

**INFLUENCE OF SOME HETEROGENEOUS CATALYSTS ON
PYROLYTIC CONVERSION OF MODEL POLYPROPYLENE AND
HIGH DENSITY POLYETHYLENE INTO FUEL LIKE PRODUCTS**



BY

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CONVERSION OF MODEL POLYPROPYLENE AND HIGH DENSITY
POLYETHYLENE INTO FUEL LIKE PRODUCTS**



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requirements for the Degree of Doctor of Philosophy in Chemistry*

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DISSERTATION ACCEPTANCE CERTIFICATE

The thesis/dissertation prepared and submitted by Mr. Mohammad Ismail Khan titled "Influence of Some Heterogeneous Catalysts on Pyrolytic Conversion of Model Poly Propylene and High-density Polyethylene into Fuel Like Products" in partial fulfillment of the requirements for the award of the Degree of Doctor of Philosophy in Chemistry was thoroughly reviewed. The dissertation was found in conformance with the synopsis and meets the standard requirement. However, the conferral of the Degree is subject to fulfillment of all departmental requirements.



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**IN THE NAME OF ALMIGHTY ALLAH,
THE MOST BENEFICENT,
THE MOST MERCIFUL**

DEDICATED TO
My LOVING CHILDREN AND WIFE



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INFLUENCE OF SOME HETEROGENEOUS CATALYSTS ON PYROLYTIC CONVERSION OF MODEL POLYPROPYLENE AND HIGH DENSITY POLYETHYLENE INTO FUEL LIKE PRODUCTS

ABSTRACT

Because of the limitations of petroleum products in terms of their high prices, scarce supplies, and the reality of petroleum depletion, emphasis must be on finding cheap, abundant & environmentally friendly alternative resources. Throughout the world, many steps are being taken in this direction to find alternatives to petroleum based fuels. Several substitute candidates including liquids from coal, biomass, spent lubricants, waste plastics, tyres, etc. are the focus of researchers in the past few decades to get fuel having properties similar to petroleum based oils. Among these, waste plastics are the promising one to get not only fuel like products to valorize petroleum and petrochemicals, but also to get rid of the disposal issues in a more environmental friendly way. The present work was aimed at catalytically converting two commonly used polyolefins i.e. PP and HDPE in a fixed-bed reactor over original and metal supported heterogeneous catalysts into useful products with emphasis on high conversion to liquid products that could be used as fuels or feed-stock in chemical industries.

Four catalyst systems i.e. original and metal impregnated titanates (BaTiO_3), prebaked clay (PBCs), bentonite clay (BCs) and activated carbon (ACs) were used to identify their potential as catalysts in conversion of PP and HDPE to liquid products with interest in gasoline and light gas oil fractions. All the laboratory prepared catalysts were calcined prior to use and characterized by using SEM, EDS, SAA, XRD and surface acidity measurements. The pyrolysis reactions were carried out in a steel made micro reactor under nitrogen environment. Preliminary experiments were performed in the temperature range of 250-400 °C in order to optimize the temperature. Time optimization study was also performed. The optimum temperature and time were decided on the basis of highest wt% yield of the liquid products. The effect of catalyst type and concentration on total conversion and conversions to liquid, gas and coke/residue was next studied. The optimum catalyst and its concentration in case of four catalysts systems were also decided on the basis of highest wt% yield of the liquid product.



The liquid products derived from both polyolefins in thermal and catalyzed runs in highest yields were subjected to compositional analyses by FTIR and GC-MS in order to study the carbon range and hydrocarbon group types distributions.

The results indicated that polyolefins (both PP and HDPE) were converted more meaningfully into useful liquid products through catalytic route compared to thermal route. The catalytic activities of the various catalysts were toward formation of C₆-C₁₂ C-range products in case of PP and C₁₃-C₁₆, and C₂₁-C₃₀ range hydrocarbons in case of HDPE. Compared to thermal runs, the derived liquids were mostly comprised of paraffinic and olefinic hydrocarbons. Some of the catalysts used caused the formation of naphthenic hydrocarbons. Formation of oxygenates and aromatics were not observed.

The standard fuel oil analyses developed for petroleum based fuels were applied to crude/lump liquids as well as their distillate fractions. The results indicated that the lump liquid pyrolysates derived from both thermal and catalytic degradation met the fuel grade criteria and may be used as feed stock to refineries or petrochemical industries. The fuel qualities of the distillate fractions (b.pt. 65-180 °C) closely matched with the gasoline and kerosene range hydrocarbons. On the other hands, the fuel characteristics of the distillates fractions (b.pt. 180-250 °C) showed that these fractions can be used as blends to marketable premium fuel products particularly gasoline & light gas oil.



Table of Contents

S.No	Title	Page #
-	Title Pages	i-v
-	ACKNOWLEDGEMENT S	vi
-	ABSTRACT	vii
-	TABLE OF CONTENTS	ix
-	LIST OF TABLES	xi
-	LIST OF FIGURES	xiv
1.	INTRODUCTION	1
1.1	SCOPE OF THE CURRENT STUDY	2
1.2	AIMS AND OBJECTIVES OF THE PRESENT WORK	4
1.3	PLASTICS	5
1.3.1	Polyethylene	9
1.3.2	Polypropylene	10
1.4	PLASTIC WASTES	11
1.4.1	Sources of Plastic Wastes	11
1.5	MANAGEMENT OF WASTE PLASTICS	13
1.5.1	Land Filling	13
1.5.2	Mechanical Recycling	14
1.5.3	Biological Recycling	14
1.5.4	Thermochemical Recycling	14
1.6	THERMAL PYROLYSIS	16
1.6.1	Mechanism of Thermal Cracking	16
1.7	CATALYTIC PYROLYSIS	20
1.7.1	Mechanism of Catalytic Cracking	20
1.7.2	Catalysts used for Plastic Conversion into Useful Products	22
1.7.3	Properties of Catalysts Used in the Plastic Conversion	26
1.8	CONVERSION PRODUCTS AND THEIR ANALYSIS	29
1.8.1	Conversion Products	29
1.8.2	Analysis of the Liquid Products	29
1.9	LITERATURE SURVEY	37
	REFERENCES	58
2	EXPERIMENTAL	62
2.1	CHEMICALS AND REAGENTS	63
2.2	CATALYSTS PREPERATION	63
2.2.1	Preparation of Original and Doped Barium Titanates (BaTiO ₃).	64
2.2.2	Preparation of Original and Transition Metal Impregnated Pre Baked Clay (PBCs) Catalysts.	64
2.2.3	Preparation of Original and Transition Metal Impregnated Bentonite (BCs) Catalysts.	65
2.2.4	Preparation of Original and Transition Metal Impregnated Activated Carbon, Darco, (ACs) Catalysts.	66
2.3	PYROLYSIS EXPERIMENTS	66
2.3.1	Pyrolysis Equipment	66



2.3.2	Process	68
2.3.3	Calculations	69
2.4	CHARACTERIZATION/ANALYSES	69
2.4.1	Analysis of Feed Polymers	70
2.4.2	Characterization of Catalysts Used	70
2.4.3	Liquids Analyses	72
	REFERENCES	79
3	RESULTS AND DISCUSSION	80
3.1	CHARACTERIZATION OF FEED POLYMERS	82
3.2	CHARACTERIZATION OF CATALYSTS USED	84
3.2.1	Characterization of Original and metal doped nanoporous titanates	84
3.2.2	Characterization of original and selected metal oxide impregnated PBCs.	88
3.2.3	Characterization of original and metal oxide impregnated BCs	94
3.2.4	Characterization of original and transition metal salts impregnated ACs.	100
3.3	THERMAL PYROLYSIS	106
3.3.1	Effect of temperature on overall yields and yields of liquid, gas, and residue/coke	109
3.3.2	Analyses of Liquid Products	114
3.4	CATALYTIC PYROLYSIS OVER NANOSTRUCTURED HETEROGENEOUS CATALYSTS	125
3.4.1	Catalytic Pyrolysis of PP	125
3.4.2	Catalytic Pyrolysis of HDPE	140
3.5	CATALYTIC PYROLYSIS OVER METAL OXIDES IMPREGNATED PBCs	155
3.5.1	Activity Tests	156
3.5.2	Liquid Product Composition	161
3.6	CATALYTIC PYROLYSIS OVER METAL OXIDES IMPREGNATED BCs	174
3.6.1	Activity Tests	175
3.6.2	Liquid Products Composition	179
3.7	CATALYTIC PYROLYSIS OVER TRANSITION METAL SALTS IMPREGNATED ACs	193
3.7.1	Activity Tests	193
3.7.2	Liquid Products Composition	197
3.8	FUEL PROPERTIES OF LIQUIDS DERIVED FROM THERMAL AND CATALYTIC PYROLYSIS OF POLYPROPYLENE AND HIGH DENSITY POLYETHYLENE	211
3.8.1	Distillation Study and Fuel Properties of the Distillate Fractions	211
3.8.2	Fuel Properties of Crude Pyrolysates and Their Distillate Fractions	215
3.9	Comparative Study	231
	CONCLUSIONS	236
	REFERENCES	237



List of Tables

Table #	Title	Page #
1.1	Some commonly used thermo-plastics and their uses	6
1.2	Some commonly used thermosetting plastics and their uses	7
1.3	Some commonly used elastomers and their uses	7
1.4	Typical properties of polyethylene (PE)	9
1.5	Typical properties of polypropylene	11
1.6	Fuel properties and their ASTM designations used for analysis of the liquid fuels	32
1.7	Calorific values of different fuels	35
3.1	Properties of feed PP and HDPE	83
3.2	EDX analysis of original and various metal doped BaTiO ₃ catalysts	86
3.3	Surface area analysis of original and various metal doped BaTiO ₃ catalysts	86
3.4	Total acidity analysis of original and various metal doped BaTiO ₃ catalysts	87
3.5	Mineralogical composition of the pre baked clay (PBC).	90
3.6	Surface area and pore size analysis of the original and metal oxides impregnated PBCs	91
3.7	Acidity of the original and metal oxides impregnated PBCs.	91
3.8	EDX analysis of original acid washed BC	96
3.9	Surface area, pore size, pore volume and active metal concentration of the acid washed and various transition metals oxides impregnated BCs	97
3.10	Acidity of original and metal oxides impregnated BCs.	97
3.11	EDX analysis of original activated carbon	102
3.12	Surface area, pore size, pore volume and active metals concentration of the original and various metals oxides impregnated ACs	103
3.13	Acidity of the original and various metal oxides impregnated ACs	103
3.14a	Yields of pyrolysates derived from thermal pyrolysis of PP and HDPE as a function of temperature	113
3.14b	Yields of pyrolysates derived from PP as a function of time.	113
3.15	Major absorption peaks observed and assigned configurations in the FT-IR spectra of the liquid products derived from thermal pyrolysis of PP and HDPE	118
3.16	Hydrocarbons identified in the liquid product derived from thermal pyrolysis of PP	120
3.17	Hydrocarbons identified in the liquid product derived from thermal pyrolysis of HDPE	122



3.18	Carbon range distributions in liquid products derived from thermal pyrolysis of PP and HDPE	124
3.19	Hydrocarbon group types distributions in liquid products derived from thermal pyrolysis of PP and HDPE	124
3.20	Yields of pyrolysates derived from catalytic pyrolysis of PP over original and metal doped BaTiO ₃ as a function of catalyst type and concentration.	129
3.21	Major absorption peaks observed and assigned configurations in the FT-IR spectra of the liquid products derived from pyrolysis of PP using BaTiO ₃ based catalysts.	134
3.22	Hydrocarbons identified in liquid product derived from catalytic pyrolysis of PP using Pb/BaTiO ₃	136
3.23	Carbon range distributions in liquid products derived from catalytic pyrolysis of PP over original and metal doped BaTiO ₃	140
3.24	Hydrocarbon group types distributions in liquid products derived from catalytic pyrolysis of PP over original and metal doped BaTiO ₃	140
3.25	Yields of pyrolysates derived from catalytic pyrolysis of HDPE over original and metal doped BaTiO ₃ as a function of catalyst type and concentration.	144
3.26	Major absorption peaks observed and assigned configurations in the FT-IR spectra of the liquid products derived from pyrolysis of HDPE using BaTiO ₃ based catalysts	150
3.27	Hydrocarbons identified in the liquid products derived from catalytic pyrolysis of HDPE over Pb-Co/ BaTiO ₃	152
3.28	C-number distribution in liquid products derived from catalytic pyrolysis of HDPE over original and metal doped BaTiO ₃	154
3.29	Hydrocarbon group types distributions in liquid products derived from catalytic pyrolysis of HDPE over original and metal doped BaTiO ₃	154
3.30	Yields of pyrolysates derived from catalytic pyrolysis of PP over original and metal oxides impregnated PBCs as a function of catalyst type and concentration.	160
3.31	Major absorption peaks observed and assigned configurations in the FT-IR spectra of the liquid products derived from catalytic pyrolysis of PP and HDPE over PBCs	166
3.32	Hydrocarbons identified in the liquid products derived from catalytic pyrolysis of PP over Fe/PBC	169
3.33	Hydrocarbons identified in the liquid product derived from catalytic pyrolysis of HDPE over Zn/PBC	171
3.34	C-number distribution in liquid products derived from catalytic pyrolysis of PP and HDPE over PBCs	173
3.35	Hydrocarbon group types distributions in liquid products derived from catalytic pyrolysis of pyrolysis of PP and HDPE over PBCs	173
3.36	Yields of pyrolysates derived from catalytic pyrolysis of PP and	178



	HDPE over original and metal oxides impregnated BCs as a function of catalyst type and concentration.	
3.37	Major absorption peaks observed and assigned configurations in the FT-IR spectra of the liquid products derived from catalytic pyrolysis of PP and HDPE over BCs	184
3.38	Hydrocarbons identified in the liquid product derived from catalytic pyrolysis over Co/BC	187
3.39	Hydrocarbons identified in the liquid product derived from catalytic pyrolysis of HDPE over Zn/BC	189
3.40	Carbon range distributions in liquid products derived from catalytic pyrolysis of PP and HDPE over BCs	192
3.41	Hydrocarbon group types distributions in liquid products derived from catalytic pyrolysis of PP and HDPE over BCs	192
3.42	Yields of pyrolysates derived from catalytic pyrolysis of PP and HDPE over original and metal salts impregnated ACs as a function of catalyst type and concentration.	196
3.43	Major absorption peaks observed and assigned configurations in the FT-IR spectra of the liquid products derived from thermal and catalytic pyrolysis of PP and HDPE over ACs	202
3.44	Hydrocarbons identified in liquid product derived from catalytic pyrolysis of PP over Fe/AC	205
3.45	Hydrocarbons identified in liquid product derived from catalytic pyrolysis of HDPE over Zn/AC	207
3.46	C-number distributions in liquid products derived from catalytic pyrolysis of PP and HDPE over ACs.	210
3.47	Hydrocarbon group types distributions in liquid products derived from catalytic pyrolysis of PP and HDPE over ACs	210
3.48	Standard Test methods used for fuel properties of PP and HDPE derived liquid products	214
3.49	Distillation behavior of crude liquid pyrolysates obtained from PP in thermal and catalytic runs	215
3.50	Distillation behavior of crude liquid pyrolysates obtained from HDPE in thermal and catalytic runs	215
3.51	Fuel properties of the crude liquid products derived from thermal and catalytic pyrolysis of PP	227
3.52	Fuel properties of the crude liquid products derived from thermal and catalytic pyrolysis of HDPE	228
3.53	Fuel properties of the distillate fractions obtained from the thermal and catalytic pyrolysates of PP	229
3.54	Fuel properties of the distillate fractions obtained from the thermal and catalytic pyrolysates of HDPE	230



List of Figures

Fig. #	Title	Page #
	Introduction	
1.1	Different types of polymers and their monomers	8
1.2	Plastic wastes management routes	14
1.3	Reaction scheme: Mechanism of thermal cracking	18
1.4	Reaction scheme: Random chain scission in polypropylene	20
1.5	Reaction scheme: Unzipping mechanism in polystyrene	20
1.6	Reaction scheme: Catalytic pyrolysis of polymer	23
	Experimental	
2.1	Schematic of the pyrolysis reactor	67
2.2	Process flow sheet	69
	Results and Discussion	
3.1	Electron micrographs of original and variously doped BaTiO ₃ catalysts	87
3.2	XRD patterns of original and variously doped BaTiO ₃ catalysts	88
3.3	SEM micrographs of original and metal oxides impregnated PBCs	92
3.4	EDX analysis of original and metal oxides impregnated PBCs	93
3.5	XRD patterns of original and metal oxide impregnated PBC	94
3.6	SEM micrographs of original and metals oxides impregnated BCs	98
3.7	EDX signatures of original and impregnated BC	99
3.8	XRD patterns of original and metal oxide impregnated BCs	100
3.9	SEM micrographs of original and metals impregnated activated carbon (AC)	104
3.10	EDX Profiles of original and metals impregnated ACs	105
3.11	XRD patterns of (a) original carbon (b) Fe/AC (c) Zn/AC	106
3.12	FT-IR spectra of liquid products derived from thermal pyrolysis of (a) PP and (b) HDPE	118
3.13	GC-MS spectrum of liquid product derived from PP by thermal pyrolysis	119
3.14	GC-MS spectrum of liquid product derived from HDPE by thermal pyrolysis	119
3.15	FT-IR spectra of liquid liquid products derived from PP in uncatalyzed and BaTiO ₃ catalyzed runs	135
3.16	GC-MS spectrum of liquid product derived from PP by pyrolysis in the presence of Pb/BaTiO ₃	136
3.17	FT-IR spectra of the liquid products derived from HDPE with	151



	original and variously doped BaTiO ₃ catalysts	
3.18	GC-MS spectrum of liquid product derived from HDPE by pyrolysis in the presence of Pb-Co/BaTiO ₃	152
3.19	FT-IR spectra of the liquid products derived from thermal and catalytic pyrolysis (a) PP thermal run (b) PP catalyzed run (c) HDPE thermal run (d) HDPE catalyzed run	167
3.20	GC-MS spectrum of liquid product derived from PP by pyrolysis in the presence of Fe/PBC	168
3.21	GC-MS spectrum of liquid product derived from HDPE by pyrolysis in the presence of Zn/PBC	168
3.22	FT-IR spectra of the liquid liquid products derived from thermal and catalytic pyrolysis (a) PP thermal run (b) PP catalyzed run (c) HDPE thermal run (d) HDPE catalyzed run	185
3.23	GC-MS spectrum of liquid product derived from PP by pyrolysis in the presence of Co/BC	186
3.24	GC-MS spectrum of liquid product derived from HDPE by pyrolysis in the presence of Zn/BC	186
3.25	FT-IR spectra of the liquid products derived from thermal and catalytic pyrolysis (a) PP thermal run (b) PP catalyzed run (c) HDPE thermal run (d) HDPE catalyzed run.	203
3.26	GC-MS spectrum of liquid product derived from PP by pyrolysis in the presence of Fe/AC	204
3.27	GC-MS spectrum of liquid product derived from HDPE by pyrolysis in the presence of Zn/AC	204



INTRODUCTION





CHAPTER-1

INTRODUCTION

1.1. SCOPE OF THE CURRENT STUDY

Plastics are enjoying popularity since as early as 1860 when these were first invented. With the passage of time, demand for both commercial as well as household uses was increased manifold. Chemically, plastics are made up by polymerization of small monomers into long chain molecules called polymers. Due to their inertness, thermal and electrical insulating properties, and light weight, plastics are more desirable for use in food and agro- based goods packaging, fabrication of electrical goods, and apparel, etc. Further, due to high demand, low production cost, lower energy consumption and low CO₂ emissions during production of plastics, worldwide plastics production and consumption has tremendously increased in recent years. Due to population growth, it is expected that per capita consumption will increase further in the coming decades. Since, the life span of plastic products is relatively short; there is a vast plastic wastes streams that reach to the trash bins in municipal sites. As plastics like LDPE, HDPE, PP, PS, PVC, PETE, PLA are non-biodegradable, and remain there in the landfills for longer period of time thereby creating serious environmental problems. This has created post consumer disposal issues as constrained by strict legislations of the environmental protection agencies.

Keeping in view, the detrimental impact on the environment, plastic wastes must be disposed off in such a way to cause minimum damage to the environment. Safe alternative processes to effectively dispose off the plastics wastes are needed to be explored. Research is underway worldwide in the field of green chemistry which could yield biodegradable/green polymers; however, commercial production and availability in the market in bulk quantities will take some time to substitute the existing non biodegradable plastics. Other alternative methods need to be sought out to curb the environmental issues and handle the menace without necessarily creating more secondary problems. In addition to environmental issues, there is much concern with the wastages



of a valuable resource. Thus, in order to avoid environmental problems associated with plastic disposal and to ensure resource recovery, emphasis must be on safe disposal through other methods like reuse, production of liquid fuel (energy recovery) and recycling.

Among the several safe disposal measures, conversion into useful products has been the focus of attention of many researchers in recent years. This approach will not only potentially reduce the waste but will conserve the natural resources. However, the constraints are still there in the form of poor liquid yields and inferior quality. Hence, further investigations are required to enhance the generation of value added products (fuel) with minimum energy requirements, improve the product quality and minimize damages to the environment.

To get these objectives, thermal and/or catalytic conversion of waste polymers into fuels or chemicals, is the focus of modern research. Thermal degradation is done with the expense of heat hence, it demands relatively high temperatures. The products are mostly olefinic and enriched in gaseous hydrocarbons. The products need further hydro-treatment which is expensive in term of hydrogen consumption. Keeping in view these limitations, this option is not considered to be applicable on commercial scale. Catalytic conversion (pyrolysis) of plastic wastes into value added products has several advantages over thermal conversion including less severe operating conditions, substantial product yield and reasonably good quality products. This route is considered as a suitable candidate process for effective conversion of plastic wastes into valuable useful products on commercial scale in the near future.

There is sufficient literature on the catalytic pyrolysis of model and waste plastics (both individual and commingled) using a number of catalysts. Silica-alumina catalysts have been found to be successful in degradation of polyethylene into valuable fuel oils at a temperature of 500 °C . Similarly, the use of commercial catalysts like ZSM-5 (Zeolite Socony Mobil-5) and meso porous MCM-41 (Mobil Catalytic Material Number 41) have also been investigated for cracking of polyolefins by many workers. Some cheap



catalysts like spent commercial Fluid Cracking Catalyst (FCC) have been tried for cracking of polystyrene and polyethylene.

Even though, most of these catalysts worked in terms of plastic wastes conversion to various useful products, but still there are shortcomings which have restricted their industrial applications. These include their high cost of production, susceptibility towards deactivation by coke deposition, sintering or coalesce, deactivation due to severe operating conditions of high temperature, extended residence time with low percentage conversion, etc. Moreover, hindrance in internal diffusion of bulky molecules into the micro pores of the catalysts is another limitation affecting the products distribution. Furthermore, textural properties and Bronsted & Lewis acidities may influence the catalytic activities of several catalysts. Hence, there is a need to investigate new catalysts with superior textural, morphological and chemical properties.

The present work aimed at catalytic conversion polypropylene (PP) and high density polyethylene (HDPE) in a fixed-bed reactor at low temperatures over original and metal impregnated nano-structured barium titanates, zeolite like pre baked clays, bentonites and carbon as catalysts into useful products that could be used as fuel and feed-stock for chemical industries with emphasis on high conversion to liquid products and products selectivity in gasoline and diesel range hydrocarbons.

1.2. AIMS AND OBJECTIVES OF THE PRESENT WORK

The aims and objectives of the present study are to:

- find out a safe route for otherwise environmentally objectionable disposition of polyolefins based waste plastic streams
- view the role of some original and metal impregnated nano-structured barium titanates, zeolite like pre-baked clays, bentonites and carbon as catalysts in conversion of polyolefins into synthetic fuels
- view the role of catalyst type and concentration on the overall yields and yields of liquid, gas & solid residue



- evaluate a highly active and selective catalyst (s) for conversion of PP and HDPE with emphasis on high conversion into liquid oils and product selectivity in narrow molecular size distributions to eliminate further product upgradation
- get specific products (liquid oils) enriched in light hydrocarbons (C_4 - C_{16}) comparable in properties with base gasoline and diesel fuel oils
- avoid formation of waxes and coke/char thereby reducing the difficulty of separating complex product mixtures
- evaluate the fuel properties of the derived liquids in comparison with the petroleum derived fuels to see their prospective uses as feed stock to refineries or as blends to the marketable premium fuel products particularly gasoline and diesel fuel oils.

1.3 . PLASTICS

Plastics are polymeric materials that are formed by polymerization of small molecules called monomers. Monomers are repeating molecular units and building blocks, which are bonded together to form a plastic. Plastics are formed by various chemical processes which include:

- Polymerization process i.e. catalytic or peroxide-initiated polymerization of monomers, e.g. ethylene, propylene, or butadiene styrene (copolymers).
- Poly condensation process of dissimilar monomers (e.g. bi-functional organic acids and alcohols or amines).
- Poly addition process of reactive monomer molecules.

Generally, plastics can be divided based on their thermal behavior and synthetic route or polymerization mode. Depending upon thermal behavior, there are two main types of plastics i.e. thermoplastics and thermosetting plastics. Whereas depending upon the mode of polymerization, plastics may be classified as addition polymers or condensation polymers.

Thermoplastics are soft plastics which can be changed into different shapes at specific temperature. These are linear chain macromolecules in which the molecules are joined end-to-end into a series of long carbon chains, without cross linking [1]. These are formed by



addition polymerization. Thermoplasts contribute to the total world's plastic consumption by roughly 80% and are used as containers, packaging, trash bags and other non-durable goods. Typical examples of thermoplasts are high and low density polyethylene (HDPE, LDPE), polyethylene terephthalate (PET), polystyrene (PS), polypropylene (PP) and polyvinyl chloride (PVC). Different types of thermoplasts along with their uses are given in the Table 1.1. Their structural formulas are given in Fig. 1.1.

Table 1.1. Some commonly used thermo-plastics and their uses

Plastic	Uses
Low density polyethylene	Plastic bags, flexible containers and bottles, cling film, some bottle caps, etc.
High density polyethylene	Rigid pipes, automotive fuel tanks, buckets, toys, plants pots, crates and bottles for detergents, bleach, milk, non carbonated drinks, etc.
Polyethylene terephthalate	Bottles for mineral water, fizzy drink and beer, fibers for clothing and carpets, food packaging.
Polypropylene	Food containers, most bottle tops, battery cases, bottle crates, drinking straws, automotive parts, potato chips bags and biscuit wrappers and fibers, etc.
Polystyrene	Dairy product containers, egg boxes, tape cassettes, vending cups disposable cutlery and plates, packing material.
Polyvinyl chloride	Window frames, credit cards, flooring, pipes, bottles, packaging film, cable insulation, and medical products.

On the other hand, thermosetting plastics are those which cannot be converted into different shapes with heating, rather these get harden upon heating. Thermosetting plastics have cross linked carbon chains, which are, therefore, deformed on heating. Thermosets are formed by condensation polymerization in which bi-functional molecules are allowed to condense inter-molecularly under suitable conditions, with the liberation of small by-products such as H_2O , HCl , etc. During this process, the monomers undergo



chemical changes i.e., condensation on heating and change into an infusible mass irreversibly. Examples of thermosetting polymers are unsaturated polyurethane (PU), unsaturated polyesters and, amide, phenolic and epoxy resins [2].

Table 1.2. Some commonly used thermosetting plastics and their uses

Plastic	Uses
Polyurethane	Coating, finishes, cushions, gears, diaphragms, mattress and car seats
Epoxy-resins	Adhesives, sports materials, electrical and automotive equipments
Phenolic-resins	Base for abrasives, electronics material. Used in the field of metal bonding, carbon materials, electronic materials and structural materials to their properties like corrosion resistance, fire resistance and high carbon residue

Table 1.3. Some commonly used elastomers and their uses

Plastic	Uses
Styrene-butadiene rubber	Radial tyres, conveyor belts, gaskets, hoses, floor tiles, footwear and adhesives.
Nitrile rubber	Gloves, health care, textile industry, automotive and aeronautical industry, etc.
Fluoroelastomers	Building industries, petrochemical and automotive industries, aerospace & aeronautics, chemical engineering, optics treatment of textile, stone, microelectronics, etc.
Chloroprene rubber	Rubber industry, adhesives, dipped articles, molded foam and improvement of bitumen.

A third category of plastics is termed as elastomers, which are rubber-type polymers. Elastomers are formed by cross-linking of polymer chains, in a less proportion than thermosets, which give elastic properties to these materials and also bear relatively good resistance [3].



Among all the plastics , polyolefins i.e. polyethylene and polypropylene have the highest share of production of any polymer type and represent around 60% in plastic wastes. For this reason, these two plastics were selected for the present study.

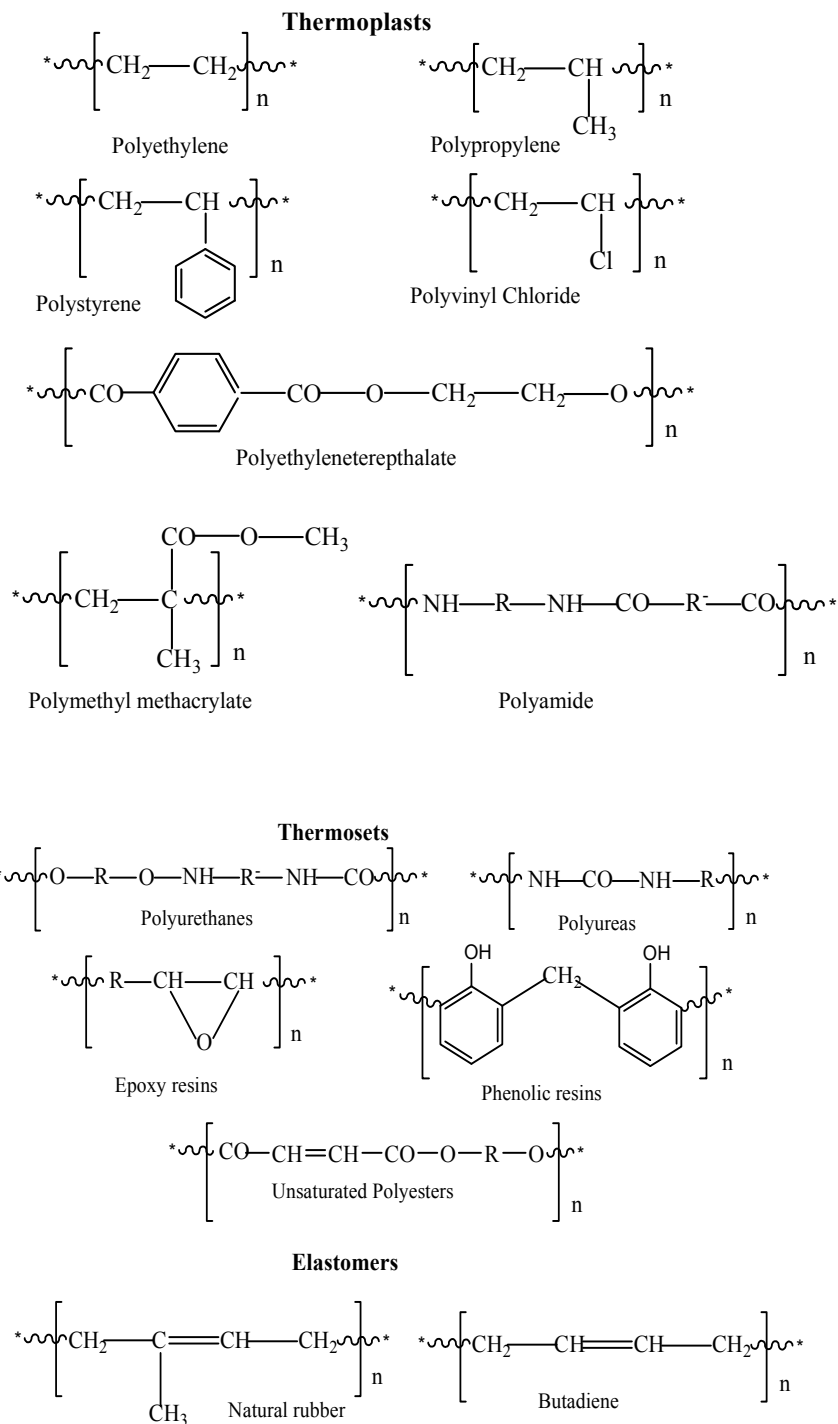


Figure. 1.1. Different types of polymers and their monomers.



1.3.1. Polyethylene ($-\text{CH}_2-$)_n

Polyethylene (PE) is one of the most common thermoplasts, which consists of ethene monomers, attached end to end forming a long chain of carbon atoms, and to each carbon atom two hydrogen atoms are attached. Polyethylene is commercially prepared by polymerization of ethylene gas. Other non-official names used for polyethylene are polythene or polymethylene. Using different production process, PE with different flexibilities and mechanical properties is manufactured. Two major types of PE are commonly used i.e. high density polyethylene and low density polyethylene. HDPE is hard to semi-flexible and strong plastic, having a soft waxy surface with excellent chemical resistance and moisture bearing properties. HDPE is commonly used for making rigid pipes, automotive fuel tanks, buckets, toys, plants pots, crates and bottles for detergents, bleach, milk, non carbonated drinks, etc. (Table 1.1)

LDPE is a low melting point, tough and flexible plastic which has waxy surface that scratches easily. It has good transparency, stable electrical properties and good moisture barrier properties. LDPE is mainly used for making plastic bags, flexible containers and bottles, cling film, some bottle caps etc. Some typical properties of PE are provided as under:

Table 1.4 . Typical properties of polyethylene (PE)

ASTM Methods	Property	LDPE	HDPE
D792	Density (g/cm ³)	0.92	0.95
D570	Water absorption, 24h (%)	<0.01	00
D638	Tensile strength (psi)	1800-2200	4600
D638	Tensile Elongation (%)	600	900
D638	Tensile modulus (psi)	-	-
D790	Flexural modulus (psi)	-	200,000
D785	Hardness, Shore D	D41-D50	D69
D3418	Melting Temperature (°C)	230/110	260/125



Generally, all polyethylene plastics have good toughness, impact resistance, stiffness, low density and acceptable food contact; therefore, these are widely used by the food, medical and other consumer industries and users for packaging, bags, piping, as laminates and liners.

Due to most wide usage, it is produced in substantial quantity i.e. in 2011 its worldwide production was about 280 million metric tons. However, due to its non biodegradable nature, it can be harmful to humans and environment because it remains in landfills for hundreds of years.

1.3.2. Polypropylene

Polypropylene is a thermoplastic polymer, comprised of propylene monomers linked together by addition polymerization. The process occurs in the presence of a catalyst, which is mostly aluminum alkyl and titanium tetrachloride. Polypropylene is also produced as a by-product during the crude oil refining processes. Polypropylene bears remarkable co-existing versatile properties such as light weight, rigidity, toughness, heat resistance, chemical resistance, and high surface gloss, good processibility, high flow, and good impact resistance, due to which it finds a large variety of applications including packaging and labeling, textiles, stationery, plastic parts and reusable containers, electrical and electronic applications and automotive interior parts. Some typical properties of polypropylene are provided in table 1.5.



Table 1.5. Typical properties of polypropylene

ASTM Method	Property	Value
D792	Specific gravity	0.90-0.91
D570	Water absorption (%)	0.01-0.03
D638	Tensile strength (psi)	4,500-6,000
D638	Elongation at break (%)	100-600
D638	Tensile modulus (psi)	16,500-22,500
D790	Flexural modulus (psi)	17,000-25,000
D256	Impact strength, Izod (ft-lb/in of notch)	0.4-1.4
D785	Hardness, Rockwell R	80-102
C177	Thermal conductivity (10^{-4} cal-cm/s-cm ² -°C)	2.4-2.8
D696	Coefficient of thermal expansion(10^{-5} in/in-°C)	8-10
D648	Deflection temperature (°F)	
	At 264 psi	120-140
	At 66 psi	225-250

1.4. PLASTIC WASTES

As plastics are extensively used in the daily life activities for different purposes like greenhouses, mulches, wiring, coating, films, packaging, covers, bags and containers, etc. therefore, the municipal solid wastes contain a considerable amount of plastic solid wastes (PSW). Plastic wastes are of major concern due to their several obnoxious effects including choking of drainage systems causing water and sewage to flood into streets and become the breeding grounds of germs and bacteria that cause diseases. Similarly, plastic bags are disposed off in streets instead of their disposal in trash bins due to unawareness. Tons of plastic bags litter the roads and in windy seasons, flying in the air causing nuisance.

In European countries, the annual production of municipal solid wastes was about 106 to 250 tonnes, which increases with the annual growth rate of 3%. A study showed that throughout the world each individual produced an average of 250 kg of MSW, and in total of 1.3 to 109 tonnes of MSW [4]. The USEPA report showed that in US, the percentage of plastic wastes in the MSW was 11 % in 2002, which increased to 12.1 % in 2007 [5, 6]. Thermoplastics have been found to constitute about 80 % of the total plastics consumption, which is mostly used in packaging and in non-plastics applications like textile fibers and coatings [7]. Some studies revealed that the percent share of plastic



wastes in different sectors of MSW in UK was about 7 % [8], whereas in US it was found to be 12.1 % by weight (USEPA 2008).

1.4.1. Sources of Plastic Wastes

The major sources responsible for plastic waste pollution include domestic or house hold, industrial and agricultural sources.

1.4.1.1. Household Waste Plastic Sources

The household sources are also called municipal sources. These include domestic items like food containers, packaging foam, disposable cups, plates, cutlery, CD and cassette boxes, fridge liners, vending cups, electronic equipment cases, drainage pipe, carbonated drinks bottles, plumbing pipes and guttering, flooring, cushioning foams, thermal insulation foams, surface coatings, etc. These items are prepared commercially from polyethylene, polypropylene, polystyrene, polyvinyl chloride, polyethylene terephthalate, etc. Although plastics are found in all categories of municipal solid wastes, however containers and packaging plastics i.e. used in bags, sacks, and wraps, other packaging, other containers, and soft drink, milk, and water containers, constitutes the largest tonnage [5, 6]. It was estimated that packaging accounts for about 37.2% of all different types of plastics consumed in Europe and over 35% in throughout the world [9].

Municipal plastic wastes are heterogeneous due to which they are unsuitable for reclamation. However, thermal cracking into hydrocarbons may provide a suitable route of recycling of such wastes, which is commonly termed as chemical recycling [10].

1.4.1.2. Industrial Waste Plastic Sources

In variety of industries, plastics are widely used, due to which industries are considered as a major source of waste plastics. Industrial plastic wastes largely come from large plastics manufacturing, processing and packaging industry. A large quantity of industrial waste plastic mainly results from construction and demolition companies (e.g. polyvinyl chloride pipes and fittings, tiles and sheets), electrical and electronics industries (e.g. switch boxes, cable sheaths, cassette boxes, TV screens, etc.) and the automotive



industries spare-parts for cars, such as fan blades, seat coverings, battery containers and front grills). Most of the industrial plastic waste exists with relatively good physical characteristics i.e. sufficiently clean and free of contamination and are available in fairly huge quantities. Also sometimes these plastics may have been exposed to high temperatures during the manufacturing process which may have decreased its characteristics, due to which these are not being used in any product applications, and discarded as such as wastes. Industrial plastics wastes are mostly homogeneous in nature; therefore, re-pelletization and remolding seem to be a simple and effective means of recycling.

1.4.1.3. Agricultural Plastic Sources

Polymers have also found wide applications in agriculture and horticulture [11]. Today, the plasticulture i.e. use of plastics in agriculture is largely contributing in increased crops yield. Application of plastic in agricultural/horticultural include use in greenhouses, small tunnels, mulching, temporary coverings of structures for fruit trees, etc. which results in production of plastics wastes. Other sources of waste plastics in agriculture include feed bags, fertilizer bags, temporary tarpaulin-like uses such as covers for hay, silage, etc. The vast majority of the protected cultivations area covered by plastic materials which is dominated by the use of plastic made out of polyethylene [12, 13]. In particular, low-density polyethylene is the most widely used polyethylene grade in agriculture, due to its relatively good mechanical and optical properties, combined with a competitive market price.

1.5 MANAGEMENT OF WASTE PLASTICS

There are a number of methods currently in use for dealing with the plastic wastes. These include land filling, mechanical recycling, biological recycling and thermo-chemical recycling.

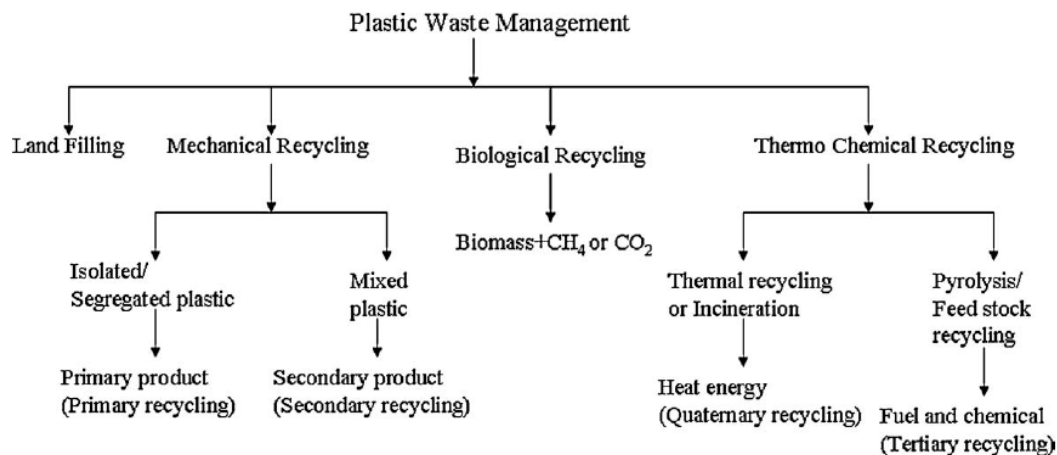


Fig.1.2. Plastic wastes management routes

1.5.1 Land Filling

Land filling is the oldest method used for solid waste disposal; however, there are strict environmental legislations with respect to this method of disposal specifically if the solid wastes contain plastics. Because of light weight, waste plastics have a high volume to weight ratio, therefore, appropriate landfill spaces are not only becoming scarce but also very expensive. More seriously, plastics are non biodegradable and remain in the landfills for years thereby creating several environmental problems, hence there is a need to replace this method with other environmentally friendly and cost effective methods. Plastic wastes are potential sources of energy, therefore, land filling of plastic wastes should be avoided as far as possible as it impart negative environmental impacts [14].

1.5.2 Mechanical Recycling

Recycling of plastics is important not only from the point of waste treatment but also from the recovery aspect of valuable materials and to form new similar products. This approach has several disadvantages including the performance level of the new products, economic viability, and practicability of such process in industrial application. Thus, mechanical recycling is an expensive and energy-intensive procedure which cannot be justified for domestic mixed plastics wastes inspite of the fact that it is widely used [15].



1.5.3 Biological Recycling

Biological recycling is the method in which plastic wastes are converted into environmentally friendly or easily degradable products. Biological reprocessing can be either aerobic or anaerobic, with anaerobic being the preferred method of decomposition because microorganisms break down faster with a lack of oxygen. This process of waste management is considered more effective for the environment than using a landfill or incineration because of the ability to form a useful synthetic gas as opposed to producing fossil fuels.

Plastics are non degradable due to the reasons that antioxidants are added during their manufacture. Current research is focused on the introduction of biodegradable plastics so that that these not only conform to user requirements but can be biologically recycled after use. This method of recycling is, however, not effective due to the reasons that these plastics will only degrade if disposed of in appropriate conditions. Furthermore, the end products will be CO₂, and H₂O, so these will increase in concentration of green house gases [16].

1.5.4 Thermochemical Recycling

Chemical recycling is referred to advanced technology processes used to convert plastic wastes into smaller molecules, usually liquids or gases, which in turn are used as chemical feed stocks for the production of new petrochemicals and plastics. Based on the high energy contents, the products can also be used as fuel [17].

Thermochemical recycling includes thermal recycling or incineration and pyrolysis.

1.5.4.1. Thermal Recycling or Incineration

The incineration is a waste management process in which plastic wastes alone or along with other wastes are combusted in a furnace for recovery of heat. The heat generated by the process is captured and turned into energy. However, the thermal degradation of polymers to low molecular weight materials requires high temperatures



typically more than 500 °C and even up to 900 °C, and has a major drawback of inferior product quality[18]. In spite of the fact that provisions are made for pollution control, there is still substantial public concern over environmental issues associated with this kind of recycling. These concerns have question marked the applicability and diminished the future operation of these facilities [19].

1.5.4.2. Pyrolysis

Pyrolysis is heating of any carbonaceous material in oxygen depleted environment or inert atmosphere. When the reaction is carried out in the absence of a catalyst, the process is called Thermolysis. Pyrolysis is capable of treating many different solid hydrocarbon based wastes producing clean fuels with high calorific value.

During pyrolysis, the polymeric materials are heated to high temperatures, so their macromolecular structures are broken down into smaller molecules and a wide range of hydrocarbons are formed. These pyrolytic products can be divided into a gas fraction, a liquid fraction consisting of paraffins, olefins, naphthenes and aromatics, and solid residues.

