	1	470	75	40	72.73

The feed to catalyst ratio, time required for conversion, temperature needed and the percentage yield of liquid products is given in the table. It clearly shows the trail with 1:3 and 1:2 feed to catalyst ratio is optimum when compared with the others with reaction time of 30 and 40 min and the reaction temperature of 510°C and 490°C with the maximum liquid products yield of 74% and which are exists in the range of diesel. This liquid was very heavy fuel when compared with the products produced from the catalytic degradation using the catalysts Si-Al and mordenite.

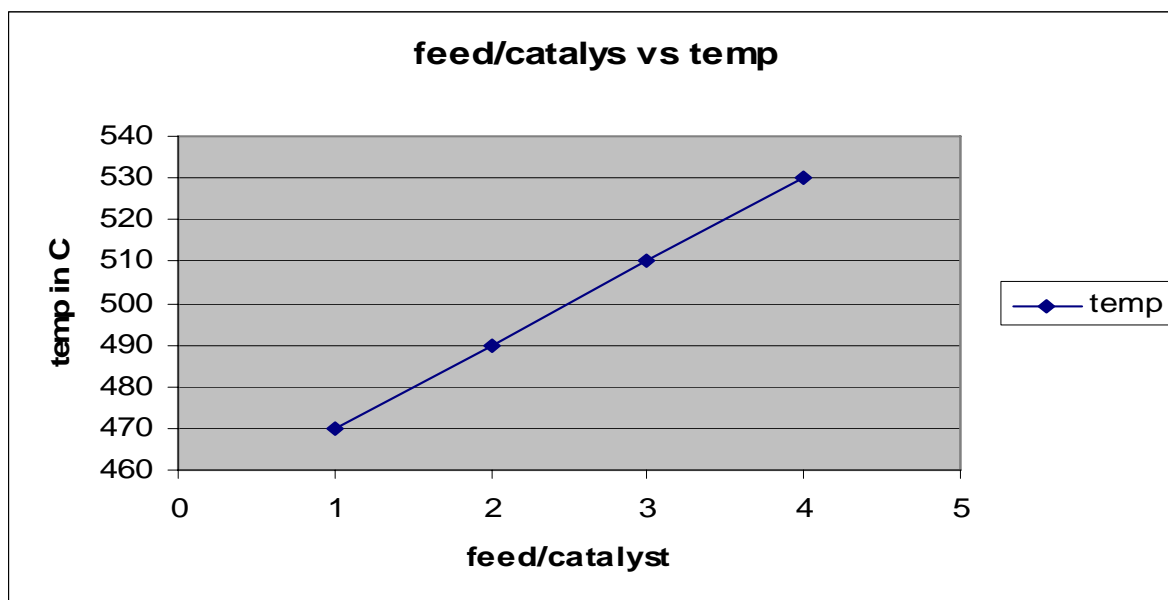


Fig 4.21: Feed / catalyst vs temp for the catalytic degradation of HDPE using A-C catalyst

The different trends of the products obtained and its relation with time, temperature, amount of catalyst used is shown below. We have observed that the reaction time increases with the

decrease in the reaction temperature and the initial rate of degradation was decreased with feed to catalyst ratio.