The liquid products are usually composed of higher boiling point hydrocarbons. In order to obtain useful gasoline-range hydrocarbons from the pyrolytic oil, fractional distillation is preferred for product separation. More valuable chemical raw materials including benzene, toluene and other condensed aromatic hydrocarbons may be obtained by refining the pyrolytic oil [20].

Pyrolysis of plastic wastes can be carried out in the absence or in the presence of catalysts, the former is referred as thermal pyrolysis and the later one using a catalyst is referred to as catalytic cracking.

1.6. THERMAL PYROLYSIS

Thermal cracking is an endothermic process, requires elevated temperature and hence is high energy consuming process. Thermal cracking of waste plastics normally requires the temperature of 350-500 °C [21-23], however, in some cases temperatures as



high as 700-900°C has also been used to obtain better product yields [20, 24, 25]. The thermal cracking processes of plastics mostly result in wide hydrocarbon distributions that require subsequent treatments to obtain valuable products. Thermal cracking of original and waste plastics has been extensively studied and a number of studies have been reported in the literature on thermal degradation of PE [21, 26, 27], PS [23, 26, 28-30], and PP [22, 28, 31], PVC [32, 33], polymethyl methacrylate [34], polyurethane [35] and polyethylene terephthalate [33].

The general features of thermal pyrolysis of polymers or plastic wastes are:

1. High yield of C₁ and C₂ range hydrocarbons in the gaseous products
2. The olefins produced are less branched
3. Some di-olefins are also produced at high temperature
4. Wide distribution of molecular weight in the liquid product (poor gasoline selectivity)
5. The percent yield of gaseous and coke product is high
6. Thermal cracking reactions are relatively slow.

1.6.1. Mechanism of Thermal Cracking

In general, the mechanism of thermal cracking of polymers involves three main steps namely initiation, propagation and termination. The initiation step involves the random homolytic cleavage to form fragments called primary radicals. In propagation step, the primary radicals undergo β -scission and H-transfer, to give secondary radicals and alkenes as products. The termination step involves the formation of a neutral molecule by the combination of secondary radicals. The general mechanism is given as below [36].



In literature, four major mechanistic routes have been proposed for thermal degradation of polymers [37], these are described as follow:

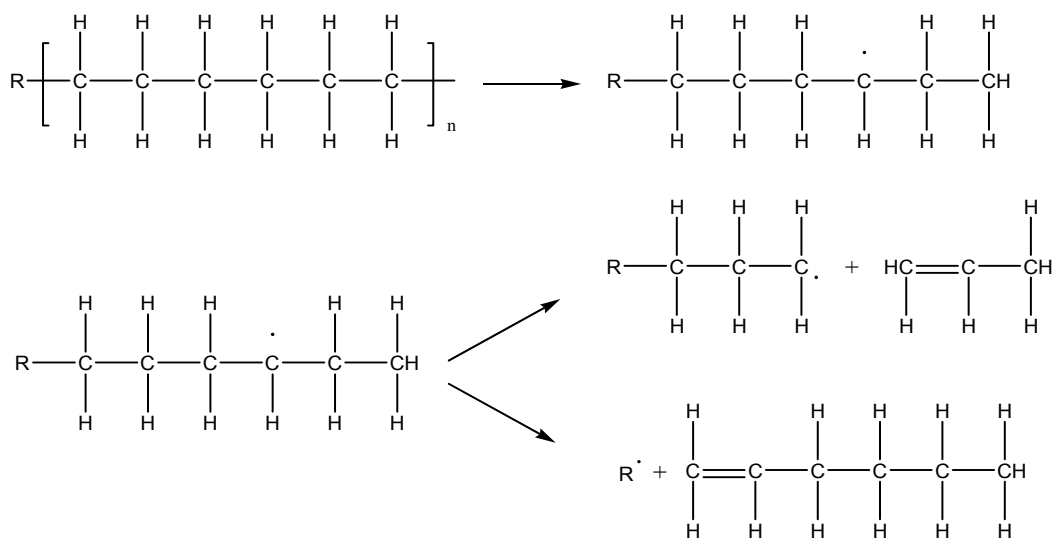
a. End-chain scission or unzipping: According to this mechanism, first scission /cracking occur at the chain ends and then proceeds successively towards the length of the polymeric length, this mostly results in the formation of monomers.

b. Random-chain scission: In this type of scission, random fragmentation along the polymer length occurs, which results in formation of monomers as well as oligomers.

c. Chain-stripping: In this case, the side chain reactions involving substituent on the polymer chain occurs.

d. Cross-linking: The two adjacent stripped polymer chains may link together which may lead to the formation of high molecular weight species leading to the formation of char.

It has been reported that thermal pyrolysis of PP and PE follow the random chain scission route, resulting in mainly oligomers and dimers [20]. Peterson, *et al.*, studied the thermal decomposition of PE by thermogravimetry, which mainly produced 1-hexene and propene [38].



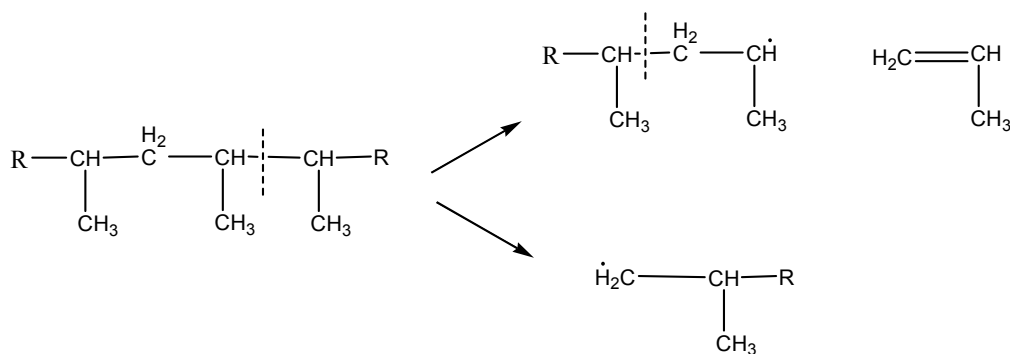


Figure 1.4. Reaction scheme: Random chain scission in polypropylene [38]

In case of PP, it was observed that during pyrolysis primary and secondary alkyl radicals are formed, which is accompanied by hydrogen abstraction and bonding of the radicals to give methane, alkenes and monomers [39]. The major products of the thermal pyrolysis of PP were found to be pentane, 2-methyl-1-pentene and 2,4-dimethyl-1-heptene [38]. Similarly, the pyrolysis of PS was found to occur through end-chain mechanism, giving the monomer as a main product [32, 40, 41].

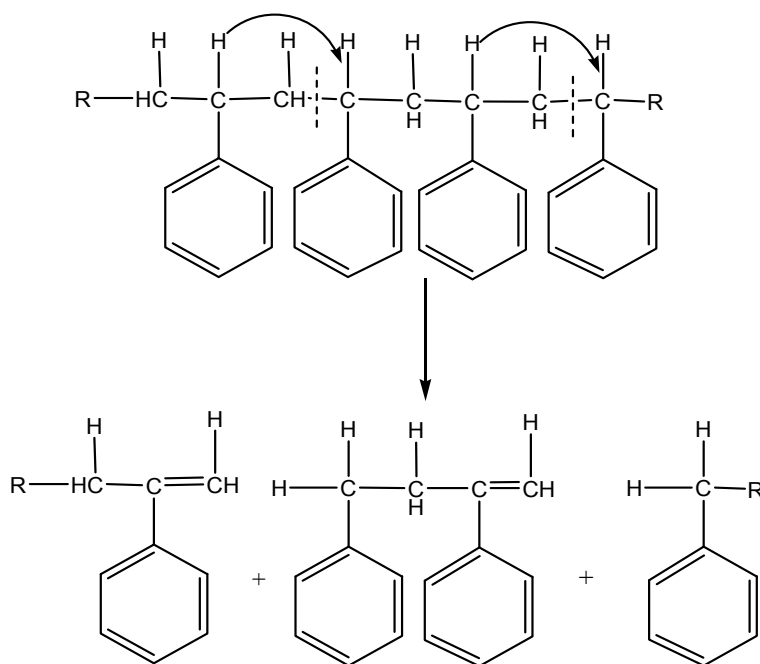


Figure 1.5. Reaction scheme: Unzipping mechanism in polystyrene [37]



1.7. CATALYTIC PYROLYSIS

The energy consumption during the thermal cracking (pyrolysis) is very high and the molecular weight distribution of the products obtained is quite broad, varying with the conditions used. However, the selectivity of the product obtained can be controlled by the use of suitable catalysts (catalytic cracking) under appropriate conditions of temperature, pressure and atmosphere (N_2 , H_2 or air). Catalytic cracking of plastics requires lower energy consumption (temperatures from 350 to 550° C) and the chemical distribution of the product is narrower than in thermal process, leading to the production of more valuable products [42]. Catalyst can also influence the product distribution. The product slate obtained in case of catalytic runs was enriched in gaseous products and leaner in condensates with changed composition compared to non catalytic runs. The gaseous products contained a large C_3 fraction, while the liquid products were mainly aromatic hydrocarbons.

The characteristic features of catalytic cracking are [43]:

1. Requires low temperature and short reaction time than thermal degradation [44].
2. Associated with high production of C_3 and C_4 range hydrocarbons in the gaseous product
3. The olefins formed as the primary products and more branched due to isomerization [45]
4. The liquid fraction is rich in C_5 - C_{10} range hydrocarbons (high gasoline selectivity) [46-48]
5. Aromatics are also produced due to olefin cyclization [48]
6. More reactive for larger molecules
7. No reaction for pure aromatics
8. Paraffins are produced by H-transfer process
9. Product distribution can be controlled by the selection of a catalyst [49-51].

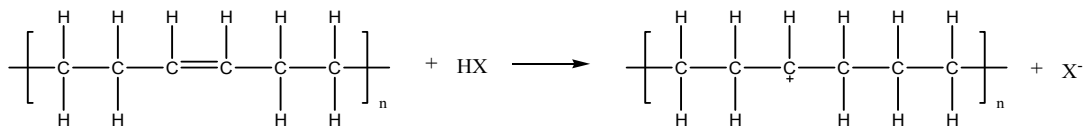
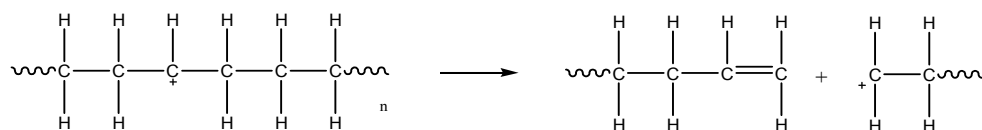
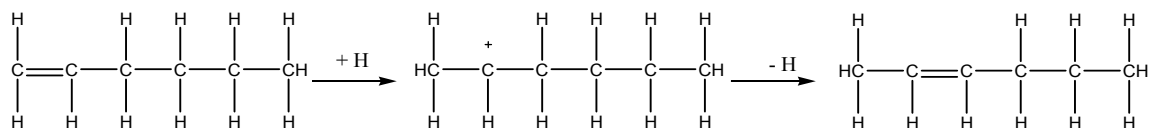
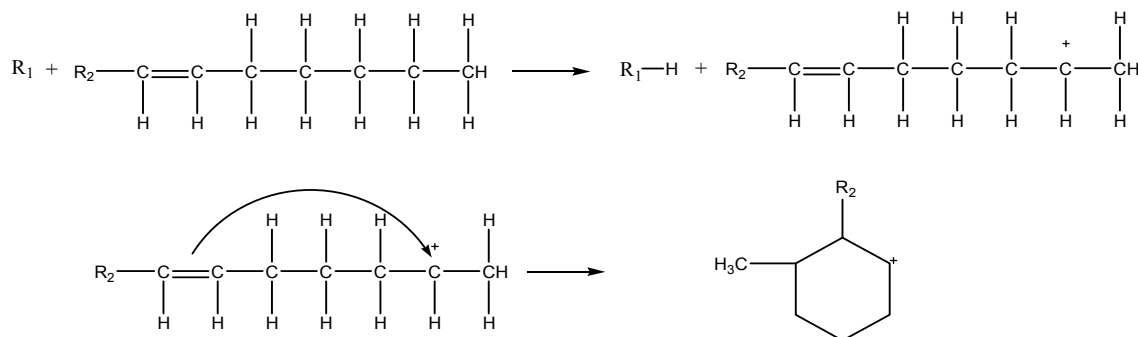
1.7.1. Mechanism of Catalytic Cracking

The catalytic pyrolysis also occurs in three distinct steps as in the case of thermal degradation i.e. initiation, propagation and termination, however, with some major



differences [52]. The reaction is initiated with the formation of the carbenium ion by protolytic cracking of alkane at the acid sites of the catalysts. It is assumed that carbenium ion may also be formed by attachment of a proton from the Bronsted centers to olefin or by hydride abstraction from paraffin by a Lewis acid center of the catalyst [53]. The propagation step involves the rearrangement, isomerization and scission of the carbenium ion. It is reported that the carbenium ion may undergo structural rearrangement in order to get more stabilize; hence the carbon chain isomerization may lead to formation of isomers [54]. Similarly, the carbenium ion may lead to the formation of olefin by β scission. It was reported that the carbenium ion may undergo the isomerization through hydrogen or carbon shifts and result in the rearrangement of the double bond position or of the skeletal carbon chain[55]. The reaction terminates by abstraction of proton from carbenium ion to give an olefin, and the acidic site of the catalyst returns to its original state.

The carbenium ion may undergo aromatization and cyclization to give naphthenes or aromatics. During the process, the carbenium ion may abstract a proton from an olefin to give a secondary carbenium ion, which by intramolecular attack of carbocation on double bond, results in cyclized products depicted as under:

**Initiation Step****Propagation Step****Beta Scission****Intramolecular H transfer****Cyclization****Figure 1.6.** Reaction scheme: Catalytic pyrolysis of polymer**1.7.2. Catalysts Used for Plastic Conversion into Useful Products**

A variety of homogeneous and heterogeneous catalysts are used in the catalytic pyrolysis of plastic wastes into value added products. Among homogeneous catalysts used are classic Lewis acids, such as aluminum trichloride and metal tetrachloroaluminates [56]. However, homogeneous catalyst systems pose several problems including the difficulty in recovery of spent catalysts from the products. In order to overcome these problems, heterogeneous catalysts have been used for the

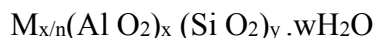


catalytic cracking of plastics. Among heterogeneous catalysts, molecular sieves are mostly used. These include conventional zeolites [57], meso porous catalysts [58], nano structured and hierarchical catalysts [56].

Other classes of catalysts have also been researched previously. These include ionic liquids [59], and Ziegler Natta [60]. However, these catalysts encountered several problems including corrosion and environmental problems. Molecular sieves include a wide range of solid materials having porous microstructures. They also possess acid or basic properties, very useful in catalytic reactions. Their classification depends on chemical composition and their pore structure. Zeolites, both natural and synthetic are promising ones. Attention has also been paid to the molecular sieves with pores larger than zeolites in recent years [61]. According to the IUPAC, zeolites are considered microporous materials, with pore sizes smaller than 2 nm, whereas MCM-41 and SBA-15 are considered meso porous materials, with pore sizes falling within the range between 2 and 50 nm.

1.7.2.1. Microporus Catalysts or Zeolites

Zeolites also referred to as molecular sieves, are naturally occurring micro porous materials with well-defined pore structures and considered as crystalline alumino-silicate with a cage structure. Chemically, they are comprised mainly of silicon, aluminum and oxygen in their framework and contain water and/or other molecules within their pores. The basic structure of the zeolites is formed by TO_4 tetrahedra ($T = Si, Al$) with oxygen atoms connecting neighboring tetrahedra. Zeolites composition may be described by three components i.e. extra-framework cations, framework and adsorbed phase. Generally, zeolites are represented by chemical formula, which is given as under:



Where,

M = metal cation

n = valency of cation

w = water contents

x & y = no of atoms of aluminum and silicon



Zeolites whether natural or synthetic are enjoying popularity in a variety of applications including in petrochemical cracking, water softening and purification, in the separation and removal of gases & solvents from industrial emanations owing to their small and uniform pores, thermal stability, and high surface area. Zeolites can be modified by metal doping. Metal doped zeolites can be used effectively in crude oil cracking, isomerization and fuel synthesis. Zeolites can also serve as oxidation or reduction catalysts, often after metals have been introduced into the framework.

Zeolites are the most widely used heterogeneous catalysts for pyrolysis of plastics due to their high micro porous nature that are formed by the linkage of SiO_4 and AlO_4 tetrahedra [62]. Zeolites are made shape selective by tailoring their pore sizes [63]. They are also called molecular sieves. On the other hand, the presence of aluminum provides the zeolites with acid properties (Brönsted and Lewis) that vary from one zeolite to another, according to their topology. The zeolite structures HY, HZSM-5, and H-Beta are the catalysts that are used industrially for the cracking of hydrocarbons [64-66].

Nanocrystalline HZSM-5 catalysts are used in the catalytic cracking of HDPE, LDPE, and PP at temperatures within the range of 340–380 °C due to high resistance to deactivation. Other zeolitic materials of catalytic interest include hierarchical zeolites, which have at least two levels of ordered porosity (usually meso pores, in addition to the zeolite micro pores). These hierarchical mesoporous-microporous materials present improved accessibility and remarkable mass-transfer properties, which is especially interesting for the processing of plastics molecules, because of their bulky nature [56].

The effect of modified zeolitic catalysts on the degradation of polymers for producing valuable hydrocarbons has been described in the literature. Several modified zeolites have been the focus of the workers. Metal impregnation may enhance the catalytic activity of the zeolite due to the formation of smaller and more reducible M-oxide species, which impart superior characteristics to the zeolites as catalyst. Metal impregnation affects the concentration of Lewis acid sites and the presence of a basic strength on zeolitic support improve the catalyst activities and limit the coke depositions [67]. Oxygen atoms in the framework of zeolites are intrinsic Lewis basic sites which



form acid-base pairs with the charge compensating cations. The basicity of zeolite can be further increased by impregnating it with a solution of alkali metal salts which can be decomposed to form oxides. The occlusion of alkali metal oxide clusters in the zeolite cages results in a further increase in basicity [68].

Uemichi, *et al.*, [69] have used a H-gallosilicate catalyst that degraded polyethylene at 425 °C in a flow reactor yielding 63.6% of liquids with a remarkable share of BTX aromatics (35.7%), that could be applied as raw chemicals. Low and high-density polyethylene and polypropylene have been degraded in a fixed-bed flow reactor system with and without H-gallosilicate catalyst at 375–550 °C to investigate the product distribution and the catalyst stability [70]. The gallosilicate exhibited a stable catalytic activity for the degradation of polyolefins when reused, because of a very low yield of coke deposited on the catalyst surface. The chemical recycling of low-density polyethylene by selective conversion into aromatic hydrocarbons using H-gallosilicate has also been reported elsewhere [71]. A fixed-bed flow reactor, in which melted polyethylene came into contact with H-gallosilicate catalyst, was highly effective in converting the polymer to aromatic hydrocarbons. The yield of aromatics was much lower when the degradation was performed by heating a mixture of the polymer and the catalyst in a batch reactor [69].

However, most of these catalysts did not prove effective in terms of plastic conversion, due to high cost. Polymeric molecules are bulky and remarkable in size; therefore, catalysts' textural properties are very important. Main disadvantage of zeolites comes from their micro porosity which hinders the access of bulky polymer molecules to the active site of the catalyst [72]. The occurrence of steric and diffusional hindrances for entering the zeolite micro pores posed by the bulky nature of the polyolefins highlighted the importance of catalysts having easily accessible acid sites, either through meso pores or by a high external surface area [73].

1.7.2.2. Mesoporous Catalysts

Because of the bulky nature of the plastic wastes which usually leads towards steric hindrances or diffusion constraints in the micro pores of the zeolitic catalysts, the



meso porous materials are gaining attention that contain highly accessible acid sites and can work effectively with the bulky nature of the plastic wastes. Mesoporous materials are potential candidates to be used as heterogeneous catalysts in a variety of applications due to high surface area (up to $1600\text{ m}^2\text{ g}^{-1}$ for meso structured silica) and mono dispersed pore diameters in the range 2–50 nm [74]. These materials possess weak acidity and can be functionalized or tailored for a specific application by introduction of metals for instance, aluminum, gallium, iron or zirconium during the synthesis [75]. Catalytic conversion of polyolefin plastic wastes into fuels over solid acid catalysts is one of the technologies that are receiving increased attention due to the interesting products obtained (gasoline, diesel, etc.) .There is ample number of works studying the performance of different catalysts (zeolites, silica–alumina and meso structured materials) in the catalytic cracking of polyolefins. Some recent studies have also employed hybrid micro/mesoporous materials [76]. Currently, hierarchical Beta zeolite with a bimodal micro-meso porosity are used extensively [77]. Ni/H-Beta proved to be an especially adequate catalyst for obtaining gasoline.

1.7.2.3. Nano structure and Hierarchical Materials

The use of engineered nano materials in consumer products and industrial processes has increased exponentially over the past decade. There are recent developments in application of nano structured catalysts employed in alkylation, dehydrogenation, hydrogenation, and selective oxidation reactions carried out for conversion of hydrocarbons (with main emphasis on fossil resources) to chemicals [78].

Several new classes of porous materials have recently emerged as catalysts while the discovery of novel ultra large-pore frameworks with desirable acidity remains largely a serendipitous process. Noble metal nano particles such as Pt, Pd, Rh, Au and their alloys with other metals have been extensively employed to catalyze a wide range of dehydrogenation, hydrogenation, and selective oxidation reactions of organic molecules [78].



1.7.3 Properties of Catalysts Used in the Plastic Conversion

The catalyst selection for conversion of plastic into useful product is always a problem due to bulky nature of the plastic molecules. However, there are certain properties of catalysts which must be considered before selection of a catalyst for the purpose. These are:

a. Textural properties: It has been shown that the textural properties such as pore size and specific surface area, etc. play an important role in the degree of cracking of the polymers and hence products distribution [79].

b. Uniform pore size distribution: Catalysts having pores of different sizes and dimensions tend to produce much more different products and byproducts. In general, mesoporous catalysts tends to favors formation of liquid products, while micro porous materials favor formation of gaseous products [79].

c. Acid strength: The acid strength or acidic site of the catalysts is characterized by Lewis and Bronsted acidity, which plays a vital role in the degradation activity of the catalyst [80-82]. Strong Bronsted acid sites lead to catalysts with high cracking activity. Strong Bronsted acid sites also tend to produce a larger proportion of gas products (rather than liquid products) and may produce larger amounts of coke.

d. Recovery from the product or residue: The efficient catalyst is one which could be recovered from the solid residue and could be regenerated. The heterogeneous catalysts with alumino siliceous nature could be recovered from the solid products easily.

e. Thermal and chemical stability: The catalyst should have high thermal and chemical stability, so it may not be suffered from thermal or chemical deactivation due to heat and the presence of impurities. Thermally or chemically unstable catalysts usually deactivate during the reaction and lose their activity [83].



1.8. CONVERSION PRODUCTS AND THEIR ANALYSES

1.8.1. Conversion Products

The products (pyrolysates) obtained from plastic pyrolysis can be classified as:

- a. Gaseous products:** These include hydrocarbons ranging from C_1 - C_4 , mostly comprise of methane, ethane, ethylene, propane, propylene, n-butane, iso-butane, 1-butene or iso-buthylene, etc.
- b. Liquid products and Waxes:** The fraction containing C_5 - C_{44} range hydrocarbons are liquid products and include oil and waxes, which mostly consists of, naphthenes, n-paraffins, olefins and their isomers. Depending upon the nature of the feed polymers and the catalysts used sometimes aromatics may also be present. These products are of most interest since these could be used as alternative fuels owing to high octane number.
- c. Coke or Char:** The coke is a byproduct mostly contains fillers, stabilizers and pigments.

1.8.2. Analysis of the Liquid Products

The liquid products obtained from the plastic wastes pyrolysis are analyzed by using a wide range of instrumental techniques, to get to know about the exact nature of the products. These techniques can be divided in the categories of spectroscopic, chromatographic and thermal analysis.

1.8.2.1. Spectroscopic Analysis

Various spectroscopic techniques used for the characterization of the liquid products include UV-Vis, FT-IR and NMR spectroscopy. UV-Vis spectroscopy is a common tool for indicating the olefins, aromatics and aliphatic hydrocarbons in the organic chemistry, however, the use of UV-Vis spectroscopy has been rarely reported for characterization of pyrolysis oil. However, UV fluorescent spectroscopy is employed to investigate and differentiate the mono, di and tri-aromatic compounds formed during the pyrolysis [84].



FT-IR spectroscopy provides consolidated information about the functional groups and the type of atomic linkage present in the organic compounds, which is most widely used in the field of plastic wastes pyrolysis [85-87]. The major information obtained from FT-IR analysis is to identify the nature of the hydrocarbons i.e. alkenes, alkanes and aromatics, carboxylates, alcohols, aldehydes, and halogenates etc. produced during the pyrolysis of polymers.

^1H and ^{13}C -NMR spectroscopy is also extensively used for products identification in the pyrolysis oil [86, 88]. ^1H -NMR data is used to deduce the relative abundance of aliphatic and aromatic hydrocarbons. The spectrum is obtained in the range of 0-8 ppm, which can be divided into two main regions, i.e. 0-3 ppm region, in which only aliphatic proton resonates and 4-8 ppm where aromatic protons can be indicated. The proportion of aromatic and aliphatic compounds is determined from ratio of signals in the both ranges [85, 89]. ^{13}C -NMR spectroscopy is also used to obtain similar information in characterization of pyrolysis oil. Generally, ^{13}C -NMR spectroscopy provides even more detailed information about the carbon atom attached to different atoms and functional groups i.e. aromatic, olefinic, carboxylic, ketonic, amine, etc. in the oil sample [85, 89].

1.8.2.2 Chromatographic Analysis

Chromatographic techniques like HPLC and GC are playing key role in products identification in the gaseous and liquid fractions obtained from wastes plastic pyrolysis. HPLC is used to indicate the group type hydrocarbons, i.e. alkanes, cycloalkanes and aromatics. This technique has been successful in quantification of mono, di and tri aromatics [84]. GC is more commonly used to obtain similar information with much better detection systems like FID and TCD, which gives a more wide range of products detection in the liquid and gaseous products [20, 60, 90-92]. However, the HPLC and GC techniques are based on identification of the products by comparison of the retention time with those of the standards compounds.

GC coupled with mass spectrometry (GC-MS) is currently extensively used to qualitatively and quantitatively characterize the pyrolysis oil without using the standard hydrocarbons [60, 88, 90]. In GC-MS, the fractions separated by the GC column are



analyzed by mass spectrometer, and the mass fragmentation obtained is used to identify the respective component. Mostly the modern units operate with a software library of the compounds, which helps in identification of the compounds using their fragmentation patterns. The data obtained is used to deduce the % distribution of different hydrocarbon range compounds and various group type hydrocarbons in the pyrolysis oil [92].

1.8.2.3. Thermal Analysis

Thermal analysis which include thermogravimetry and Differential Scanning Calorimetry (DSC) analysis are used to obtain the data of weight loss of the sample with increasing the temperature. Mostly, TGA and DSC studied are carried out as a model reaction of the polymer wastes in order to study the pyrolysis behavior of the sample, and obtain the optimum cracking temperature [87, 90]. The TGA and DSC curves obtained are used to know the thermal stability and degradation temperature of the polymer. The gaseous products obtained in thermal studied can be collected and analyzed by other analytical techniques like gas chromatography [93].

1.8.2.4 Fuel Properties

Since the liquid products has the potential to be used as liquid fuels, hence their fuel properties are also analyzed by using different standard (ASTM) methods used for analysis of petroleum and petroleum based products. These are given in Table 1.6.

In order to investigate the potential of the liquid pyrolysate obtained from pyrolysis of polymers to be used as liquid fuels for production of energy, various fuel properties of the pyrolysates are evaluated as used for the characterization of petroleum products. Some of the properties [94] that may be conveniently used to evaluate the fuel characteristics of petroleum products are discussed below:

1.8.2.4.1. Specific Gravity and API Gravity

The specific gravity and API gravity are the important properties that are widely used for preliminary characterization of the petroleum products. Specific gravity denoted by the ratio of density of the liquid to that of water at a standard temperature in petroleum



industries which is 60 °F. Although specific gravity is a more common unit, however, in petroleum industry the API gravity is more preferred property for general assessment of the nature of the petroleum fractions. The relation of specific gravity and the API gravity is given as following:

$$\text{API gravity} = \frac{141.5}{\text{specific gravity}} - 131.5$$

Table 1.6 . Fuel properties and their ASTM designations used for analysis of liquid fuels

Parameter	Method
API gravity @ 60°F	ASTM D4052
Density @ 15 °C 0.7442 g/cm ³	ASTM D4052
Gross heat of combustion	ASTM D240
Sulfur content (0.0003 Wt%)	ASTM D5453
PIONA	ASTM D5134
Say bolt Color Units	ASTM D156
Distillation behavior	ASTM D86
Dry vapor pressure equivalent	ASTM D5191
Free water and/or particulates	ASTM D4176
Kinematic viscosity @ specified temp.	ASTM D445
Base number	ASTM D974
Ash	ASTM D482
Carbon content	ASTM D5291
Hydrogen content	ASTM D5291
Nitrogen content	ASTM D5291
Carbon/hydrogen	ASTM D5291
Non Volatile matter	ASTM D1353



1.8.2.4.2. Kinematic Viscosity

Viscosity is the measure of the resistance to flow of a fluid, which may be thought as a sort of internal friction that prevents a liquid from freely flowing. Kinematic viscosity may be determined as dynamic viscosity or kinematic viscosity. Dynamic viscosity is defined as the force per unit area that is required to maintain a unit velocity gradient in the fluid [95]. The unit of dynamic viscosity is force x time/ length² and the SI unit given is N s.m⁻², whereas the common unit is poise, which is given as:

$$1 \text{ poise (dyne. S/cm}^2\text{)} = 0.1 \text{ Ns/m}^2$$

Kinematic viscosity is defined as dynamic viscosity divided by density. Viscosity is mostly determined by the time of flow in a capillary tube under its own weight. The unit of the kinematic viscosity is force x time x length/mass, its SI unit is m²/s and common unit is stokes, which is given by the relation as follow:

$$1 \text{ stoke (dyne.s.cm/g)} = 10^{-4} \text{ m}^2/\text{s}$$

1.8.2.4.3. Flash Point and Fire Point

The flash point of the fuel is defined as the temperature at which a flash (slight flame) appears instantaneously and propagates itself over the surface of the liquid oil. The oil flashes because the oil vapors mix with air to form a flammable mixture as it is heated to specific temperature. The flash point of the oil roughly corresponds to vapor pressure of 3 to 5 mm Hg. When an ignition source is brought close to the surface of the oil, the oil vapors and mixture at the surface burn momentarily and then extinguish at its critical temperature is reached. The flash point of gasoline and kerosene normally occurs at a temperature range of 38 to 43 °C.

As the name indicates, fire point of liquid fuel refers to a temperature at which a sustained flame results on the oil surface that remains for longer than four seconds. The fire point of oil always occurs at temperature higher than the flash point. The fire point of gasoline and kerosene appears at 43 to 45 °C, and sometimes may reach upto 58 °C.



1.8.2.4.4. Aniline Point

Aniline point is defined as the lowest temperature at which the oil becomes completely miscible with an equal volume of aniline. Aniline point gives an estimation of the paraffinicity and aromatic contents of the fuel oil and hence its ignition quality of a fuel. Fuels containing high aromatics are miscible with aniline at low temperature, and, therefore, have high ignition properties. Generally kerosene and diesel oil have high aniline point than gasoline.

1.8.2.4.5. Pour Point

The pour point of liquid fuels is the lowest temperature at which the oil will cease to flow, when cooled without agitation. It is the measure of the amount of the long chain paraffins in the petroleum fraction. High paraffin containing fuels have usually high wax contents, which solidifies at low temperature, and, therefore, makes the transportation and storage of the oil difficult. The pour point is a very significant property, specifically in the areas where temperature falls below freezing point, and the liquid fuel may lead to the blockage of the supply to the combustion chamber. Different types of chemical compounds called pour point depressants are usually added to improve the flow properties of the oil.

Long chain paraffins i.e. C_{16} to C_{60} are usually responsible for precipitation [96]. About 1% of waxes in middle distillates may lead to solidification of the oil [96].

1.8.2.4.6. Ash Contents

Ash content is the measure of the metallic contamination in the liquid fuel, which form ash after burning. The ash formed after completely burning of the oil usually consists of stable metallic salts, metal oxides and silicon oxide [96]. The ash forming contamination (metals) are considered undesirable in oil because these are responsible for wearing of the materials of engines and oil refineries. Generally, light distillates fractions have smaller ash contents, whereas the heavy fraction contains high ash contents.



1.8.2.4.7. Carbon Residue

Liquid fuels (petroleum distillates fractions) contain a number of compounds having different physical and chemical properties. Some of these compounds are volatile and vaporizes completely in the absence of the air at atmospheric pressure with no residue remaining, while others are non volatile and leave some carbonaceous residue upon destructive distillation under such conditions. The residue left behind after the hydrocarbon mixture is heated in the absence of air at atmospheric pressure is termed as carbon residue, which gives an indication of the heaviness of the crude oil (liquid fuel). Carbon residue gives an estimation of the carbonaceous depositing characteristics of fuels, which helps it using in certain types of combustion equipment or engines.

1.8.2.4.8. Calorific Value

The quantity of the heat released per unit mass of fuel burnt under excess of oxygen under constant pressure, is termed as calorific value. Generally, a fuel having high hydrogen to carbon ratio exhibit high calorific value than the one with low hydrogen to carbon ratio. The units used for calorific value is calorie per gram or Btu per gram. Calorific value is determined in specially designed equipment called bomb calorimeter, which allows the combustion of the fuel in controlled environment under high pressure of oxygen, and the total heat released can be determined accurately. The calorific values of different fuels compared with polymers are given in the Table 1.7 [55].

Table 1.7. Calorific values of different fuels

Fuel	Calorific Value (MJ/kg)
Coal	25-28
Wood	7-14
Heating oil/Fuel oil	40-48
Gasoline	46
Polyethylene	44



1.8.2.4 .9. Diesel Index

Diesel index is a very useful relation which indicates the burning quality of distillate fuels. It shows the smoke character of the fuel and hence its aromatic contents. Diesel index is given by the following relation:

$$\text{Diesel Index} = \frac{\text{Anilinepoint} \times \text{APIgravity}}{100}$$

1.8.2.4.10. Octane Number

Octane number is defined as the ratio of iso-octane to n-heptanes in a fuel. Octane number is actually the measure of the tendency of the resistance of the fuel to auto ignition or detonation. Iso-octane has been assigned the octane number of 100, which has a boiling point of 125 °C, and can resist auto ignition in the internal combustion engine, whereas n-heptanes has been given the octane number of 0. In normal spark ignition engines, the air fuel mixture is compressed to high pressure, due to which the temperature raises; however ignition is triggered by spark plug or ignition system. If a fuel with low octane number is used, the fuel detonates or self ignites under high temperature, before the piston completes its cycle, which leads to knocking or pining sound. In severe cases, it may lead to breaking of connecting rods, blow head gaskets, melt piston, damage bearings or other components. It is, therefore, required to use fuel with high octane rating that is resistant to explosive ignition under such conditions. The higher the octane number, the more is the fuel resistant to self ignition.

The octane rating is measured in a test engine by comparison with a mixture of iso-octane (2,2,4-trimethylpentane) and n-heptanes in a definite proportion that would have the same anti knocking characteristics as like the fuel under test. The percent volume of the iso-octane in the mixture designates the octane number i.e. the fuel having octane number of 90 means it resembles the knocking characteristics of 90:10 mixture of iso-octane and n-heptanes [97]. Thus, the octane rating of 90 does not mean that the fuel contains iso-octane in same amount but it has same auto ignition resistance as same amount of iso-octane. As fuel contains a number of compounds that are more knock



resistance than iso-octane, therefore, the definition has been extended to allow for octane numbers higher than 100.

Commonly octane rating is designated as research octane number (RON) and motor octane number (MON). RON is determined by testing the knocking characteristics in a test engine operating with about 600 rpm speed and variable compression ratio under same conditions, the results are compared with mixtures of iso-octane and n-heptanes. RON is a common type of octane rating used worldwide.

MON is the type of octane rating determined in similar test engine as used for RON, but under load, i.e. operating with about 900 rpm speed, variable ignition timing and preheated fuel mixture. Generally, depending upon the composition of the fuel, the value for MON is 8 to 10 numbers less than RON, however, there is no direct relation between MON and RON. In most countries, the term anti knock index (AKI) is used instead of MON and RON, which is the average of RON and MON i.e. $\text{RON} + \text{MON}/2$.



1.9. LITERATURE SURVEY

Pyrolysis of waste plastics has been extensively studied in the last few decades. Several factors influencing the pyrolysis behavior were the focus of research carried out in the past two decades.

1. Type of pyrolysis; single stage, and two stage.
2. Feed/Waste type; individual, mixed or commingled, and mixing ratio, co-feeding with biomass, etc.
3. The type and structure of the degrading polymers and their pretreatments; microwaves thawing, irradiation, etc.
4. Temperature; low, intermediate, high, very high.
5. Reaction time, Short or extended.
6. Pressure; ambient , low, intermediate, and high.
7. Solvent.
8. Different kinetic parameters, activation energy, rate constant.
9. Heating rate; slow, intermediate, rapid, and flash.
10. Type of reactor & mode of contact of reactants: Gray–King , semi-batch, conical spouted bed reactor, fixed bed, fluid bed, the rate of fluidizing gas, un stirred, and stirred, continuous flow.
11. Catalyst type, catalyst particle size, concentration, plastic to catalyst mass ratio, pore structure, macro, meso, micro porous nature, unique acid properties, Bronsted and Lewis acidities.
12. Catalyst stability; chemical and mechanical, regeneration and recycling.
13. Presence and absence of oxygen, nitrogen & hydrogen environment, etc.
14. Possible reaction mechanism routes; end chain, random chain scission reactions.

In the proceeding section, main contributions to address the influence of the above mentioned factors and recent advances in the field are presented in detail. This compilation allows the readers to understand the pyrolysis of waste plastics without spending time in searching many resources.



Ding *et al.* in 1997 [98] studied the catalytic depolymerization of high density polyethylene and commingled post-consumer plastic waste (CP#2) using a 27-cm³ tubing reactor and a 150-cm³ autoclave reactor. The cracking experiments were conducted at 400 to 435 °C, for 60 min, in N₂ or H₂ atmosphere, and with or without TiCl₃ or HZSM-5 catalyst. It was reported that no significant non-catalytic reactions occurred until the reaction temperature reached 430°C, in case both, HDPE and CP#2. The optimum yield obtained was 88.7% for HDPE and 86.6% for CP#2 at 435°C using TiCl₃ catalyst, while the maximum gas yields of 21.2% for HDPE and 17.6% for CP#2, were attained using HZSM-5 catalyst. It was concluded that HZSM-5 favored cyclization and aromatization reactions while TiCl₃ catalyzed recombination and disproportionation reactions. Detailed product analyses and characterization lead to a reasonable explanation of reaction pathways and mechanisms.

In 1997, **Uddin *et al.*** [99] investigated the degradation of four different types of polyethylene including high density PE (HDPE), low density PE (LDPE), linear low density PE (LLDPE), and cross-linked PE (XLPE) at 430 °C in a batch operation with and without silica-alumina as a solid acid catalyst. Results indicated that in case of thermal degradation, the HDPE and XLPE gave larger amount of wax-like compounds than LDPE and LLDPE, however, the yields of liquid products given by HDPE and XLPE (58–63 wt%) was smaller than given by thermal degradation of LDPE and LLDPE (76–77 wt%). These results indicated that the composition of the products and its yield was largely influenced by structure of the degrading polymers. The liquid fractions obtained in thermal degradation comprised of hydrocarbons with carbons ranges of n-C₅ to n-C₂₅ (boiling point range, 36–405 °C). In case of catalytic degradation in the presence of silica-alumina catalyst, the yield of liquid fractions of all the polyethylene samples were very high, about 77–83 wt % with no formation of waxes. The liquid products of the catalytic degradation were distributed in the hydrocarbon range of n-C₅ to n-C₂₀ with C₅–C₁₂ as in a major proportion. Results showed that the solid acid catalyst degraded the different polyethylene samples indiscriminately into light fuels with an improved rate.

Williams *et al.* in 1999 [100] investigated the pyrolysis of six main plastics in municipal solid waste individually including HDPE, LDPE, PP, PS, PVC, and PET in a



fixed-bed reactor at a temperature of 700 °C gradually heated at 25 °C min⁻¹. The authors also pyrolyzed the mixture of polystyrene with each of the other five plastics in a 1:1 ratio using a fixed-bed reactor under the same conditions as used for individual plastics. Results indicated that the gaseous products of pyrolysis obtained from the pyrolysis of individual plastic mainly included hydrogen, methane, ethane, ethene, propane, propene, butane, and butene, in case of PET plastic carbon dioxide and carbon monoxide, and in case of PVC hydrogen chloride was also formed. The analysis of the oil or waxes produced from polyalkene plastics, HDPE, LDPE, and PP, indicated that these products mainly comprised of aliphatic hydrocarbons containing alkanes, alkenes, and alkadienes series. The PVC, PS and PET mainly gave oil rich in aromatics, because they had aromatic groups in their structures. The mixture of plastics with PS gave a high yield of gases and poor yield of oil or waxes, than the individual plastics. Similarly, the average molecular weight of the oil or wax obtained from mixed plastics was smaller than expected from individual molecular weights.

In 1999, **Uemichi *et al.*** [101] conducted a study on two-stage catalytic degradation of polyethylene in the presence of amorphous silica–alumina and HZSM-5 as catalysts to convert the polymer into high-quality gasoline-range fuels. In comparison to one-stage degradation using each catalyst, the two-stage method was found to be more advantageous. The yield and octane number of gasoline obtained in two stage processes was higher despite of low aromatics content. In case of using silica–alumina and HZSM-5 in flow reactor, in a weight ratio of 9:1 as upper and lower catalysts, respectively, promising results were obtained. The favorable catalyzing of the polymer into liquid hydrocarbons by the silica–alumina loaded in the upper layer was attributed to the moderate acidity of the catalyst. The oil obtained showed low quality, which was transformed into high-quality gasoline by the strongly acidic sites of the HZSM-5 loaded in the lower layer (second stage) at the expense of oil yield. During the lower layer reaction, the concentration of iso paraffins and aromatics was increased which upgraded the quality of oil.

In 2000, the catalytic degradation of high-density polyethylene to hydrocarbons was studied by **Manos *et al.*** [102] using different zeolites as catalysts to investigate the



effect of zeolite morphology on the products distribution. It was found that the product were typically between C_3 and C_{15} hydrocarbons. Distinctive patterns of product distribution were found with different zeolitic structures. Over large-pore ultra stable Y, Y, and β zeolites, alkanes were the main products with less alkenes and aromatics and only very small amounts of cycloalkanes and cycloalkenes. Medium-pore mordenite and ZSM-5 gave significantly more olefins. In the medium-pore zeolites, secondary bimolecular reactions were sterically hindered, resulting in higher amounts of alkenes as primary products. The hydrocarbons formed with medium-pore zeolites were lighter than those formed with large-pore zeolites. The following order was found regarding the carbon number distribution: (lighter products) ZSM-5 < mordenite < β < Y < US-Y (heavier products). A similar order was found regarding the bond saturation: (more alkenes) ZSM-5 < mordenite < β < Y < US-Y (more alkanes). Dependent upon the chosen zeolite, a variety of products was obtained with high values as fuel, confirming catalytic degradation of polymers as a promising method of waste plastic recycling.

Kiran *et al.* in the year 2000, employed a Gray–King reactor for the pyrolysis of waste PE and PS individually and in combination with different compositions [40]. The critical temperature effective for pyrolysis of wastes plastics was determined from their thermo gravimetric analysis. The selected heating rate was low in order to attain higher liquid yields. It was found that the waste PS gave the high yield of liquid, and waste PE yielded high yield of gaseous products. The major product in the liquid fraction obtained from PS was styrene whereas from waste PE, propenylbenzene was the most abundant dominant pyrolysis product.

In 2001, **Takuma *et al.*** [69] reported the degradation of low and high density polyethylene and polypropylene in a fixed bed flow reactor system with and without H-gallosilicate catalyst at the temperature range of 375 to 550 °C to study the product distribution and the catalyst stability. Results indicated that the thermal degradation of the polyolefins produced mostly waxy hydrocarbons, the yield of which related to the type of polymer used. While the catalytic degradation using gallosilicate as catalyst, the products obtained were lighter hydrocarbon mixtures, which was rich in various important aromatics, mostly toluene, xylene and benzene. The nature of the products was also



dependant on the structure of the polymer feed upto some extent. This can be due to the mechanism of the reaction which involved the frequent skeletal isomerization of decomposed fragments. The reaction intermediates, which are unsaturated fragments frequently isomerizes in the presence of acidic gallosilicate, and leads to the formation of isomers that are distributed in thermodynamically equilibrated concentrations. The polyolefin's degradation with the catalysts thus proceeds by similar intermediates formation regardless of the structure of the degrading polymers, and leads leading to almost similar product distributions. The gallosilicate catalysts were found to be stable in catalytic activity in the degradation of polyolefins in repeated use because of the less coke deposited on its catalyst surface.

Aguado *et al.* in 2001 [103] investigated the conversion of a plastic mixture consisting of polypropylene and both low- and high-density polyethylene using a mesoporous HMCM-41 type and nano sized HZSM-5 (n-HZSM-5) zeolite as catalysts. The influence of the plastic to catalyst mass ratio and reaction temperature was studied in a batch reactor. The catalysts used showed high activity during the conversion of the polyolefin mixture by giving total plastic conversion as the temperature was raised 375 to 450 °C or plastic to catalyst ratio was varied from 200 to 4. The nature of the product obtained with different catalysts was different due to the prevailing cracking mechanism. It was shown that the catalysts n-HZSM-5 zeolite, having strong acidic sites and high external surface area, promoted end-chain scission reactions in the polymer degradation, due to which light hydrocarbons with about 80–90 % of C₃–C₆ range hydrocarbons were obtained. On the other hand, in case of HMCM-41 catalyst random scission reactions were predominant due to its mild acidity and large pore size, leading to formation of heavier products (C₅–C₁₂ and C₁₃–C₂₂ range hydrocarbons).

Alia *et al.* in 2002 [104] investigated the catalytic degradation of HDPE under nitrogen atmosphere in a laboratory scale fluidized bed reactor. The experiments were conducted at 360 °C with 2:1 ratio of catalyst to polymer feed under nitrogen atmosphere, and at 450 °C with 6:1 ratio of catalyst to polymer feed under atmospheric pressure. The catalysts used included ZSM-5, US-Y, ASA, fresh FCC catalyst (Cat-A) and equilibrium FCC catalysts with different levels of metal poisoning. The results of the initial set of



experiments carried out at 360 °C, the activity of the catalysts in terms of the yield of volatile hydrocarbon products was: model catalysts > commercial FCC catalyst > E-Cats. However, under the process conditions resembling to FCC conditions, the fresh commercial FCC catalyst was more active in terms of the yield of volatile hydrocarbons. It was also shown that the level of metal contamination did not affect the product composition.

Marcilla in 2002 [105] studied the catalytic decomposition of various PE polymers having different characteristics i.e. density and melt flow index using solid acid catalyst (MCM-41). Thermo gravimetric analysis of the polymers at different heating rates in the presence of the catalysts (MCM-41) in different percentages was carried out. The kinetic investigation of the process was also conducted. Results indicated that there was no significant difference between the thermal decomposition of different polymers. However, in the presence of the catalysts prominent differences were observed in the decomposition temperatures of the PE samples used, which showed that the structure of the polymer has some influence on degradation in presence of the catalyst.

Dawood *et al.* in 2002 [106] studied the effect of exposing PP to γ -irradiation before the catalytic pyrolysis using HY-zeolite in a thermo balance and semi-batch reactor. It was shown that there was significant increase in rate of the catalytic pyrolysis after exposing the PP to irradiation dose of 10 kGy. The enhanced reactivity of the irradiated PP was indicated by the poor yield of the coke and solid residue, and high yield of C₇-C₁₀ range hydrocarbons in the liquid fractions. The effect of temperature on the pyrolysis showed that the catalytic pyrolysis is favored at high temperature, the optimum temperature was found to be ranging from 325–375 °C. Based on the experimental results and the literature reports, the authors devised the possible reaction mechanism.

Catalytic cracking of a plastic mixture containing LDPE and EVA copolymer in the weight ratio of 86/14, was studied by **Serrano *et al.*** in 2003 [107] using mesoporous Al-SBA-15, Al-MCM-41 and nano crystalline HZSM-5 zeolite as catalysts in a batch reactor at 400 to 420 °C. The authors showed that the decomposition of EVA releases acetic acid, which was observed in the temperature range 350 to 400 °C. Amongst the



catalysts used, the nanosized HZSM-5 was the most active, which led to complete conversion of the plastic mixture at 420 °C. It was also found that the cracking of the polymer mixture was more difficult than thermal as well as catalytic cracking of pure LDPE. This was attributed to the occurrence of cross-linking reactions which leads to deactivation by coke fouling, especially in the presence of mesoporous Al-MCM-41 and Al-SBA-15 catalysts due to their open structure. The HZSM-5 catalysts showed high selectivity towards C₁–C₅ hydrocarbons, about 75%, majority of which included C₃ to C₄ range olefins. Group type analysis of the C₆–C₁₂ range hydrocarbons fraction obtained at 420 °C showed mostly the presence of olefins and some amount aromatics (>15%).

Qian *et al.* in 2004 [108] investigated the thermal and catalytic degradation of LDPE and PP over modified ZSM-5 zeolite, DeLaZSM-5 catalysts. Results indicated that in the presence of DeLaZSM-5 catalysts, the degradation behavior of LDPE and PP was quite different from the thermal degradation and reported literature using USY catalysts. Further, it was shown that over DeLaZSM-5, LDPE exhibited much higher level of degradation than PP did, particularly in relatively lower temperature stage, showing that DeLaZSM-5 has shape-selectivity in catalytic degradation of LDPE and PP. The factors affecting the shape-selectivity effect of DeLaZSM-5, were found to be the pore structure, unique acid properties of the DeLaZSM-5, and the proper reaction temperature.

The catalytic degradation of polyethylene was studied by **Gobin *et al.*** in 2004 [109] in a semi batch reactor over various microporous materials as catalysts including zeolites, zeolite-based commercial cracking catalysts, clays and their pillared analogues. The products given by all catalysts showed the boiling point distribution in the range of motor engine fuels. Amongst zeolitic catalysts, ZSM-5 gave mostly gaseous products and no coking was observed due to its shape selectivity. The commercial cracking catalysts resulted in complete degradation of the polymers giving higher liquid yield and lower coke content than its parent USY zeolite. Different clays i.e. saponite, Zenith-N, montmorillonite and their pillared analogues showed lower activity than zeolites, however, they completely degraded the polymer, showing high liquid formation, due to their mild acidity, and less coke formation. The regenerated pillared clays also showed



similar activity as fresh samples, but their original performance was lost after removal from the formed coke.

Lin et al. in 2004 [18] studied the pyrolysis of HDPE over different catalysts using a laboratory scale fluidized-bed reactor operating isothermally at ambient pressure. Results indicated that degradation with HZSM-5 zeolite give the high yield of volatile hydrocarbons as compared with non-zeolitic catalysts i.e. MCM-41 and SAHA. In case of using HZSM-5 catalysts as a cracking additive combined with non-zeolitic MCM-41 and $\text{SiO}_2\text{-Al}_2\text{O}_3$, low yield of gaseous products with lower loss of gasoline range hydrocarbon was observed as compared to only HZSM-5 catalyst. The MCM-41 catalyst having large mesopores and SAHA having weaker acidic sites gave high yield of olefins hydrocarbons ranging between $\text{C}_3\text{-C}_7$. It was found that both the catalysts i.e. SAHA and MCM-41, allowed bulky reactions to occur which led to formation of coke and subsequently resulted in deactivation of the catalyst.

In 2005, **Hakki et al.** [110] investigated the conversion of polyolefins (HDPE, LDPE and PP) into naphtha range feedstock by hydro liquefaction process. The hydro liquefaction was conducted in cold hydrogen under the pressure of 5 MPa at the temperatures range of 375 and 450 °C without using any catalyst. Two types commercial catalysts were used, a hydrocracking catalyst (DHC-8) and a hydrogenation catalyst (HYDROBON). The effect of temperature and catalyst type on product yields and composition of gas and liquid products was investigated. The temperature was the main effect in hydro liquefaction. DHC-8 showed good cracking activity, but it gave the liquid product containing high olefin content same as thermal run. Although HYDROBON catalyst produced the sufficient amount of liquid (and naphtha fraction) at the higher temperature, it gave the liquid product with very low olefin content. The naphtha fractions obtained from polyolefins under the optimal hydrocracking conditions were analyzed by PIONA instrument to determine the hydrocarbon groups. PIONA analysis showed that the naphtha obtained from hydroliquefaction over hydrocarbon catalyst could be used as a petrochemical feedstock. However, the naphtha obtained in presence of DHC-8 catalyst, which is to be used a feedstock, was needed further hydrogenation treatment.



Serrano *et al.* in the year 2005 [111] used a novel approach to study the catalytic degradation of low-density polyethylene (LDPE), which is called pyrolysis coupled with gas chromatographic separation and mass spectrometry detection (Py–GC/MS). This technique provides rapid screening of the catalytic activity of the solid acidic catalysts and allows the direct analysis of the resulting products. The authors synthesized and characterized three different solid acid catalysts including microporous HZSM-5, nano crystalline *n*-HZSM-5 and Al-MCM-41. The catalytic activity was investigated by thermo gravimetric (TG) analysis in the degradation of LDPE. A program was obtained from the Py–GC/MS analysis of pure LDPE at 700 °C, which indicated characteristic triplets, corresponding to straight chain diene, alkene and alkane hydrocarbons of different chain lengths. Catalytic degradation of LDPE in the presence of HZSM-5 zeolites gave same range of products with a promising increase in light olefins and aromatic fractions (e.g. benzene, toluene, and xylene) whereas the heavier olefin and paraffin hydrocarbons were completely eliminated. On the other hand, the mesoporous Al-MCM-41 did not show selectivity in the products, rather it gave a low proportion of aromatics and a higher content of olefin and paraffinic hydrocarbons.

In 2007, **Achilias *et al.*** [112] examined the recycling of model polymers and waste products i.e. LDPE, HDPE or PP by using the dissolution-precipitation method, and pyrolysis method. In dissolution-precipitation technique, the model and commercial polymers were examined with different solvents/non-solvents in different ratio and at different temperatures. In each case, the recovery of polymer was more than 90%. The polymer samples were characterized by FT-IR analysis and tensile mechanical properties analysis, before and after recycling. The catalytic pyrolysis of the model and wastes polymer samples was also investigated in the laboratory fixed bed reactor using FCC catalyst. Analytical results indicated that the catalytic pyrolysis resulted in the formation of aliphatic products mainly consisting of a series of hydrocarbons (alkanes and alkenes), which can be recycled back for the production of plastics or liquid fuels.

Macilla *et al.* in 2006 [113] investigated the catalytic pyrolysis of four samples of commercial polymers (LDPE, PP, PS and EVA copolymer), using a thermo balance under nitrogen atmosphere at a heating rate of 10 °C/min in the presence of HZSM-5,



MCM-41a and MCM-41b catalysts having different chemical and physical properties. The catalysts synthesized in the laboratory and were characterized by X-ray powder diffraction (XRD), surface area, pore size analysis, and ^{27}Al and ^{29}Si solid state NMR spectroscopy. Results showed that the two meso porous catalysts (MCM) having larger pore size, showed high activity than HZSM-5 zeolite in the catalytic pyrolysis of each of the four polymers. Among the two mesoporous catalysts, the MCM-41 bb was the most active due to high acidity.

Marcilla *et al.* in 2008 [114] studied the catalytic pyrolysis of low and high density polyethylene i.e. LDPE and HDPE in the presence of HZSM5 catalyst using a batch reactor. The products obtained in the process were characterized. It was found that the catalysts mostly formed the gaseous products. The composition of the pyrolysis products was dependent upon the structure of the polyethylene feed, particularly at the beginning of the degradation process, during which the catalytic cracking of LDPE gave olefins as major compounds in both the gaseous and condensed phases. With the increase in temperature, the composition of the gases remained same but in case of the condensed fraction, the yield of olefins decreased, due to which aromatic compounds were predominantly generated. In case of HDPE, in the beginning of the process, high yield of paraffins and aromatics were formed in the gaseous and condensed products, respectively. However, at high temperature, the products distribution was same as in case of LDPE.

Lin *et al.* in 2008 [115] studied the pyrolysis of mixture of post-consumer polyethylene waste (HDPE/LDPE) over various catalysts in a fluidized-bed reactor at the temperature range of 290–430 °C at atmospheric pressure. Results indicated that the zeolitic catalysts gave the high yield of the volatile hydrocarbons (HZSM-5 > HUSY > HMOR), than the non zeolitic catalysts i.e. SAHA $\approx$ MCM-41, which was attributed to the nature of catalyst and the reaction temperature. The product obtained with HZSM-5 contained olefinic contents of about 60 wt % in the range of $\text{C}_3\text{--C}_5$. On the other hand, the product obtained with HMOR and HUSY comprised of high paraffinic streams, with large amounts of isobutane (*i*-C₄), however, these both catalysts deactivated during the



reaction. The products obtained with MCM-41 and SAHA were rich in olefins having the broad carbon range of C₃–C₇ compounds.

Antonio *et al.* in 2008 [116] conducted a study to explore the possibility of using refinery facilities to carry out the plastic cracking and also maximize the products obtained. In this study, a blend of LDPE and VGO in different proportions was degraded in presence of FCC equilibrium catalyst. The reactor used was a laboratory scale sand fluidized bed reactor maintained at 500 °C, in which initially a 7:1, catalyst to LDPE/VGO blend ratio was cracked in order to simulate the operating conditions in a large scale industrial reactor. The blends of polyethylene evaluated included the relative proportion of LDPE of 0, 6, 25, 75 and 100 % wt/ wt. The gaseous and liquid fractions obtained were collected and quantified. The results of the catalytic run were also compared with those obtained in the thermal cracking. In all cases, the FCC equilibrium catalyst was found to show high selectivity to the production of isobutane and isopentane in among the volatile compounds and also to aromatics in the liquid products. The results given showed the viability of introducing plastics into FCC unit, to produce potentially valuable products from low value materials.

Siddiqui *et al.* in 2009 [117] carried out thermal and catalytic pyrolysis of polystyrene (PS) with LDPE, HDPE, PP, PET in a 25 cm³ stainless steel micro reactor at about 430 to 440 °C under 5.5–6.0 MPa N₂ pressure and for 1 h. Pyrolysis of each plastic was studied with different ratios of PS i.e. 1:1, 1:2 and 1:3 to explore the role of PS and its reactivity. Results showed that the pyrolysis under 1:1 ratio gave the best yields in the form pyrolytic oils. SIM distillation of the hexane soluble fraction indicated that hydrocarbons with boiling point above 96 °C were present whereas low boiling fractions were not found, which was attributed to the vaporization of highly volatile components. GC analysis showed the presence of some very important chemical compounds present in the liquid products obtained from the pyrolysis of mixed plastics.

In 2009, **Marcilla *et al.*** [118] investigated the thermal degradation of LDPE and HDPE in a batch reactor under dynamic conditions. The pyrolysis behavior of LDPE and HDPE was compared, which showed no major difference in the quantity and weight



fraction of the gaseous products obtained. In case of both polymers, initially n-paraffins were the major products, however, as the decomposition proceeds, 1-olefins were the major product. The difference in the behavior of LDPE and HDPE at the beginning of the degradation process was revealed by the analysis of the condensed fraction that was much larger than the gaseous fraction. However, at high temperature, similar trends were observed, as 1-olefins, n-paraffins, dienes and olefins with wide carbon number distributions were the most important condensed compounds obtained in the thermal degradation of both polyethylene. Results showed that the formation of 1-olefins and n-paraffins starts at lower temperatures than the dienes and olefins. While as the temperature increases, the amount of low and high molecular weight compounds raises at the expense of intermediate molecular weight products. This behavior was correlated to the thermal cracking of waxes by secondary reactions.

In 2010, **Huang *et al.*** [119] investigated the pyrolysis of a mixture of hospital post-commercial polymer waste (LDPE/HDPE/PP/PS) in the presence of various catalysts using a fluidized-bed reactor operating isothermally at ambient pressure. Results indicated that with zeolitic catalysts, the yield of volatile hydrocarbons were higher (ZSM-5 > MOR > USY) than the non-zeolitic catalysts (MCM-41 > ASA). The mesoporous MCM-41 and ASA with weaker acid sites gave a mixture rich in olefinic contents and wide carbon number distribution, whereas USY resulted the products having higher saturates, and wide carbon number distribution, as well as substantial coke levels. It was shown that the application of different catalysts improves the yield of hydrocarbon products and provides better selectivity in the product distributions. A developed model based on basis of kinetic and mechanistic approaches was investigated in this work, which considers the chemical reactions and catalyst deactivation for the catalytic degradation of commingled polymer wastes. The model represents the advantage of product selectivity in term of chemical composition such as alkanes, alkenes, aromatics and coke in relation to the performance of the catalyst particle size and reaction temperature.

Pyrolysis of mixture of polymer waste (LDPE/HDPE/PP) was studied by **Wie *et al.*** in 2010 [120] over various zeolitic catalysts using a laboratory fluidized-bed reactor



isothermally operating at ambient pressure. It was reported that in the presence of various catalysts the yield of hydrocarbon products is improved and better selectivity in the product distributions is obtained. Results indicated that the yield of volatile hydrocarbons for zeolitic catalysts (ZSM-5 > MOR > USY) was higher than the non-zeolitic catalysts (MCM-41 > ASA). The meso porous MCM-41 and weakly acidic ASA gave the products with high olefinic content and wide carbon number distribution, whereas USY gave a saturate-rich mixture with a wide carbon number distribution and higher coke levels. A kinetic and mechanism based model was developed in this work for chemical reactions and catalyst deactivation during the catalytic degradation of commingled polymer waste. On practical point of view, this study provides promising results as an alternative technique for the cracking and recycling of post-consumer polymer waste.

Lin *et al.* in 2009 [121] experimented the cracking of mixture of post-consumer polymer waste including PE, PP and PS over cracking catalysts using a fluidized reactor similar to the FCC process operating isothermally at ambient pressure. Results indicated that greater product selectivity was attained in case of commercial FCC equilibrium catalyst (FCC-E1), which gave the products with about 53 wt % olefins in the C₃–C₆ range. A kinetic model based on a lumping reaction scheme was also investigated for the observed products and catalyst coking behavior. The results of the model were in good agreement with the experimental results, it also gives the advantage of lumping product selectivity, relating to catalysts activity, its particle size selected and the influence of the operation conditions, like temperature and the rate of fluidizing gas. Furthermore, the authors showed that using appropriate reaction temperatures and suitable catalysts, both the product yield and product distribution from polymer degradation can be controlled, which can lead to a potentially cheaper process with more valuable products.

Yang *et al.* in 2010 [122] conducted a study to identify the possible routes for the reaction mechanism for the pyrolysis of a plastic waste mixture. Kinetic investigation of mixture of same percentages of different polymers including polyethylene (PE), polypropylene (PP), and polystyrene (PS) were carried out in order to find that whether direct conversion of plastic wastes is favored into gases, liquids, and solid products, or then some parallel reactions or reversible elementary steps are required. The pyrolysis



experiments were conducted in six different micro autoclaves, and on the basis of results obtained under different temperatures and reaction times, a reaction mechanism was proposed. The experimental data was fitted in kinetic model, which revealed that the data reasonably fitted the results and provided satisfactory explanation for the results of the waste plastic degradation. The authors also estimated different kinetic parameters, which indicated that there was a direct dependence of the activation energy and pre-exponential factor on the reaction temperature. These results also verified that the rate constant of some reactions were dependent nonlinearly on temperature in the logarithmic form, showing that the temperature influences the reaction mechanism.

Lina *et al.* 2010 [92] investigated the catalytic pyrolysis of a mixture of post-consumer consisted of PE/PP/PS/PVC over cracking catalysts using a fluidized reaction system operating isothermally at ambient pressure. The effect of different factors on the cracking reaction was examined; these included the catalyst type, reaction temperature, ratios of catalyst to plastic feed, flow rates of fluidizing gas, catalyst particle sizes, etc. A model was developed which was based on kinetic and mechanistic considerations associated with the chemical reactions and catalyst deactivation in the acid-catalyzed degradation of polymer wastes, which provided results in good agreement with experimental data.

Lopez *et al.* in 2011 [123] conducted a study on the regeneration and recycling of ZSM-5 zeolite during the pyrolysis of a plastic mixture using a semi-batch reactor at 440 °C. The results of the fresh and used catalysts were compared with each other and the non catalytic (thermal) run under same conditions. It was reported that fresh catalyst was more active, producing gases rich in C₃–C₄ hydrocarbons and H₂, as well as less aromatics were produced in the liquid fraction. Results indicated that after one pyrolysis experiment, the zeolite loses its major activity, both in terms of yields and the products quality; however, by regeneration through heating at 550 °C in oxygen atmosphere, the initial activity of the catalysts could be recovered.

Aboulkas *et al.* in 2010 [124] studied the decomposition kinetics polymer recycling on industrial scale by estimating the activation energy and the reaction model



of the pyrolysis of HDPE, LDPE and PP from non-isothermal kinetic results. The activation energies determined by Friedman, Kissinger–Akahira–Sunose and Flynn–Wall–Ozawa iso-conversional methods, for HDPE, LDPE and PP were found to be 238–247 kJ/mol, 215–221 kJ/mol and 179–188 kJ/mol, respectively. The authors also interpreted the conversion process using appropriate conversion model including Coats–Redfern and Criado methods.

Lopez *et al.* in 2011 [125] studied the influence of ZSM-5 zeolite and Red Mud in the pyrolysis of plastic wastes. The catalysts were characterized by BET surface area, pore size, and acidity analysis. The zeolite showed weak and strong acid sites and high BET surface area of about $412.0 \text{ m}^2 \cdot \text{g}^{-1}$, however, Red Mud showed lower acidity having also weak and strong acid sites, meso-macro pores and smaller BET surface area of $27.49 \text{ m}^2 \cdot \text{g}^{-1}$. The catalysts were tested for the pyrolysis of a mixture of plastics resembling to the municipal plastic wastes at temperatures of 440 and 500 °C using a 3.5 dm^3 semi-batch reactor. The results showed that ZSM-5 zeolite had a strong effect in the characteristics and distribution of pyrolysis products, by giving high yield of gases and liquids with a higher aromatic content at both temperatures. Whereas Red Mud required higher temperatures than ZSM-5 zeolite to show its activity in pyrolysis, as the results obtained at 440 °C were same as without catalysts, however, at 500 °C, high yield of gaseous products and a high aromatics containing liquid fractions were obtained.

In the year 2011, **Lopez *et al.*** [126] investigated the catalytic pyrolysis of plastic waste streams which were the rejects of the industrial packing wastes sorting plant. Pyrolysis was conducted in a 3.5 dm^3 semi batch reactor in the presence of commercial ZSM-5 as catalysts at 440 °C for 30 min under nitrogen atmosphere. In all pyrolysis runs, high yield of useful gases and liquids were obtained which can be used as fuels starting materials for different chemicals. Solid residue consisting of inorganic material present in the feed and some char is also formed during the pyrolysis. The zeolite showed high activity by giving the liquid fraction rich in aromatics and C_3 – C_4 hydrocarbon range gases, from the feed comprised of polyolefins. The characteristics of the products obtained in pyrolysis and the activity of the catalyst is steered by the composition of the



feed (raw material). In case of using paper rich samples in pyrolysis, the ZSM-5 zeolite leads to high water and less CO and CO₂ formation.

Sarker *et al.* in 2011 [127] reported that the thermal pyrolysis of polymer wastes gives significant quantities of (C₆–C₁₄) range light naphtha liquids, but in addition, a residual fraction was also obtained which can be used as a potential feedstock for upgrading. The authors obtained a liquid fraction by thermal degradation of waste plastics comprising of about 29 % of +110 °C naphtha range hydrocarbons, and subjected it to thermal reactions in the presence of commercial HZSM-5 zeolite catalyst. Results indicated that there was a good conversion to naphtha.

In the year 2011, a detailed review of the different methods for recycling of plastic wastes was presented by **Kumar *et al.*** [128]. The authors discussed the production and consumption of HDPE, and different methods for its recycling with special reference to pyrolysis into useful products of fuel values. The review also focused on different factors which affect the degradation of plastics, the kinetics and mechanism of the reaction involved in the pyrolysis reaction.

In 2012, **Arabiourrutia *et al.*** [129] carried out the thermal pyrolysis of three different polyolefin plastics including HDPE, LDPE and PP using a conical spouted bed reactor. This technique was used for the high selectivity to waxes due to the low residence times and high heating rates which reduce secondary reactions and increase the yield of primary pyrolysis products i.e. waxes. Pyrolysis experiments were carried out at 450, 500 and 600 °C and the products obtained were completely characterized by using different techniques like, gel permeation chromatography (GPC), FT-IR spectrophotometry, simulated distillation, heating values and melting points determination. The operating conditions and the feed type were found to be the major factors affecting the properties of the waxes obtained.

Lopez *et al.* in 2012 [130] investigated the influence of temperature and time on the products obtained in the pyrolysis of plastic wastes. The authors studied the thermal behavior of a plastic mixture in a thermo gravimetric analyzer as well as in a lab scale semi-batch reactor under atmospheric pressure in order to establish an appropriate



relative time and temperature combination for pyrolysis of plastic waste. Results indicated that temperature affected the characteristics of pyrolysis liquids than gas and solid properties. 500 °C temperature and 15-30 min were found to be the optimum temperature and time for the reaction. At lowest temperature (460 °C), the liquid obtained was highly viscous containing high proportion of long hydrocarbon chains, whereas at high temperature (600 °C), less liquid with high aromatic contents were obtained.

Ding *et al.* in 2012 [131] investigated the pyrolysis of polymers in a stainless-steel autoclave at different temperatures, i.e. 360, 380, 400 and 420 °C under initial pressure of 6.325 kPa and reaction times of 0–240 min. From the experimental results, a kinetic model was developed to interpret the formation of different range fractions i.e. light, middle and heavy fraction. This model proved well for operation in different conditions, also the model showed that the pyrolysis of a polymer, its mixture and mixed plastics containing additives can be described. The optimization experiment showed that the yield of heavy fractions was 70 wt % in the pyrolysis of HDPE at 380 °C in 250 min, whereas in case of thermal pyrolysis of plastic mixtures, the yield of heavy fractions was about 50 wt% in 30 min at 400 °C. The activation energy for HDPE conversion was 217.66 kJ mol⁻¹ and that of plastic mixtures was about 178.49 kJ mol⁻¹, respectively.

Seerano *et al.* in 2012 [73] presented a review on the catalytic cracking of polyolefins over solid acids focusing on the role played by the catalysts toward the synthesis of fuels and chemicals as well as on the reaction systems currently used. Initially, conventional solid acids, such as micrometer sized crystal zeolites and silica–alumina were used to establish the relationship among their activity, selectivity, and deactivation in the polyolefin cracking and the inherent properties of the catalysts (acidity, pore structure); however, the occurrence of steric and diffusional hindrances for entering the zeolite micro pores posed by the bulky nature of the polyolefins highlighted the importance of having easily accessible acid sites, either through meso pores or by a high external surface area. This fact led toward the investigation of mesoporous materials (Al-MCM-41, Al-SBA-15) and nano zeolites, which allowed increasing the catalytic activities, especially in the case of polypropylene. Further advances included the application of hierarchical zeolites whose bimodal micropore-mesopore size distribution



has turned them into the most active catalysts for polymer cracking. In this regard, hierarchical zeolites may be regarded as a clear breakthrough and it is expected that future research on them will bring new achievements in the field of catalytic cracking of polyolefins. In addition, other materials with high accessibility toward the active sites such as extra-large pore zeolites, delaminated zeolites, or pillared zeolite nano sheets can also be considered potentially promising catalysts. From a commercial point of view, two-step processes seem to be the most feasible option including a combination of thermal treatments with subsequent catalytic conversion and reforming, which allows the catalytic activity to be preserved against different types of deactivation.

Adrados *et al.* in 2012 [132] conducted a study on pyrolysis as an alternative for the reclamation of rejected streams of waste plastic e.g. PE, PP, PS, PVC, PET, acrylonitrile butadiene styrene (ABS), aluminum, tetra-brick, and film which are typically sent to landfills or incinerators. The authors investigated the pyrolysis of a plastic mixture and waste plastic samples obtained from a sorting plant using a non-stirred semi-batch reactor in the presence of red mud as a catalyst. Results indicated that even using same volume of the feed material, the pyrolysis yield showed a noteworthy difference. In case of pyrolysis of real samples, less liquid and more gaseous products were obtained. The pyrolyzed products of different feeds also showed significant differences in the composition.

The catalytic and stepwise pyrolysis of mixture of different polymers including PE, PP, PS, PET and PVC was investigated by **Lopez, *et al.*** in 2012 using a 3.5 dm³ semi-batch reactor at 440 °C for 30 min in the presence of ZSM-5 zeolite as catalyst [133]. In this study, dechlorination step was carried out at low temperature (300 °C) both with and without catalyst. Results showed that by applying the dechlorination step, about 75 wt% chlorine could be reduced in the liquid fraction. However, the dechlorination step leads to negative impact on the catalyst in terms of reducing its activity, which could be avoided by carrying out the dechlorination step in the absence of the catalysts and the second step with the catalyst.



Wilk *et al.*[134] in 2013 studied the steam gasification of various plastic materials including PE, PP, and mixtures of PE & PS, PE & PET and PE & PP using a dual fluidized bed gasification pilot plant (DFB). Results showed that product gas obtained from PE was rich in CH₄ and C₂H₄, and the LCV of the gas was 25 MJ/m³. Whereas the gas product given by mixture of PE with other polymers showed that the concentration of CH₄ and C₂H₄ increased with increasing the ratio of PE. The proportion of CH₄ was high in the product gas obtained from pure PP and that of C₂H₄ was higher in gas derived from PE. In case of polymer mixtures i.e. PE & PP or PE & PS, the relative distribution of H₂ and CO was larger, whereas the mixture of PE and PET gave the high yield of CO₂, about 28 %. It was concluded that oxygen containing polymers gave high yield of CO₂, and the non oxygen polymers gives smaller yield of CO₂, which actually comes from the reactions of water. It was further revealed that the product gas obtained from gasification of polymers, also contained tar in the range of 100 g/m³, the GC-MS analysis of the tar indicated that it is mainly composed of PAH and aromatics, out of which naphthalene was one of the important compounds.

The pyrolysis study of mixtures of palm shell and polystyrene waste was conducted by **Abnisa *et al.*** in 2013 [135] in order to obtain liquid oil which could be used as fuel. Various reaction variables including temperature, feed ratio and reaction times were screened to select the optimized conditions. The optimum conditions were found to be, 600 °C temperature, palm shell and polystyrene ratio of 40:60, and the reaction time of 45 min, under which the maximum oil yield of 68.3 % was attained. The product analysis indicated that the heating value of the oil was 40.34 MJ/kg, containing 1.9 wt % of water and 4.24 wt % of oxygen, and mainly consisted of aliphatic and aromatic hydrocarbons.

Miranda *et al.* in 2013 [136] investigated the possible routes for the pyrolysis mechanism of various polymer wastes including rubber tyre (RT), PE, PP and PS. The authors used the mixture of the polymers which consisted of 30% RT, 20% PE, 30% PP and 20% PS for the pyrolysis study to obtain the liquid oil of fuel value. Experiments were carried out at different temperatures and times in batch mode, and the experimental data was used to study different kinetic models. The data led to develop new kinetic



models and reaction pathways were proposed, which helped to explain the wastes thermal degradation. Kinetic parameters were estimated and temperature dependence of activation energy and pre-exponential factor was evaluated. In case of some reactions, the rate constant showed non linear temperature dependence on the Arrhenius law in its logarithmic form, which strongly suggested that pyrolysis mechanism of polymer wastes is temperature dependent.

Miskolczi *et al.* in 2013 [137] studied the pyrolysis of municipal plastic wastes (MPW) and its co-pyrolysis with municipal solid wastes in a batch reactor at different temperatures i.e. 500, 550 and 600 °C in the presence of various catalysts. The catalyst used included Y zeolite, b-zeolite, equilibrium FCC catalysts, MoO₃, Ni/Mo, HZSM-5 and Al(OH)₃, etc. The liquid oil obtained during the pyrolysis was characterized by viscosity determination, compositional analysis and determination of various contaminants in the oil. Results indicated that the viscosity of the oil is reduced by using b-zeolite and MoO₃ catalysts. It was observed from the morphological and textural analysis of the char produced that more coke deposits on the catalysts surface while using MSW in the feed. Different contaminants found in the pyrolysis oils included K, S, P Cl, Ca, Zn, Fe, Cr, Br and Sb.

After going through the literature review, it can be observed that most of the previous work is devoted to the use of catalysts with emphasis on high product yields, and product quality. The results obtained in most of the studies are promising in term of conversion of plastics into useful products. However, due to bulky nature of the polymeric molecules, properties of the catalysts need to be tailored further with emphasis on textural, surface and chemical properties to render them more active.

The present work aimed at catalytically converting PP and HDPE in a fixed-bed reactor at low temperatures over original and metal impregnated nano-structured barium titanates, zeolitic pre baked clays, bentonites and carbon as catalysts into useful products that could be used as fuel and feed-stock for chemical industries with emphasis on high conversion to liquid products and products selectivity in gasoline and diesel range hydrocarbons.



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EXPERIMENTAL





CHAPTER-2 EXPERIMENTAL

2.1. CHEMICALS AND REAGENTS

All chemicals used were of analytical grade (Merck, Aldrich, BDH, Alfa Aesar, and Fluka). Nitrogen gas (99 % purity) was purchased from British Oxygen Company, Peshawar. The model polyolefins i.e. poly (propylene) and high density poly (ethylene) were collected from local industrial market. Their proximate analysis i.e. moisture, ash, loss on ignition & fixed carbon (wt %) and ultimate analysis i.e. carbon, hydrogen, nitrogen & sulphur (wt %) were determined according to American Society for Testing and Materials (ASTM) Standards/ Institute of Petroleum (IP) designated methods. Pre baked clay was collected from local brick kiln. Run of mine (ROM) bentonite was provided by Pakistan Mineral Development Corporation (PMDC), Government of Khyber Pakhtunkhwa and activated carbon, Darco (20-40 mesh) granular was purchased from Aldrich. Other reagents used included BaCO_3 (99 % Alfa Aesar) and TiO_2 (99 % Merck), PbO (99 % Fluka), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99 % Merck), FeCl_3 (79 %), CoCl_2 (99 %), $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (98 %), $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (99 %), and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99 %).

2.2 .CATALYSTS PREPERATION

A number of heterogeneous catalysts listed as under were prepared in the laboratory. The incipient witness method [1] was followed to impregnate the corresponding metal salt solutions on to each catalyst.

- I. Original and metal doped barium titanates (BaTiO_3 , Pb/BaTiO_3 , Co/BaTiO_3 and Pb-Co/ BaTiO_3)
- II. Original and transition metal impregnated prebaked clay (PBC, Zn /PBC , Ni/PBC , Co/PBC , Fe/PBC , and Mn/PBC)
- III. Original and transition metal impregnated bentonites (BC, Zn/BC , Ni/BC , Co/BC , Fe/BC , and Mn/BC) and
- IV. Original and transition metal impregnated activated carbon, Darco (AC, Zn/AC , Ni/AC , Co/AC , Fe/AC , and Mn/AC).



2.2.1. Preparation of Original and Metal Doped Barium Titanates (BaTiO_3)

Materials: BaCO_3 (99 % Alfa Aesar) and TiO_2 (99 % Merck) were used in synthesis of BaTiO_3 , PbO (99 % Fluka) and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99 % Merck) were used as Pb and Co precursors for doping.

Procedure: The catalysts i.e. BaTiO_3 , Pb/BaTiO_3 , Co/BaTiO_3 and $\text{Pb-Co}/\text{BaTiO}_3$ were synthesized by reactive calcination method [2]. For synthesis of original BaTiO_3 , stoichiometric quantities of BaCO_3 and TiO_2 were slurried using doubled de-ionized water in a tungsten carbide jar for about 4 h in planetary ball mill (Fritz) using ZrO_2 (sintered) balls of 2 mm diameter in size. After milling, the slurry was dried in an oven at 90 °C for 6 h. The dried solid phase material was then pressed into pellets using a hydraulic press. Further, the pellets were calcined in a muffle furnace at 950 °C for 4 h with temperature increment of 5 °C/min and cooling rate of 10 °C/min, in order to get the required perovskite phase. After calcination, the pellets were ground to a fine powder and sieved through 80 μm screen. The powdered catalyst was milled again in a ball mill for 8 h in the presence of double distilled water. The sample was dried in an oven and then stored in a glass vial for further use.

The doped catalysts i.e. Pb/BaTiO_3 , Co/BaTiO_3 and $\text{Pb-Co}/\text{BaTiO}_3$ were prepared using the same procedure, with the only modification of adding the stoichiometric quantities of dopants like PbO and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ as Pb and Co precursors.

2.2.2. Preparation of Original and Metal oxides Impregnated PBCs

Materials: Pre-baked clay (PBC) was collected from a brick kiln and used as zeolitic source. Transition metals salts used for the preparation of metals impregnated PBC included FeCl_3 (79 %), CoCl_2 (99 %), $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (98 %), $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (99 %), and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99 %) as metal precursors.

Procedure: The transition metals salts were impregnated on PBC by using incipient wetness method [1]. Before impregnation, PBC was purified by de-siltation and exhaustive washing with copious amount of de-ionized water (DI), dried in an oven at



100 °C for time duration of 3 hours, screened through 125 µm screen and stored as original PBC.

For preparation of impregnated catalysts, stoichiometric quantity of each metal salt, required for attaining 2 % wt loading, was dissolved in 100 mL of DI. The solution was transferred to a 250 mL beaker and added 3 g of purified PBC. The resultant suspension was stirred at 70 °C for 5 hours using a hot plate cum magnetic stirrer. Catalyst was recovered by vacuum filtration, and dried in an oven at 90 °C for time duration of 24 hours. After drying, the resulting impregnated catalyst was ground to a fine powder and then calcined at 550 °C for four hours in a muffle furnace.

All the catalysts were stored in air tight glass vials, and used as such for catalytic activities in further pyrolysis experiments.

2.2.3. Preparation of Original and Metal Oxides Impregnated BCs (BC, Zn/BC, Ni/BC, CO/BC, Fe/BC, and Mn/BC) Catalysts

Materials: Different transition metal salts used as precursor included i.e. FeCl₃ (79 %), CoCl₂ (99 %), Zn (NO₃)₂·6H₂O (98 %), MnCl₂·4H₂O (99 %), and Ni(NO₃)₂·6H₂O (99 %). Acid modified bentonite clay was used.

Procedure: Before metal impregnation, the clay was acid modified. In a 250 mL round bottom flask, about 150 mL aliquot of 0.1 N HCl solution was taken, and about 50 g of the clay sample was added to it. The suspension was refluxed for 3 hours with constant stirring. The clay sample was collected through vacuum filtration and washed with copious amount of distilled water. The sample was dried in an oven at 100 °C for about 12 h. The dried clay was crushed to a fine powder and then screened through 125 µm sieve. The clay sample was then calcined at 550 °C for 5 hours. After calcination, the sample was stored in a glass vial and used as such for metal impregnation.

Metal Impregnation: Transition metal salts impregnation on bentonite clay was performed by incipient wetness method [1]. In a typical run, stoichiometric quantity of metal salt was weighed and dissolved in 100 mL of de-ionized water in a 250 mL beaker. About 3 g of acid modified clay was added to the salt solution and stirred at 65 °C for



about 4 h. The suspension was dried at 100 °C in an oven. The catalyst was crushed, calcined in the supply of air at 500 °C for 4 h in a muffle furnace and stored for further use.

2.2.4. Preparation of Original and Transition Metal Salts Impregnated ACs (AC, Zn/AC, Ni/AC, CO/AC, Fe/AC, and Mn/AC) Catalysts

Materials: Different transition metal salts i.e. FeCl_3 (79 %), CoCl_2 (99 %), $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (98 %), $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (99 %), and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99 %) were used in impregnation study. Activated granular carbon was ground to a fine powder, sieved through 75 μm sieve, and used for impregnation.

Procedure: The transition metals were impregnated on activated carbon accordingly by wet impregnation method. Before impregnation, the granular carbon was ground into a fine powder. Stoichiometric quantity of each metal salt required for 2 wt % loading was dissolved in 100 mL de-ionized water in a 250 mL beaker, separately. A 5 g portion of powdered carbon was added to the salt solution and stirred at 65 °C for 4 h under vigorous stirring. The sample was dried in an oven at 90 °C overnight and stored in glass vials for further catalytic activities.

2.3. PYROLYSIS EXPERIMENTS

Pyrolysis experiments of the PP and HDPE were carried out with and without catalysts, separately.

2.3.1. Pyrolysis Equipment

The pyrolysis equipment used was comprised of a steel reactor, furnace, condenser, liquid receiving flask, and gas outlet. The schematic of the pyrolysis assembly is provided in Fig. 2.1. The assembly consisted of:

A. Furnace: A tube furnace equipped with a thermocouple and automatic temperature controller was used for heating purpose. The reactor was placed in the furnace horizontally and heated up to the desired temperature electrically. Reactor skin temperature was measured by using a thermocouple.

B. Reactor: The reactor used was stainless steel made (25.4 cm x 2.1 cm).

- C. Nitrogen Flow:** The reactor was connected with nitrogen cylinder for nitrogen supply required during the pyrolysis reactions.
- D. Condenser:** The reactor was connected with a water cooled glass reflux condenser to condense the vapors leaving the reactor
- E. & F. Water Inlet and Outlet:** The condensation was done via water circulation through E (inlet) and F (out let).
- G. Gas Exit:** The non condensed gases were expelled through a gas exit
- H. Receiving Flask:** The condensates were collected in receiving flask connected next to the condenser and stored for further analysis.

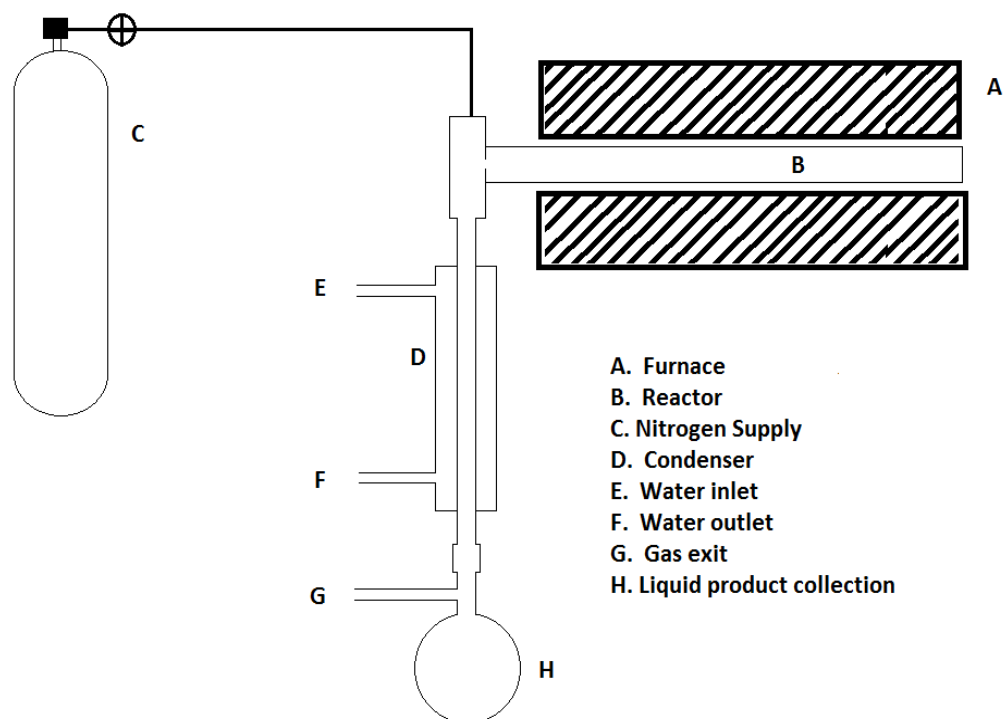


Fig. 2. 1. Schematic of the pyrolysis reactor

2.3.2. Process

2.3.2.1. Thermal Pyrolysis

In a typical run, a definite amount of the feed sample was taken in the reactor. The reactor was purged twice with nitrogen to remove the air and heated to the desired



temperature in non sweeping environment of nitrogen. The heating was controlled to get the desired temperature by using a thermocouple. The sample was held at the desired temperature till no recovery of the liquid. The time at the completion of reaction was noted. The vapors leaving the reactor were allowed to flow through a Liebig condenser set up where the liquid condensed by using water as cooling medium. The gaseous products were vented after cooling by passing through traps containing water to recover any more condensates. After completion of reaction, the reactor was cooled to ambient conditions/temperature. The liquid collected in the reservoir was measured by weight and used for further analysis. The residue was collected as char and weighed. The process flow sheet is provided in Fig.2.2.

Thermal pyrolysis experiments were carried out to determine the optimum temperature and time for maximum liquid yields.

2.3.2.1.1. Temperature Optimization Study

Some preliminary experiments were performed at different temperatures ranging from range 250- 400 °C for optimization. The optimum temperature was decided on the basis of highest wt% yield of the liquid product.

2.3.2.1.2. Contact Time Optimization Study

Pyrolysis experiments were carried out at optimized temperature while varying the time from 10-60 minutes. The optimum time was decided on the basis of highest wt% yield of the liquid product.