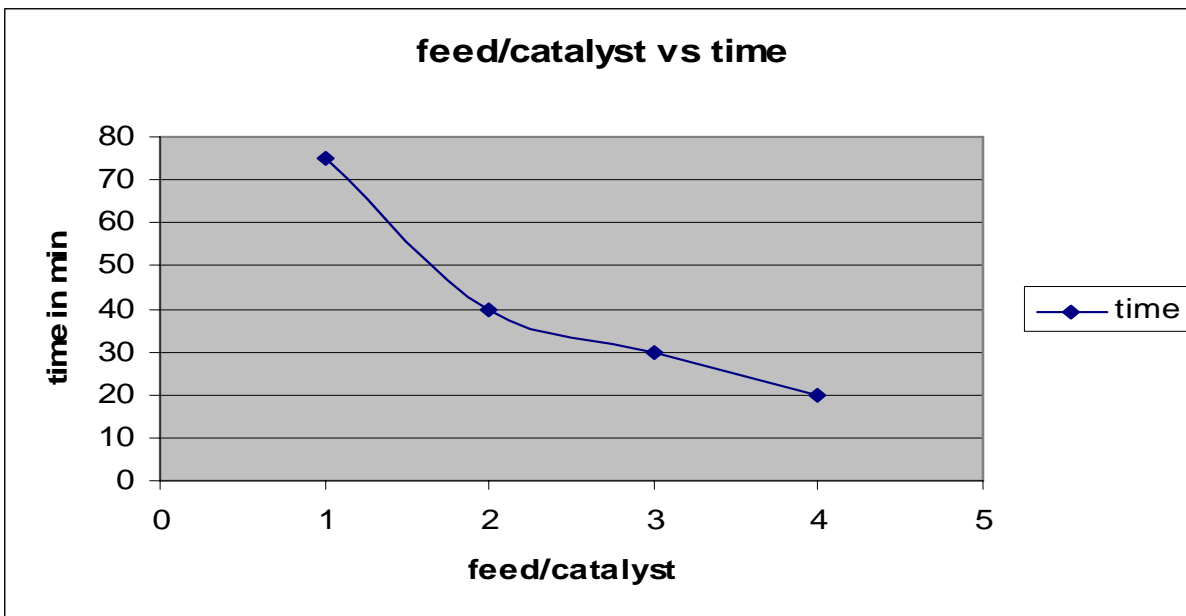


Fig 4.22: Feed / catalyst vs time for the catalytic degradation of HDPE using A-C catalyst.

The reaction temperature was very much less like mordenite when compared with all other catalysts. We could find that 470°C as the minimum degradation temperature in this case by using activated carbon as catalyst.

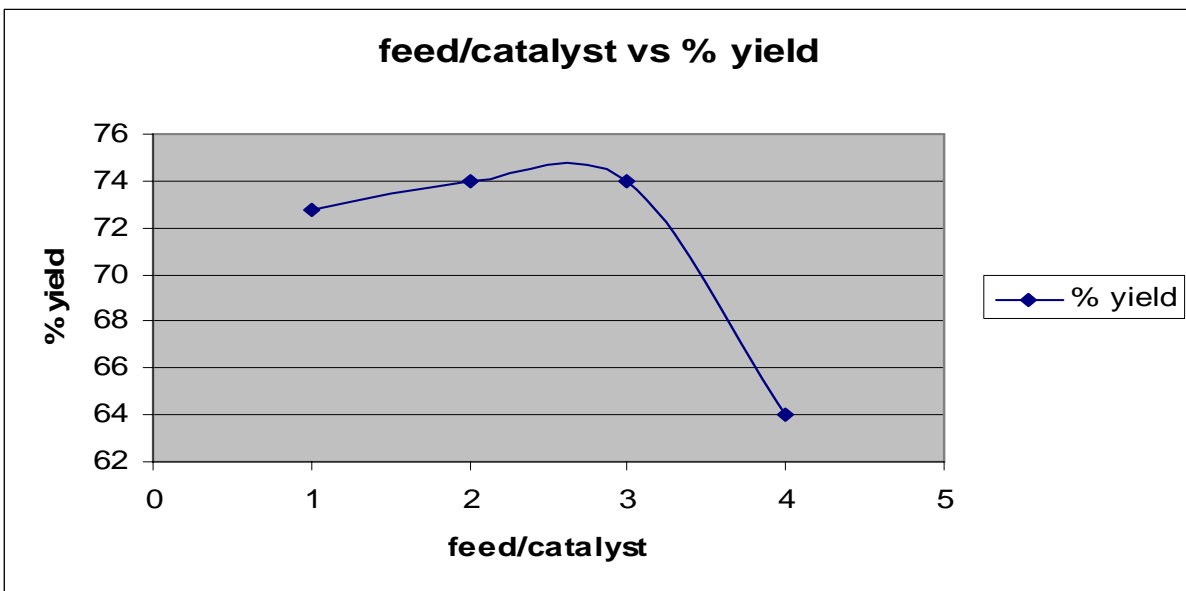


Fig 4.23: Feed / catalyst vs %yield for the catalytic degradation of HDPE using A-C catalyst.

At minimum reaction temperature the time required for the completion of the reaction was very high i.e., about 75 min for the feed/catalyst ratio 1:1. But the products coming were heavy fuels.