2.3.2.2 .Catalytic Pyrolysis

Catalytic pyrolysis was carried out by using the same procedure out lined as above. In a typical run, the feed sample (2 g) was taken in the reactor, to which added the solid catalyst in desired concentration. The contents were pyrolyzed under optimized conditions of temperature and contact time. In order to study the influence of catalyst type and concentration, samples were pyrolyzed unstirred using 2 g of plastic loaded with each catalyst in concentration range of 0.5-10 wt%, seperately. The optimum catalyst



type and its concentration were decided on the basis of highest wt% yield of the liquid products.

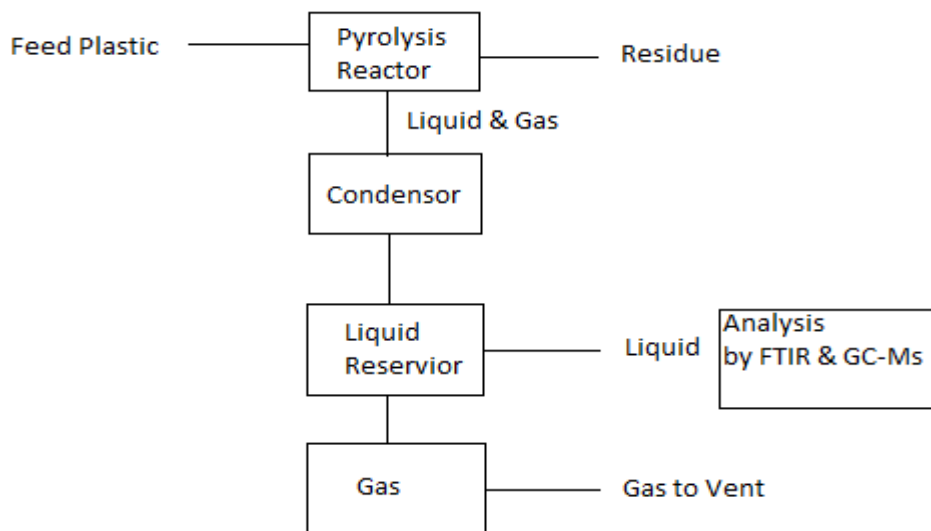


Fig. 2.2. Process flow sheet

2.3.3. Calculations

Overall % yields and yields of liquid, gas and coke/residue (wt %) were calculated as under:

$$\text{Overall yield (T wt \%)} = \frac{WP - WR}{WP} \times 100$$

$$\text{Liquid yield (L wt \%)} = \frac{WL}{WP} \times 100$$

$$\text{Gas yield (G wt \%)} = 100 - [\% \text{ L} + \% \text{ R}]$$

$$\text{Residue yield (R wt \%)} = \frac{WR}{WP} \times 100$$

Where WP, WL, and WR are the weight of feed, liquid oil and residual polymer



2.4. CHARACTERIZATION/ANALYSES

The feed polymers, catalysts used, and the liquids derived under optimized conditions were analyzed by different analytical techniques described as following:

2.4.1. Analysis of Feed Polymers

2.4.1.1. Proximate Analysis

Proximate analysis of feed polymers (PP & HDPE) including moisture, volatile mater, ash, & fixed carbon (wt %) was performed using standard ASTM designated methods.

2.4.1.2. Ultimate Analysis

Ultimate analysis including determination of carbon, nitrogen, hydrogen and sulfur (wt %) was performed using CHNS analyzer.

2.4.2. Characterization of Catalysts Used

All catalysts in original and impregnated form were characterized by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), surface area & pore size, X-ray diffractometry and total acidity measurment.

2.4.2.1. Scanning Electron Microscopy (SEM)/ Energy Dispersive X-ray Spectroscopy (EDX)

The surface morphologies of the catalysts used were examined by using Scanning Electron Microscope (Model JEOL-JSM-5910; Japan). The instrument was equipped with Schottky field emission source that produces an electron probe with a diameter of about 3 to 8 nm at the sample. The accelerating voltage and emission current used for SEM imaging were 15 kV and 6 nA. The samples mounted on stubs were kept at a working distance of 19.8 to 22.4 mm, and were tilted at an angle of 30° from the primary electron beam to face the electron energy analyzer. The elemental analysis was performed by EDX equipped with SEM.



2.4.2.2. Surface Area Analysis (SAA)

The surface area and pore size analysis was carried out by using surface area analyzer (Quantachrome Nova Station A) using nitrogen adsorption method. Each sample was initially degassed at 200 °C for 4 h. Surface area of each of the catalysts was calculated from the nitrogen adsorption-desorption isotherms data using Brunauer, Emmett and Teller (BET) equation. The pore size and pore volume were calculated from N₂ physisorption isotherm data with the help of Barrett, Joyner, Halenda (BJH) method.

2.4.2.3. X-ray Diffractometry

All catalysts prepared in the laboratory were characterized by using X-ray diffractometer (XRD; Model JDX-9C, JOEL, Japan) at room temperature, with CuK α radiation and a nickel filter. The diffraction spectra were obtained using CuK- α) radiation having ($k=1.54178 \text{ \AA}$).

2.4.2.4. Total Acidity Determination

Total acidity of the original and variously impregnated catalysts was determined by the modified procedure reported in the literature [3]. The corresponding data is compiled in Table-2.

A 0.1 g aliquot of catalyst was taken in a screw cap vial and added 10 ml of KOH (0.01 N) solution. The contents were agitated and kept in contact over night in order to establish equilibrium between the catalyst and KOH solution. The solution was then decanted in a separate volumetric flask and thoroughly shaken and added phenolphthalein indicator. The contents were subsequently titrated against freshly prepared HCl (0.01 N) solution using a micro burette. The end point was noted when the color of the indicator changed. The volume of HCl consumed was noted as V₁. A blank test was carried out and the volume of HCl consumed was noted as V₂.

Total acidity was calculated using the following expression:

$$\text{Total acidity (mg KOH/g)} = 56.1 \times V_n \times N/W$$



Where

56.1 = Equivalent weight of KOH.

$V_n: V_2 - V_1$

V_1 = Volume of HCl used in case of sample.

V_2 = Volume of HCl used in case of blank.

N = Normality of HCl.

W_t = Weight of sample taken.

2.4.3. Liquids Analyses

The liquids derived under optimized conditions were analyzed by physicochemical and spectroscopic analyses.

2.4.3.1. Physicochemical/ Fuel Properties

The standard fuel oil analyses developed for petroleum based fuels were applied to crude/lump pyrolysis liquids. These include physical properties (density, specific gravity & API gravity, Conradson carbon residue, and ash), flow properties (kinematic & dynamic viscosities and pour point), volatility properties (flash point, % distillate volume), combustion properties (aniline point, heating value, and diesel index), and antiknock properties (octane number, cetane number, and anti knock index). The results were compared with petroleum-derived products to look for their fuel oil qualities in chemical and thermal applications using standard ASTM/IP methods [4, 5] (Table-2.2).

2.4.3.1.1. Physical Properties

Density, Specific Gravity and API Gravity

Density was determined by weighing a fixed mass of the oil of a definite volume. In a typical experiment, a 25 mL pycnometer having an accuracy of ± 0.05 mL was weighed (m_1) and carefully filled with the liquid fraction. The pycnometer was capped to avoid any evaporation and remove air bubbles. The mass of the liquid filled pycnometer



was measured (m_2) using a Sartorius balance (± 0.01 g). The density (ρ) was measured using the expression:

$$\rho = \frac{m}{v}$$

Where m = mass of the liquid ($m_2 - m_1$)

Specific gravity (SG) of the sample was calculated as follows:

$$SG = \frac{\rho_s}{\rho_w}$$

Where

ρ_s = density of sample

ρ_w = density of water

The API gravity was determined as:

$$\text{API gravity} = \frac{141.5}{SG} - 131.5$$

Conradson Carbon Residue

A portion of 10 g of sample was weighed into tarred porcelain; this crucible was placed in the center of the Skidmore crucible. The Skidmore crucible was then placed in a sand bath. Loose covers were applied to both Skidmore and the iron crucible to allow free exit to the vapors as formed. The whole assembly was hooded in order to distribute the heat uniformly during the process. Heat was provided through the gas burner and continued till the sample ignited and the bottom of the iron crucible got cherry red. The heating source was removed, when the flame was ceased and no further blue smoke observed. The burner was removed and the apparatus was allowed to cool. The cover of the Skidmore crucible was removed. The porcelain crucible was then removed with heated tongs, placed in a desiccator, cooled and weighed.

The CCR was calculates as:



$$CCR = \left[\frac{m_1 - m_2}{M} \right] \times 100$$

Where: m_1 = mass of crucible containing residual carbon (g) m_2 = mass of empty crucible (g), and M = mass of sample (g).

Ash

An aliquot of 5 g of sample was weighed in a predried and preweighed china dish. The dish was placed on a tripod and heated until the contents were ignited by the flame. The sample was allowed to burn at a uniform and moderate rate in order to get carbonaceous residue. The heating was discontinued when the burning ceased.

The dish was placed in the muffle furnace maintained at 775 °C and heated until all carbonaceous material has disappeared, cooled to room temperature in a desiccator and weighed. The mass of the ash as a percentage of the original samples was calculated as follows:

$$\text{Ash \%} = \left[\frac{w}{W} \right] \times 100$$

Where: w = mass of ash (g), and W = mass of sample (g).

2.4.3.1. 2. Flow Properties

Kinematic and Dynamic Viscosities

The kinematic viscosity was determined using kinematic viscometer model Stanhope Seta (UK made). In a typical experiment, the liquid was filled into the viscometer. The sample was allowed to flow under its own weight. The time elapsed during the moment of sample front between the two points marked on the viscometer was noted. The kinematic viscosity measurement was made as under.

The viscometer bath was filled with paraffin oil as bath liquid. A clean, well dried viscometer was fitted into the bath. The heater was turned on and the bath liquid was heated up to the desired temperature. A small amount of the sample was filtered prior to analysis to remove any foreign particles and was put into the viscometer and allowed to



flow by its own weight. With the sample flowing freely, the time was measured in seconds when the sample front was advanced from the first timing mark to the second one using an inbuilt timer. The kinematic viscosity was calculated using the following expression from measured flow time.

$$\nu = Ct$$

Where

ν = kinematic viscosity, mm²/s, C = calibration constant of the viscometer, (mm²/s)/s, and t = mean flow time, s.

Pour Point

The sample was taken into the test jar of the pour point apparatus to the level mark. The jar was closed with the cork carrying the high-pour thermometer in such a way that the bulb immersed in the sample. The sample jar was immersed in the jacket containing a coolant and allowed to cool. The temperature at which haziness was observed in the sample jar was noted as onset of the pour point. The cooling was continued and the jar was periodically removed. The flow of the sample was observed. The temperature at which the sample flow ceased was noted as the pour point. The pour point was reported as multiple of 4 °C.

2.4.3.1. 3. Volatility Properties

Flash Point

The cup of the Pensky Martin closed cup tester was cleaned and filled with the sample upto the filling mark and placed on the center of the heater. The heater was turned on and the sample was allowed to heat slowly at a rate of 25 to 30 °F/min. The flame was then lit on and the pilot was adjusted to a diameter of 3.2 to 4.8 mm. The test flame was applied momentarily across the center of the test cup. The temperature was recorded as flash point at the time when the test flame caused a distinct flash in the interior of the test cup.



Distillation

The distillation apparatus (*Stahhope Seta*) was used which embodies a round bottom flask (100 mL), an inbuilt heater for heating, a liquid bath with a condensate tube and a graduated cylinder covered with blotting paper used as a calibrated volume receiver. A mercury thermometer was centered at the distillate end to monitor the temperature of the leaving vapors.

In a typical run, a 100 ml of the liquid oil was taken in the distillation flask, which was connected to an inbuilt condenser. The contents were heated using inbuilt heater. The temperature when first drop of the condensate was appeared was noted as initial boiling point. The heating was continued till temperature ceased to rise. Two different fractions, fraction A (upto boiling range of 180 °C) and fraction B (boiling range above 180 °C) were collected. The relative proportion of fraction A and B were determined in each sample. The residue left in each sample was also calculated.

2.4.3.1.4. Combustion Properties

Aniline Point

In a typical run, equal volume of sample and aniline was taken in aniline point apparatus. The contents were heated and the temperature at which complete miscibility of the two phases observed was noted as T_1 . The contents were cooled and the temperature at which complete separation was observed was noted as T_2 . Aniline point was recorded as the average temperature $(T_1+T_2/2)$.

Heat of Combustion by Bomb Calorimeter

The heating value (gross) was determined via ASTM method D4809 using a bomb calorimeter model Gallenkamp (UK made). In a typical run, a portion of 1g of sample was weighed into the sample cup. The cup was placed in the curved electrode and the fuse wire was tied between the two electrodes so that the central portion of the loop pressed down on the center of the cup. A cotton thread was tied to the nichrome wire and used as wick to burn the sample. With the test sample and fuse in place, the bomb was



charged slowly with oxygen to 3.0-MPa (30-atm) gauge pressure at room temperature and was immersed in a bucket containing water. The calorimeter was turned on to equilibrate the temperature of water in the outer jacket and bucket. The sample was then fired and the temperature rise was noted using a magnifier.

The gross calorific value was calculated as:

$$Q \text{ (gross)} = E \times T$$

Where:

E= energy equivalent of the calorimeter

T= corrected temperature rise of calorimeter in °C.

Diesel Index

Diesel index was calculated using the following expression:

$$\text{Diesel Index} = \frac{(\text{API gravity} \times \text{Aniline point})}{100}$$

2.4.3.1. 5. Anti Knock Properties

Octane and Cetane Numbers

Octane and cetane numbers were determined using a pre-calibrated portable octanometer Model SX-100 M, Russia (SHATAX) based on measurement of the dielectric constant with accuracy and repeatability equivalent to ASTM approved CFR engines test methods (ASTM D2699 and D2700 for Octane Number and ASTM D613 for Cetane Number). Sample of test oil was filled into the sample holder upto the level mark, and then the imitator was capped tightly on the sample holder. The instrument was pre-calibrated and the octane number, cetane number and antiknock index were determined and directly read from the display.



Anti Knock Index

Anti Knock Index (AKI) was also calculated using the following expression for cross check:

$$\text{Anti Knock Index (AKI)} = \left(\frac{\text{RON} + \text{MON}}{2} \right)$$

Where RON= Research octane number and MON= Motor octane number

2.4.3 .2. Spectroscopic analysis

The liquid products obtained from thermal and catalytic pyrolysis were submitted to FT-IR and GC-MS analyses to investigate the nature of the hydrocarbons, C-number distribution, and hydrocarbon group types.

2.4.3 .2.1. FT-IR Analysis

The FT-IR analysis of the liquid products was carried out using FT-IR spectrophotometer (FTIR Prestige-21, Shimadzu, Japan). The spectrum of each of the liquid oil samples was collected over the wave number range of 4000 to 400 cm⁻¹.

2.4.3 .2.2. GC-MS Analysis

GC-MS analysis of the liquid products was carried out by gas chromatograph coupled with MS analyzer (Model GCMS-QP2010, Shimadzu, Japan) equipped with an auto injector (ADC-201) and DB-5MS column (25 m x 0.25 mm i.d., 0.25 μm). The standard conditions used were:

Carrier gas used	: Helium
Flow rate of carrier gas (ml/min)	: 1.3
Split ratio	: 50
Injector temperature (°C)	: 300
Sample injection volume (μl)	: 1



The initial oven temperature (°C) : 35

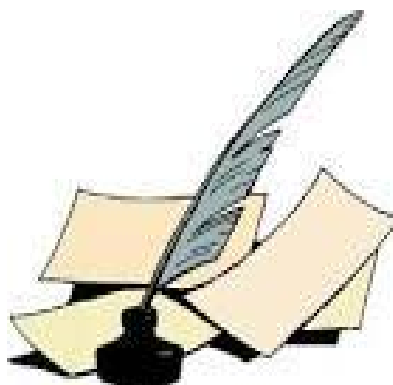
The initial oven temperatures was ramped to 100 °C at a rate of 5 °C min⁻¹ and hold time of 5 min, then to 150 °C at a rate of 10 °C min⁻¹ and hold time of 10 min. The temperature was finally raised to 290 °C at the rate of 2.5 °C min⁻¹ with an isothermal held of 10 min. The product peaks in the chromatogram were identified by NIST-MS library.

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RESULTS AND DISCUSSION





CHAPTER-3

RESULTS AND DISCUSSION

The present work was aimed at converting individual polypropylene and high density polyethylene thermally as well as catalytically in a fixed-bed reactor at low temperatures into useful products that could be used as fuel and feed-stock for chemical industries with emphases on high conversion to liquid products and product selectivity in gasoline and diesel range hydrocarbons. For this purpose, pyrolysis of PP and HDPE was investigated in nitrogen environment, separately in the absence and presence of various catalysts to evaluate their effectiveness in pyrolysis of polyolefins to get fuel like liquid products. The carbon range and hydrocarbons group types distributions of the liquid products obtained under optimum conditions (temperature, time, catalysts type and concentration) were also studied. The research was carried in the following phases:

Phase-1: In the first phase, the feed polymers were characterized using standard ASTM methods. In addition, the various catalysts including type A, B, C, and D were prepared in the laboratory and characterized by using SEM, EDX, surface area & pore size, XRD, and total acidity analysis.

- A. Original and metal doped titanates (BaTiO_3 , Pb/ BaTiO_3 , Co/ BaTiO_3 , and Pb-Co/ BaTiO_3)
- B. Original and metal oxide impregnated zeolitic clays (PBCs) (PBC, Zn/PBC, Ni/PBC, Co/PBC, Fe/PBC, and Mn/PBC)
- C. Original and metal oxide impregnated Bentonites (BCs) (BC, Zn/BC, Ni/BC, Co/BC, Fe/BC, and Mn/BC), and
- D. Original and metal salts impregnated carbons (ACs) ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}/\text{AC}$, $6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}/\text{AC}$, CoCl_2/AC , FeCl_3/AC , and $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}/\text{AC}$).

Phase-2: In the second phase, some preliminary experiments were performed in case of both polyolefins at different temperatures ranging from 250-400 °C. Pyrolysis was investigated at different temperatures i.e. 250, 300, 350 and 400 °C in non sweeping



nitrogen atmosphere for temperature optimization study, which was decided on the basis of highest yield of liquid products. Temperature optimization study was also carried out by varying time from 10-60 minutes.

Phase-3: In the third phase, four catalyst systems (A, B, C, and D) were used, separately to evaluate their effectiveness in pyrolysis of PP and HDPE into useful fuel like products. Optimum catalyst in case of each system was decided on the basis of highest liquid yields. Morphological, surface properties and total acidity of the catalyst systems were considered in evaluating their activity & selectivity in term of products yields (over all yields and yields of liquids, gases & residues), and their influence on the desired liquid products composition. The results obtained in each catalysts system were compared also to evaluate a more active and selective catalyst.

Phase-4: In the fourth phase, the liquids derived in both thermal and catalyzed runs (optimum temperature, time and catalyst type & concentration) were subjected to distillation study to further fractionate the lump liquids into light, middle and heavy oils on the basis of their boiling range. The fuel properties including density, API gravity, kinematic viscosity, gross heat of combustion, carbon residue, ash, cetane number, octane number (MON/RON), pour point, flash point, aniline point and diesel index of lump liquids as well as their distillate fractions of gasoline and diesel range were performed. For this purpose, standard Institute of Petroleum (IP) or American Society for Testing and Materials (ASTM) tests/designated methods were used. The results were cross analyzed/compared with the standard fuel properties in order to decide about the quality of the derived liquids.

The results of thermal and various catalyzed runs are discussed in the proceeding sections.

3.1. CHARACTERIZATION OF FEED POLYMERS

The proximate and ultimate analyses of both feed polymers were performed using ASTM designated methods. The results are provided in Table 3.1.

**Table 3.1.** Properties of feed PP and HDPE

Analysis (wt %)	PP	HDPE
Proximate analysis (ASTM D 3173-75)		
Moisture (ASTM D 3173)	0.00	0.00
Volatile matter (ASTM D 3173)	99.90	99.81
Ash (ASTM D 3174)	0.01	0.18
Fixed Carbon (ASTM D 3172 – 89)	0.09	0.01
Carbon residue (ASTM D 189)	0.20	0.61
Ultimate analysis		
Carbon	83.10	84.74
Hydrogen	11.77	11.65
Nitrogen	0.14	0.02
Sulfur	0.16	0.66
Thermal analysis		
Decomposition Temperature (°C)	405	590

The proximate analysis data compiled in Table 3.1 indicated that the volatile matter values (V.M) were quite high (>99 %) in case of both feed polymers. The values of ash and fixed carbons were found to be less than < 0.02 wt%. Similarly, the levels of carbon residue were found to be <1 wt %, in case of both feed PP and HDPE. More volatile matter produces more liquid and gaseous products during pyrolysis, hence their presence is considered to be beneficial for conversion of PP and HDPE into liquid and gas products. It can be observed that both PP and HDPE were decomposed without giving a significant amount of ash and carbon residue. These products are considered detrimental due to their catalysts deactivation activities [1]. Analytical grade PP and HDPE contain 100 % volatile matter with no ash and carbon residue [2]. The ash and carbon residue may be resulted due to the presence of additives and other impurities present in samples under study.

The ultimate analysis in terms of carbon, hydrogen, nitrogen, and sulphur was also determined. The results compiled in Table 3.1 indicated that PP contained carbon; 83.10 %, and hydrogen; 11.77 %, while HDPE contains carbon; 84.74 %, and hydrogen; 11.65 %. Nitrogen and sulphur contents were also determined. The levels of nitrogen



were found to be 0.14 and 0.02 % and that of sulphur contents were found to be 0.16 and 0.66 % in PP and HDPE, respectively.

Feed samples were also characterized on the basis of their thermal degradation temperatures by using TGA analysis. Both polymers degraded completely in nitrogen environment by giving sharp exotherms without leaving any noticeable residue. In case of PP, the de-volatilization/ weight loss rate showed a maximum at 405 °C and in case of HDPE at 590 °C which indicated that HDPE is thermally more stable as compared to PP.

3.2. CHARACTERIZATION OF CATALYSTS USED

Among type A catalysts which were used as novel catalysts in the current study, all forms i.e. BaTiO₃, Pb/ BaTiO₃, Co/ BaTiO₃, & Pb-Co/ BaTiO₃ were analyzed. Among type B; Fe/PBC, & Zn /PBC, among type C; Co/BC & Zn/BC and among type D; Fe/AC & Zn/AC catalysts which gave maximum liquid yields were characterized. Type A catalysts were prepared in the laboratory by reactive calcination method, type B & C by wet impregnation method followed by calcination and type D by wet impregnation method & used without prior calcination.

Morphological characterization was performed by using Scanning Electron Microscopy (SEM) Elemental analysis was carried out by using Energy Dispersive x-ray (EDX). Surface properties were determined by using Surface Area Analyzer (SAA). Textural properties were determined by X-ray Diffractometry (XRD) and total acidity by titration method.

3.2.1. Characterization of Original and metal doped nano porous titanates (BaTiO₃, Pb/ BaTiO₃, Co/ BaTiO₃, and Pb-Co/ BaTiO₃)

The surface morphology of the original BaTiO₃, and doped i.e. Pb/ BaTiO₃, Co/ BaTiO₃ and Pb-Co/ BaTiO₃ was studied by SEM. Electron micrographs of the catalysts are provided in Fig.1 (a-d). The SEM of the original BaTiO₃ indicated the presence of granular particles of about 200 to 400 nm in size distributed throughout the surface. Most of the particles appeared to have been agglomerated in the form of stacks like formations upon calcination. The micrograph of the Pb/BaTiO₃ showed some granules, however,



particles agglomeration in this case is more prominent which have caused abnormal grain growth. Also, the granule size is larger comprised of many particles interweaved with each other compared to un-doped BaTiO₃. Similarly, the micrograph of Co/BaTiO₃ showed highly agglomerated particles mostly resulted from particles inter weaving. The granules of Pb-Co/ BaTiO₃ appeared to be large in size and mostly exfoliated to give serrated formations. This significant increase in size may be due to the incorporation of Pb and Co ions into the matrix of original BaTiO₃.

The elemental composition was also studied by EDX (Table- 3.2). It can be observed that the original BaTiO₃ contained Ba, Ti and O in concentrations of 58.45, 20.53 and 20.58 wt%, respectively. In case of Co/BaTiO₃ and Pb/ BaTiO₃, the concentrations (% wt) of Co and Pb were found to be 4.00 and 0.25 %, respectively, whereas in case of Pb-Co/BaTiO₃, their concentrations were found to be 3.94 and 0.25 %, respectively. The results indicated that compositions (% wt) of all catalysts are very close to their theoretically calculated values.

The surface properties of the catalysts are given in Table- 3.3. The results indicated that the surface area, pore volume and pore diameter were increased in case of doped samples. In case of Pb-Co/ BaTiO₃, a significant (almost threefold) increase in the surface area and pore volume can be observed compared to the original BaTiO₃. The surface area determined in case of original BaTiO₃ was found to be 98.53 m².g⁻¹, whereas their levels in case of Pb/ BaTiO₃ and Co/ BaTiO₃ were found to be 198.88 and 131.5 m².g⁻¹, respectively. On the other hand, the surface area determined in case of Pb-Co/ BaTiO₃ was significantly increased to 269.59 m².g⁻¹. This marked increase in surface area with doping may be attributed to increase in the galleries spacing due to incorporation of the Pb and Co cations in the original titanate lattices [3]. The results indicated that doping caused a synergistic effect on the increase in surface area.

The perovskite phase of the catalysts under study was confirmed by XRD analysis. The XRD patterns of original and various metal doped BaTiO₃ are given in Fig. 3.2. The profiles exhibited major peaks mostly appeared at 32, 37, 45 and 58° 2θ, which showed resemblance to the characteristic patterns of perovskite phase [4]. On the other



hand, the broadness in peaks indicated the cubic phase. Cubic phase perovskite rather than tetragonal phase predominates in calcined samples [5]. This further confirmed that calcination has caused phase change from tetragonal to cubic. No major changes were observed in the XRD patterns of metal doped BaTiO₃, which indicated that the lattice structure of the perovskite remained intact even after doping, and the dopants occupied the crystal lattices by replacing Ba with Pb and Ti with Co.

The total acidity of each catalyst was also determined. The results are given in Table 3.4, which indicated that the acidities of the original as well as doped catalysts are almost comparable.

Table 3.2. EDX analysis of original and various metal doped BaTiO₃ catalysts

Catalyst	wt %				
	Ba	Ti	O	Co	Pb
Original BaTiO ₃	58.45	20.53	20.58	-	-
Pb/BaTiO ₃	54.69	20.42	20.68	-	4.00
Co/BaTiO ₃	58.75	20.32	20.49	0.25	-
Pb-Co/BaTiO ₃	55.45	20.05	20.29	0.25	3.94

Table 3.3. Surface area, pore volume and pore diameter analysis of original and various metal doped BaTiO₃ catalysts

Catalyst	BJH Surface area (m ² g ⁻¹)	Pore size (°A)	Pore volume (cm ³ g ⁻¹)
Original BaTiO ₃	98.53	127.03	0.24
Pb/BaTiO ₃	198.88	127.01	0.62
Co/BaTiO ₃	131.52	129.50	0.38
Pb-Co/BaTiO ₃	269.59	130.36	0.87

Table 3.4. Total acidity of original and various metal doped BaTiO₃ catalysts

Catalyst	Acidity(mg KOH /g)
Original BaTiO ₃	2.85
Pb/BaTiO ₃	3.40
Co/BaTiO ₃	3.00
Pb-Co/BaTiO ₃	3.20

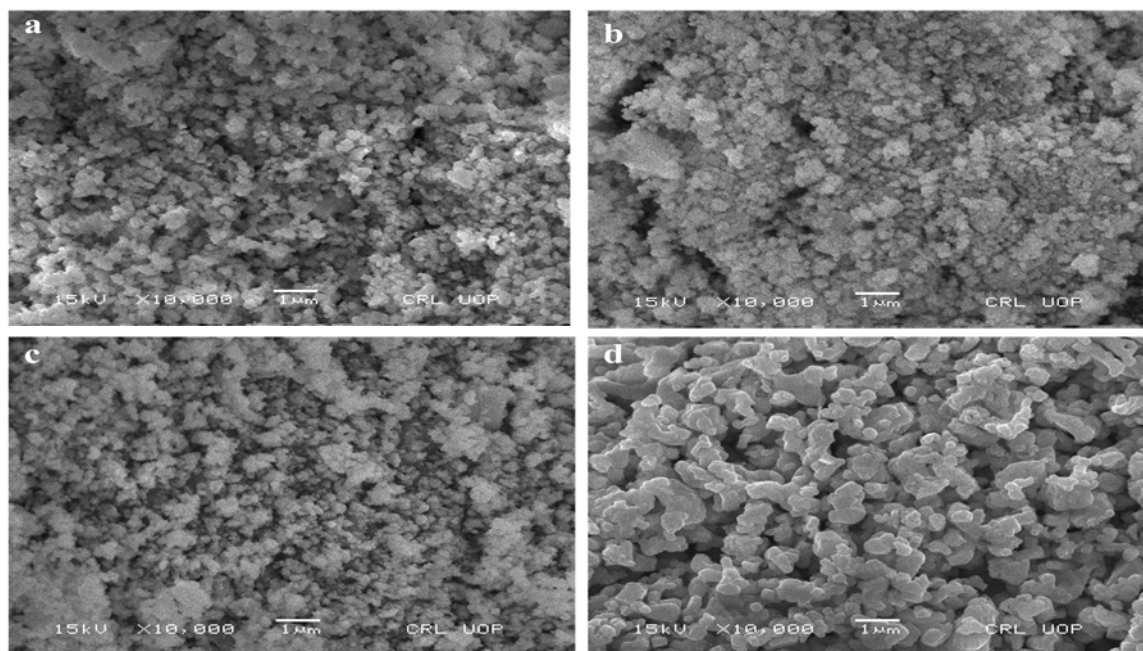


Figure 3.1. Electron micrographs of original and various metal doped BaTiO₃ catalysts
(a) un-doped BaTiO₃ (b) Pb/BaTiO₃ (c) Co/BaTiO₃ (d) Pb–Co/BaTiO₃

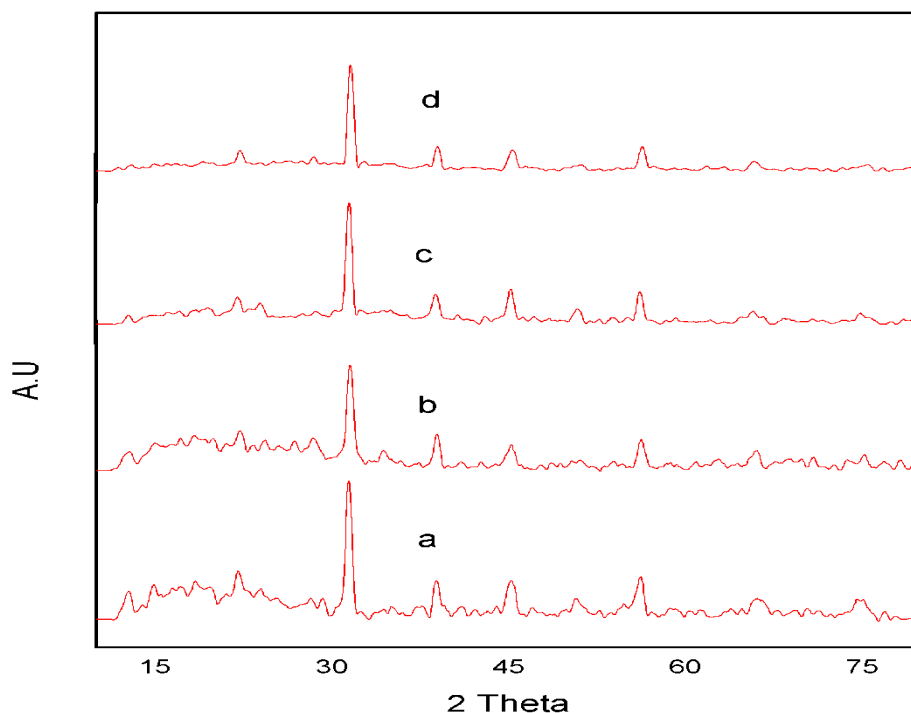


Figure 3.2. XRD patterns of original and variously doped BaTiO₃ catalysts (a) un-doped BaTiO₃ (b) Pb/ BaTiO₃ (c) Co/ BaTiO₃ and (d) Pb-Co/ BaTiO₃

3.2.2. Characterization of original and selected metal oxide impregnated PBCs

The SEM study of the selected catalysts was performed. The micrographs are given in Fig 3.3. The morphological features of the original PBC as shown in Fig. 3.3 (a) indicated its layered morphology with prominent tunnels and large caves distributed throughout the surface. The surface appeared to be not uniform, rather comprised of different sized granules with empty spaces in between. Most of the particles appeared to have been agglomerated in the form of clusters.

The SEM micrographs of Fe/PBC and Zn/PBC are provided in Fig. 3.3 (b) and Fig. 3.3 (c). It can be observed that due to impregnation, the catalysts surface turned to be more porous and uniform compared to original PBC. The surface layering increased as observed in the form of flake like features.

The mineralogical compositions of the original and variously metal oxide impregnated PBCs were studied by EDX analysis. The results obtained are compiled in Table-3.5. The EDX signatures of PBCs are provided in Fig. 3.4 (a-c). The results



indicated that the original PBC mostly contained SiO_2 and Al_2O_3 (about 50 %), which supposed to have formed the zeolitic frame work. Furthermore, various inorganic elements i.e. Na, Mg, K, Ca, Fe and Zn were also found to be present in different concentrations ranged from 0.7 to 5.03 %, except Fe which was present in high concentration; more than 23 wt %. In addition, PBC also contained carbon and oxygen in high concentration. The occurrence of high wt % of C and O suggested that carbonates were present as major impurities in the clay.

As in the current study, only Fe/PBC and Zn/PBC were found to be the most active catalysts for the cracking of PP and HDPE, respectively in terms of giving high liquid yields. Therefore, further EDX analysis was performed for these catalysts only. The analyses compiled in Table-3.6 showed that in case of Fe/PBC, the concentrations of the active metals was found to be 1.9 and in case of Zn/PBC, the concentration of active metal Zn was 25.7 %. It is pertinent to add here that the concentration of Fe in the original PBC was quite high (23 %), therefore, upon impregnation, the wt % of Fe in Fe/PBC attained a concentration of 25.7 wt%.

The surface area analysis data given in Table-3.6 showed that the original PBC has high surface area and small pore dimensions. The BET and BJH surface areas were found to be 74.54 and 300.26 $\text{m}^2 \text{g}^{-1}$, respectively. The pore size and the pore volume were found to be 122.78 $\text{\AA}$ and 0.92 cm^3/g , respectively. The BET surface area values increased up to 77, and 83 $\text{m}^2 \text{g}^{-1}$ in case of Zn/PBC, and Fe/PBC, respectively. Similarly, the pore size and the pore volume of these catalysts were found to be increased. The increase in the surface area might be corresponded to increase in the layers spacing of the PBC which might be due to pillaring effect exhibited by the metal oxides during impregnation and subsequent calcination. The pillaring effect of various metals has already been reported in the literature [6].

The XRD patterns of the original and metal oxides impregnated pre-backed clay are displayed in Fig. 3.5. The patterns indicated that the original PBC was mixed clay with kaolinite and montmorillonite being the major components. Further, it also contained non clayey materials in the form of impurities. Among the impurities found included mica, α -chrysothalite and quartz [7-9]. The XRD patterns of Fe/PBC and Zn/PBC indicated



similar configurations compared to original PBC clay. However, some additional diffraction peaks were appeared which can be corresponded to the impregnated metal oxides. The XRD patterns of Fe/PBC and Zn/PBC showed characteristic peaks corresponded to α -Fe₂O₃ [10] and ZnO [11], respectively. The results indicated that the impregnated Fe and Zn, were changed to respective oxides i.e. α -Fe₂O₃ and ZnO upon calcination.

The results of total acidity have been compiled in Table 3.7. A significant increase is observed in case of Fe/PBC followed by Zn/AC compared to original PBC. The acidities determined in case of other catalysts are almost comparable.

Table 3.5. Mineralogical composition of PBC

Element	wt (%)
C	10.45
O	26.97
Na	0.75
Mg	1.21
Al	8.89
Si	19.37
K	2.47
Ca	5.03
Fe	23.97
Zn	0.89
Total	100

**Table 3.6.** Surface area, pore size, pore volume, and active metals concentration of original and metal oxides impregnated PBCs

Catalyst	BET Surface area (m ² g ⁻¹)	BJH Surface area (m ² g ⁻¹)	Pore size (°A)	Pore volume (cm ³ g ⁻¹)	Active metals Conc. (wt %)
PBC	74.54	300.26	122.78	0.92	-
Zn/PBC	80.71	422.53	132.57	1.4	1.9
Ni/PBC	65.34	221.03	110.6	0.53	-
Co/PBC	70.11	156.21	103.9	0.32	-
Fe/PBC	77.88	223.07	125.64	0.69	1.8
Mn/PBC	62.65	239.45	121.8	0.73	-

Table 3.7. Acidity of the original and metal oxides impregnated PBCs

Catalyst	Acidity(mgKOH/g)
PBC	2.02
Fe/PBC	5.53
Zn/PBC	3.00
Ni/PBC	1.97
Mn/PBC	2.84
Co/PBC	1.95

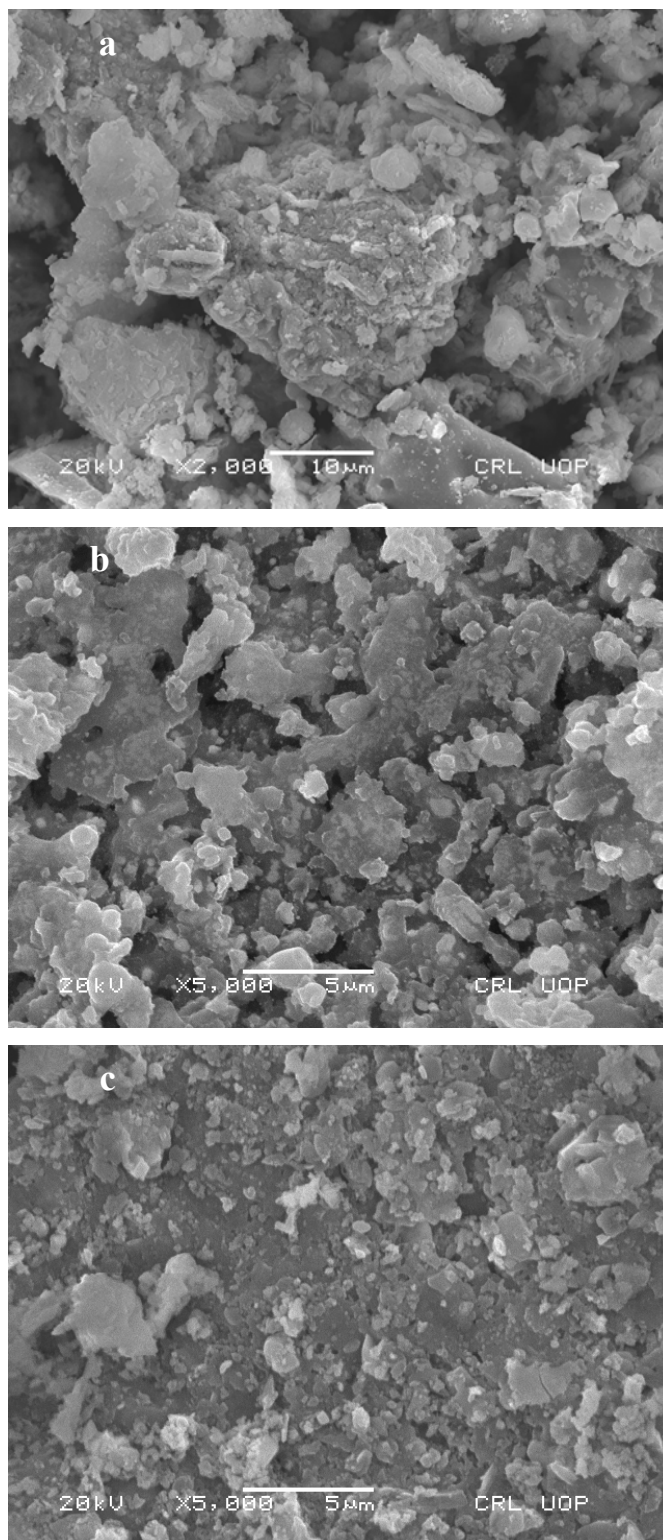


Figure 3.3. SEM micrographs of original and metal oxides impregnated PBCs (a) original PBC (b) Fe/PBC and (c) Zn/PBC

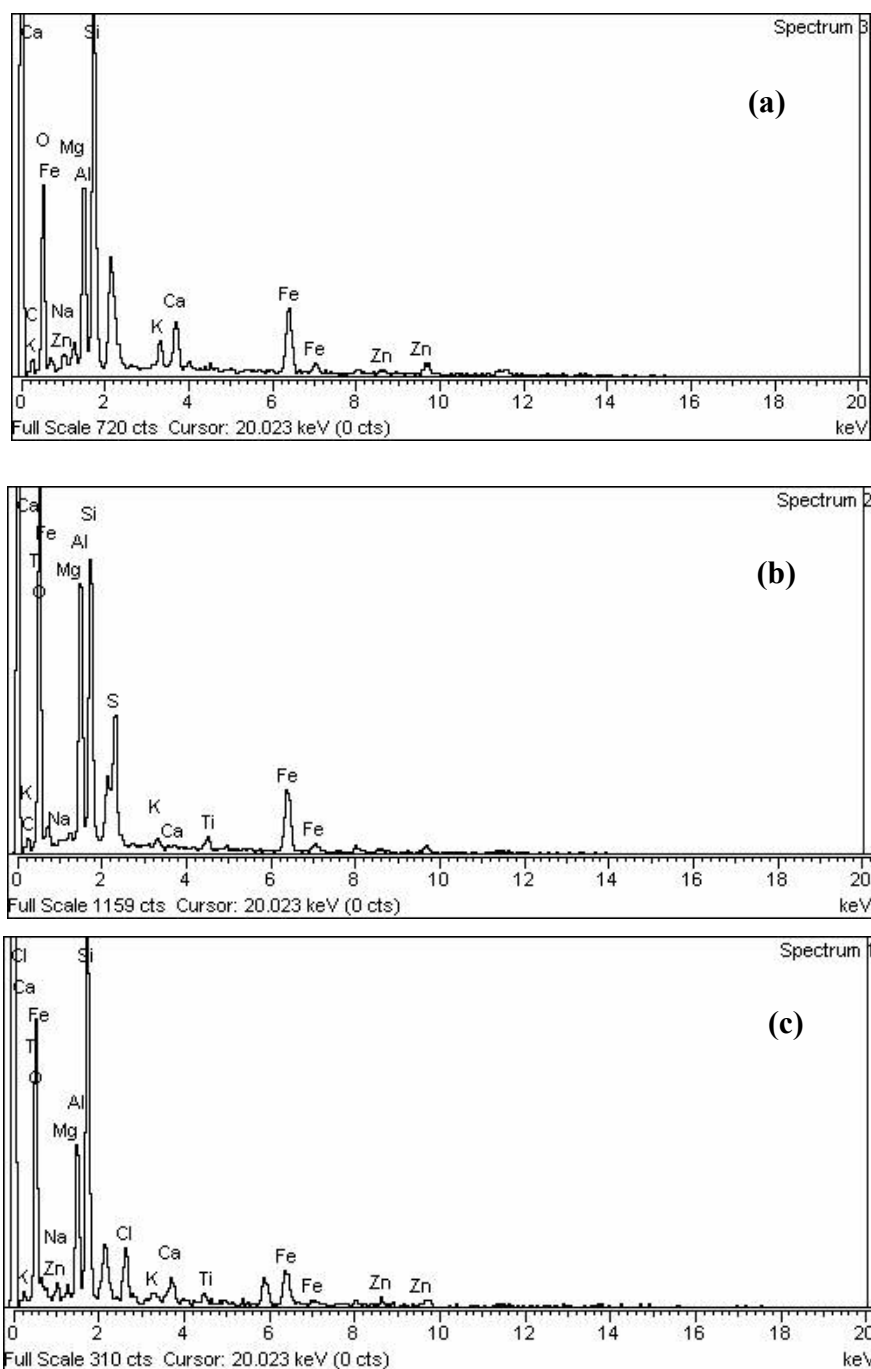


Figure 3.4. EDX signatures of original and metal oxides impregnated PBCs (a) original PBC (b) Fe/PBC and (c) Zn/PBC

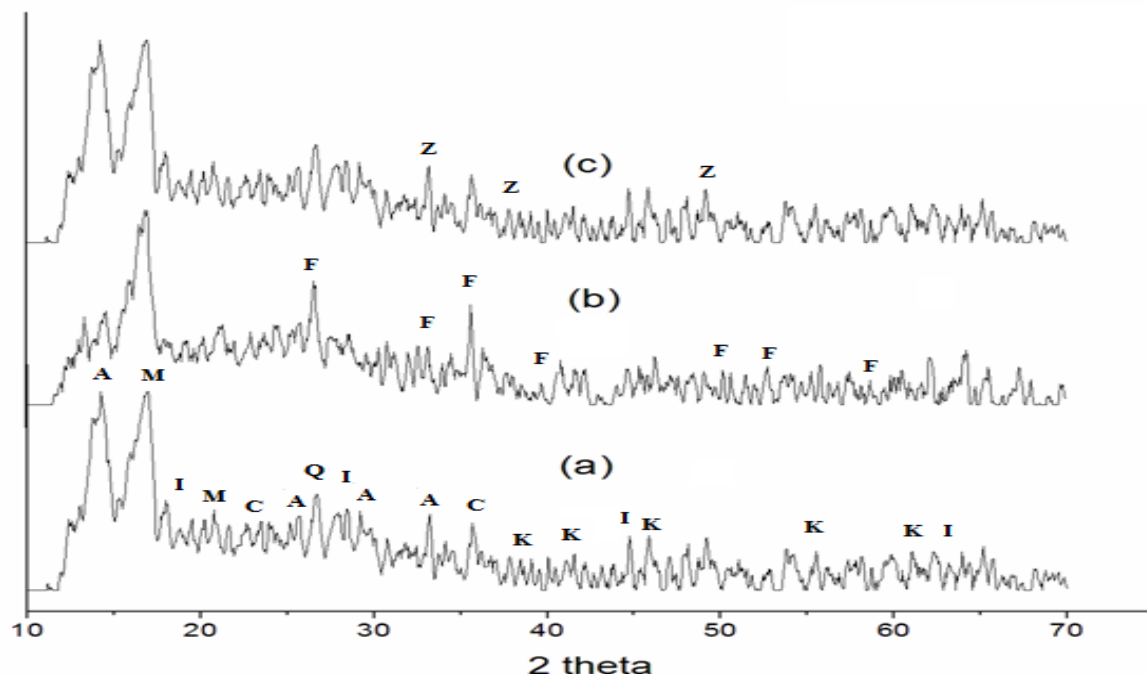


Figure 3.5. XRD patterns of original and metal oxides impregnated PBCs (a) original PBC (b) Fe/PBC (c) Zn/PBC,

Where, *A* = *Albeit*, *M* = *Montmorollinite*, *I* = *Iolite/mica*, *C* = α -*Chrystobalite*, *Q* = *Quartz*, *K* = *Kaolinite*, *F* = Fe_2O_3 , and *Z* = *ZnO*.

3.2.3. Characterization of original and metal oxide impregnated BCs (BC, Zn/BC, Ni/BC, Co/BC, Fe/BC, and Mn/BC)

On the basis of maximum liquid yields, Co/BC and Zn/BC proved to be the optimum catalysts for the pyrolysis of the PP and HDPE, respectively, therefore, morphological analysis of original BC and these two catalysts was performed. The micrograph of the original BC is provided in Fig. 3.6 (a) which indicated a layered surface morphology. Some ill developed features in the form of plateaues, micro fissures and channels can be seen throughout the surface. Further, some distinct and separately identifiable features mostly in the form of grains of different sizes can also be observed. The SEMs of metal oxide impregnated betonies, i.e. Co/BC and Zn/BC featured different surface morphologies compared to original BC. Both of these catalysts exhibited layered surfaces with minute fissures, cracks and cavities. In case of Co/BC, the surface was



mostly consisted of various formations like flakes stacked upon each other, whereas in case of Zn/BC, the surface showed formations like spherules/particles coalesced among themselves resulting aggregates.

The elemental analysis of the original and impregnated BCs was also carried out. The EDS signatures are provided in Fig 3.7 (a-c) and the data is given in Table. 3.8. The results showed that original BC (Fig 3.7 a) mostly contained O, Si and Al in higher concentrations i.e. 43.43, 32.38 and 11.23 wt %, respectively which indicated the predominance of SiO₂ and Al₂O₃. Other elements found in different concentrations ranged from 0.29 to 4.53 wt % included K, Mg, Ca, Na and Fe. It is suggested that these elements may be present in the form of their cations attached to the alumina-silicate frame work of the clay under study or as discrete minerals uniformly distributed in the matrix as impurities.

The EDX analysis of the selected impregnated BCs is given in Fig. 3.7 (b), Fig. 3.7 (c). and Table. 3.8. The corresponding EDX signatures indicated that the concentrations of Co and Zn in Co/BC and Zn/BC were quite high and found to be 2.27 and 1.37 wt %, respectively. The results showed that their concentrations were found to be very close to the theoretical value of 2 wt %.

The surface properties of the catalysts under study were also determined. The results are provided in Table. 3.9. The BET and BJH surface area values of the original BC were found to be 89.87 and 155.65 m² g⁻¹, respectively, whereas the levels of pore volume and pore size were found to be 0.46 cm³/g and 125.56 °A, respectively. The results obtained in case of impregnated samples indicated that the surface properties greatly altered and the surface areas and pore volumes of BCs were markedly decreased upon impregnation. Among the impregnated BCs, the highest BET surface area of 36.37 m² g⁻¹ was observed in case of Zn/BC, whereas the lowest of 21.08 m² g⁻¹ in case of Mn/BC. Similar changes were observed in case of pore width, which was decreased from 125.56 °A (original BC) to 57.77 °A (Zn/BC). The pore volume determined in case of all impregnated BCs was also found to decrease from 0.46 cm³g⁻¹ (original BC) to 0.04 cm³g⁻¹ (Fe/BC and Mn/BC). The decrease in surface area, pore volume and pore size may



be attributed to blinding of micro pores in the BC matrix due to impregnation of metal oxides [12].

The XRD patterns of the original and metal oxides BCs (oxides of Co and Zn) are provided in Fig 3.8 (a-c). The X-ray diffractogram of the original BC confirmed that the precursor clay contained montmorillonite as a major component [13] which consist of alternate layers of silica tetrahedral sheets and aluminum octahedral sheets, interconnected by hydroxyl sheets [14]. The other minerals identified included kaolinite, quarts and illite [15]. The XRD patterns of the metals oxides impregnated clay samples exhibited minerals configurations identical to the precursor clay. However, some additional peaks were also appeared which can be corresponded to metal oxides configurations. The X-ray diffractogram of Zn/BC showed characteristic peaks corresponded to ZnO [11]. Similarly, the pattern of Co/BC indicated the characteristic peaks corresponded to crystalline planes of Co_2O_3 [16]. Hence, it can be concluded that during calcination, the metallic precursors i.e. Co and Zn were converted to their respective oxides i.e. ZnO and Co_2O_3 .

The acidity data is provided in Table 3.10. The results indicated that the values of the impregnated BCs show an increase compared to original BC. The acidity values of the impregnated BCs are comparable with each other.

Table 3.8. EDX analysis of acid washed BC

Element	weight %
O	43.43
Si	32.38
Al	11.23
Mg	2.82
Na	0.29
K	1.37
Ca	4.53
Fe	3.96
Totals	100

**Table 3. 9.** Surface area, pore size, pore volume and active metal concentration of original acid washed and various transition metal oxides impregnated BCs

Catalyst	Surface area (m ² g ⁻¹)		Pore size (°A)	Pore volume (cm ³ g ⁻¹)	Active metals Conc. (wt %)
BC	89.87	155.65	125.56	0.46	-
Ni/BC	24.88	52.02	77.99	0.14	-
Co/BC	23.09	28.14	76.26	0.06	2.27
Fe/BC	24.23	22.36	75.30	0.04	-
Mn/BC	21.08	19.42	76.81	0.04	-
Zn/BC	36.37	73.05	57.77	0.14	1.73

Table 3.10. Acidity of original and metal oxides impregnated BCs

Catalyst	Acidity(mg/g)
BC	3.20
Fe/BC	4.80
Zn/BC	4.20
Ni/BC	4.48
Mn/BC	4.04
Co/BC	4.85

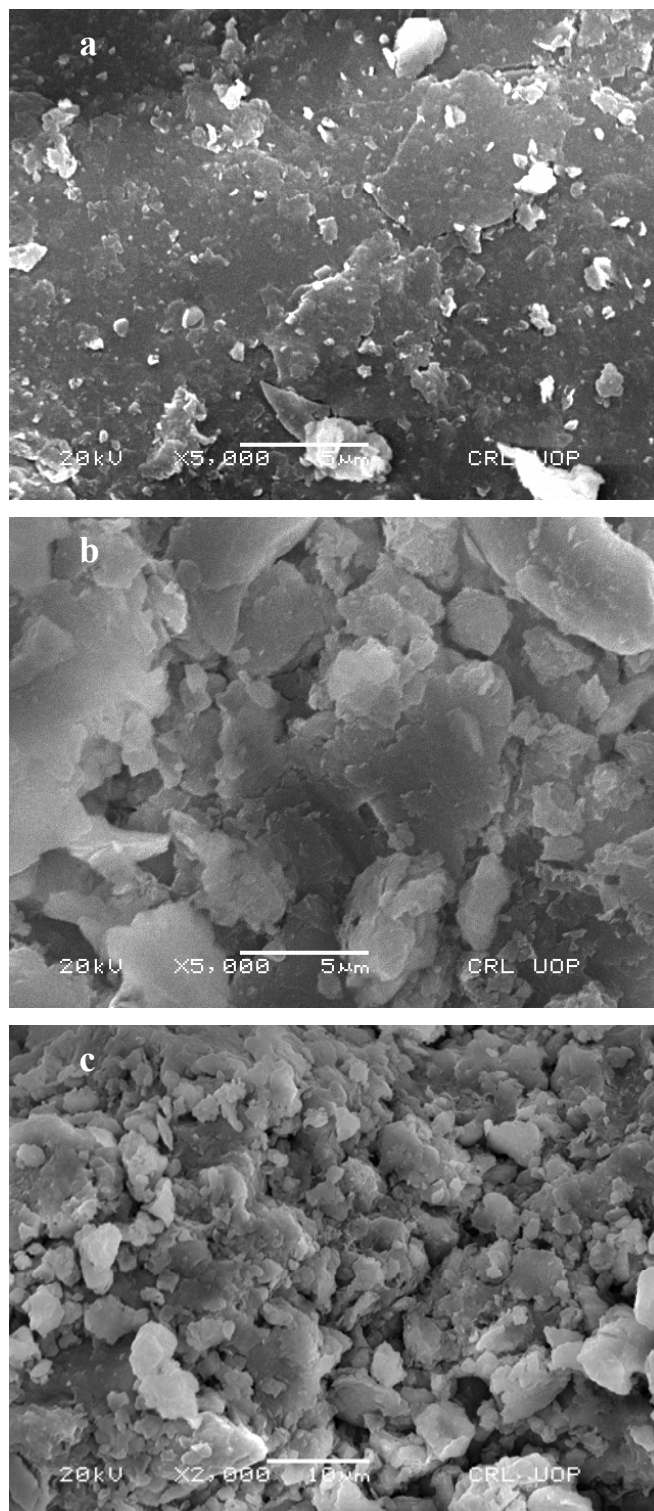
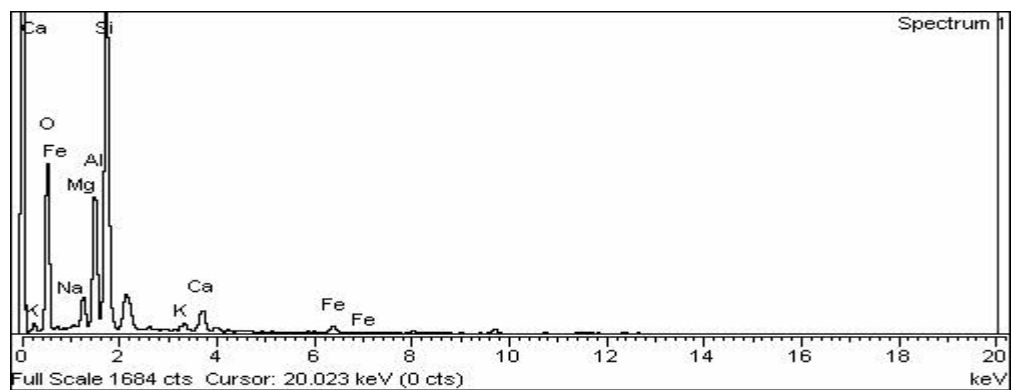
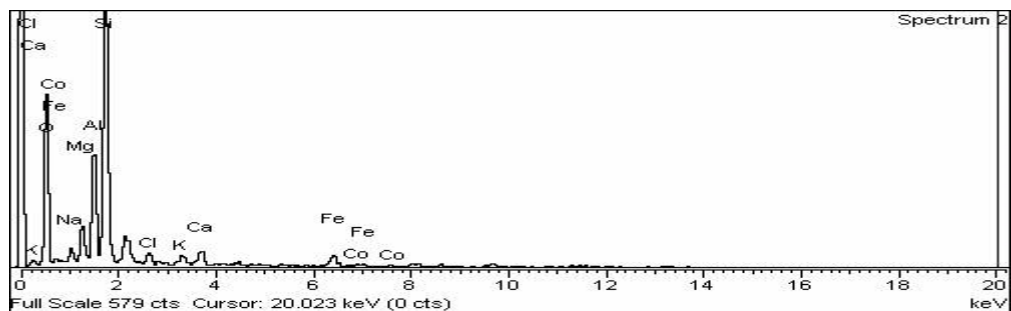


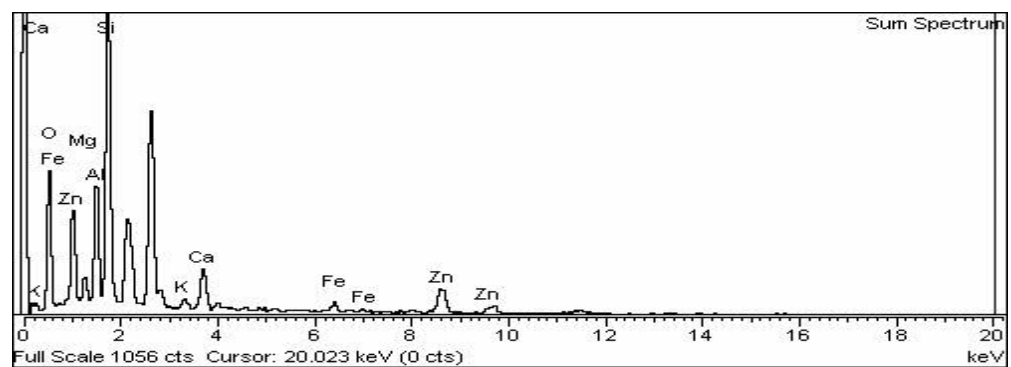
Figure 3.6. SEM micrographs of original and metal oxides impregnated BCs (a) original BC (b) Co/BC and (c) Zn/BC



(a)



(b)



(c)

Figure 3.7. EDX signatures of original and metal oxides impregnated BCs (a) original BC (b) Co/BC and (c) Zn/PBC

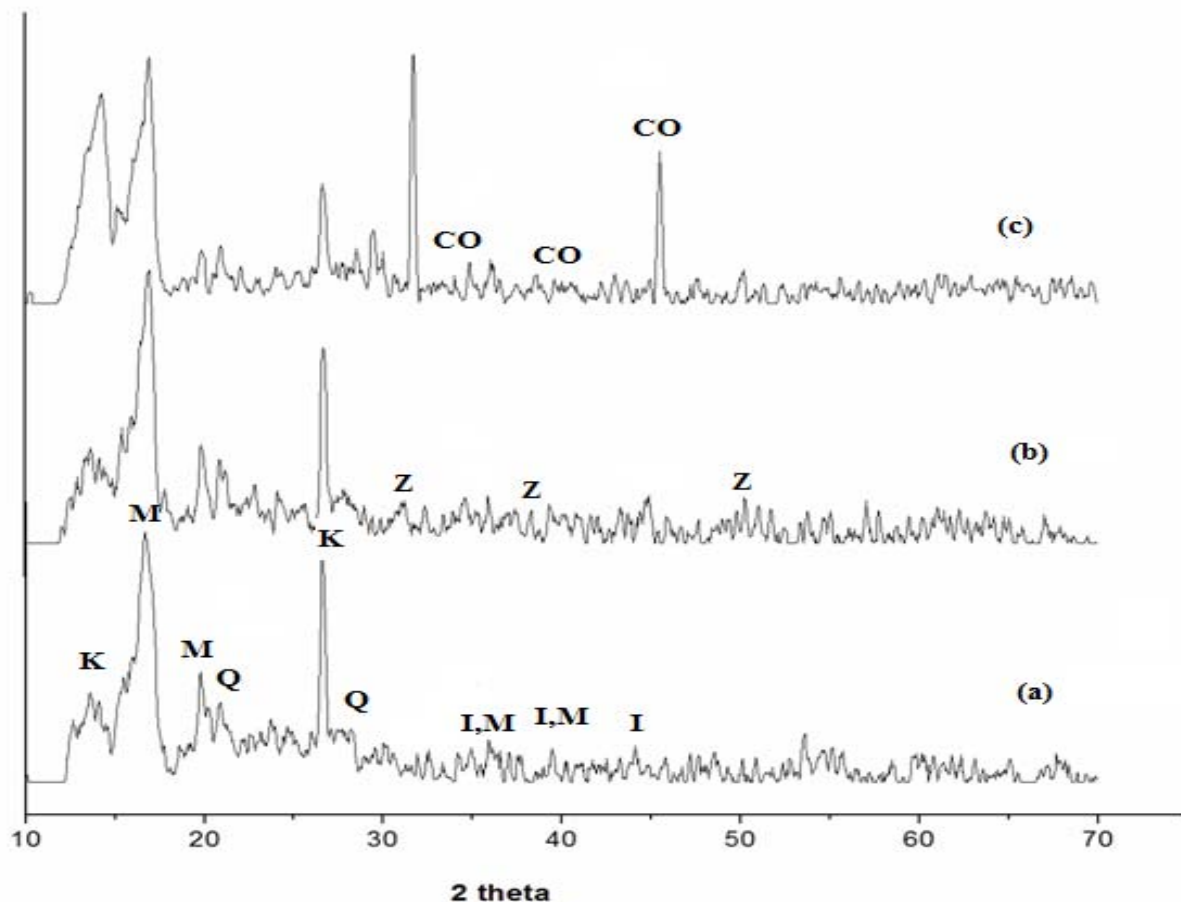


Figure 3.8. XRD patterns of original and metal oxide impregnated BCs
(a) original BC (b) Zn/BC (c) Co/BC

Where, *M*= Montmorillonite, *I*= Illite, *Q* = Quartz, *K*= Kaolinite, *Z*= ZnO and *Co*= Co_2O_3 .

3.2.4. Characterization of original and metal salts impregnated ACs ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}/\text{AC}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}/\text{AC}$, CoCl_2/AC , FeCl_3/AC , and $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}/\text{AC}$).

The morphologies of the original and metals impregnated carbons were investigated by SEM analysis. The corresponding micrographs are provided in Fig. 3.9 (a-c). The micrograph of the original AC is given in Fig. 3.9 (a) which featured several vertical formations stacked together with observable spaces among them. Some uniformly sized pores extended into the matrix can also be observed. In addition, the



surface appeared to be consisted of formations like ridges or channels. The micrographs of Fe/AC and Zn/AC pictured in Fig. 3.9 (b) and Fig. 3.9 (c) indicated porous and layered surface morphologies. However, most of the pores observed to be distributed randomly through the surface. Some of the pores appeared to have been clogged or blocked by the impregnated metal phase. In addition, some formations like channels having large and small diameters randomly distributed in the matrix were observed.

The EDX analysis of original AC is provided in Table 3.11 and Fig 3.10 (a-c). It can be observed that it has 85 % carbon and about 15 % oxygen. In the present study, impregnated ACs i.e. Zn/AC and Fe/AC were found to be more active in the pyrolysis of PP and HDPE, therefore, further EDX analysis was performed only for these two catalysts. The EDX signature of Zn/AC is given in Fig 3 (b) which showed that the concentration of the active metal i.e. Zn was found to be 9.5 wt %. Similarly, the EDX signature of Fe/AC given in Fig 3 (c) showed the concentration of Fe to be 11.1 wt %. The results indicated that the concentrations of these metals were found to be very close to the theoretical value of 10 %.

The properties of the original and impregnated ACs were determined by N₂ adsorption-desorption method using BET and BJH adsorption models. Results are displayed in Table 3.12. The surface area of the original AC was found to be 117.84 m² g⁻¹, whereas the pore size and the pore volume were found to be 35 °A and 0.17 cm³/g, respectively. In case of impregnated ACs, an increase in the surface area can be observed. An appreciable increase in the surface area was observed in case of Fe/AC, followed by Zn/AC, where the surface areas determined were found to be 209.01, and 135.45 m² g⁻¹, respectively. This increase may be attributed to an increase in the interlayer spacing due to interposition of the inorganic elements into the carbon matrix. Likewise, an increase in the pore size of the catalysts was also observed with increase in the surface area in case of these catalysts.

The XRD patterns of the original and variously impregnated ACs are provided in Fig 3.11 (a-d). XRD pattern of original AC given in Fig 3.11 (a) showed the existence of an amorphous carbon along with polycrystalline hexagonal phase by giving peaks at 2θ



of 27 and 45° [17]. On the other hand, the XRD patterns of the metals impregnated ACs (Fig 3.11 (b-d)) showed amorphous structures, which indicated metal phases dispersed on the surface of the matrix [18].

Total acidity analysis is provided in Table-3.13. The results indicated an increase in acidity in case of Fe/AC and Zn/AC while in case of other catalysts, the acidities are almost comparable with the original AC.

Table 3.11. EDX analysis of original activated carbon

Element	weight %
C	81.64
O	18.36
Totals	100



Table 3.12. Surface area, pore size, pore volume and active metals concentration of original and various transition metal salts impregnated ACs

Catalyst	BJH surface area (m² g⁻¹)	Pore size (°A)	Pore volume (cm³ g⁻¹)	Active metals Conc. (wt %)
AC	117.84	35.00	0.17	-
Fe/AC	209.01	120.39	0.60	11.20
Ni/AC	105.61	34.83	0.16	-
Zn/AC	135.75	77.30	0.20	9.50
Mn/AC	122.31	35.08	0.22	-
Co/ AC	87.43	35.14	0.13	-

Table 3.13. Total acidity of the original and variously transition metal salts impregnated ACs

Catalyst	Acidity(mg/g)
AC	3.60
Fe/AC	5.20
Zn/AC	4.50
Ni/AC	3.20
Mn/AC	3.15
Co/AC	2.99

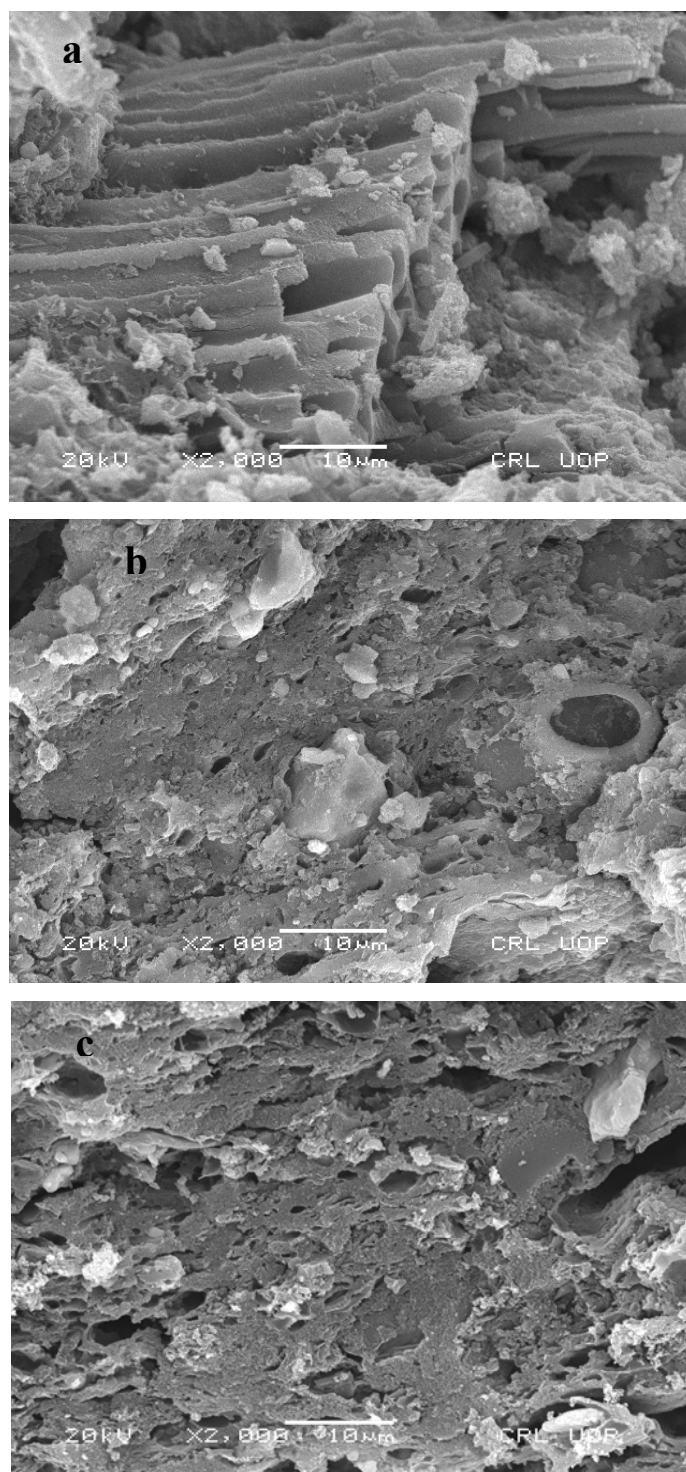
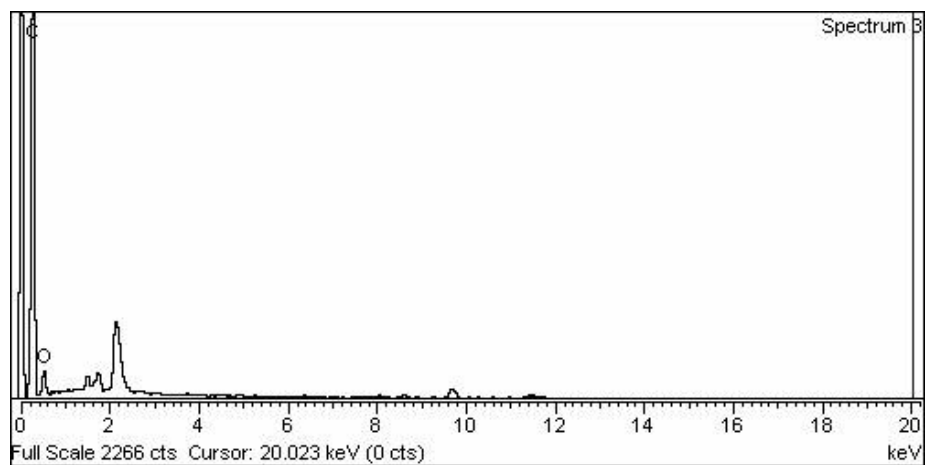
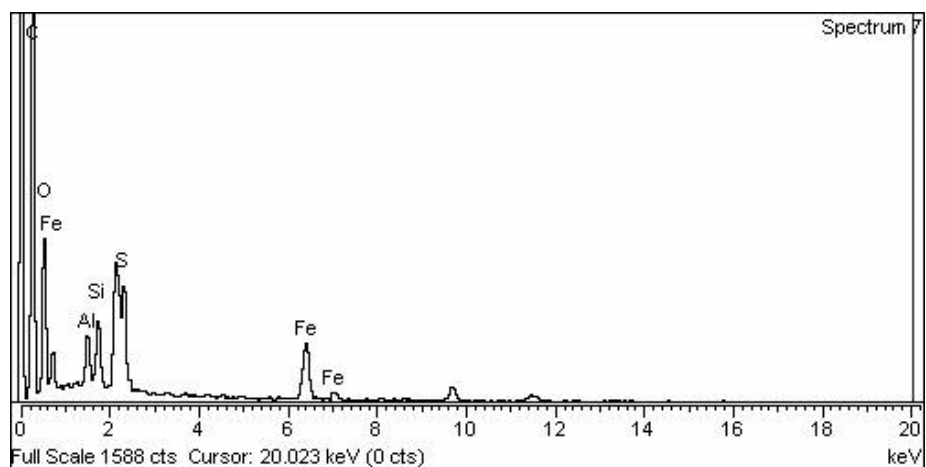


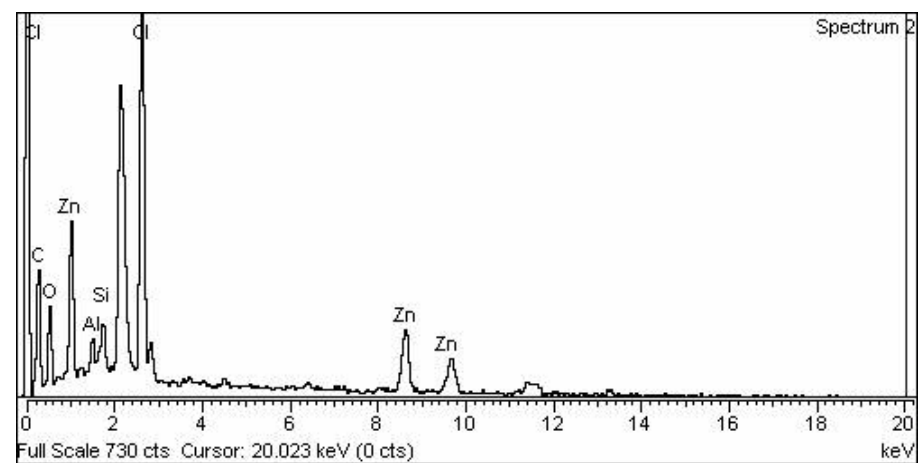
Figure 3.9. SEM micrographs of original and transition metal salts impregnated ACs
(a) original AC (b) Fe/AC and (c) Zn/AC



(a)



(b)



(c)

Figure 3.10. EDX profiles of original and transition metal salts impregnated ACs (a) original AC (b) Fe/AC (c) Zn/AC

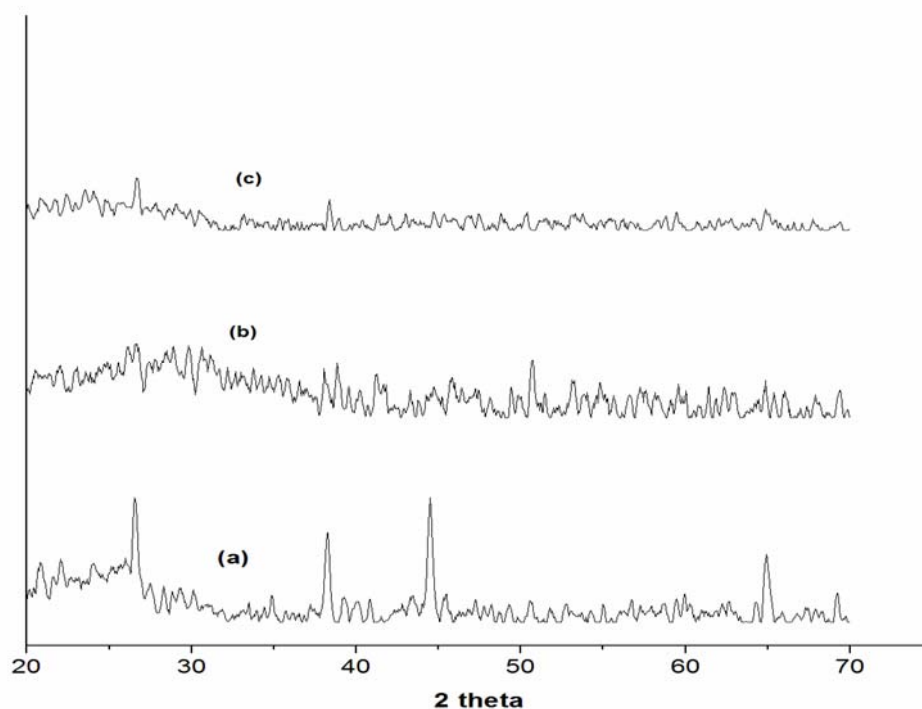


Figure 3.11. XRD patterns of original and transition metal salts impregnated ACs (a) original carbon (b) Fe/AC (c) Zn/AC

3.3. THERMAL PYROLYSIS

Pyrolysis experiments were performed using two model polyolefins; PP and HDPE. The effect of temperature on formation of various cracking products was studied. Pyrolysis was investigated at different temperatures i.e. 250, 300, 350 and 400 °C in non sweeping nitrogen atmosphere. Several verification experiments were performed to verify the optimum temperature.

Temperature and time optimization study

Some preliminary experiments were performed at different temperatures ranging from 250- 400 °C for optimization. Similarly, experiments were carried out at optimum temperature for different time durations ranged from 10 to 60 minutes. The optimum



temperature and time were decided on the basis of highest wt% yield of the liquid products.

The effect of temperature on conversions to liquid products was studied. The results are provided in Table-3.14 (a). The effect on the formation of the liquid products is observable from the results which indicated that the liquid yield increased to a maximum when the temperature was increased from 250 to 300 °C and then began to decrease with the increase in temperature from 300 to 350 °C and 350 to 400 °C. Based on the results, 300 °C was found to be optimum temperature. Temperature was also optimized in case of HDPE. The results are compiled in Table-3.14 (a). A temperature of 350 °C was found to be the optimum temperature.

In order to optimize time, reactions were carried out for time duration range from 10-60 minutes in case of PP as well as HDPE. The results are given in Table 3.14 b. The results indicated an increase in total conversion as well as formation of liquid product with the increase in time from 10 min to 30 minutes. Extension in time beyond 30 min caused similar yields compared to those achieved at 30 minutes; hence 30 min was found to be the optimum time in case of both polyolefins.

The results can be explained on the basis of the given mechanism. It is well established that the pyrolysis reaction takes place through three progressive steps: initiation, propagation and termination. Initiation reaction cracks the large polymer molecules into free radicals. The free radicals and molecular species can be further cracked into smaller radicals and molecules during the propagation reactions. Finally, the radicals generated are unstable and ultimately combined together into stable molecules through termination reactions.

The mechanism of thermal cracking (free radical route, random chain scission) can be depicted as under:

Initiation (thermolysis)



*Propagation*

A radical may disproportionate thereby forming an olefinic hydrocarbon and a small chain free radical depicted as under:



A radical may fragment giving a small chain radical and aliphatic hydrocarbon depicted as under:

*Termination*

Hydrogen abstraction (produced by shuttling) leading to formation of aliphatic hydrocarbons depicted as under:

*Retrogressive Recombination*

If sufficient hydrogen is not available for capping, the free radicals may undergo recombination depicted as under:



At low temperature, the thermal scissions of the bonds are less likely. When the temperature is increased, the bond breaking is more frequent leading to formation of free radicals which upon quenching give rise to the formation of liquid products. However, when the temperature is further increased (beyond the optimum one), the liquid products formed are suffered from thermal cleavages leading to formation of gaseous products.

The effect of time can also be explained on this proposition. Extension in time causing the thermal fragmentation of the liquid products formed which cause a decline in their yields.



In the proceeding section, the effect of temperature on overall yields and yields of liquid, gas and coke is presented in a more detail.

3.3.1. Effect of temperature on overall yields and yields of liquid, gas, and residue/coke

3.3.1.1. Overall yields (combined liquid + gas)

The effect of temperature on overall yields and yields of liquid, gas and coke achieved in case of PP and HDPE was studied. The product yields as a function of temperature obtained in case of PP is provided in Table 3.14 (a). From the data compiled, a marked effect of temperature on the cracking behavior of the PP towards total conversion can be seen. It can be observed that with the increase in temperature, the overall yield was increased from 86.32 % (at 250 °C) to 98.66 % (at 300 °C). This is due to the reason that PP is an easily degradable polyolefin due to its branched structure [19]. Another reason may be the high proportion of tertiary carbons present in the polypropylene chains, which promotes the thermal cleavage of C–C bonds [20] leading to the formation of free radicals.

Further increase in temperature from 300 to 350 °C, and then from 350 to 400 °C caused the total conversion to decrease. This is due to recombination of thermal cracking products via retrogressive reunion of the thermally generated free radicals (secondary reactions) leading to formation of char [21]. The results obtained during current investigation are in consonance with other studies which have also reported similar effect of temperature on the overall yields of degradation products [22, 23].

The influence of temperature on total conversion and conversions to liquid, gas and coke upon pyrolysis of HDPE was also investigated. The results are compiled in Table 3.14 (a). On contrary to PP, the behavior of HDPE was different. At 250 °C, the HDPE was almost intact and no conversion was observed. Further increase caused the total conversion to increase linearly with the increase in temperature and conversion up to 60 wt% was attained when the temperature was increased from 250 to 300 °C. Similarly, conversion as high as 98.34 wt% was achieved at 350 °C. It was observed that the increase in temperature from 250 to 300 °C, and then from 300 to 350 °C caused a



significant increase in total conversion (overall yields) which can be thought to be due to frequent bond scissions in this temperature range.

3.3.1.2. Liquid yields

The effect of temperature on conversions of PP to liquid, gas and residue (PP not volatile at the pyrolysis temperature + coke) was also studied. The effect is observable (Table-3.14 a). It can be seen that the liquid yield increased to a maximum and then began to decrease with further increase in temperature. With the increase in temperature from 250 to 300 °C, the yield of liquid products increased from 57.27 to 69.82 wt%. Upon further increase in temperature from 300 to 350 °C and then from 350 and 400 °C, the yields decreased to 67.74 and 63.23 wt%, respectively. It can be observed that the yield of the liquid products was increased with the increase in temperature from 250-300 °C. Increasing temperature after 300 °C caused the liquid product to decline. This can be attributed to the fact that at low temperature, the degradation reactions are not favored thermodynamically resulting in incomplete conversion, whereas at elevated temperature higher than 300 °C, coke formation dominates leading to low yield of liquid products. Carbonaceous deposits/coke may be formed by recombination of cracking fragments as reported earlier [24].

The HDPE behaved differently in terms of formation of liquid products as a function of temperature (Table 3.14 a). This is due to different skeletal structure of HDPE compared to PP. The difference in skeletal structure can influence the product distribution. HDPE has a high molecular weight, and thereby have a low melt index and high T_m . [25]. Conversion to liquid products was not observed at 250 °C compared to PP. This is attributed due to the reason that HDPE has very little branching along the hydrocarbon chains, hence the crystallinity is 95 wt% or better. As a result, the van der Waal's attractions between the chains are greater and so it has a higher melting point. Its density is also higher because of the better packing and smaller amount of wasted space in the structure [26], hence requires more severe conditions to crack. As reported earlier, polymers with high crystallinity are less vulnerable to thermo-degradation than low crystalline polymers [27]. When the temperature was increased from 250 to 300 °C and



then 300 to 350 °C, the yields of liquid products attained levels of about 30, and 80 wt%, respectively which can be corresponded to more frequent bond scissions in the feed polymer.

3.3.1.3. Gas yields

The effect of temperature on the formation of gaseous products in case of PP is also evident from the data compiled in Table 3.14 (a). It can be seen that increase in temperature has not affected the formation of gaseous products to a greater extent. The yields of gaseous products were in the range of 29-31 wt% which indicated a very slight increase in the yield with the increase in temperature from 250 to 400 °C. At 250 and 300 °C, the yields of gaseous products achieved were 29.05 and 28.84 wt%, respectively and at 350 and 400 °C, an increase in yields up to 30 and 31.07 wt% was achieved.

In case of HDPE, the yield pattern of the gas yield with the change in temperature is different compared to the liquid products (Table 3.14 a). At temperature of 250 °C, no cracking was observed. However, with the increase in temperature, the yield of gaseous products increased. At 300 °C, the yield of gas was 30.17 wt%. Upon further increase in temperature from 300- 350 °C, the gas yields increased to around 38 wt%.

3.3.1.4. Residue yields

The influence of temperature on the formation of residue/char was also investigated. It is evident from the data that the yield of solid residue/coke in case of PP changed inversely with increase in temperature from 250-300°C and linearly with the increase from 300-400 °C. The residue/coke decreased when the temperature was increased from 250-300 °C; but increased upon further increase in temperature from 300-400 °C. The yield of solid residue was highest at temperature of 250 °C (13.68 wt %), which decreased to 1.34 wt% with the increase in temperature to 300 °C. The yield of solid residue remained unaffected till 350 °C, however, it increased again to about 5.7 wt% at 400 °C. This is due to the reason that at elevated temperatures, the liquid products formed, subsequently undergo further cracking to form gas (rare) and coke (dominant). Residue/coke yield as high as 13 wt% at 250 °C, is indicative of secondary reactions mostly recombination or condensation reactions. Another reason can be thought



is the interaction of the escaping nascent, hot pyrolysis vapors with the surrounding decomposing solid. These interactions involve exothermic reactions, which lead to the formation of char [28].

The temperature effect on the formation of solid residue in case of HDPE was also investigated. The yield of solid residue was as high as 100 % at 250 °C, which decreased with the increase in pyrolysis temperature. At 300 °C, the residue reduced to around 39 wt%, and further to < 1wt% at 350 °C. The results indicated that the cracking reactions were enroute till 350 °C and after 350 °C, the recombination reactions dominated which led to the formation of coke/char.

After examining the effect of temperature on total conversion and conversions to liquid products, gas and residue, it is concluded that both polymers showed high conversions. This behavior is explained considering the presence of tertiary carbons in the structure of the plastics under study that provide favorable positions for the initiation of the polymer chain cracking [20]. However, both polymers behaved differently in terms of conversions to liquid, gas and residue and gave reasonably high yields under less severe conditions compared to previously reported cracking experiments carried out under continuous or semi-continuous conditions. In case of PP, the optimum temperature for formation of maximum desirable liquid products was found to be 300 °C among the investigated temperature range of 250 -400°C, while in case of HDPE, it was found to be 350 °C. Furthermore, PP gave maximum liquid yield of around ~70 wt% (at 300 °C) which was around ~80 wt% (350 °C) in case of HDPE. As far as the gaseous products are concerned, PP gave around 31 wt% (at 400 °C) while HDPE gave around 45 wt% (at 400 °C). Thus, it is concluded that PP is more susceptible to cracking in terms of giving more liquid products at optimum temperature compared to HDPE which is more susceptible to cracking in terms of gaseous products.



Table 3.14 a . Yields of pyrolysates (over all yields and yields of liquid, gas and coke) derived from thermal pyrolysis of PP and HDPE as a function of temperature.

Polyolefin	Temperature (°C)	Total yield (wt %)	Conversions to liquid, gas, and residue (wt %)		
			Liquid	Gas	Solid residue
Polypropylene	250	86.32	57.27	29.05	13.68
	300	98.66	69.82	28.84	1.34
	350	97.74	67.74	30.00	1.56
	400	94.30	63.23	31.07	5.70
Polyethylene	250	ND	ND	ND	ND
	300	66.95	30.70	36.25	33.05
	350	98.12	80.88	17.24	1.88
	400	99.46	54.17	45.29	0.54

ND: Not Determined

Table 3.14 b . Yields of pyrolysates (over all yields and yields of liquid, gas and coke) derived from thermal pyrolysis of PP and HDPE as a function of time.

Polyolefin	Temperature (°C)	Total yield (wt%)	Conversions to liquid, gas, and residue (wt %)		
			Liquid	Gas	Solid residue
Polypropylene	10	67.30	45.36	21.94	32.70
	20	87.35	62.71	24.64	12.65
	30	98.66	69.82	28.84	1.34
	40	98.67	69.81	28.86	1.33
	50	98.73	69.91	28.92	1.27
	60	98.79	69.78	29.01	1.21
Polyethylene	10	64.39	47.69	16.70	35.61
	20	85.44	68.52	16.92	14.56
	30	98.12	80.88	17.24	1.88
	40	98.18	78.37	19.81	1.82
	50	98.50	75.13	23.37	1.50
	60	99.13	71.46	27.67	0.87

Temperature: 300 °C in case of PP and 350 °C in case of HDPE



3.3.2. Analyses of Liquid Products

The liquid products derived from PP and HDPE at optimum temperatures were characterized by FT-IR and GC-MS analysis.

3.3.2.1. FT-IR analysis

FT-IR analysis of the pyrolysis oils derived from PP and HDPE in thermal as well as catalytic runs was carried out in order to know about the nature of the hydrocarbons produced in terms of various functional groups. The FT-IR spectra of liquid products derived from PP and HDPE under optimum conditions is provided in Fig 3.12 (a-b) and the corresponding peak data is given in Table 3.15. The results showed similar chemical nature of the derived liquids.

The FT-IR spectrum of pyrolysate derived from PP by thermal pyrolysis is provided in Fig 3.12 (a) which exhibits strong absorption peaks around 2953 and 2868 cm^{-1} . These peaks can be corresponded to aliphatic C-H stretching vibrations of methyl (CH_3) and methylene (CH_2) [29]. A weak absorption peak appearing at 1620 cm^{-1} indicate the presence of olefinic $\text{C}=\text{C}$, and a strong absorption peak appearing at 1456 cm^{-1} can be corresponded to $\text{C}=\text{C}$ stretching in alkenes [30]. A medium intensity weak absorption peak at the wave number range of 1377 cm^{-1} indicating C-H scissoring and bending vibrations of alkanes [31]. The results indicated that the liquid fraction was mainly consisted of aliphatic and olefinic hydrocarbons.