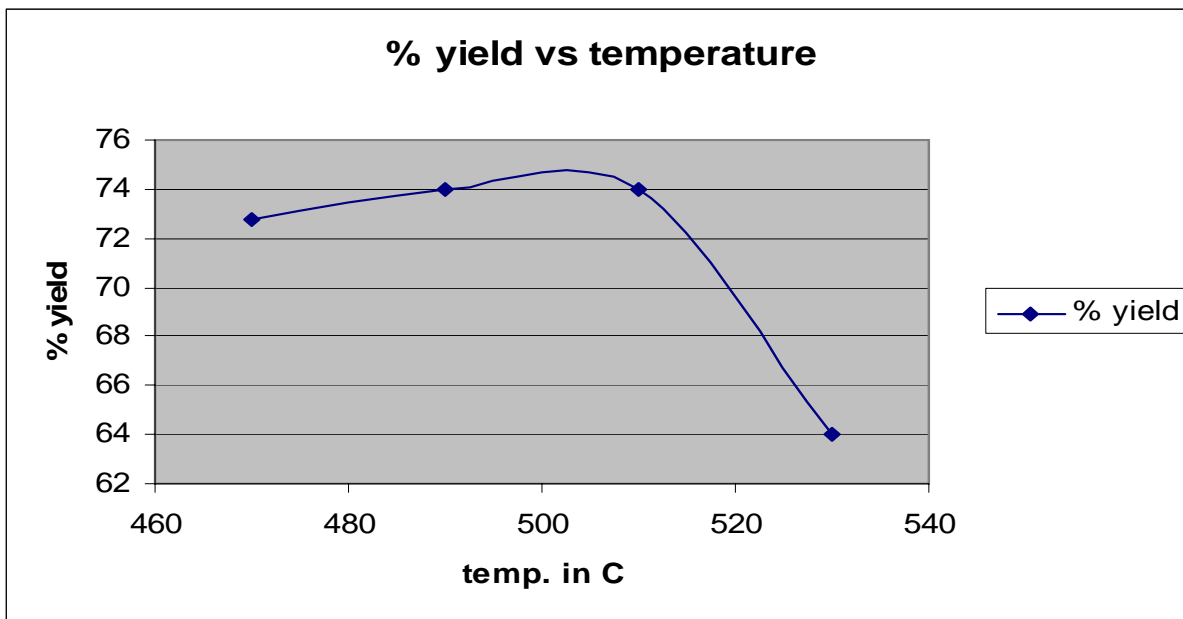


Fig 4.24: Temperature vs liquid product yield for the catalytic degradation of HDPE using A-C catalyst.

We may observe that the liquid product yield is very high in the temperature range of 500-510°C as shown in the fig.4.25