The FT-IR spectrum of the pyrolytic liquid derived from thermal pyrolysis of HDPE is provided in Fig.3.12 (b). The spectrum shows strong absorption peaks mostly positioned at 2920 and 2852 cm^{-1} . These peaks can be corresponded to asymmetric stretching of C-H of CH_3 and CH_2 , respectively. A weak intensity absorption peak appearing at 1525 cm^{-1} indicated $\text{C}=\text{C}$ of olefins, and a medium peaks centered at 1456 cm^{-1} showing $\text{C}=\text{C}$ stretching of olefins. The results indicated that the liquid fraction mostly contained paraffinic and olefinic hydrocarbons, whereas no aromatics and oxygenates were found.



3.3.2.2. GC-MS analysis

Individual component analysis

The individual component analysis of raw/crude liquid pyrolysates derived from PP (obtained under optimum temperature in case of thermal runs) was performed. The GC-MS spectrum is provided in Fig 3.13. Different hydrocarbons identified in thermally derived liquid fractions are listed in Table 3.16 (PP) along with their retention times, peak areas and % concentration. The data was used to deduce the % distribution of different carbon range hydrocarbons and hydrocarbon types in each of the pyrolysate. Furthermore, the GC-MS data indicated the specific types of hydrocarbons molecules formed during the thermal runs carried out at optimized temperatures. The results showed that most of the product molecules were similar during thermal cracking, but the difference observed only in their relative distribution.

It can be seen that the liquid derived from PP contained naphthenes, olefins and paraffins with preponderance of paraffins. Among the naphthenes, the individual molecules identified in high concentration were; 2, 4-diethyl-1-methyl cyclohexane, 1-isopropyl-1, 4, 5-trimethylcyclohexane, 1-heptyl-2-methyl cyclopropane, and 1, 3-dimethylcyclopentane.

Among the olefins, 1-octene, 4-methyl 2-decene, 5-octadecene, (E), 8-methyl 1-undecene, 1-hexadecene, 1, dodecene, 3-hexadecene, 2-methyl-2-docosene, 1-pentadecene, 1-tetradecene, 5-tetradecene, hexadecene, and heptadecene were the most abundant compounds.

Among the paraffins, hexadecane, tetradecane, pentadecane, heptane, octane, tetratetracontane, 2, 6, 11-trimethyl dodecane, undecane, dodecane, 4,6-dimethyl dodecane, tetradecane, 2,3,5,8-tetramethyl decane, nonadecane, heneicosane, heptadecane, pentatriacontane, docosane, octadecane, tetratriacontane, and octacosane were found in high concentrations.

The GC-MS spectrum of liquid pyrolysate derived from HDPE at optimum temperature is provided in Fig. 3.14. The individual component molecules identified in the liquid fraction derived from HDPE in thermal run (optimum temperature) by GC-MS



are presented in Table 3.17. Among the naphthenes, I, 1-bicyclohexyl-2-(1-methylethyl)-trans, 1-isopropyl-1, 4, 5-trimethylcyclohexane, and 1, 3, 5-trimethyl cyclohexane, eicosyl cyclohexane were identified in high concentration. Among the olefins; 4, 5-dimethyl -2-Undecene, 4,5-dimethyl -2-Undecene, 3-eicosene (E), 19-eicosadiene, 7-tetradecene (E), 2-ethyl-2-docosene, 1-tricosene, 5-eicosene(E), 1- hexadecene, 4-tetradecene, 2, 3, 4-trimethyl-1-tricosene, 2, 3,4-trimethyl -6- tetradecene and 1-heptadecene were observed in high concentration. Among paraffins, 2-Isopropyl-5-ethyl-I-octane, octacosane, 2, 6, 10-trimethyl hexadecane, heptadecane, 2-methyl-I-dodecane, 2-heptyl-I-decane, 2-hexyl-I-octane, 2, 6, 10-trimethyl-hexadecane, nonadecane, heneicosane, tetratetracontane, and hexatriacontane were found in high concentration.

It is evident from the results that the thermally derived liquids in case of both PP and HDPE were enriched in paraffins followed by olefins followed by naphthenes. No oxygenates and aromatics were observed in case of both polyolefins.

C-number distribution

The distribution of hydrocarbons with different carbon chain length in the PP and HDPE derived liquid products was investigated by GC-MS. Results compiled in Table 3.18 showed that in PP derived liquid product, the distributions of different hydrocarbons range products, i.e. C₆-C₁₂, C₁₃-C₁₆, C₁₇-C₂₀, C₂₁ to C₃₀ and above C₃₀ were found to be 15.16, 33.04, 12.99, 24.97 and 8.05 %, respectively. Results showed that the liquid products were enriched in C₁₃ to C₁₆ (33.04 %), and C₁₇-C₂₀ (24.97%), which indicated that the liquid product is enriched in diesel range hydrocarbons. Further, about 50 wt% of the liquid product has composition very similar to light naphtha range hydrocarbons (C₆-C₁₆).

Similarly, in case of HDPE derived liquid product, the product distributions in C₆-C₁₂, C₁₃-C₁₆, C₁₇-C₂₀, C₂₁-C₃₀ and > C₃₀ range hydrocarbons were found to be 32.56, 30.80, 14.19, 12.35 and 10.95 %, respectively which indicated that the liquid product is enriched in low boiling naphtha range hydrocarbons i.e. C₆ -C₁₆ (32.56 %) and C₁₃-C₁₆ (30.8 %). About 63% hydrocarbons were in the gasoline and diesel range, whereas C₁₇ - C₃₀ constituted about 34 %.



Hydrocarbon group types distribution

The relative proportion of olefins, cycloalkanes, aliphatic and aromatic components in the PP and HDPE derived liquid products is provided in Table 3.19. The data showed that in case of PP derived liquid product, the proportions of different types of hydrocarbons i.e. olefins, naphthenes and paraffins were 25, 7 and 66 %, respectively, whereas in case of HDPE derived liquid product, the % distributions of olefinic, naphthenic and paraffinic components were found to be 31, 8 and 59 %, respectively. Upon comparing the hydrocarbon group types yields, both PP and HDPE gave high yields of paraffinic followed by olefins followed by naphthenes. As combustion of paraffinic hydrocarbon give more energy compared to aromatic or naphthenic hydrocarbons, hence the PP derived liquid fraction is suggested to be more value added compared to HDPE.

It is concluded from the above study that thermal cracking of PP and HDPE was very effective. Total conversion as high as 98.66 wt% (liquid; 69.82%, gas; 28.84%, and residue; 1.34 %) was achieved at 300 °C in case of PP and as high as 98.12 % (liquid; 80.88 %, gas; 17.24 %, and residue; 1.88 %) in case of HDPE at 350 °C. The optimum temperatures were decided to be 300, and 350 °C in case of PP and HDPE, respectively. FTIR and GC-MS results showed that the liquid product was mostly consisted of a wide spectrum of hydrocarbons mainly distributed within the C₆–C₁₆ carbon number range products. The liquid fraction derived from PP was enriched in the naphtha range hydrocarbons with preponderance in diesel range hydrocarbons (C₆–C₁₆; ~50%, C₁₃–C₁₆; 33.04 %). Similarly, the liquid product obtained in case of HDPE was also enriched in naphtha range hydrocarbons with preponderance of both gasoline and diesel range hydrocarbons (C₆ to C₁₆; ~63%), C₆–C₁₂; 32.56% and C₁₃–C₁₆; 30.8 %). The % distributions of paraffinic, olefinic, and naphthenic hydrocarbons in liquid product derived from PP were found to be 66.55, 25.7, and 7.58 %, respectively, whereas in case of liquid product derived from HDPE, their % distributions were 59.70, 31.90, and 8.40 %, respectively. Upon comparing the hydrocarbon group types yields, both PP and HDPE gave high yield of paraffinic hydrocarbons followed by olefins followed by naphthenes.

Table 3.15. Major absorption peaks observed and assigned configurations in the FT-IR spectra of the liquid products derived from thermal pyrolysis of PP and HDPE

Sample	Position (cm ⁻¹)	Intensity	Assigned configuration
Liquid pyrolysate (PP)	2953	strong	CH ₃ (aliphatic)
	2868	strong	CH ₂ (aliphatic)
	1620	weak	C=C (olefinic)
	1456	strong	CH ₂ bending
	1375	medium	C-H scissoring/bending
	887	strong	C-H (olefinic)
Liquid pyrolysate (HDPE)	2920	strong	CH ₃ (aliphatic)
	2852	strong	CH ₂ (aliphatic)
	1525	weak	C=C (olefinic)
	1456	medium	CH ₂ bending
	908	strong	C-H (olefinic)

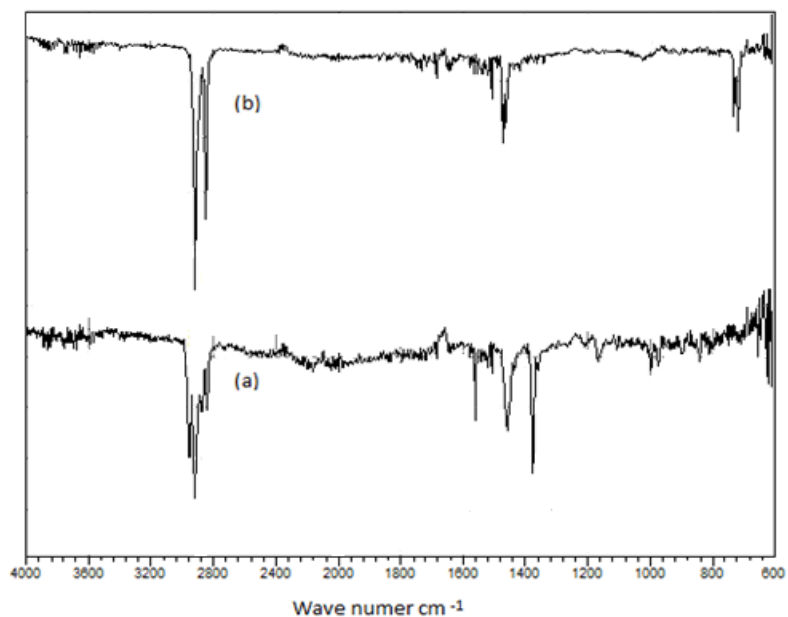


Figure 3.12. FT-IR spectra of liquid products derived from thermal pyrolysis of polyolefins (a) PP and (b) HDPE

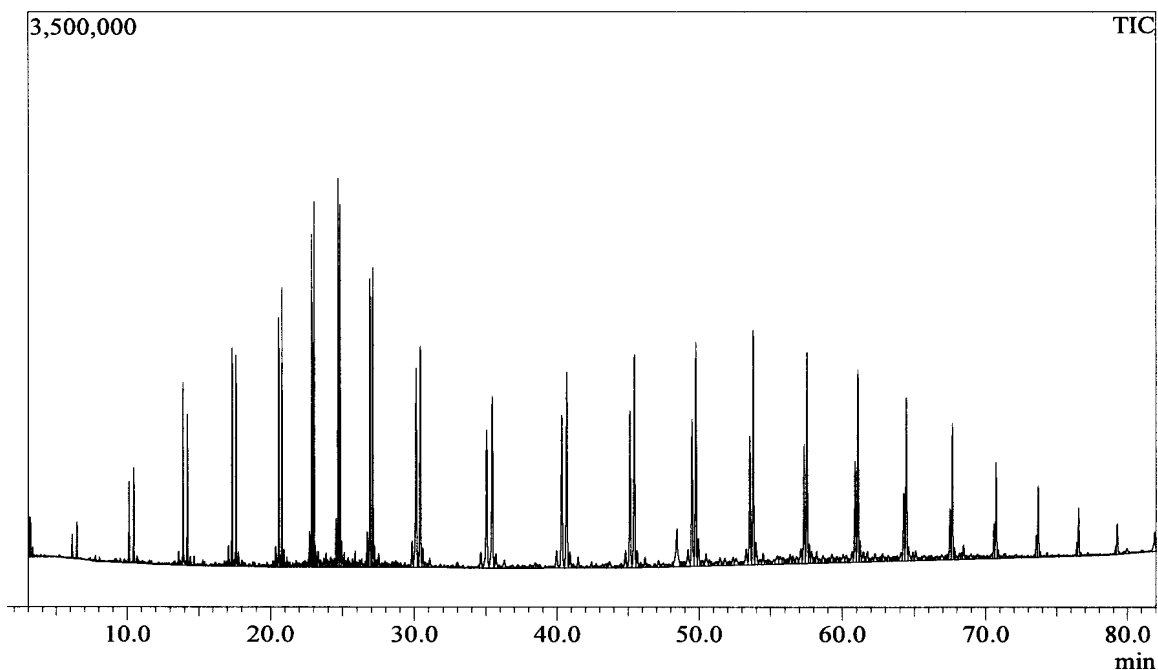


Figure 3.13. GC-MS spectrum of liquid product derived from PP by thermal pyrolysis

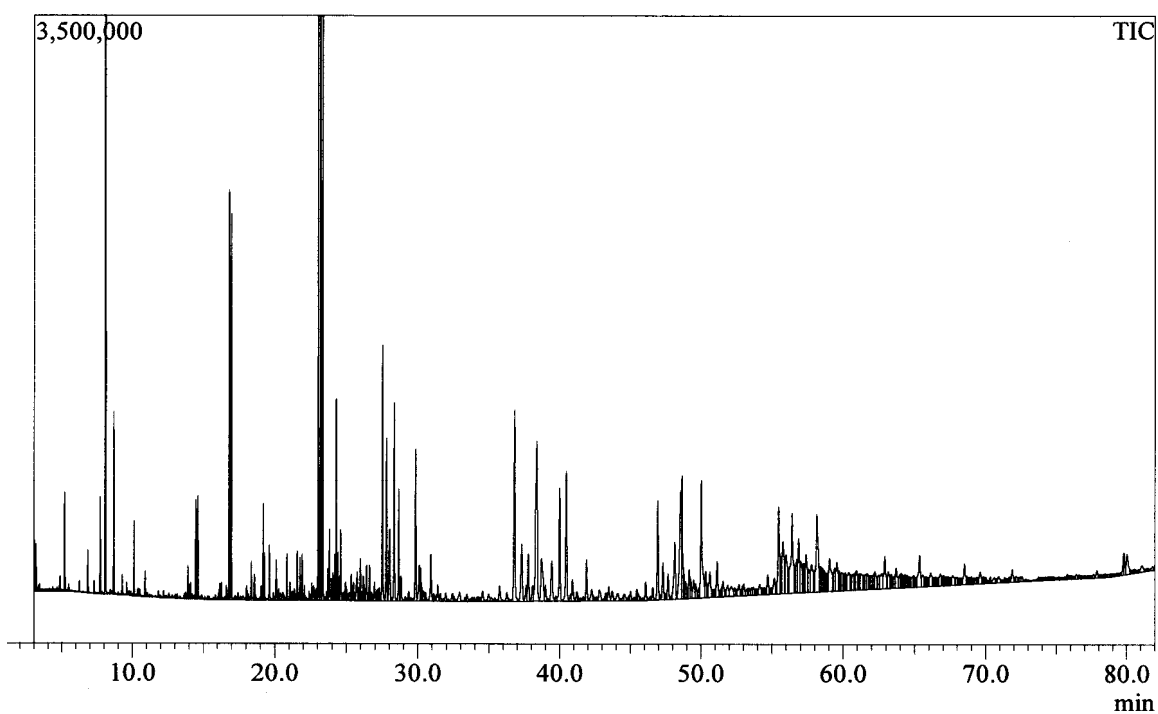


Figure 3.14. GC-MS spectrum of the liquid product derived from HDPE by thermal pyrolysis

**Table 3.16.** Hydrocarbons identified in the liquid product derived from thermal pyrolysis of PP

ID#	Compound	t _R	% peak area/ Relative conc.
Naphthenes			
1	1,3-Dimethylcyclopentane	3.041	1.32
2	Cyclopentane, 1,2-dimethyl (cis)	3.091	0.15
3	Cyclopentane, 1,2-dimethyl (trans)	3.142	0.32
4	Cyclohexane, methyl -	3.876	0.16
5	Cyclopropane, 1-heptyl-2-methyl -	13.907	1.39
6	1- Isopropyl-1,4,5-trimethylcyclohexane	16.44	1.61
7	Cyclohexane, 2,4-diethyl-1-methyl -	19.918	2.03
8	1,1 -Bicyclohexyl, 2-(1-methylethyl) -	23.843	0.14
9	Cyclohexane, 1-pentanedimethyl -	23.843	0.46
Total yield			7.58
Olefins			
1	1-octene	6.114	3.21
2	2-Decene, 4-methyl -	14.033	2.48
3	2-Undecene, 4,5-dimethyl -	17.341	0.03
4	1-Undecene, 8-methyl -	18.034	1.64
5	1- Dodecene	20.58	1.45
6	5-Tetradecene. (E)	20.929	0.43
7	2-Heptene, 5-ethyl-2,4-dimethyl -	22.378	0.64
8	1- Tridecene	22.862	0.05
9	5-Eicosene, (E)	24.019	0.43
10	3-Hexadecene, (Z)	24.683	0.31
11	2- Methyl-2-docosene	25.467	1.02
12	1,9- Tetradecadiene	26.704	0.02
13	1- Pentadecene, (E)	26.899	0.28
14	1- Pentadecene, (Z)	30.115	0.69
15	1- Tetradecene	35.033	1.27
16	5-Eicosene, (E)	39.952	1.38
17	1- Hexadecene	40.325	1.55
18	5-octadecene, (E)	41.477	1.69
19	1,15- Hexadecadiene	44.798	1.47
20	1-Heptadecene	45.117	0.26
21	1- Tricosene, (E)	45.623	1.21
22	1- Tricosene, (Z)	49.496	0.13



23	1- Heptadecene	53.535	1.16
24	Z-5-Nonadecene	64.268	1.46
25	4- Tetradecene, 2,3,4-trimethyl -	65.362	0.64
26	9-Hexacosene	67.496	0.24
27	9- Tricosene, (Z)	73.553	0.73
Total yield			25.87
Paraffins			
1	Heptane	3.302	4.11
2	Octane	6.448	3.71
3	Nonane	10.453	2.47
4	Undecane	17.612	3.23
5	Dodecane	20.799	2.64
6	Dodecane, 4,6-dimethyl -	22.162	2.61
7	Decane, 2,3,5,8-tetramethyl-	22.162	3.21
8	Pentadecane	24.83	4.73
9	Dodecane, 4,6-dimethyl, trans	26.022	2.61
10	Tetradecane	27.097	4.89
11	Dodecane, 2,6,11-trimethyl -	30.409	3.45
12	Hexadecane	35.433	5.16
13	Nonadecane	40.678	2.18
14	Heneicosane	45.431	1.43
15	Heptadecane	49.768	1.04
16	Hexadecane, 2,6,10, 14-tetramethyl -	53.784	2.23
17	Docosane	57.544	1.24
18	Oetadecane	61.086	2.29
19	Tetratetracontane	64.448	3.58
20	Tetratriacontane	67.658	2.84
21	Oetacosane	70.727	1.04
22	Pentadecane, 8-hexyl -	73.682	0.43
23	Hexatriacontane	76.528	2.56
24	Triacontane	79.274	2.87
Total yield			66.55

**Table 3.17.** Hydrocarbons identified in the liquid product derived from thermal pyrolysis of HDPE

ID#	Compound	t _R	% peak area/ Relative conc.
Naphthenes			
1	1, 3-Dimethylcyclopentane	3.057	0.38
2	Cyclopentane, 1,2-dimethyl- (cis)	3.107	0.21
3	Cyclopentane 1,2-dimethyl (trans)	3.158	0.34
4	Cyclohexane, methyl -	3.895	0.01
5	Cyclopentane, 1, 1 ,3,4-tetramethyl-, cis	6.853	0.26
6	Cyclohexane, 1,3,5-trimethyl -	7.726	1.27
7	Cyclohexane, eicosyl -	16.274	1.26
8	1- Isopropyl- 1,4,5-trimethylcyclohexane	16.625	1.32
9	Cyclohexane, 2,4-diethyl-1-methyl -	19.628	0.26
10	Cyclohexane, 1 2-diethyl-3-methyl -	20.11	0.23
11	1, 1-Bicyclohexyl, 2-(1-methylethyl), cis	23.703	0.23
12	Cyclohexane, 1-(1, 5-pentanedimethyl) -	24.127	0.18
13	1, 1-Bicyclohexyl, 2-(1-methylethyl), trans	29.841	2.18
14	Cyclopentane, 1, 2-dibutyl -	40.902	0.27
Total yield			8.40
Olefins			
1	2,4-Dimethyl-1-heptene	8.105	1.33
2	1- Nonene	10.12	1.06
3	1 6-Octadiene 2,6-dimethyl (Z)	10.909	0.29
4	2-Decene, 4-methyl (Z)	14.099	0.19
5	2-Decene, 2, 4-dimethyl -	16.162	0.30
6	1-Undecene 7-methyl-	16.83	0.32
7	2-Undecene 4, 5-dimethyl -	16.971	3.23
8	1-Undecene,8-methyl	18.368	0.34
9	2-Undecene, 8-methyl- (Z)	18.587	0.23
10	3-Undecene 8-methyl	19.064	0.11
11	1,7-Nonadiene, 4, 8-dimethyl -	19.288	0.59
12	1-Dodecene	20.646	0.02
13	2-Undecene, 4,5-dimethyl -	21.064	2.18
14	2-Heptene, 5-ethyl-2,4-dimethyl -	22.399	0.12
15	9-Eicosene (E)	24.051	1.12
16	5-Eicosene (E)	23.959	0.14
17	3-Eicosene (E)	24.204	1.23
18	1, 19-Eicosadiene	24.279	1.36



19	7- Tetradecene, (E)	24.933	2.67
20	2-ethyl-2-docosene	25.498	1.74
21	1- Tricosene	28.666	2.53
22	5-Eicosene (E)	39.999	2.62
23	1- Hexadecene	40.466	1.13
24	4- Tetradecene, 2, 3,4-trimethyl -	41.901	1.45
25	1- Tricosene	46.082	2.57
26	6- Tetradecene, 2, 3,4-trimethyl -	51.145	1.61
27	1- Heptadecene	53.558	1.41
Total yield			31.89
Paraffins			
1	Heptane	3.32	1.25
2	Heptane, 4-methyl -	5.196	1.19
3	Octane	6.477	0.55
4	Heptane, 2,4-dimethyl -	7.3	0.24
5	Nonane, 2,6-dimethyl -	14.464	1.29
6	Decane 4-methyl -	14.612	1.31
7	Dodecane	20.651	0.36
8	Dodecane, 4, 6-dimethyl -	21.763	2.42
9	Decane, 2,3,5,8-tetramethyl -	21.916	1.32
10	2-Isopropyl-5-ethyl octane	23.03	5.44
11	Dodecane, 2-methyl-	23.191	2.44
12	Dodecane 2, 4, 6-triethyl -	23.348	1.36
13	Pentadecane	24.835	0.44
14	Dodecane, 3, 6-dimethyl -	25.983	1.37
15	Decane, 3, 3,6-trimethyl -	26.175	1.78
16	Dodecane, 4, 6-dimethyl -	26.409	1.45
17	Tetradecane	27.12	1.47
18	Decane, 2-heptyl -	27.52	2.46
19	2-Hexyl octane	27.802	2.73
20	Dodecane, 2, 6, 11-trimethyl -	30.438	1.49
21	Hexadecane, 2,6, 10-trimethyl -	35.734	3.21
22	Nonadecane	40.773	1.38
23	Heneicosane	45.45	3.62
24	Octane, 2-butyl-	47.325	0.52
25	Heptane, 2, 4-diethyl -	48.158	0.57
26	Heptadecane	49.881	2.25
27	Hexadecane, 2,6, 10, 14-tetramethyl -	54.002	1.52
28	Pentatriacontane	55.469	1.17



29	Docosane	57.586	1.43
30	Octadecane	61.115	1.34
31	Tetratetracontane	64.308	2.32
32	Tetratriacontane	67.671	0.43
33	Octacosane	70.582	3.44
34	Hexatriacontane	76.528	2.63
35	Triacontane	79.274	1.51
Total Yield			59.70

Table 3.18. Carbon range distributions in liquid products derived from thermal pyrolysis of PP and HDPE

Polyolefin	Distribution (wt%)				
	C₆-C₁₂	C₁₃-C₁₆	C₁₇-C₂₀	C₂₁-C₃₀	>C₃₀
PP	15.16	33.04	12.99	24.97	8.05
HDPE	32.56	30.80	14.19	12.35	10.95

Table 3.19. Hydrocarbon group types distributions in liquid products derived from thermal pyrolysis of PP and HDPE

Polyolefin	Distribution (wt%)			
	Paraffins	Olefins	Naphthenes	Aromatics
PP	66.55	25.87	7.58	00.00
HDPE	59.70	31.90	8.40	00.00



3.4. CATALYTIC PYROLYSIS OVER GROUP-A (ORIGINAL AND METAL DOPED BARIUM TITANATES)

3.4.1. Catalytic Pyrolysis of PP

The efficacy of original, as well as Pb, Co and Pb & Co co-doped barium titanates in pyrolysis of polypropylene PP into useful products is reported in this section. The effect of each catalyst and its concentration on over all yields (combined liquid + gas) and yields of liquid, gas and residue was studied.

The use of heterogeneous catalysts in unsupported and supported forms has been reported in the literature [32-36]. However, most of the previous work is devoted to the use of catalysts to get high product yields and the results of such studies are promising. However, due to bulky nature of the polymeric molecules, the efficiency of each catalyst has not been established yet. This is due to several reasons including catalyst deactivation by sintering, coke deposition, and loss in surface due to mechanical stresses during pyrolysis [37-39]. In order to maintain the activity throughout the reaction, properties of the catalysts in use need to be tailored further with emphasis on their textural, surface and chemical properties or new & novel catalysts possessing such properties need to be explored.

Nano structure materials have been extensively investigated in recent years as catalysts in a variety of applications [40-42], due to their excellent surface properties, thermal stability and resistant to deactivation by coke deposition. Among these, barium titanates have been proved to be effective catalysts or catalyst carriers [43, 44]. Lead and cobalt have been used in cracking of petroleum and petroleum based oils [45, 46].

The present work aimed at catalytically converting PP in a fixed-bed reactor over original and Pb, Co, and Pb-Co co- doped barium titanates into useful products with emphasis on high conversion to liquid products that could be used as fuel or feed-stock in chemical industries.



3.4.1.1. Activity tests

The pyrolysis of PP was investigated in the absence and presence of original and various metal doped barium titanates. Each catalyst was used in different concentrations. The effect of catalyst type and concentration on over all yields and yields of liquid, gas and solid coke was studied. The results are displayed in Table 3.20.

3.4.1.1.1. Over all yields (combined liquid + gas)

The effect of individual catalyst and its concentration on over all yields was studied. The results are compiled in Table 3.20 and compared with the yield achieved in case of un-catalyzed run. It can be seen that none of the catalysts altered the overall yields, however, an increase of 0.46 wt % was observed (from 98.66 to 99.12 wt %) in case of run catalyzed with Pb/BaTiO₃ when used in 1 wt % concentration. In rest of the runs, the overall yields were decreased.

3.4.1.1.2. Liquid yields

The effect of individual catalyst and its concentration on liquid yields was also studied. The results obtained are displayed in Table 3.20. A better catalytic activity towards formation of liquid products can be observed when some of these catalysts were used in low concentration compared to thermal run. Among these, Pb/ BaTiO₃ caused the yield to increase, and exhibited high activity by giving highest liquid yield of 92 wt %. A noticeable increase in liquid yields can also be observed in case of runs catalyzed by Co/BaTiO₃ (1%) and Pb-Co/BaTiO₃ (1%) which gave 83 and 84 wt % yields, respectively. Compared with the thermal run, both catalysts exhibited high activities next to Pb/ BaTiO₃.

The high yields achieved in case of Pb/ BaTiO₃ can be attributed to its surface properties i.e. high surface area and topology (micro pores). High surface area and large pore volume have been reported to be responsible for high conversion of bulky polyolefins molecules [47]. Moreover, PP has many tertiary carbons in the chain, and its cracking does not require strong acidities [48]. The acidity of metal ions relates with ionic size, the higher the ionic size, the poorer is acidity. As the ionic size of Pb ion is large



(covalent radii, 1.54Å and ionic radii 1.20Å) [49], hence it has poor acidity. In current study, doping BaTiO₃ with Pb might have caused a small change in its acidity.

On contrary, some of the catalysts including un-doped BaTiO₃ showed poor activity and gave the lowest yield of ~64 wt % which is even less than the one achieved in case of thermal run. The lowest yield can be attributed to the topology of the catalyst i.e. surface area and pore volume which might have offered internal diffusion hindrances to the bulky polymer molecules and have reduced the access of the polymer molecules to the active sites present within the pores.

3.4.1.1.3. Gas yields

The influence of catalysts under study was also studied in terms of the formation of gaseous products. It can be observed from the data compiled in Table 3.20 that both catalyst type and concentration greatly affected the gas yields. The highest gas yield of 49.28 wt % was achieved in case of run catalyzed with un-doped BaTiO₃ (5 wt %) and the lowest yield of 6.21 wt % in case of Pb/doped BaTiO₃ (1 wt%) catalyzed run. The results indicated that un-doped BaTiO₃ (5 wt %) favored the formation of gases. This increase corresponded to a decrease in liquid yield which can be attributed to high acidity of the catalyst required for over cracking reactions thereby leading to the formation of small molecules that were collected mainly as gas [50]. Moreover, as earlier reported, there is a relationship between gas production and the strength of the catalyst acid sites [50]. Though, BaTiO₃ has been reported to have extremely low Lewis acidity [51], but in comparison to the variously doped titanates, it still retained acidic sites.

3.4.1.1.4. Coke yields

As earlier reported, coke may be generated during cracking due to retrogressive reunion of the thermally fragmented free radicals. Moreover, it may be contributed by un-volatilized PP or PP remnants together with the residual catalyst [52]. The effect of individual catalyst and concentration on the formation of coke/residue was also studied. The data is provided in Table 3.20. It can be observed that the residue obtained in case of thermal run was quite low and found to be 1.88 wt % compared to most of the catalyzed runs. The results showed that the yields of solid residue obtained in case of different catalyzed runs were in the range of 0.8 to 12.76 wt %. The highest yield of 12.76 wt%



was achieved in case of Pb-Co/ BaTiO₃ catalyzed run. This can be corresponded to the decrease in gas yields (8.13 wt %). The reason can be thought is the secondary reactions (retrogressive) undergone in gas molecules. Such reactions are leading to carbon deposition at the surface of the catalysts and render it inactive. The coke formed covers the surface and makes it inaccessible for the reactants. This surface coverage by the coke might have influenced the desirable reactions by favoring retrogressive/de-propagation reactions thereby causing the coke yields to increase. In case of Pb/ BaTiO₃ (1 %) catalyzed run, negligible amount of carbon residue (0.88 wt %) was achieved. This can be attributed to much less over cracking reactions occurring in the pyrolysates, which are responsible for coke formation. The catalysts used might have suppressed severe over cracking reactions in the primary liquid products as earlier reported [50].

Based on the formation of highest liquid and lowest coke yields, Pb/BaTiO₃ is suggested to be the most active catalyst for deriving liquid fractions in large amount particularly when used in low concentration. The catalyst may favor formation of gas when used in high concentration.



Table 3.20. Yields of pyrolysates (over all yields and yields of liquid, gas and coke) derived from catalytic pyrolysis of PP over original and metal doped BaTiO₃ as a function of catalyst type and concentration.

Catalyst type	Catalyst Conc. (wt %)	Yields (wt %)			
		TC	L	G	SR/Coke
Thermal Run	00	98.66	69.82	28.84	1.34
Un-doped BaTiO ₃	0.5	96.72	66.21	30.51	3.28
	1.0	94.99	64.34	30.65	5.01
	2.5	91.24	60.01	31.23	8.76
	5.0	89.88	40.60	49.28	10.12
	10	87.79	38.91	48.88	12.21
Pb/BaTiO ₃	0.5	98.66	80.45	18.21	1.34
	1.0	99.12	92.91	6.21	0.88
	2.5	96.23	69.21	27.02	3.77
	5.0	94.21	60.49	33.72	5.82
	10	93.40	59.4	34.00	6.13
Co/BaTiO ₃	0.5	98.49	79.94	18.55	1.51
	1.0	98.54	83.43	15.11	1.46
	2.5	98.29	78.63	19.66	1.71
	5.0	96.37	74.76	21.61	3.63
	10	94.19	69.76	24.43	5.81
Pb-Co/BaTiO ₃	0.5	89.49	81.34	8.15	10.51
	1.0	90.90	84.46	6.44	9.10
	2.5	88.89	80.23	8.66	11.11
	5.0	87.24	79.11	8.13	12.76
	10	88.65	78.80	9.85	11.35
TC: Total conversion		L: Liquids	G: Gas	SR: Solid residue	

3.4.1.2. Liquid Products Composition

3.4.1.2. 1. FTIR Analysis

The liquid products derived from PP in the presence of all catalysts used were characterized by FT-IR. The peaks data is compiled in Table 3.21. The spectrum of uncatalyzed run (Fig.3.15 a) shows many peaks appearing mostly in the wave number range of 2960-2840 cm⁻¹. The presence of these peaks can be corresponded to C-H stretching.



Peaks can also be observed at 1520 cm^{-1} which can be assigned to C=C, and those appearing in the wave number range at $1460\text{--}1350\text{ cm}^{-1}$ to C-H bending vibrations. The spectrum of the liquid product obtained in case of un-doped BaTiO₃ catalyzed run (Fig.3.15 b) exhibits several peaks which can be confidently corresponded to aliphatic hydrocarbons. The spectra of the liquid fractions obtained in case of Pb/ BaTiO₃, Co/ BaTiO₃ and Pb-Co doped BaTiO₃ catalyzed runs (Fig.3.15 c-e) are identical in shape and their intensities indicate the compositional similarities. However, the spectrum of liquid product obtained in case of Pb/ BaTiO₃ catalyzed run (Fig.3.15 c) features some additional peaks which can be corresponded to olefinic C=C configurations. From the compiled results, it can be observed that un-doped BaTiO₃ enhanced the formation of paraffins while Pb-BaTiO₃, enhanced the olefins fractions in the derived liquid products.

3.4.1.2. 2. GC-MS Analysis

Individual component analysis

In case of PP, maximum yield of liquid pyrolysate was obtained with Pb/BaTiO₃. The major hydrocarbon compounds identified in the GC-MS spectrum (Fig.3.16) are indicated in Table 3.22.

It is evident from the data that among naphthenes, the highly abundant hydrocarbons found were; 2-(1-methylethyl)-1,1-bicyclohexyl, 1,5,5-trimethyl cyclohexane, 2,4,6-trimethyl cyclohexane, 1,3,5-trimethyl cyclohexane, eicosyl cyclohexane, and 2,4-diethyl-1-methyl cyclohexane.

Among various olefinic compounds, the mostly occurring hydrocarbons found were; 7- tetradecene, (E), 1-dodecene, E-I0-pentadecene, 2-hexyl- 1-decene, 7-methyl I-undecene, and I-isopropyl-1, 4, 5-trimethylcyclohexane.

The major paraffinic compounds were found to be; 2,4-diethyl heptane, 2-isopropyl-5-methyl-heptane, 2,5-diethyl heptane, 2-methyl decane, 2-butyl octane, 2,4-dimethyl heptane, heptadecane, and 2,6, 10, 14-tetramethyl hexadecane.

*C-range distribution*

Some selected liquid products derived from un-catalyzed and catalyzed runs were analyzed by GC-MS. The carbon range distribution of the derived liquid products is provided in Table 3.23. The data indicated that in case of thermal run, the yields of different carbon range products i.e. C₆-C₁₂, C₁₃-C₁₆, C₁₇-C₂₀, C₂₁-C₃₀ and > C₃₀ were found to be 15.16, 33.04, 12.99, 24.97, 24.97 and 8.05 wt%, respectively. In case of run catalyzed with un-doped BaTiO₃, the yield of C₆-C₁₂ range hydrocarbons was found to increase (18 %). However, the yield of C₁₃-C₁₆ range hydrocarbons was found to decrease (26.77 %). The results indicated that the catalyst favored the formation of light liquid products and inhibited the formation of middle range products. It can be observed from the results that the catalyst decreased the formation of C₁₇-C₂₀, and increased C₂₁-C₃₀ hydrocarbon range products slightly (22.63, and 25.67 %). Products in the carbon range >C₃₀ were found to decrease (5.32 %) compared to thermal run. The results indicated that the catalyst assisted in cracking of the high boiling range hydrocarbons (>30) to yield lighter products. In case of run catalyzed with Pb//BaTiO₃, the yield of low carbon range products was found to be significant compared to both of the thermal and un-doped BaTiO₃ catalyzed runs. The yield of C₆-C₁₂ products was found to be increased (47.37 %). The formation of C₁₃-C₁₆ products was comparable with the thermal run (32.92 %). On contrary, the formation of products like C₁₇-C₂₀ (7.16 %) and C₂₀-C₃₀ (11.28%) were found to decrease.

As afore mentioned, the catalyst under study has caused a decrease in gas yields, hence, the gaseous molecules might have been consumed/recombined and generated C₆-C₁₂ hydrocarbon range products through olefin dimerization and oligomerization. Bronsted (HX) acids exhibit high activity in the oligomerization of unsaturated hydrocarbons as earlier reported [53]. There is a synergic effect of Lewis and Brønsted acid sites of titanates on several reactions [54]. In current study, doping with Pb, might have generated more redox centers in the catalyst under study thereby causing predominance of catalytically active sites at the surface as well as within the matrix [55] to favor pyrolytic conversion of PP in light hydrocarbon range products.



Liquid products obtained in case of runs catalyzed with Co//BaTiO₃ showed higher proportion of C₆-C₁₂ (35.22 %) and C₁₃-C₁₆ (54.91 %) range hydrocarbons compared to thermal run. Similarly, Pb-Co/BaTiO₃ also significantly increased the yield of C₆-C₁₂ range products (43.83 %), but decreased the yield of C₁₃-C₁₆ range products (25.22 %). Also, in case of both catalysts, the least abundance of C₁₇-C₂₀ (4.23 and 11.26 %), C₂₁-C₃₀ (4.51 and 17.97 %) and > C₃₀ (2.57, and 00 %) range hydrocarbons in the derived liquid products confirmed the cracking ability of these catalysts towards formation of light range hydrocarbons compared to heavy hydrocarbons. With respect to formation of light carbon range products, it can be seen that among the two catalysts used, Co/BaTiO₃ favored the yield of C₁₃-C₁₆ range products where as Pb-Co/BaTiO₃ enhanced the yield of C₆-C₁₂.

Hydrocarbon group type distribution

The relative proportions of hydrocarbon group types i.e. paraffins, olefins, cycloalkanes, and aromatic components in the liquid fractions obtained in case of thermal and catalyzed runs were determined in order to evaluate the cracking abilities of the catalysts under study. The data is compiled in Table 3.24.

The proportion of different types of hydrocarbons i.e. paraffins, olefins, and naphthenes determined in case of thermal run were found to be 66.55, 25.87, and 7.85 wt %, respectively. Similarly, the yields achieved in case of run catalyzed with un-doped BaTiO₃ were found to be 69.95, 25.8, and 4.25 wt%, respectively. The results showed that the catalyst has caused an increase in the yield of paraffins and decrease in the yield of naphthenes when compared with thermal run. The yields of olefins remained unaffected. In case of Pb/BaTiO₃ catalyzed run, the yield of paraffins was found to be significantly reduced to 46 wt% where as olefinic and naphthenic components were found to increase up to 43 and 10 wt%, respectively compared to thermal run.

On contrary, in case of Co/BaTiO₃ catalyzed run, the yields of paraffins and olefins were found to be 62 and 23 %, respectively where as the naphthenes content was found to be 14 %. The results exhibited an increase when compared with the thermal run. In case of Pb-Co/ BaTiO₃ catalyzed run, the yields of paraffins, olefins and naphthenes



were found to be 64.14, 21.51, and 14.36 % respectively. The results indicated that all catalysts influenced the formation of different hydrocarbon group types and showed preponderance of paraffinic hydrocarbons. This is due to the predominance of hydrogen transfer reactions occurred at the catalyst surface. The hydrogen required for saturation of olefinic configurations may generate from dehydrogenation of olefins and naphthenes which helps in formation of paraffins as earlier reported [56].

The results indicated activity of some of these catalysts towards formation of naphthenes. This can be attributed to their textural properties and cyclization, isomerization and oligomerization activities. For such reactions to undergo, textural properties of the catalysts play a key role [57]. No aromatics were observed in case of catalyzed runs. The results showed that all catalysts disfavored those reactions which are leading to the formation of aromatics. Aromatics are usually formed through dehydro cyclization [21]. Hence, the activities of all the catalysts under study towards de-hydro cyclization reactions were not established.

It can be inferred from the results that the catalyst type and concentration have no role to play in increasing the overall yields. Comparing the results with thermal run performed under similar conditions, all catalysts altered the conversion to liquid, gas and solid residue particularly Pb/BaTiO₃ appeared to have caused a significant increase in liquid yields and inhibited the coke formation. Further, some of the catalysts (Pb/BaTiO₃, Co BaTiO₃ and Pb-Co/BaTiO₃) greatly affected the formation of different carbon range products and hydrocarbon group types in the liquid products and appreciably increased the paraffinic hydrocarbons followed by naphthenic hydrocarbons. Doping with Pb helped in the formation of olefins in the liquid product. It appeared that the catalytic activities of the variously doped catalysts were toward formation of paraffins and naphthenes. Due to absence of aromatics in the liquid products, aromatization activities of all BaTiO₃ based catalysts were not established.

**Table 3.21.** Major absorption peaks observed and assigned configurations in the FT-IR spectra of the liquid products derived from pyrolysis of PP using BaTiO₃ based catalysts

Pyrolysis obtained with	Position (cm ⁻¹)	Intensity	Assigned configuration
Thermal run	2953	strong	CH ₃ (aliphatic)
	2868	strong	CH ₂ (aliphatic)
	1620	weak	C=C (olefinic)
	1456	strong	CH ₂ bending
	1375	medium	C-H scissoring/bending
	887	strong	C-H (olefinic)
BaTiO ₃	2920	strong	CH ₃ (aliphatic)
	2852	strong	CH ₂ (aliphatic)
	1620	medium	C=C (olefinic)
	1455	weak	CH ₂ bending
	908	medium	C-H (olefinic)
Pb/ BaTiO ₃	2954	strong	CH ₃ (aliphatic)
	2912	strong	CH ₃ (aliphatic)
	2872	strong	CH ₂ (aliphatic)
	1625	medium	C=C (olefinic)
	1456	strong	CH ₂ bending
	1377	strong	C-H scissoring/bending
	887	medium	C-H (olefinic)
Co/ BaTiO ₃	2954	strong	CH ₃ (aliphatic)
	2916	strong	CH ₃ (aliphatic)
	2868	strong	CH ₂ (aliphatic)
	1620	weak	C=C (olefinic)
	1525	weak	CH ₂ bending
	1456	strong	CH ₂ bending
	1377	medium	C-H scissoring/bending
	887	strong	C-H (olefinic)
Pb-Co/ BaTiO ₃	2953	strong	CH ₃ (aliphatic)
	2914	strong	CH ₃ (aliphatic)
	1560	medium	C=C (olefinic)
	1456	medium	CH ₂ bending
	887	strong	C-H (olefinic)

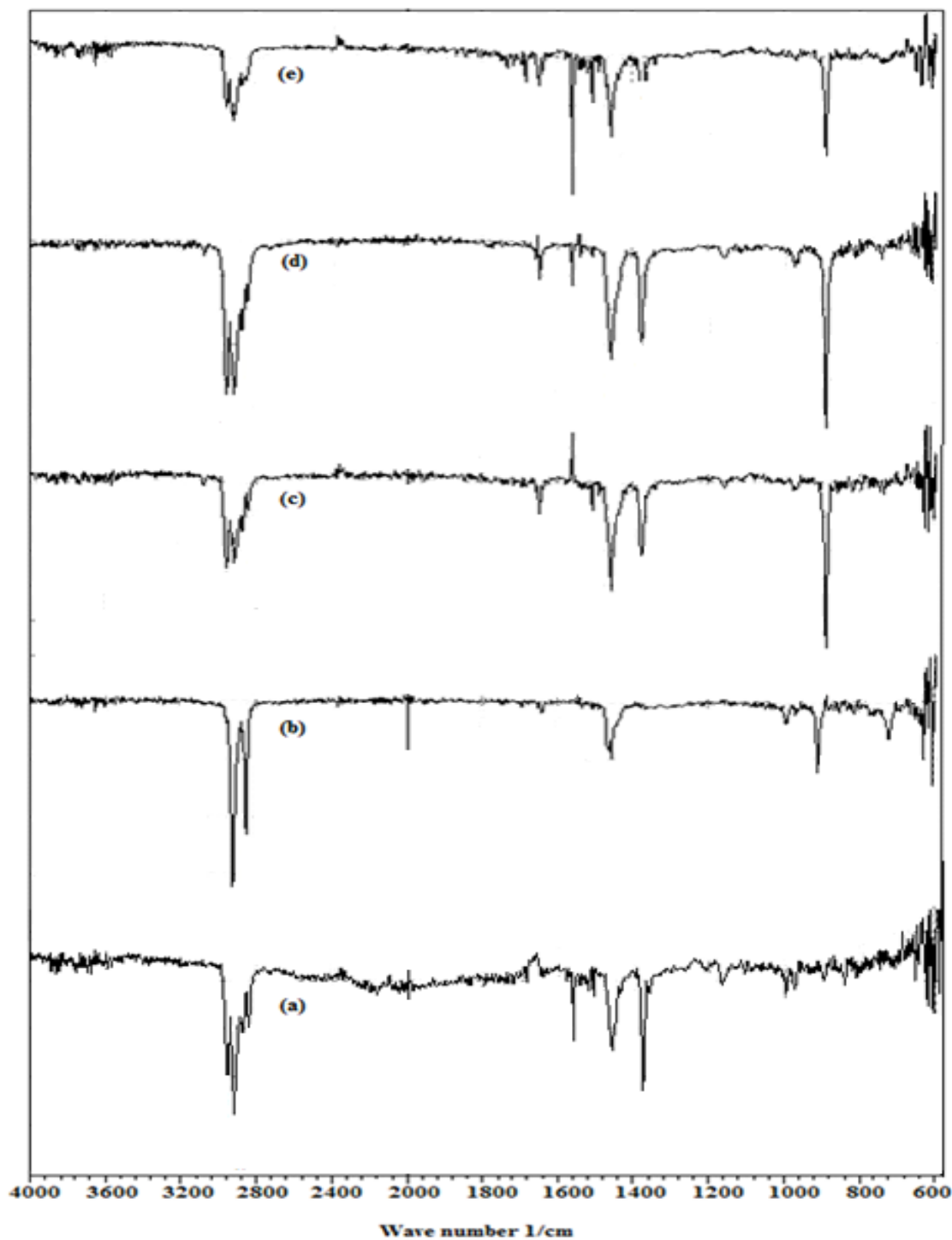


Figure 3.15. FT-IR spectra of liquid products derived from PP in un-catalyzed and catalyzed runs (a) Thermal run (b) un-doped BaTiO₃ catalyzed run (c) Pb/ BaTiO₃ catalyzed run (d) Co/ BaTiO₃ catalyzed run and (e) Pb-Co/ BaTiO₃ catalyzed run.