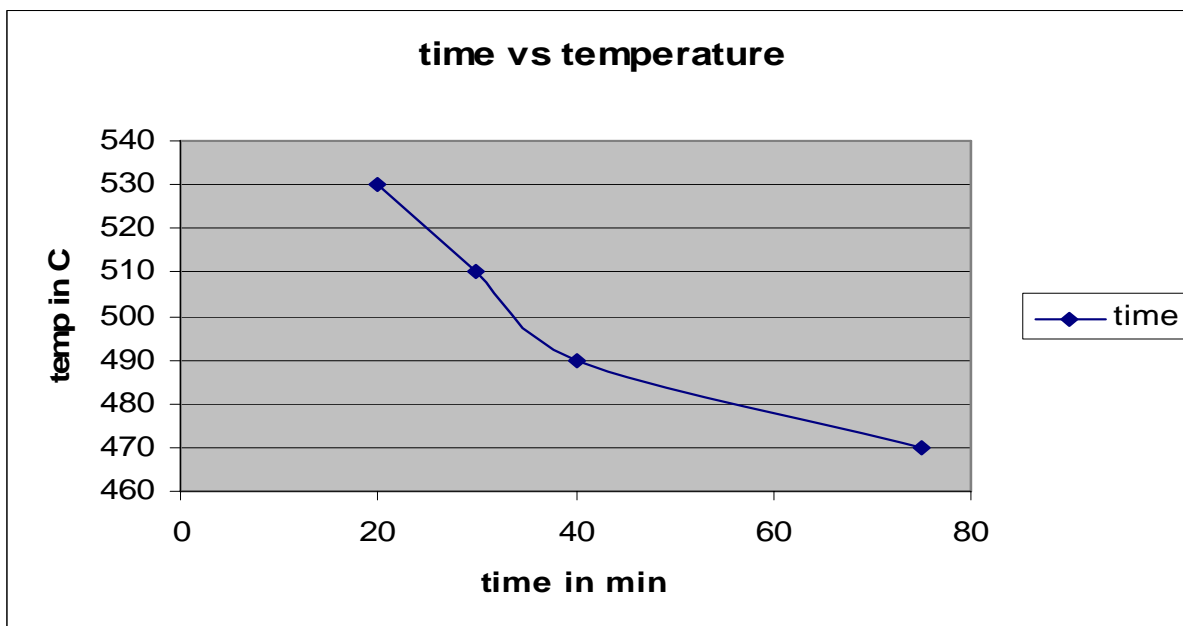


Fig 4.25: Time vs temperature for the catalytic degradation of HDPE using A-C catalyst

Activated Carbon catalyst supports the process at 470-510°C to give better liquid product yield and with minimum reaction time as show in fig. But the products are not much stable in liquid form as in the case of thermal degradation.

4.2.4 Isothermal Catalytic and Non-Catalytic Degradation of Waste HDPE Plastics:

All the previous methods and experiments were done for the individual catalysts and thermal techniques for waste HDPE plastic's degradation. And we have seen that how the process parameters especially yield of the liquid hydrocarbons varied with different feed/ catalysts ratios, by the application of different ranges of reaction temperatures, with their individual lapsed times for the completion of the reactions. But here we have observed many things by the isothermal techniques with constant feed/catalyst ratios of all the catalysts. The table shows the product distribution of the isothermal catalytic and non-catalytic degradation of waste HDPE plastics. The reaction temperature applied here was 500°C, the feed/ catalyst ratio taken was 4:1 and the reaction time was 30 min.

Table 4.8: product distribution of Catalytic and non-catalytic degradation of waste HDPE plastics at F/C ratio 4:1

Process	%Solids	%Liquids	%Gases	Time (min)	Nature of the Products
Non-catalytic (Thermal)	2.85	70	27.15	30	Not Solidified
Catalytic (Silica Alumina)	3.18	74	22.88	30	Not Solidified
Catalytic (Mordenite)	3.21	76	20.79	30	Not Solidified
Catalytic (Activated carbon)	3.11	84	12.89	15	Solidified

The process with Activated carbon was very fast and the yield of the liquid product was also more when compared with the others but the liquid fuel was solidified quickly. The time taken for the completion of the reaction was very less about 15 min only. The liquid fuels

from thermal degradation at this 500°C were very stable in liquid form when compared with all other non-isothermal non-catalytic degradation processes.