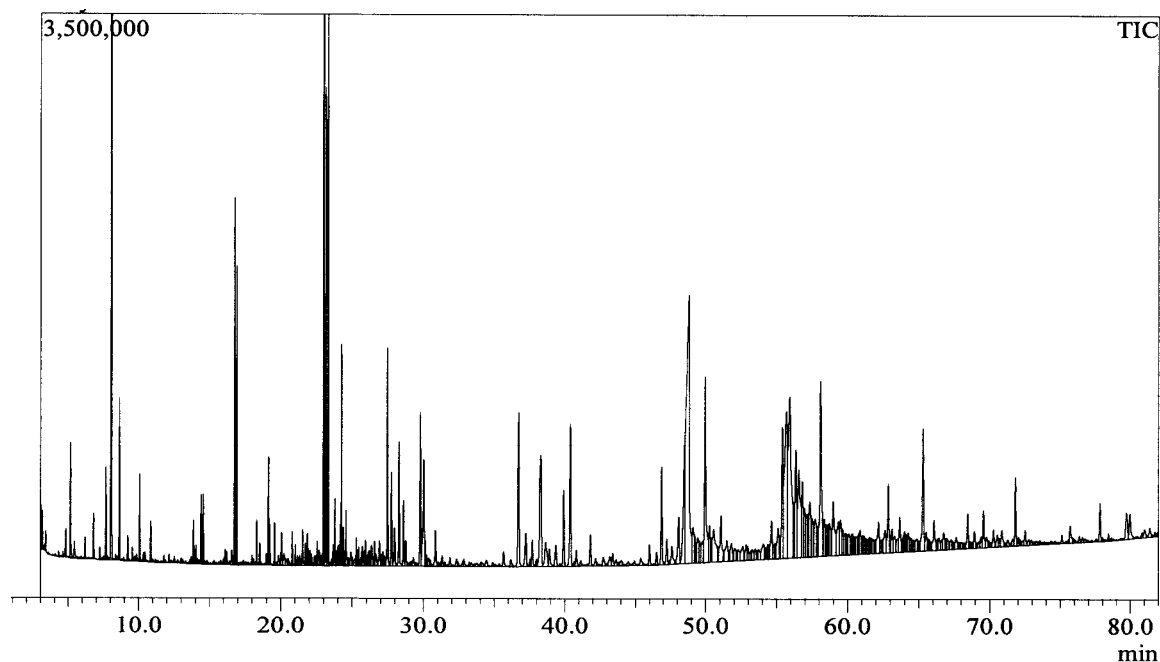


Figure 3.16. GC-MS spectrum of liquid product derived from pyrolysis of PP using Pb/BaTiO₃

Table 3.22. Hydrocarbons identified in liquid products derived from pyrolysis of PP using Pb/BaTiO₃

S.#	Compound	t _R	% peak area/ relative conc.
Naphthenes			
1.	1,3-Dimethylcyclopentane	3.033	0.38
2.	Cyclopentane, 1,2-dimethyl, cis	3.083	0.19
3.	Cyclopentane, 1,2-dimethyl -	3.133	0.37
4.	Cyclohexane, methyl -	3.861	0.01
5.	Cyclopentane, 1,1,3,4-tetramethyl, cis	6.806	0.43
6.	Cyclohexane, 1,3,5-trimethyl, cis	7.682	1.31
7.	Cyclohexane, 1,5,5-trimethyl -	8.638	1.70
8.	Cyclohexene, 3,5,5-trimethyl -	9.229	0.11
9.	Cyclohexane, eicosyl	16.23	0.50
10.	2,4,6-Trimethylcyclohexane	19.155	1.37
11.	Cyclohexane, 2,4-diethyl-1-methyl -	19.584	0.45



12.	Cyclohexane, 1,2-diethyl-3-methyl -	20.07	0.32
13.	2,4,6- Trimethyl cyclohexane	22.562	0.25
14.	Cyclohexane, 1,1 -(1,5-pentanediy)	24.1	0.37
15.	1,1-Bicyclohexyl, 2-(1-methylethyl),cis	29.779	2.12
16.	Cyclopentane, 1,2-dibutyl -	40.82	0.41
Total yield			10.29
Olefins			
17.	1-Nonene	10.073	1.53
18.	1,6-Octadiene, 2,6-dimethyl, (Z)	10.861	0.87
19.	2-Decene, 4-methyl- (Z) -	14.053	0.17
20.	2-Decene, 2,4-dimethyl -	16.119	0.74
21.	1-Isopropyl-1,4,5-trimethyl cyclohexane	16.58	2.21
22.	1-Undecene,7-methyl -	16.782	2.42
23.	2-Undecene, 4,5-dimethyl -	16.923	1.86
24.	1-Undecene, 5-methyl -	18.323	0.39
25.	2-Undecene, 8-methyl, (Z)	18.542	0.26
26.	1,7-Nonadiene,4,8-dimethyl -	19.242	0.52
27.	1-Dodecene	21.03	3.42
28.	2-Undecene, 4,5-dimethyl -	21.03	0.22
29.	2-Heptene, 5-ethyl-2,4-dimethyl -	22.369	1.46
30.	E-10-Pentadecene	22.563	2.86
31.	9-Eicosene, (E)	24.025	0.15
32.	5-Eicosene, (E)	23.932	0.13
33.	3-Eicosene, (E)	24.176	0.32
34.	1,19-Eicosadiene	24.251	1.37
35.	18- Nonadecene	24.39	0.22
36.	7- Tetradecene, (E)	24.993	8.98
37.	2-Methyl-2-docosene	25.463	0.19
38.	1-Decene, 2-hexyl -	27.473	2.57
39.	1- Tricosene	28.293	1.77



40.	Isotridecane	35.647	1.73
41.	5-Eicosene	39.909	1.47
42.	4-Tetradecene, 2,3,4-trimethyl -	41.813	1.56
43.	1,15-Hexadecadiene	44.488	0.06
44.	3-Tricosene	45.783	0.08
45.	11-Dodecene, 2,4,6-trimethyl -	49.955	0.06
46.	4-Tetradecene, 2,3,4-trimethyl -	51.073	0.56
47.	4-Tetradecene, 2,4,6-trimethyl -	58.988	1.54
48.	4-Tetradecene, 2,3,4-trimethyl -	65.284	1.70
Total yield			43.39
Paraffins			
49.	Heptane	3.293	0.06
50.	Heptane, 4-methyl -	5.15	1.17
51.	Heptane, 2,4-dimethyl -	7.253	2.71
52.	2,6-Dimethyl heptane	8.045	1.44
53.	Nonane, 2,6-dimethyl -	14.416	0.75
54.	Decane 2-methyl -	14.565	0.93
55.	Undecane	17.588	1.53
56.	Dodecane	20.616	0.51
57.	Hexane, 5-methyl-2-(1-methylethyl) -	21.533	0.55
58.	Dodecane, 4,6-dimethyl -	21.73	0.41
59.	Decane, 2,3,5,8-tetramethyl -	21.883	0.96
60.	2-Isopropyl-5-methyl heptane	23	4.78
61.	Decane 2-methyl -	23.16	3.43
62.	Heptane, 2,4-diethyl -	23.317	5.08
63.	Decane, 2-hexyl	23.788	0.57
64.	Isotridecane	25.295	0.36
65.	Dodecane, 4,6-dimethyl -	25.946	0.35
66.	Decane, 3,3,6-trimethyl -	26.136	0.24
67.	Dodecane, 4,6-dimethyl -	26.37	0.35



68.	Octane, 2-butyl -	27.032	3.22
69.	Tetradecane	27.042	0.3
70.	2- Hexyl octane	27.756	1.4
71.	Decane,2-methyl -	27.963	0.72
72.	Hexadecane, 3,7,11, 15-tetramethyl -	28.765	0.38
73.	Dodecane, 2,6,11-trimethyl -	30.37	0.11
74.	Hexadecane	35.367	0.13
75.	Hentetracontane	37.233	0.51
76.	Heptane, 2,5-diethyl -	38.294	3.46
77.	Nonadecane	40.672	1.01
78.	Heneicosane	45.37	0.34
79.	Octane, 2-butyl -	47.248	1.53
80.	Hexadecane, 3,7,11,15-tetramethyl -	47.607	0.28
81.	Heptadecane	49.739	1.98
82.	Hexadecane, 2,6, 10, 14-tetramethyl-	53.74	1.75
83.	Docosane	57.514	0.48
84.	Octadecane	61.165	0.37
85.	Octane, 4-butyl -	62.854	1.26
86.	Octacosane, 2,4,6,8-tetramethyl -	63.649	0.01
87.	Tetratetracontane	64.361	0.02
88.	Octacosane	70.69	0.22
89.	Pentadecane, 8-hexyl -	73.543	0.02
90.	Hexatriacontane	76.553	0.01
Total yield			45.69

Concentration of Co/BaTiO₃: (1%)

**Table 3.23.** Carbon range distributions in liquid products derived from catalytic pyrolysis of PP over original and metal doped BaTiO₃

Catalyst	Distribution (wt %)				
	C ₆ -C ₁₂	C ₁₃ -C ₁₆	C ₁₇ -C ₂₀	C ₂₁ -C ₃₀	>C ₃₀
No catalyst	15.16	33.04	12.99	24.97	8.05
BaTiO ₃	18.55	26.77	22.63	25.67	5.32
Pb/BaTiO ₃	47.37	32.92	7.16	11.28	0.06
Co/BaTiO ₃	35.22	54.91	4.23	4.51	2.57
Pb-Co/BaTiO ₃	43.83	25.25	11.26	17.97	0.00

Catalyst concentration: 1 wt%

Table 3.24. Hydrocarbon group types distributions in liquid products derived from catalytic pyrolysis of PP over original and metal doped BaTiO₃

Catalyst	Distribution (wt %)			
	Paraffins	Olefins	Naphthenes	Aromatics
No catalyst	66.55	25.87	7.58	0.00
BaTiO ₃	69.95	25.8	4.25	0.00
Pb/BaTiO ₃	45.69	43.39	10.29	0.00
Co/BaTiO ₃	62.65	22.86	14.49	0.00
Pb-Co/BaTiO ₃	64.14	21.51	14.36	0.00

Catalyst concentration: 1 wt%

3.4.2. Catalytic Pyrolysis of HDPE

The catalytic pyrolysis of high density polyethylene (HDPE) into useful products was investigated in the presence of BaTiO₃ based catalysts. The product yields (overall yields and liquid, gas and coke/residue) as a function of catalyst type and concentration were studied.

There is ample body of literature on the catalytic pyrolysis of model and waste plastics (individual and comingled) using a variety of catalysts. Silica-alumina catalysts have been found to successfully effectuate the degradation of polyethylene into valuable fuel oil at a temperature of 500 °C [58, 59]. Similarly, ZSM-5 and meso porous MCM-41 have also been investigated for cracking of polyolefins [60-63]. Cracking of polystyrene



and polyethylene was also reported in the presence of spent commercial FCC catalyst [64]. The catalytic conversion of polyolefins into liquid fuels was investigated in the presence of MCM-41, silica-alumina and ZSM-5 catalysts at 400°C. It was found that MCM-41 gave high conversion as compared to silica–alumina and ZSM-5 zeolite catalysts [65-67].

Even though, most of these catalysts worked in terms of plastic waste conversion, but still they are associated with either high cost of production or the operating conditions which may not be industrially feasible as high temperature and extended residence time with low percentage conversion [68], hence the properties of these catalysts need to be tailored further to improve their textural properties.

In the preset work, we have investigated the cracking of high density polyethylene at 350 °C in the presence of some mild acidic nano-structured catalysts which included, BaTiO₃, Pb/BaTiO₃, Co/BaTiO₃ and Pb-Co/BaTiO₃. The aim of the study was to obtain high yield of liquid products, enriched with light hydrocarbons exploiting the unique textural properties of the un-doped and various metal doped BaTiO₃ catalysts.

3.4.2.1. Activity Tests

Our preliminary pyrolysis experiments showed that 350 °C is the optimum temperature for cracking of high density polyethylene in un-catalyzed run. Hence, for further experiments, 350 °C was used as optimum temperature. The nano-structured solid acid catalysts used included un-doped BaTiO₃, and variously doped Pb/ BaTiO₃, Co/BaTiO₃ and Pb-Co/ BaTiO₃. Results of overall conversion yields and yields of liquid, gas and solid residue/coke as a function of individual catalyst type and concentration are given in Table 3.25.

3.4.2. 1.1. Overall product yields (combined liquid+ gas)

The overall conversion yield was already significant in case of un-catalyzed run (98.12 wt %). It can be observed that all catalysts did not alter the total conversion compared to un catalyzed run and only marginal increase (from 1.4 to 1.5 wt %) in overall yields can be seen. An optimum over all yield of 99.64 wt % was achieved in run



catalyzed with Pb-Co/BaTiO₃ (5 wt% loading). A marginal increase (99.52 wt %) was also observed in case of Co/BaTiO₃ (10 wt% loading). In the rest of the catalytic runs, the overall yields were decreased. A significant decrease from 98.12 wt % to 78.84 wt % was observed in case of un-doped BaTiO₃ (0.5 wt% loading) catalyzed run.

3.4.2. 1.2. Liquid yields

The effect of individual catalyst and its concentration on conversion to liquid products was also investigated. The results indicated in Table 3.25 show that the use of catalysts under study significantly altered the product spectrum in term of liquid yields. It can be seen from the results that liquid yields in the product slates were dominant in some of the catalyzed runs compared to thermal run where the yield achieved was found to be about 80 %, whereas in case of Co/ BaTiO₃ (1 % loading) and Pb-Co/BaTiO₃ (1 % loading) catalyzed runs, the yields achieved were found to be 83 and 85 wt %, respectively. Similarly, in case of Pb/BaTiO₃ (0.5 % loading) catalyzed run; a maximum yield of 83 % was achieved. Among the catalysts used, Pb-Co/ BaTiO₃ gave the highest yield (85 wt %) and showed high activity while un-doped BaTiO₃ gave the lowest yield (~80 wt %) and showed poor activity. The lowest yield in case of un doped BaTiO₃ may be correlated to its low surface area (98 m².g⁻¹) and small pore volume, due to which the bulky polymer molecules experienced hindrance in internal diffusion thereby caused the yields to decline. Hindrance in internal diffusion of bulky molecules into the micropores of the catalysts is already reported in the literature [69]. Correlation between surface properties and catalytic activity of several catalysts has also been reported elsewhere [69]. The high yields achieved in case of Pb-Co/ BaTiO₃ can be attributed to its high surface area (269 m².g⁻¹) and hence its topology (micro pores). High surface area and large pore volume have been reported to be responsible for high conversion of bulky polyolefins molecules [47]. Similarly, the surface area and pore dimensions of the Pb/BaTiO₃ and Co/ BaTiO₃ are analogous to the un-doped and Pb-Co/ BaTiO₃ and showed moderate activity in attaining maximum liquid yield (83 wt%). Moreover, as reported earlier, HDPE has many tertiary carbons in the chain, and its cracking do not requires strong acidities [48]. The change in acidity of un-doped BaTiO₃ with doping might be the other reason.



3.4.2.1.3 . Gas yields

The effect of solid acid catalysts was also studied on the formation of gaseous products. Results indicated that all the catalysts used influenced the gas yields. The maximum gas yield (50.15 wt %) was attained in case of Pb-Co/ BaTiO₃ (10 wt % loading) catalyzed run, whereas the minimum (0.5 wt %) in case of un-doped BaTiO₃ (1 wt % loading) catalyzed run. This showed that Pb-Co/BaTiO₃ (5 wt % loading) favored the formation of gases, which corresponded to a decrease in the liquid yield from 80.88 to 52.95 wt %. More specifically, the effect of the polymer to catalyst ratio expressed as the acidity content of the polymer/catalyst system is believed to have influenced the formation of liquid hydrocarbons. The liquid yield seemed to have a negative correlation to the acidity content as earlier reported [70].

3.4.2.1.4 . Residue Yields

The effect of individual catalyst on the formation of coke/residue (combination of coke and residual PE) is provided in Table 3.25. Results indicated that the yield of solid residue in case of thermal run was very minute (1.88 wt %), as compared to most of the catalyzed runs. The maximum residue yield (21.13 %) was given by un-doped BaTiO₃ (0.5 wt % loading), whereas the minimum yield (0.36 wt %) by Pb-Co/ BaTiO₃ (5 wt %). The data also showed that the yield of solid residue or coke inversely corresponded to the yield of gaseous products. The low yield of gaseous product and hence high yield of solid residue may be attributed to the secondary reactions taken place between molecules in gas phase, mostly at the catalyst surface that resulted in coke formation. Besides, the low degree of over cracking may also be responsible for high coke formation, which might have inhibited severe over cracking of primary liquid products as earlier reported [50].

It can be suggested from the above discussion that Pb-Co/BaTiO₃ is the most active among the studied catalysts as it leads to high liquid yields and lowest residue yield, which was the main objective of the current study.



Table. 3.25. Yields of pyrolysates (over all yields and yields of liquid, gas and coke) derived from catalytic pyrolysis of HDPE over original and metal doped BaTiO₃ as a function of catalyst type and concentration.

Catalyst	Catalyst quantity (wt %)	Yields (wt %)			
		Total	Liquid	Gases	Solid residue/coke
Thermal Run	00	98.12	80.88	17.24	1.88
Original BaTiO ₃	0.5	78.84	78.34	0.5	21.13
	1.0	79.59	79.15	0.44	20.41
	2.5	94.29	81.97	12.32	5.71
	5.0	91.55	70.35	21.2	8.45
	10	88.64	65.45	23.19	11.36
	0.5	93.37	83.21	10.16	6.33
Pb/BaTiO ₃	1.0	91.14	76.64	14.50	8.86
	2.5	90.33	74.85	15.48	9.67
	5.0	89.52	70.38	19.14	10.48
	10	88.55	68.41	20.14	11.45
	0.5	91.50	73.17	18.33	8.50
Co/BaTiO ₃	1.0	95.95	83.43	12.52	4.05
	2.5	99.3	78.63	20.67	0.70
	5.0	99.43	70.54	28.89	0.57
	10	99.52	60.72	38.80	0.48
	0.5	98.86	69.82	29.04	1.14
Pb-Co/BaTiO ₃	1.0	95.27	85.17	10.10	4.13
	2.5	92.69	74.64	18.05	7.31
	5.0	99.64	52.95	46.69	0.36
	10	98.40	48.25	50.15	1.60
	0.5	98.86	69.82	29.04	1.14

3.4.2.2 . Liquid Products Composition

3.4.2.2.1. FTIR Analysis

In order to investigate the composition of the liquid products derived from various catalyzed runs, the products were characterized by FT-IR. The data is compiled in Table 3.26. The FT-IR spectra (Fig. 3.17 a-e) show almost the same configurations. Fig.3.17 (a) represents the spectrum of derived liquids in case of thermal run. The spectrum features



several peaks in the scanned wave number range. The spectrum of liquid product derived from un-doped BaTiO₃ catalyzed run is given in Fig 3.14 (b). Major peaks appearing at the wave number range of 2960-2840 cm⁻¹ can be corresponded to methyl and methylene C-H stretching vibrations. A peak appearing at 1520-1600 cm⁻¹ shows olefinic C=C, and peaks in the wave number range of 1460-1350 cm⁻¹ show C-H bending vibrations. The FT-IR spectra of the liquid product derived in runs catalyzed with different catalysts (Fig 3.17 b-d) feature several signals which can be corresponded to paraffinic and olefinic configurations. However, in case of liquid products obtained in the presence of Pb/BaTiO₃ and Co/BaTiO₃, (Fig 3.17 b, c), the peaks which can be assigned to olefinic configurations are less prominent and ill developed. This indicated that the catalysts favored the formation of paraffins compared to olefins. On the other hand, the spectrum of the liquid products obtained in the presence of Pb-Co/ BaTiO₃ (Fig 3.17 d) feature peaks can be corresponded to both paraffins and olefins, which indicated the selectivity of the catalyst towards formation of paraffins and olefins with preponderance of the former one.

3.4.2.2.2. GC-MS Analysis

Individual component analysis

The GC-MS spectrum of the liquid pyrolysate derived from HDPE using Pb-Co/BaTiO₃ as catalyst is provided in Fig. 3.18. Data given in Table 3.27 shows the hydrocarbons identified along with their retention times and relative abundance.

The data showed that among different different naphthenic compounds identified included 1,2-dimethyl -3-cyclopentane, ,methyl-5-cyclohexane, 1-heptyl-2-methyl-cyclopropane, 1-Isopropyl-1,4,5-trimethylcyclohexane and 2,4-diethyl-I-methyl cyclohexane were observed.

Among olefinic compounds, the major compounds were found to be dodecene, pentadecene, tetradecene and heptadecene. Whereas the most abundant paraffins were found to be nonane, undecane, dodecane, pentadecane, tetradecane, 2,6,11-trimethyl



dodecane, hexadecane, nonadecane, heneicosane, heptadecane, , 2,6, 10, 14-tetramethyl hexadecane, docosane, octadecane, tetratetracontane, tetratriacontane and octacosane.

Upon comparing the composition of thermally and catalytically derived liquid pyrolysates of HDPE, it can be concluded that most of the compounds detected were of the same chemical nature. However, the difference was in their relative abundance.

C-number distribution

The nature of the liquid products obtained in case of un-catalyzed and catalyzed runs was investigated by GC-MS analysis, which helped to determine the distribution of different hydrocarbon range products. The carbon number distributions of the derived liquid products is provided in Table 3.28. Results showed that in case of the liquid product obtained in thermal run, the yields of different carbon range products i.e. C₆-C₁₂, C₁₃-C₁₆, C₁₇-C₂₀, and > C₃₀ were found to be 32.56, 30.80, 14.19, 12.35 and 10.95 wt %, respectively. One can see that the shift is towards the formation of lighter products. In case of run catalyzed with un-doped BaTiO₃, the yield of the C₆-C₁₂ range hydrocarbons was decreased to 15 %, and those of C₁₃-C₁₆ and C₁₇-C₂₀ were slightly increased (by average of 2 %). Similarly, the yield of C₂₁-C₃₀ range hydrocarbons increased almost two fold i.e. 24 %, hence the shift is towards formation of heavy products. It was expected that the catalysts will assist in formation of C₆-C₁₂ range hydrocarbons; however, the results are not in agreement with this proposition which confirmed the non selectivity of the catalyst in terms of formation of lighter products (naphtha range hydrocarbons) in substantial quantity. On the other hand, a significant increase in yield of the high carbon range hydrocarbons (C₂₁-C₃₀) indicated that the catalyst had limited cracking activity towards high molecular weight hydrocarbons to yield lower molecular weight hydrocarbons. As clear from the data, the un-doped BaTiO₃ catalyst has led to a very low yield of gaseous products when used in low concentration. It may, therefore, be suggested that gas molecules might have been consumed in the formation of C₁₇-C₂₀ hydrocarbon range products through olefin dimerization and oligomerization. It has been reported earlier that Bronsted (HX) acids exhibit high activity in the oligomerization of unsaturated hydrocarbons [53]. Furthermore, there is a synergic effect of Lewis and



Brønsted acid sites of titanates on several reactions [54]. The same reasons may be thought for the above yield pattern. The acidity of the catalysts used can be thought a valid reason for product distribution enriched in high carbon range products.

Regarding the distribution of different range hydrocarbons in the liquid products, the results obtained with Pb/ BaTiO₃ are similar to that of un-doped BaTiO₃. In case of run catalyzed with Pb/BaTiO₃, the yield of low range hydrocarbons (C₆-C₁₂) was decreased to half as compared with the un catalyzed run, and the yield of hydrocarbons with carbon number of C₇-C₁₆ was decreased slightly (27.45 %). However, the yield of products ranging from C₁₇-C₂₀ was increased by about 7 % and that of C₂₁-C₃₀ range products was increased by 19 %. Hence, the same phenomenon of olefin dimerization and oligomaerization might be involved here, which caused the yield of high C-range products to be substantially high [53].

The catalytic behavior of Co/BaTiO₃ and Pb-Co/BaTiO₃ was different from the aforementioned catalysts. In case of run catalyzed with Co/BaTiO₃, the liquid products showed a decrease in the C₆-C₁₂ range hydrocarbons (24.34 %), the yields of C₁₃-C₁₆ and C₁₇-C₂₀ range hydrocarbons were increased by 5 to 8 %, respectively, whereas the yield of C₂₁-C₃₀ (13.05 %) was almost unaffected. Similarly, in the presence of Pb-Co/BaTiO₃ catalyst, the yields of different carbon range products i.e. C₆-C₁₂, C₁₃-C₁₆, C₁₇-C₂₀, and > C₃₀ were found to be 18.55, 31.34, 25.7, 16.02 and 7.88 wt %, respectively. The results showed non selectivity of the later catalyst. However, a general conclusion can be drawn from these results, that Pb/BaTiO₃ increased the yield of high hydrocarbon range products (C₁₇-C₃₀) and decreased the yield of low hydrocarbons range products (C₆-C₁₆), whereas Co/BaTiO₃ favored the yield of middle hydrocarbons range products (C₁₃-C₂₀) and decreased the yield of low hydrocarbons range products (C₆-C₁₂). The yield of heavy range hydrocarbons remained unaffected. On the other hand, in the presence of Pb-Co/BaTiO₃ catalyst, the yield pattern of different range hydrocarbons remained unchanged, which indicated that the effect of Pb and Co on the distribution of the products is counter balanced in case of Pb-Co/BaTiO₃ catalyzed run. As earlier reported, the product distribution in term of lighter and heavier components corresponded to the acidity of the catalyst. High acidity can cause formation of lighter/volatile products, while



acidity less than the critical value lead to formation of heavier products [50]. This effect may be correlated here to the relative weaker acidity of the catalyst due to doping with Pb and Co ions. Doping with basic cations may alter the intrinsic acidity [71]. It is inferred from the results that the distribution of different range hydrocarbons is steered by the acidity of the catalysts used.

Hydrocarbon group types

The relative abundance of hydrocarbons types i.e. paraffins, olefins, naphthenes, and aromatics in the liquid products obtained in case of un-catalyzed and catalyzed runs was also calculated with the help of GC-MS analysis. The data is compiled in Table 3.29, which indicated that all the liquid products are lean in aromatics. It has been reported previously that the aromatics are usually formed through dehydro-cyclization process [71], hence, all the catalysts did not prove to be effective in assisting de-hydro cyclization reactions. In case of un-catalyzed run, the proportions of paraffins, olefins, and naphthenes in the liquid product were found to be 59.70, 31.90, and 8.40 %, respectively. The un-doped BaTiO₃ catalyst selectively increased the yield of paraffins by 6 % and reduced the yield of naphthenes by 6 %, whereas the yield of olefins remained the same, as compared to the yield pattern obtained in case of un-catalyzed run. The activity of Pb/ BaTiO₃ and Co/BaTiO₃ was almost the same in terms of the formation of paraffins, olefins, and naphthenes and both of the catalysts selectively increased the yield of paraffins to 73 and 76 %, respectively, and decreased the yield of olefins (by 8 to 11 %) & naphthenes (by 4 to 5 %).

In case of Pb-Co/BaTiO₃, the yields of paraffins, olefins and naphthenes were found to be 70.73, 24.64 and 4.38 %, respectively, which indicated that the catalyst used decreased the yield of olefins and naphthenes and increased the yield of paraffins, as compared to un-catalyzed run. The results obtained in case of all catalyzed runs showed that the catalysts favored the formation of paraffins at the expense of olefins and naphthenes, however, the yield of paraffins given by Pb-Co/BaTiO₃ is relatively smaller than Pb/BaTiO₃ and Co/BaTiO₃ catalysts. This may be attributed to the ability of the later catalysts to undergo the hydrogen transfer reactions at their surface. It has been reported



that the hydrogen that leads to the formation of paraffins is provided by shuttling i. e. the dehydrogenation of olefins and naphthenes [56]. This also indicated that these catalysts promoted the dehydrogenation of olefins and naphthenes, which caused their low yield and thus favored the formation of paraffins. The low yield of the naphthenes also suggested the poor selectivity of these catalysts towards cyclization, isomerization and oligomerization, which in turn depend upon the textural properties of the catalysts [57]. Hence, it may be suggested that in case of doped BaTiO₃ catalysts, the dopants i.e. Pb and Co together, steered the texture of the catalysts due to which the activity of the resultant catalysts is enhanced towards hydrogen transfer reactions, thereby giving high yield of paraffins.

The catalytic cracking of HDPE was investigated in the presence of un-doped BaTiO₃, Pb/BaTiO₃, Co/BaTiO₃ and Pb-Co/BaTiO₃, at 350 °C and in nitrogen environment. It was found that these catalysts markedly enhanced the yield of liquid products as compared to un-catalyzed run, particularly with Pb-Co/BaTiO₃ catalyst, the liquid yield of 86 % was attained. The catalysts also influenced the formation of different carbon range products and hydrocarbon group types. In comparison to un-catalyzed run, the un-doped BaTiO₃ catalyst decreased the yield of the C₆-C₁₂ and increased the yield of C₂₁-C₃₀ range hydrocarbons significantly. Comparing the liquid yield samples obtained, the ones obtained in case of catalyzed runs contained heavier components reflecting poor cracking abilities of all the catalysts employed. Similarly, Pb/BaTiO₃ and Co/BaTiO₃ enhanced the formation of C₁₃-C₁₆, and C₂₁-C₃₀ range hydrocarbons. On the other hand, Pb-Co/BaTiO₃ catalyst gave the average yield (20 to 25 wt %) of different range hydrocarbons. Regarding the hydrocarbon type distribution, all the catalysts enhanced the yield of paraffins and reduced the formation of naphthenes and olefins, which showed that the catalysts are active in catalyzing the hydrogen transfer reactions.



Table- 3.26. Major absorption peaks observed and assigned configurations in the FT-IR spectra of the liquid products derived from pyrolysis of HDPE using BaTiO₃ based catalysts

Pyrolysis state obtained with	Position (cm ⁻¹)	Intensity	Assigned configuration
Thermal run	2953	strong	CH ₃ (aliphatic)
	2868	strong	CH ₂ (aliphatic)
	1620	weak	C=C (olefinic)
	1456	strong	CH ₂ bending
	1375	medium	C-H scissoring/bending
	887	strong	C-H (olefinic)
BaTiO ₃	2920	strong	CH ₃ (aliphatic)
	2852	strong	CH ₂ (aliphatic)
	1620	medium	C=C (olefinic)
	1455	weak	CH ₂ bending
	908	medium	C-H (olefinic)
Pb/ BaTiO ₃	2954	strong	CH ₃ (aliphatic)
	2912	strong	CH ₃ (aliphatic)
	2872	strong	CH ₂ (aliphatic)
	1625	medium	C=C (olefinic)
	1456	strong	CH ₂ bending
	1377	strong	C-H scissoring/bending
	887	medium	C-H (olefinic)
Co/ BaTiO ₃	2954	strong	CH ₃ (aliphatic)
	2916	strong	CH ₃ (aliphatic)
	2868	strong	CH ₂ (aliphatic)
	1620	weak	C=C (olefinic)
	1525	weak	CH ₂ bending
	1456	strong	CH ₂ bending
	1377	medium	C-H scissoring/bending
	887	strong	C-H (olefinic)
Pb-Co/ BaTiO ₃	2953	strong	CH ₃ (aliphatic)
	2914	strong	CH ₃ (aliphatic)
	1560	medium	C=C (olefinic)
	1456	medium	CH ₂ bending
	887	strong	C-H (olefinic)

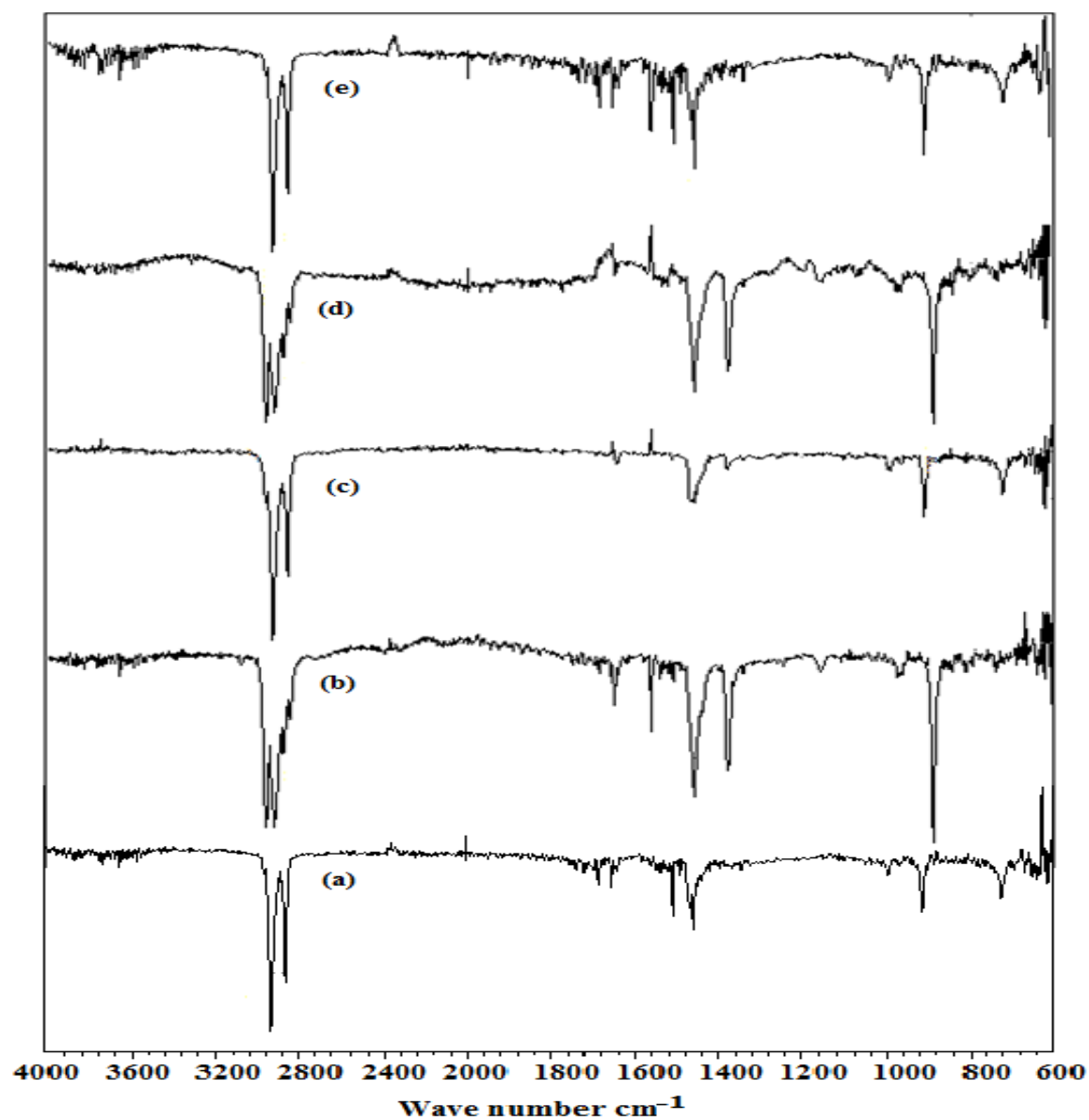


Fig. 3.17. FT-IR spectra of the liquid products derived from catalytic pyrolysis of HDPE over original and variously doped BaTiO₃ (a) Thermal run (b) un-doped BaTiO₃ (c) Pb/BaTiO₃ (d) Co/ BaTiO₃ and (e) Pb-Co/ BaTiO₃

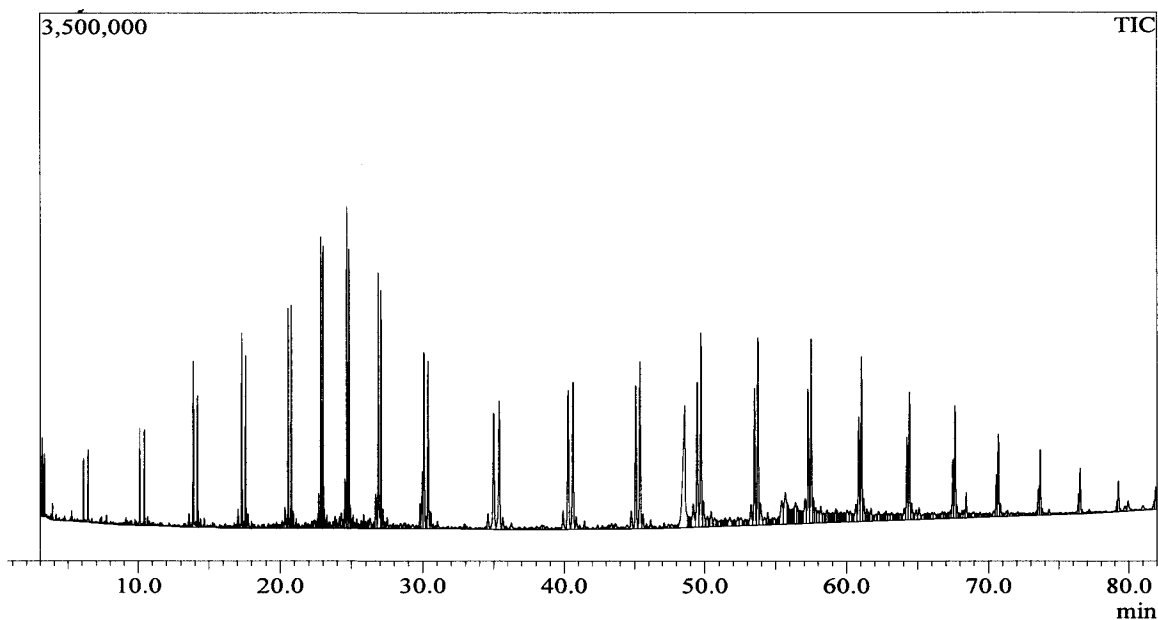


Figure 3.18. GC-MS spectrum of liquid product derived from HDPE by pyrolysis in the presence of Pb-Co/BaTiO₃

Table 3.27. Hydrocarbons identified in the liquid product derived from catalytic pyrolysis of HDPE over Pb-Co/ BaTiO₃

S.No	Compound	t _R	% peak area/ relative conc.
Olefins			
1.	1-Octene	6.098	0.66
2.	2,4-Dimethyl-1-heptene	8.03	0.55
3.	1-Undecene, 8-methyl -	18.012	0.03
4.	1-Dodecene	20.563	1.59
5.	5- Tetradecene, (E)	20.912	0.64
6.	2-Undecene, 4,5-dimethyl -	20.656	0.09
7.	1- Tridecene	22.849	1.71
8.	5-Eicosene, (E)	24.01	0.01
9.	3-Eicosene, (E)	24.01	0.01
10.	1,19-Eicosadiene	24.16	0.06
11.	3-Hexadecene, (Z)	24.672	2.02
12.	1,9- Tetradecadiene	26.689	0.33
13.	1- Pentadecene	26.883	1.88
14.	4- Pentadecene	30.095	1.86
15.	1-Tetradecene	35.007	1.84



16.	5-Eicosene, (E)	39.939	0.22
17.	1- Hexadecene	40.299	1.77
18.	5-Octadecene, (E)	41.45	0.15
19.	1,15- Hexadecadiene	44.767	0.83
20.	1- Heptadecene	45.089	1.97
21.	1- Tricosene (E)	45.602	0.15
22.	Z-5- Nonadecene	64.252	1.51
23.	9-Hexacosene	67.472	0.69
24.	1- Tricosene	49.477	1.88
25.	6- Heptadecene	53.517	1.68
26.	9- Tricosene, (Z)	73.536	0.26
Total concentration (%)			24.39
Naphthenes			
27.	1,3-Dimethylcyclopentane	3.034	0.3
28.	Cyclopentane, 1,2-dimethyl-cis	3.083	0.19
29.	Cyclopentane, 1,2-dimethyl-trans	3.137	0.76
30.	Cyclohexane, methyl -	3.866	0.2
31.	Cyclopropane, 1-heptyl-2-methyl -	13.892	1.49
32.	1-Isopropyl-1,4,5-trimethylcyclohexane	16.415	0.51
33.	Cyclohexane, 2,4-diethyl-1-methyl -	19.897	0.51
34.	1,1-Bicyclohexyl, 2-(1-methylethyl) -	23.431	0.31
35.	Cyclohexane, 1,1-(1,5-pentanediy) bis	23.832	0.11
Total concentration (%)			4.38
Paraffins			
36.	Heptane	3.295	0.84
37.	Heptane, 4-methyl -	5.15	0.03
38.	Octane	6.432	1.55
39.	Heptane, 2,4-dimethyl -	7.658	1.01
40.	Nonane	10.439	1.81
41.	Undecane	17.588	2.99
42.	Dodecane	20.781	3.42
43.	Pentadecane	24.818	3.92
44.	Dodecane, 4,6-dimethyl -	25.777	0.03
45.	Decane, 3,3,6-trimethyl -	26.008	0.51
46.	Dodecane,4,6-dimethyl -	26.616	0.02
47.	Tetradecane	27.079	4.45
48.	Dodecane, 2,6,11-trimethyl -	30.382	4.51
49.	Hexadecane	35.398	4.62
50.	Nonadecane	40.645	4.76



51.	Heneicosane	45.398	4.98
52.	Heptadecane	49.744	5.07
53.	Hexadecane, 2,6, 10, 14-tetramethyl -	53.76	4.96
54.	Pentatriacontane	55.9	0.51
55.	Docosane	57.523	4.66
56.	Octadecane	61.064	4.14
57.	Tetratetracontane	64.428	3.49
58.	Tetratriacontane	67.636	2.76
59.	Octacosane	70.706	2.12
60.	Pentadecane, 8-hexyl -	73.66	1.55
61.	Hexatriacontane	76.511	1.12
62.	Triacontane	79.259	0.90
Total concentration (%)			70.73

Catalyst concentration: 1%

Table. 3.28. C-number distribution in liquid product derived from catalytic pyrolysis of HDPE over original and metal doped BaTiO₃

Catalyst*	Distribution (%)				
	C₆-C₁₂	C₁₃-C₁₆	C₁₇-C₂₀	C₂₁-C₃₀	> C₃₀
No catalyst	32.56	30.80	14.19	12.35	10.95
Original BaTiO ₃	15.45	33.83	16.71	24.38	8.05
Pb/BaTiO ₃	17.91	27.45	19.64	31.49	3.49
Co/BaTiO ₃	24.34	35.45	22.42	13.05	4.40
Pb-Co/BaTiO ₃	18.55	31.34	25.71	16.02	7.88

* Catalyst concentration: 1%

Table. 3.29. Hydrocarbon group types distributions in liquids derived from catalytic pyrolysis of HDPE over original and metal doped BaTiO₃

Catalyst*	Distribution (%)			
	Olefins	Naphthenes	Paraffins	Aromatics
No catalyst	31.90	8.40	59.70	0.00
Original BaTiO ₃	32.17	2.22	65.61	0.00
Pb/BaTiO ₃	22.50	4.14	73.36	0.00
Co/BaTiO ₃	19.92	3.2	76.89	0.00
Pb-Co/BaTiO ₃	24.64	4.38	70.73	0.00

* Catalyst concentration: 1%



3.5 CATALYTIC PYROLYSIS OVER TYPE B CATALYSTS (METAL IMPREGNATED ZEOLITES)

Pyrolysis of PP and HDPE over original and metal oxide impregnated pre baked clays (PBCs) as catalysts under optimized conditions (Temperature; 300 °C for PP and 350 °C for HDPE, residence time; 30 minutes) was carried out. PBC was used as source of zeolite and impregnated with Fe, Co, Zn, Mn and Ni containing salts in different concentrations. The effect of catalyst type and concentration on total conversion and conversion to liquid, gas and coke/residue was studied.