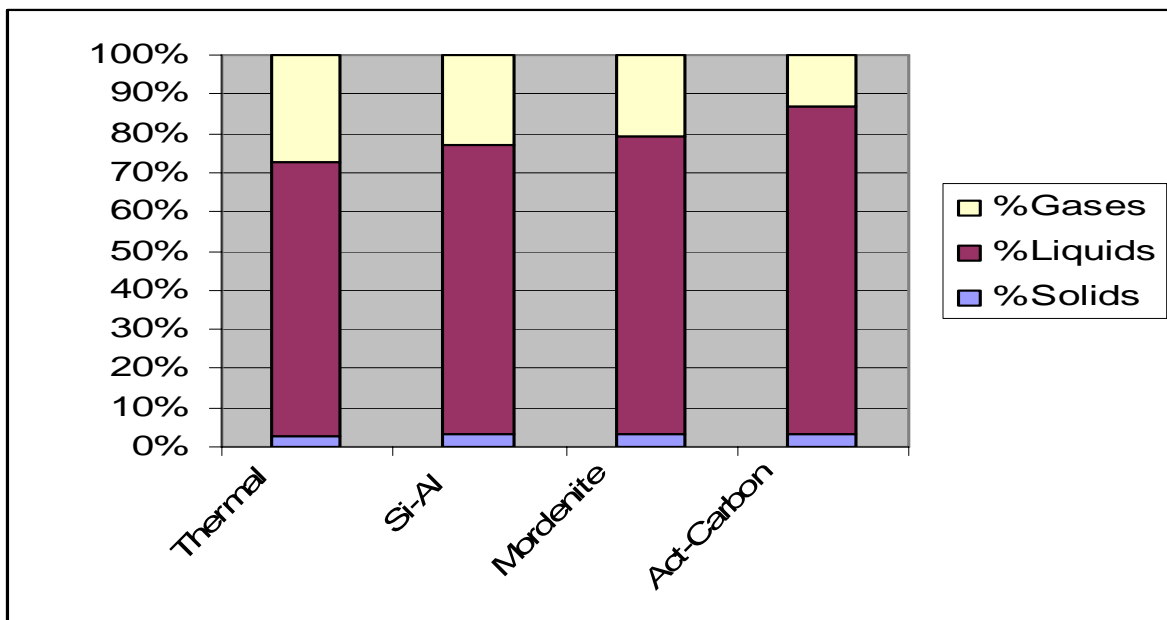


Fig 4.26: Product Distribution of Isothermal degradation of Waste HDPE at 500°C & 4:1 of Feed/catalyst. Ratio.

The liquid fuels of all other processes were very stable in liquid form and the time taken for the completion of the reaction was almost same about 30 min. But for the mordenite it was taken about 60 min and the liquid produced was very light and much qualitative and quantitative. We got maximum yield of 76% stable liquid fuels in the range of gasoline oils by using mordenite.

4.3 Physical Analysis of Liquid Products:

Different composition of liquid product was obtained for different catalyst and its different ratio with plastic feed. The liquid obtained was highest for a particular ratio at a particular temperature. This was the optimum range for the particular catalyst. It was seen that Mordenite given the maximum yield of liquid product and it was the minimum from thermal cracking. The quality of product obtained was also better in case of catalytic cracking. In every process minimum 2% of carbon was obtained as final residue.



Fig 4.27: Different liquid products samples obtained during cracking.

1. Si-Al (sample1) 2.Si-Al (sample2) 3. Activated Carbon (sample1) 4. Activated Carbon (sample 2) 5. New Catalyst (sample1) 6. New Catalyst (sample2) 7. Mordenite (sample1) 8. Mordenite (sample2) 9. Solidified Liquid fuel 10. Thermal (sample1) 11.Si-Al (sample3) 12. New Catalyst (sample3) 13. Thermal (sample2) 14. Si-Al (sample4).

4.3.1 Solid Residue:



Fig 4.28: Solid carbon residue obtained after cracking

The residue formed in this process was appears as a very good colorant. And the literature says it may use as activated carbon for cracking processes. Its pure carbonaceous fine powder.

4.3.2 Liquid Hydrocarbon Products:

We got different types of liquid hydrocarbon products from the both catalytic and non-catalytic cracking methods. The catalysts used were effectively worked to change the yield and composition of the liquid products. We got the products in different colors as shown in fig.4.27 and we tried to test them for finding their composition but we failed to do that because of economical reasons. Hence, we turned for checking physical properties mainly we tested for specific gravity, pour point and flash point and tabulated all the values.

4.3.2.1 Physical properties of Liquid Fuels

The samples collected were tested for some of their physical properties. The properties tested were specific gravity, pour point, flash point and fire point.

4.3.2.1.1 Specific Gravity & Density:

It determines the maximum power/(weight/volume). Hydrocarbons of low specific gravity passes the maximum thermal energy /volume. Hydrocarbons of high specific gravity (aromatics) posses the maximum thermal energy/weight.

It gives the idea about:

- (a) Required for the conversion of measured volumes to volumes at the standard temperature of 15°C.
- (b) Higher specific gravity means higher C: H₂. Hence, heavier the oils have lower gross calorific value on weight basis but higher gross calorific value on volumes basis.
- (c) Increase in specific gravity means decreases in paraffin content, an increase in specific gravity increases the amount of heat/volume.

The specific gravity was found for all the liquid products by using a 10 ml specific gravity bottle. 10 ml of the sample was collected in a pipette and the pre-weighted bottle was filled to its brim. The final weight of the bottle was taken. This gave the weight of the sample which when divided by 10 gave the specific gravity and hence the density of the sample. All the values were showed in the table.

4.3.2.1.2 Pour Point:

For finding the pour point, the sample was taken in a test tube and kept in a Ultra Low Temperature Refrigerator. The refrigerator has a capacity of giving temperature up to -85°C. After every 5°C drop in temperature, the sample was taken out and its fluidity was checked. At a particular temperature the liquid ceases to flow, this temperature was taken as the pour point of the fluid.

4.3.2.1.3 Flash Point:

It is the lowest temperature at which oil gives out sufficient vapor to form an inflammable mixture with air and catches fire momentarily flashes when the applied.

Flash point gives the idea about:

- (a) Volatility of the liquid fuels.
- (b) Amount of low boiling fraction present in the liquid fuel.
- (c) Explosion hazards.

(d) Nature of boiling point diagram of the system.

Apparatus: Pensky-Martin (Flash point $>50^{\circ}\text{C}$) and Abel closed cup (flash point $<50^{\circ}\text{C}$)

Procedure: The flash point of the sample was determined by using Pensky Martin Apparatus. About 30 ml of the sample was taken in the cup of the apparatus and it was cooled by using a water bath. Continuous stirring was done during the process. After every 1°C fall in temperature, the vapour of the sample was exposed to a flame. The point at which fire starts with a flash is known as the flash point.

Many liquid products were turned to solidified. Whatever the samples remained stable in liquid form only tested to find these physical properties. All the values are comparable with gasoline and diesel range of products.

Table 4.9: Some of the physical properties of the liquid products.

Catalyst	Ratio	Specific Gravity	Pour Point C	Flash Point C
Non-catalytic		0.842	-75	31
Silica Alumina	1			31.5
Silica Alumina	2	0.8038	-60	31.5
Silica Alumina	3	0.7787	-60	32.5
Silica Alumina	4	0.785	-60	31.5
Modernite	1			
Modernite	2	0.754	-80	32
Modernite	3			
Modernite	4	0.761		33
Activated Carbon	1	0.8506	-80	31
Activated Carbon	2		-80	31
Activated Carbon	3			
Activated Carbon	4			

The range of specific gravity given for the gasoline were 0.72 to 0.78 and it was up to 0.85 for diesel range of products [39].

Chapter 5

CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS AND RECOMMENDATIONS

We have studied extensively the cracking nature of HDPE both under catalytic and non-catalytic methods with the application of some important suitable catalysts, and about the catalyst characterization by the application of SEM and XRD.

The cracking temperature of HDPE was very high when compare with other plastics as we have observed from the literature. It was minimum 460°C. We have reached better yield (76%) of liquid products with the application of mordenite catalyst at this temperature. But the time taken for the completion of the reaction was very high about one hr.

We have conducted the experiments on semi batch reactor without any application of stirring. That's why we applied maximum temperature for the cracking.

The initial temperature of degradation and the time to complete the reaction were different for every process. These were the effective parameters along with feed/catalyst composition, type of the polymer and the type of the catalyst.

At the application of maximum reaction temperature for both thermal degradation and catalytic degradation, we observed the minimum time taken for the completion of the reaction. It meant if the reaction temperature increases the time for the completion of reaction decreases. The rate of the reaction depends on the size and shape of the material and catalyst. We have used irregular shape of the material that's why we got some disorders in reaction time and temperatures.

The yield and the composition of the liquid product vary along with feed to catalyst ratio and reaction temperature. And all the liquid products we got were analyzed for their physical properties. The specific gravities of all the samples were existed in the range of gasoline and diesel range of fuels. We have also tested pour point, flash point and fire point. These were varied along with their individual composition.

Whenever the time taken for the completion of the reaction was very short there we observed that the liquid product turned to solidify into wax type material.

The maximum yield (96%) of liquid fuel we get with the application of a new catalyst at 550°C. But it was solidified. And we got 80% yield at 500°C with the feed / catalyst ratio of 4:1 with the application of the same catalyst. It was very stable and very light fuel of specific gravity 0.77 which exists in the range of gasoline fuels.

If we used the mixed plastics then the reaction temperature decreases further. The maximum temperature needs for the cracking of HDPE only when compared with all other types waste plastics.

The yield of gases was more in case of thermal degradation when compared with all other catalytic methods. And it increases along with the rise in reaction temperature. We have observed the maximum gaseous product's yield as 61.06% at 650°C with the application of thermal degradation.

The solid residue remained was about 3% for the HDPE which we have used. And it was looking like pure carbon.

All the catalysts Silica Alumina, Mordenite and Activated Carbon were analyzed for their physical structure and composition. We have observed many things from their analysis. We got better yield of liquid product by the application of a very new catalyst because of its large number of pores and with high surface area when compared with all other catalysts.

The catalysts can be reusable as the solid residue, which was formed on the surface of catalyst was solid coke, which have the properties of carbon. Or in other wards if we pretreated them we will use them further.

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