Heterogeneous catalysts including conventional zeolites [72], meso porous catalysts [73], nano structured and hierarchical catalysts were used in the past with great success [34]. Among these, the zeolite based catalysts were the focus of attention of many researchers [72, 74, 75]. However, most of these catalysts did not prove effective in term of plastic conversion due to their textural properties, wide range of acidity, high cost, and access of bulky polymer molecules to the active sites of the catalysts [76, 77]. These draw backs have necessitated the development of new zeolitic catalysts with improved activity and selectivity toward degradation of polyolefins.

Metal impregnation may enhance the catalytic activity due to formation of smaller and more reducible M-oxide species, which impart superior characteristics to the zeolites as catalysts. It also affects the concentration of Lewis acid sites and the presence of a basic strength on zeolitic support which in turn not only improves the catalyst properties but also limits the coke deposition [78]. The presence of oxygen atoms in the framework of zeolites generates intrinsic Lewis basic sites which form acid-base pairs with the charge compensating cations. The basicity of zeolite can be further increased by impregnating it with a solution of alkali metal salts which can be decomposed to form oxides upon calcination. The occlusion of alkali metal oxide clusters in the zeolite cages results in a further increase in basicity [79].

The present work aimed at catalytically converting PP and HDPE in a fixed-bed reactor at low temperature using various transition metal salts impregnated on zeolitic base as catalysts into useful products that could be used as fuel and feed-stock for



chemical industries. The emphasis was on high conversion and liquid products enrichment in desirable hydrocarbons.

Pyrolysis experiments of PP and HDPE over original and Fe, Co, Zn, Mn and Ni oxide impregnated PBCs were carried out. The influence of catalyst type and concentration on overall yields and yields of liquid, gas and residue was studied. Each catalyst was used in concentration range of 0.5-10 wt %. The results of catalytic viz. thermal run are presented in the subsequent section.

3.5.1. Activity Tests

3.5.1.1. Overall product yields

The influence of catalyst types and concentration on the overall yields was studied in case of PP and HDPE, separately. The results obtained are given in Table 3.30. The results obtained are discussed in comparison to un catalyzed run (thermal run).

In case of PP, the highest overall yields were achieved over Co/PBC, 1 % loading (99.95 wt %) and Fe/PBC, 1 % loading (99.81 wt %), while the lowest yield was obtained over non impregnated PBC, 10 % loading (85.75 wt %). No appreciable change in yield pattern was observed over other catalysts when compared with the thermal run (98.66 wt %). Based on the results, Co/ PBC and Fe/ PBC were found to be the most active catalysts in terms of overall yields particularly when used in low concentration (1 wt %). When these catalysts were used in highest concentration (10 %), the yield decreased sharply.

The catalytic activities of the original and variously impregnated PBCs were also evaluated in case of HDPE. The results are compiled in Table 3.30. It can be observed that the maximum overall yields achieved over Co/PBC, Mn/PBC and Zn/PBC, 1 % loading were found to be 99.84, 98.89, and 99.89 wt %, respectively. Upon comparing with thermal run (98.12 wt %), the yields were found to be almost unaffected. It is inferred from the results that the synergistic role of catalysts in enhancing the overall yields in most of the cases was not established particularly when used in higher concentrations, where a decline in yields was observed compared to thermal run.



3.5.1.2. Liquid yields

The influence of afore-mentioned catalysts on liquid yields was also studied. The yields as a function of catalyst type and its concentration are displayed in Table 3.30. It can be observed that the liquid yields greatly affected with the type and concentration of the catalysts used. It can be noticed that optimum yield of 96.7 wt% was achieved over Fe/PBC (2.5 wt % loading) followed by 91.1 wt% over Fe/PBC (1 wt % loading) when compared with un-catalyzed run (69.82 wt %). Catalyst like Zn/PBC (2.5 wt % loading) enhanced the liquid yield up to 90 wt% and showed a significant catalytic activity next to Fe/PBC. It can be observed that all catalysts when used in low concentration caused the liquid yields to increase by 2-26 wt%. However, with the increase in concentration beyond 2.5 wt %, the liquid yields decreased sharply (upto 56.3 wt %) particularly in case of pyrolysis over original PBC (10 wt% loading).

The influence of catalyst types and concentration was also studied in case of HDPE (Table 3.20). It can be observed that all the catalysts did not appreciably increase the yield of the liquid products, even when used in high concentrations, as compared to un-catalyzed run (80.88 wt %). In case of pyrolysis over Zn/PBC (5 % loading), an optimum yield of 93.60 % was achieved followed by 79.86 % over Mn/PBC (1 % loading) and 78.33 % over Fe/PBC (5 % loading). The yield got decreased up to 58.81 wt % in case of pyrolysis over original PBC (10 % loading) followed by 55.80 wt% achieved over Ni/PBC (10 % loading). It can be observed that the catalysts exhibited their effectiveness when used in low concentrations. As concentration was increased, the yields got declined.

It is inferred from the results that in case of PP, Fe/PBC (2.5 wt % loading) while in case of HDPE, Zn/PBC (5 % loading) were found to be the most active catalysts in term of formation of liquid products in high yields.

3.5.1.3. Gas yields

Gas yields were also studied in case of pyrolysis carried out with and without catalysts. The corresponding data is given in Table 3.30. It can be observed that all the



catalysts did not appreciably increase the yield. A significant variation can be observed in gas yields in most of the catalyzed runs when compared with uncatalyzed run. In case of pyrolysis of PP without catalysts, the gas yield was found to be 24 % which increased up to a maximum of about 29 % in case of pyrolysis carried out over original PBC. In case of pyrolysis over Fe/PBC and Zn/PBC (2.5 wt % loading), the gas yields declined upto 3 and 4 %, respectively which are quite low compared to un-catalyzed run. In case of increasing concentration using same catalysts, the gas yields increased. However, this increase was found to be at the expense of liquid yields as evident from the liquid yields. It was observed that during pyrolysis of PP, the gas yield was found to be inversely proportional to the yield of the liquid products.

Unlike the pyrolysis of PP, in case of HDPE, the yield of gas in un-catalyzed run was found to be about 17 % (Table 3.30). On the other hand, almost all catalysts gave high yield of gaseous products, except Zn/PBC (5 wt % loading) which gave the minimum gas yield of 6 %.

It is inferred from the results that HDPE is more susceptible to gas formation compared to PP particularly in the presence of catalysts when used in high concentrations.

3.5.1.4. Residue yields

The effect of catalysts on the residue yields was also studied, which remained unaffected in case of some of the catalyzed runs when compared with thermal run. In case of PP (Table 3.30). the yield of the solid residue in un-catalyzed run was found to be about 1.34 wt% which decreased significantly in case of pyrolysis over Fe/PBC catalyst (0.1 wt%). The concentration of the catalysts used greatly affected the formation of residue and it increased with the increase in concentration of the catalysts under study.

The yield of the solid residue in case of HDPE was almost unaffected compared to un-catalyzed run which was found to be 1.88 wt% whereas in case of pyrolysis over catalysts under study, it increased within a range of 2 -10 wt% (Table 3.30). The catalysts which significantly reduced the yield of solid residue were Co/PBC and Zn/PBC, when



used in concentration range of 2.5- 5 wt %, where less than 0.2 wt % yields were attained.

During all these runs, surprisingly no waxes were produced in contrast to the previously reported several studies [80-83] in spite of the fact that the temperature was not sufficiently high. However, several reasons have been reported for diverse product slates including negative and synergistic effects of the experimental conditions of temperature and residence time [84], plastic type [85], the type and concentration of catalysts [86], the type of reactor used [87], etc.

It is concluded from the above discussion that both catalyst type and concentration have influenced the yields of liquid, gas and solid residue. The increase in gas yields can be linked with the decrease in liquid yields. Similarly, the increase or decrease in residue yields can also be linked with the increase or decrease in gas or liquid yields. Among the two model polyolefins, PP was found to be more susceptible to catalytic cracking in terms of formation of liquid products in the presence of Fe/PCB compared to HDPE which showed susceptibility towards liquid formation in the presence of Zn/PCB. The highest yields achieved over Fe/PBC (surface area of $77.88 \text{ m}^2 \text{ g}^{-1}$) and Zn/PBC (surface area of $80.71 \text{ m}^2 \text{ g}^{-1}$) can be attributed to high surface area which in turn gave more sites for molecular level recombination reactions leading to the formation of liquid products.



Table -3.30. Yields of pyrolysates (over all yields and yields of liquid, gas and coke) derived from catalytic pyrolysis of PP over original and metal oxides impregnated PBCs as a function of catalyst type and concentration

Catalysts	Catalyst quantity (wt %)	Product yield of PP (%)				Product yield of HDPE (%)			
		Total yield	Liquid	Gases	Solid residue	Total yield	Liquid	Gases	Solid residue
No Cat.	0	98.66	69.82	28.84	1.34	98.12	80.88	17.24	1.88
PBC	0.5	90.48	70.27	20.21	9.52	93.59	70.20	23.39	6.41
	1	93.33	75.68	17.65	6.67	93.69	72.31	21.38	6.31
	2.5	88.19	66.34	21.85	11.81	91.86	63.78	28.08	8.14
	5	88.39	64.66	23.73	11.61	89.55	58.96	30.59	10.55
	10	85.75	56.30	29.45	14.25	89.07	58.81	30.26	10.93
Ni/PBC	0.5	98.29	83.47	14.82	1.71	94.22	65.3	28.92	5.78
	1	95.92	85.31	10.61	4.08	95.73	73.98	21.75	4.27
	2.5	98.32	89.57	8.75	1.68	93.2	60.30	32.9	6.80
	5.0	98.75	81.04	17.71	1.25	92.27	57.14	35.13	7.73
	10	98.28	80.11	18.17	1.72	92.04	55.80	36.24	7.96
Co/PBC	0.5	99.96	85.12	14.84	0.04	98.29	61.07	37.22	1.71
	1.0	99.95	86.75	13.2	0.05	99.84	63.81	36.03	0.16
	2.5	98.63	83.81	14.82	1.37	99.73	66.39	33.34	0.27
	5.0	92.78	76.65	16.13	7.22	99.60	68.21	31.60	0.32
	10	90.90	71.19	19.71	9.11	98.07	59.14	38.93	1.93
Fe/PBC	0.5	99.17	89.22	9.95	0.83	93.77	61.95	31.82	6.23
	1.0	99.81	91.01	8.80	0.10	95.85	64.86	30.99	4.15
	2.5	99.74	96.70	3.04	0.26	96.16	70.16	26.01	3.84
	5.0	96.03	78.02	18.01	3.97	97.88	78.33	19.55	2.16
	10	93.14	73.53	19.61	6.68	93.52	56.17	37.35	6.48
Mn/PBC	0.5	97.88	83.04	14.84	2.12	98.89	75.61	23.28	1.11
	1.0	95.77	85.32	10.45	4.23	99.24	79.86	19.38	0.76
	2.5	97.50	80.15	17.35	2.50	90.98	63.17	27.81	9.02
	5.0	91.17	70.63	20.54	8.83	90.77	63.01	27.76	9.23
	10	90.42	67.78	22.64	9.58	91.19	59.89	31.30	8.81
Zn/PBC	0.5	95.88	81.18	14.7	4.12	98.66	74.36	24.30	1.34
	1.0	99.04	86.73	12.31	0.96	98.69	77.16	21.53	1.31
	2.5	95.06	90.9	4.16	4.94	99.45	79.81	19.64	0.55
	5.0	93.46	77.35	16.11	6.54	99.88	93.60	6.28	0.12
	10	90.49	71.19	19.30	9.51	95.71	71.02	24.71	4.29



3.4.2. Liquid Product Composition

On the basis of highest liquid yields, Fe/PBC is reported to be highly active catalyst in case of PP and Zn/PBC in case of HDPE. The liquids obtained in case of pyrolysis over these catalysts were further submitted to compositional analyses by FTIR and GC-MS.

3.4.2.1. FTIR Analysis

FT-IR spectroscopy plays an important role in identification of functional groups in organic compounds. This spectroscopic technique is also extensively used in characterization of the pyrolytic oil obtained from waste polymers, to investigate the hydrocarbon types or functional groups in the liquid fractions. The FT-IR spectra of liquid products derived from PP and HDPE by thermal as well as catalytic pyrolysis, under optimum conditions is provided Fig 3.19, whereas the corresponding peaks data is compiled in Table 3.31. The FT-IR spectrum of liquid product derived from PP by thermal pyrolysis (Fig 3.19 a) features some strong absorption peaks appearing around 2953 and 2868 cm^{-1} which can be corresponded to aliphatic C-H stretching vibrations of methyl (CH_3) and methylene (CH_2). A weak absorption peak around 1620 cm^{-1} indicates olefinic C=C stretching can be corresponded to alkenes, and a strong absorption peak appearing at 1456 cm^{-1} can be ascribed to CH_2 bending vibrations. A medium weak absorption peak appearing at the wave number range of 1377 cm^{-1} indicates C-H scissoring and bending vibrations of alkanes. The results indicated that the liquid product under study is consisted of aliphatic and olefinic hydrocarbons.

The spectrum of the pyrolysate derived from PP using Co/BC as catalyst (Fig 3.19 b) shows identical configurations which can be corresponded to methyl, methylene and olefinic functionalities as observed in case of thermally derived liquid. However, the peak intensities corresponded to olefinic C=C found to be high than observed in case of thermally derived liquid product. Moreover, a new weak peak was also appeared at 1510 cm^{-1} which can be corresponded to C=C (olefinic). The results indicated that the relative proportion of olefins increased in case of catalytically derived liquid product.



The FT-IR spectrum of the pyrolytic liquid product obtained by thermal pyrolysis of HDPE (Fig 3.19 c) features strong absorption peaks mostly positioned at 2920 and 2852 cm^{-1} which can be corresponded to asymmetric stretching of C-H of CH_3 and CH_2 , respectively [29]. A weak absorption peak at 1525 cm^{-1} indicates C=C of olefins [31], and a medium peak centered at 1456 cm^{-1} shows CH_2 bending vibrations. The results indicated that the liquid product contained paraffinic and olefinic hydrocarbons, whereas no aromatics and oxygenates were found.

The spectrum of the catalytically derived liquid product from HDPE using Zn/BC (Fig 3.19 d) shows configurations almost identical to the thermal pyrolysate. The spectrum of the catalytic run exhibits peaks which can be corresponded to methyl, methylene and olefinic groups. A new peak of medium intensity was appeared at 2868 cm^{-1} can be corresponded to CH_2 (aliphatic) indicated that the olefins are less pronounced compared to thermal run.

3.5.1.2. GC-MS Analysis

Individual component analysis

As mentioned in the previous sections, that optimum yield of liquid was obtained from PP and HDPE in case of catalytic cracking using Fe/PBC and Zn/PBC catalysts, respectively; therefore, the compositional analysis of these fractions was carried out to investigate the type of hydrocarbons formed during the cracking reactions. The GC-MS spectra of the liquid products derived from PP using Fe/PBC and HDPE using Zn/PBC are provided in Fig. 3.20 and Fig. 3.21. Table 3.32 and Table 3.33 report the compounds identified in the derived liquid products from PP and HDPE.

In case of PP, the major naphthenic compounds included; 1,3,5-trimethyl (cis) cyclohexane, 1,3,5-trimethyl (trans) cyclohexane, 1,1-bicyclohexyl 2-(1-methylethyl), 1,2-dibutyl cyclopentane, 1,1-bicyclohexyl, 2-(methylethyl) (cis), and 2,4-diethyl-1-methyl cyclohexane.

Among the olefinic compounds, the most abundant were found to be 7-methyl-1-undecene, 4,5-dimethyl-2-undecene, 1,19-eicosadiene, 1-tricosene, 5-eicosene, (E), 2,4,6-



trimethyl-11-dodecene, , 2,3,4-trimethyl-4-tetradecene, 2,4,6-trimethyl-11-dodecene and 2,3,4-trimethyl-4-tetradecene.

The paraffinic hydrocarbons were present in high proportion, out of which the common compounds included 4-methyl heptane, 2,6-dimethyl nonane, 4-methyl decane, dodecane, 4,6-dimethyl decane, 2-isopropyl-5-methyl-1-pentane, 2-methyl-1-decane, 2,4-diethyl-1- heptane, 2-hexyl-1-decane, 4,6-dimethyl dodecane, 2-hexyl 1-decane, 3-isopropyl-5-methyl-1-heptane, 3,7,11,15-tetramethyl-1-hexadecane, 2,4-diethyl-1-heptane, 1-hentetracontane, 3,7,11, 15-tetramethyl, 1-hexadecane, and 4-diethyl-heptane,

In case of liquid product derived from HDPE in catalyzed run, the most common naphthenic compounds were found to be 1,2-dimethyl (trans)cyclopentane, 1-heptyl-2-methyl- cyclopropane, 2,4-diethyl-1-methyl cyclohexane and 1,1-bicyclohexyl 2-(methylethyl). Among olefinic compounds, the abundantly occurring compounds included; 5-tetradecene, 1-tridecene, 3-hexadecene, 1-pentadecene, 1-tetradecene, 11-hexadecene, 11-heptadecene, 1-tricosene, 11-heptadecene, and Z-5-nonadecene.

Like liquid pyrolysate of PP, in case of liquid oil derived from HDPE, the paraffinic compounds were present in greater concentration. The most abundant paraffinic hydrocarbons included nonane, undecane, dodecane, pentadecane, 2,6,11-trimethyl- dodecane, hexadecane, nonadecane, heneicosane, heptadecane, 2,6,10,14-tetramethyl- hexadecane, n-docosane, 17-octadecane, tetratetracontane, tetratriacontane, octacosane, and 8-hexyl pentadecane.

C-number distribution

GC-MS analysis was carried out to decide about the C-number distributions in the thermal and catalytically derived liquids. Results of C-number distributions are provided in Table 3.34 which indicated that the catalyst used greatly affected the composition of the derived liquids. In case of PP derived liquid from the thermal run, the % distributions of different carbon range products i.e. C₆-C₁₂, C₁₃-C₁₆, C₁₇-C₂₀, and > C₃₀ were found to be 15.16, 33.04, 18.77, 24.97 and 8.05 wt %, respectively. Whereas in case of liquid derived from pyrolysis over Fe/PBC catalyst, the distributions were altered significantly.



The yield of C₆-C₁₂ range hydrocarbons was increased by 32 %, whereas the yields of C₁₃-C₁₆, C₁₇-C₂₀, C₂₁-C₃₀ and >C₃₀ range hydrocarbons were reduced by 7, 2, 22 and 3 %, respectively. The results indicated that the catalyst exhibited high activity in enhancing the formation of light hydrocarbons.

Similarly, the % distributions of different carbon range products i.e. C₆-C₁₂, C₁₃-C₁₆, C₁₇-C₂₀, and > C₃₀ in the liquid product derived from HDPE thermal pyrolysis were found to be 32.56, 30.80, 14.19, 12.35 and 10.95 wt %, respectively. Where their levels in case of pyrolysis over Zn/PBC were found to be 13.09, 35.67, 31.88, 11.09 and 7.8 %, respectively. Unlike PP, here the catalyst enhanced the yields of middle range hydrocarbons i.e. C₁₃-C₁₆ and C₁₇-C₂₀ by 4 and 16 % , respectively, whereas the yield of low carbon range products (C₆-C₁₂) was decreased by about 19 % while that of high carbon range products (>C₂₁) remained the same.

It can be observed that the catalysts used altered the product distribution of light and middle carbon range products and did not affect the formation of heavy carbon range products in case of both polyolefins. As the emphasis of the present study was to get enrichment of the derived liquids in low to middle carbon number hydrocarbons, hence the activities of these catalysts were established in converting PP predominantly into lighter and HDPE into middle range hydrocarbons.

Hydrocarbon group types

The catalysts also affected the hydrocarbon group type's distribution in the derived liquid products i.e. the yields of the alkanic and alkenic contents (olefins, and non-aromatic hydrocarbons branched hydrocarbons, etc.). Results compiled in Table 3.35 showed that in case of liquid product derived from PP in thermal run gave the paraffinic, olefinic and naphthenic contents of 66.55, 25.87 and 7.58%, respectively. Whereas in case of pyrolysis over Fe/PBC, their levels were found to be 64.81, 21.07 and 13.45 %, respectively. The results showed that Fe/PBC has enhanced the formation of naphthenes and reduced the formation of olefins, whereas the formation of paraffins remained unaffected. The formation of paraffins and olefins are reported to be produced by a different degradation mechanisms [88]. Paraffins are produced by random scission mechanism and



olefins by end-chain scission of large straight hydrocarbon intermediates. The results indicated that the catalyst has favored the random scissions rather than end chain scissions. The naphthenes were increased which are considered to be resulted due to cyclization of light straight hydrocarbons [88]. The results indicated that the catalyst assisted some cyclization reactions and yielded naphthenic hydrocarbons.

In case of HDPE, the yields of paraffins, olefins and naphthenes in un-catalyzed (thermal) were found to be 59.70, 31.90 and 8.40 %, respectively, whereas the catalyzed run gave yields of 74.09, 22.21 and 3.7 %, respectively. The results showed that Zn/PBC has significantly increased the formation of paraffinic hydrocarbons and decreased the naphthenic hydrocarbons to almost 60 %. As far as HDPE results are concerned, these can be rationalized in terms of a carbonium ion mechanism involving extensive skeletal isomerization and attendant β -cleavage reactions leading to formation of low branched paraffins as final products.

It is inferred from the results that catalytic effects prevailed over the thermal one and has changed the composition of liquid products in terms of hydrocarbon group types by producing liquids having predominantly naphthenes in case of PP and paraffins in case of HDPE compared to thermal run. Paraffins (multibranched) are desired hydrocarbons which represent potential blending components for reformulated, non-aromatic gasoline [89]. Hence these catalysts can be recommended to be useful in conversion of both polyolefins into products having fuel value.



Table -3.31. Major absorption peaks observed and assigned configurations in the FT-IR spectra of the liquid products derived from catalytic pyrolysis of PP and HDPE over PBCs

Sample	Position (cm ⁻¹)	Intensity	Assigned configuration
Thermal pyrolysis of PP	2953	strong	CH ₃ (aliphatic)
	2868	strong	CH ₂ (aliphatic)
	1620	weak	C=C (Olefinic)
	1456	strong	CH ₂ bending
	1375	medium	C-H scissoring/bending
	887	strong	C-H (olefinic)
Catalytic pyrolysis of PP using Co/BC	2954	strong	CH ₃ (aliphatic)
	2912	strong	CH ₂ (aliphatic)
	1625	weak	C=C (Olefinic)
	1510	weak	C=C (Olefinic)
	1456	strong	CH ₂ bending
	1377	medium	C-H scissoring/bending
	887	strong	C-H (olefinic)
Thermal pyrolysis of HDPE	2920	strong	CH ₃ (aliphatic)
	2852	strong	CH ₂ (aliphatic)
	1525	weak	C=C (olefinic)
	1456	medium	CH ₂ bending
	908	strong	C-H (olefinic)
Catalytic pyrolysis of HDPE using Zn/BC	2953	strong	CH ₃ (aliphatic)
	2912	strong	CH ₂ (aliphatic)
	2868	medium	CH ₂ (aliphatic)
	1456	medium	CH ₂ bending
	1377	medium	C-H scissoring/bending
	887	strong	C-H (olefinic)

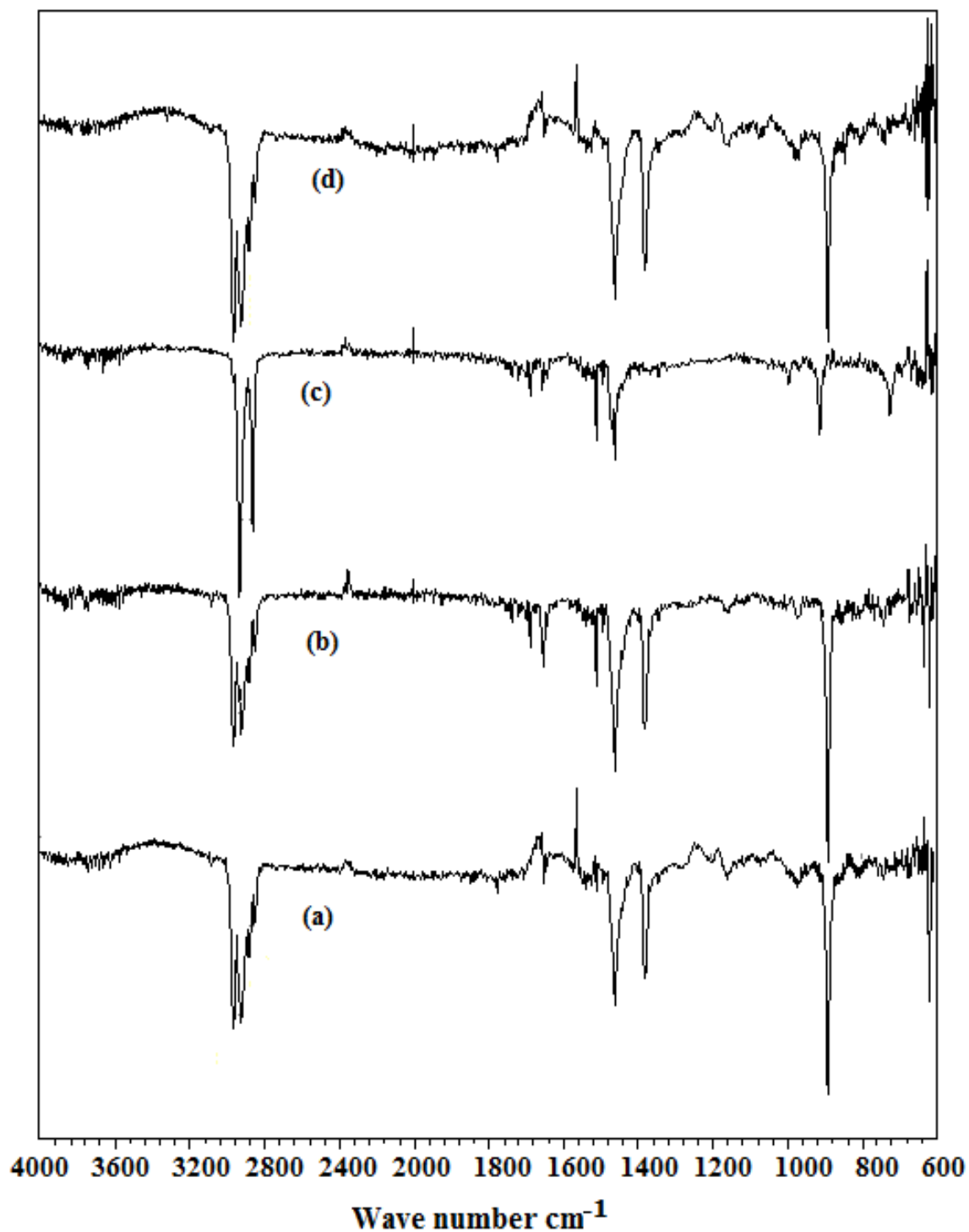


Fig. 3.19. FT-IR spectra of the liquid products derived from thermal and catalytic pyrolysis of polyolefins over PBCs (a) PP thermal run (b) PP catalyzed run (c) HDPE thermal run (d) HDPE catalyzed run.

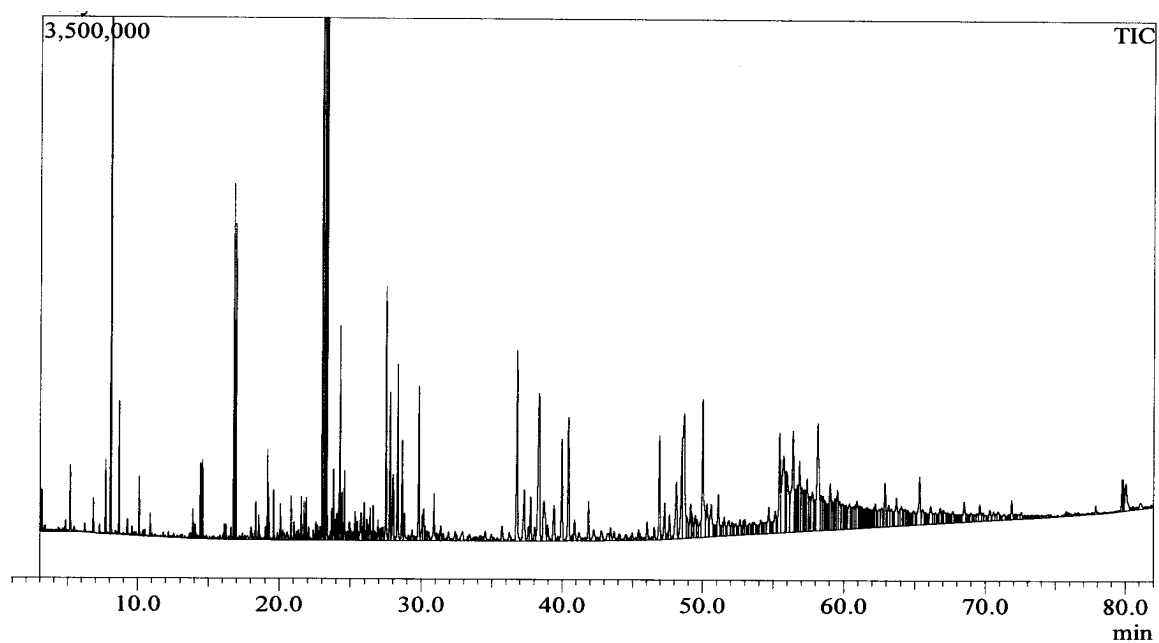


Figure-3-20. GC-MS spectrum of liquid product derived from PP by pyrolysis in the presence of Fe/PBC

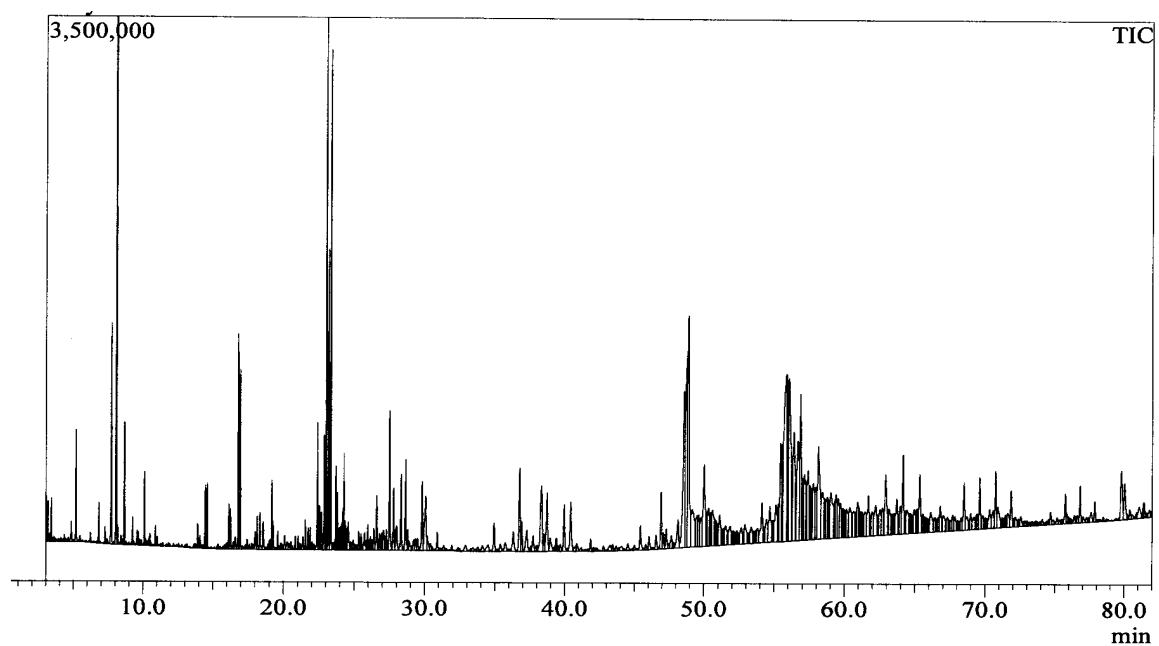


Figure 3.21. GC-MS spectrum of liquid product derived from HDPE by pyrolysis in the presence of Zn/PBC

**Table 3.32.** Hydrocarbons identified in the liquid products derived from catalytic pyrolysis of PP over Fe/PBC

ID#	Compound	t _R	% peak area/ relative conc.
Naphthenes			
1.	3-Dimethyle cyclopentane	3.047	0.36
2.	Cyclopentane, 1,2-dimethyl, cis	3.097	0.2
3.	Cyclopentane, 1,2-dimethyl, trans	3.148	0.33
4.	Cyclopentane, 1,1,3,4-tetramethyl, cis	6.836	0.42
5.	Cyclohexane, 1,3,5-trimethyl, cis	7.71	1.23
6.	Cyclohexane, 1,3,5-trimethyl, trans	8.671	2.12
7.	Cyclohexene, 3,5,5-trimethyl, cis	9.263	0.18
8.	Cyclohexane, eicosyl	16.258	0.18
9.	1-Isopropyl-1,4,5-trimethylcyclohexane	16.61	0.21
10.	2,4,6- Trimethylcyclohexane	19.187	0.07
11.	Cyclohexane, 2,4-diethyl-1-methyl -	19.614	1.15
12.	Cyclohexane, 1,2-diethyl-3-methyl -	20.097	0.63
13.	Cyclohexane, 1,1'-(1,5-pentanediy)bis	24.117	0.15
14.	1,1-Bicyclohexyl, 2-(1-methylethyl) -	29.821	2.31
15.	Cyclopentane, 1,2-dibutyl -	40.876	1.51
16.	1,1-Bicyclohexyl, 2-(methylethyl)- trans	58.153	2.31
Total concentration (%)			13.45
Olefins			
17.	1-Nonene	10.104	0.92
18.	1,6-Octadiene, 2,6-dimethyl (Z)	10.893	0.28
19.	2-Decene, 4-methyl-, (Z)	14.083	0.18
20.	2-Decene, 2,4-dimethyl -	16.148	0.30
21.	1-Undecene, 7-methyl -	16.814	2.46
22.	2-Undecene, 4,5-dimethyl -	16.955	2.32
23.	1-Undecene, 5-methyl -	18.353	0.36
24.	2-Undecene, 8-methyl, (Z)	18.572	0.23
25.	3-Undecene, 8-methyl -	19.048	0.10
26.	1,7-Nonadiene, 4,8-dimethyl -	19.272	0.57
27.	1-Dodecene	20.636	0.02
28.	2-Undecene, 4,5-dimethyl -	21.051	0.21
29.	2-Heptene, 5-ethyl-2,4-dimethyl -	22.387	0.15
30.	9-Eicosene, (E)	23.955	0.13
31.	5-Eicosene, (E)	24.045	0.21



32.	3-Eicosene, (E)	24.193	0.25
33.	1,19-Eicosadiene	24.269	1.57
34.	18-Nonadecene	24.408	0.31
35.	3-Hexadecene, (Z)	24.697	0.02
36.	7-Tetradecene, (E)	24.921	0.20
37.	2-Methyl-2-docosene	25.486	0.16
38.	1-Tricosene	28.648	1.03
39.	5-Eicosene, (E)	39.969	1.66
40.	11-Dodecene, 2,4,6-trimethyl -	40.443	1.09
41.	4-Tetradecene, 2,3,4-trimethyl -	41.872	1.14
42.	11-Dodecene, 2,4,6-trimethyl -	50.005	3.02
43.	4-Tetradecene, 2,3,6-trimethyl -	51.125	0.70
44.	4-Tetradecene, 2,3,4-trimethyl -	59.036	1.48
Total concentration (%)			21.07
Paraffins			
45.	Heptane	3.31	0.55
46.	Heptane, 4-methyl -	5.18	2.38
47.	Heptane, 2,4-dimethyl -	7.284	0.18
48.	Nonane, 2,6-dimethyl -	14.447	1.53
49.	Decane, 4-methyl -	14.597	1.67
50.	Decane, 2,4-dimethyl -	16.148	0.32
51.	Undecane	17.601	0.03
52.	Hexane, 5-methyl-2-(1-methylethyl) -	21.553	0.37
53.	Dodecane, 4,6-dimethyl -	21.751	2.04
54.	Decane, 2,3,5,8-tetramethyl -	21.904	3.31
55.	2-Isopropyl-5-methyl pentane	23.021	6.01
56.	Decane, 2-methyl -	23.182	4.46
57.	Heptane, 2,4-diethyl -	23.339	5.55
58.	Decane,2-hexyl -	23.804	1.45
59.	Pentadecane	24.825	0.64
60.	Dodecane, 4,6-dimethyl -	25.969	2.36
61.	Decane, 3,3,6-trimethyl -	26.161	0.27
62.	Dodecane, 4,6-dimethyl -	26.394	0.36
63.	Octane, 2-butyl -	26.599	0.32
64.	Decane, 2-hexyl -	27.506	2.56
65.	3-Isopropyl-5-methyl heptane	28.33	2.14
66.	Hexadecane, 3,7,11,15-tetramethy -	28.805	2.57
67.	Dodecane, 2,6, 11-trimethyl -	30.411	0.15
68.	Heptane, 2,4-diethyl -	38.349	4.11



69.	Nonadecane	40.742	0.58
70.	Cyclopentane, 1,2-dibutyl -	40.876	1.51
71.	Hentetracontane	46.932	2.79
72.	Octane, 4-butyl -	47.304	1.64
73.	Hexadecane, 3,7,11, 15-tetramethyl -	47.658	3.39
74.	Heptane, 4-diethyl -	48.137	2.31
75.	Pentatriacontane	55.448	1.25
76.	Tetrapentacontane	56.397	1.12
77.	Hentetracontane	56.856	0.38
78.	Docosane	57.569	1.53
79.	Octadecane	61.109	2.05
80.	Tetratetracontane	64.296	0.12
81.	Tetratriacontane	67.671	0.35
82.	Pentacosane	70.32	0.22
83.	Octacosane	70.582	0.24
Total concentration (%)			64.81

Fe/PBC: 2.5 wt % loading

Table 3.33. Hydrocarbons identified in the liquid products derived from catalytic pyrolysis of HDPE over Zn/PBC

ID#	Compounds name	R.Time	% peak area/ relative conc.
Naphthenes			
1.	3-Dimethylcyclopentane	3.045	0.36
2.	Cyclopentane, 1,2-dimethyl, cis	3.095	0.16
3.	Cyclopentane, 1,2-dimethyl, trans	3.147	0.45
4.	Cyclohexane, methyl -	3.882	0.05
5.	2,4-Dimethyl-1-heptene	8.049	0.03
6.	Cyclopropane, 1-heptyl-2-methyl -	13.913	1.38
7.	Cyclohexane, 2,4-diethyl-1-methyl -	19.921	0.01
8.	1,1-Bicyclohexyl, 2-(methylethyl) -	23.844	1.13
9.	Cyclohexane, 1,1-(1,5-pentanedimethyl)	23.844	0.13
Total concentration (%)			3.7
Olefins			
10.	1-Octene	6.119	0.29
11.	2,4-Dimethyl-1-heptene	8.049	0.03
12.	1-Undecene, 5-methyl -	18.04	0.03
13.	1-Dodecene	20.582	0.53



14.	5- Tetradecene, (E)	20.931	1.12
15.	1- Tridecene	22.863	1.64
16.	3-Hexadecene, (Z)	24.683	1.94
17.	2-Methyl-2-docosene	25.057	0.01
18.	1,9- Tetradecadiene	26.704	0.76
19.	1-Pentadecene	26.897	1.82
20.	1-Pentadecene	30.118	1.83
21.	1- Tetradecene	35.04	1.78
22.	5-Eicosene	39.959	0.13
23.	11-Hexadecene	40.329	1.74
24.	Octadecene, (E)	41.48	0.16
25.	1, 15-Hexadecadiene	44.802	0.26
26.	11-Heptadecene	45.12	1.83
27.	1- Tricosene	45.634	2.16
28.	11- Heptadecene	53.542	1.56
29.	Z-5-Nonadecene	64.271	1.87
30.	1,37-octatriacontadiene	65.361	0.01
31.	9-Hexacosene	67.493	0.56
32.	9-Tricosene, (Z)	73.552	0.15
Total concentration (%)			22.21
Paraffins			
33.	Heptane	3.307	0.55
34.	5-Cyclohexane, methyl -	3.882	0.05
35.	Octane	6.453	0.87
36.	Nonane	10.457	2.68
37.	Undecane	17.617	2.11
38.	Dodecane	20.8	3.59
39.	Pentadecane	24.83	4.30
40.	Dodecane, 4,6-dimethyl -	25.793	1.64
41.	Decane, 3,3,6-trimethyl -	25.793	0.53
42.	Tetradecane	27.095	4.8
43.	Dodecane, 2,6, 11-trimethyl -	30.41	4.99
44.	Hexadecane	35.433	5.10
45.	Nonadecane	40.676	5.32
46.	1 Heneicosane	45.432	5.55
47.	Heptadecane	49.774	5.64
48.	Hexadecane, 2,6, 10, 14-tetramethyl -	53.786	5.61
49.	Docosane	57.549	5.31
50.	Octadecane	61.09	4.57



51.	Tetratetracontane	64.451	3.70
52.	Tetratriacontane	67.663	2.72
53.	Octacosane	70.726	1.87
54.	Pentadecane, 8-hexyl -	73.681	1.22
55.	Hexatriacontane	76.531	0.79
56.	Triacontane	79.271	0.58
Total concentration (%)		74.09	

Zn/PBC: 5 wt %

Table 3.34. C-number distribution in liquids product from catalytic pyrolysis of PP and HDPE over PBCs

Polyolefin	Catalyst*	Distribution (%)				
		C ₆ -C ₁₂	C ₁₃ -C ₁₆	C ₁₇ -C ₂₀	C ₂₁ -C ₃₀	> C ₃₀
PP	No catalyst	15.16	33.04	18.77	24.97	8.05
	Fe/PBC	47.98	26.34	16.24	2.86	5.92
HDPE	No catalyst	32.56	30.80	14.19	12.35	10.95
	Zn/PBC	13.09	35.67	31.88	11.09	7.80

*Fe/PBC: 2.5 wt %, Zn/PBC: 5 wt %

Table 3.35. Hydrocarbon group types distributions in liquid product derived from catalytic pyrolysis of PP and HDPE over PBCs

Polyolefins	Catalyst*	Distribution (%)			
		Paraffins	Olefins	Naphthenes	Aromatics
PP	No catalyst	66.55	25.87	7.58	0.00
	Fe/PBC	64.81	21.08	13.45	0.00
HDPE	No catalyst	59.70	31.90	8.40	0.00
	Zn/PBC	74.09	22.21	3.70	0.00

* Fe/PBC: 2.5 %, Zn/PBC: 5 wt %



3.6 CATALYTIC PYROLYSIS OVER TYPE C CATALYSTS (METAL OXIDES SUPPORTED BENTONITES)

The pyrolysis reactions of PP and HDPE were carried out in the presence of metal oxides impregnated bentonites as catalysts (BC, Zn/BC, Cr/BC, Ni/BC, Co/BC, Fe/BC, and Mn/BC), separately. Catalytic runs were pyrolyzed at 300 in case of PP and at 350 °C in case of HDPE for time duration of 30 minutes. The effect of individual catalysts and their concentration on overall yields and yields of liquid, gas and residue was studied.

Pillared clays are enjoying popularity as catalysts in a variety of processes including cracking, hydro-isomerisation, dehydration, dehydrogenation, hydrogenation, aromatisation, disproportionation, esterification, alkylation and selective catalytic reduction [90] owing to their textural and chemical properties. Among these, bentonites as catalysts have been the focus of many researchers for hydrocracking of heavy fuel oils owing to their high surface areas [91]. Different types of bentonites, named after the respective dominant element, such as potassium (K), sodium (Na), calcium (Ca), and aluminum (Al) have been only recently reported as catalysts for polymer degradation [92]. However, there is insufficient literature regarding the use of metal oxides impregnated bentonites as catalysts or support for plastics degradation.

In the present work, original (Al-Si-dominant) and various metal oxides impregnated bentonites were used to evaluate their catalytic effects in cracking of polyolefins (PP and HDPE). The activity of each individual catalyst in term of yields of end products (liquid, gas and residue) particularly liquid products and the selectivity in terms of C-number (C_6 - $>C_{30}$ hydrocarbons) as well as hydrocarbon group types distributions (paraffins, naphthene, olefins and aromatics) in the liquid products are reported.

The influence of acid modified and variously impregnated BCs on the pyrolysis behavior of polyolefins under study was studied. The yields of pyrolysates i.e. overall yields and yields of liquids, gas, and solid residue as a function of individual catalysts and their concentration are provided in Table. 3.36.



3.6.1. Activity Tests

3.6.1.1. Overall product yields

The influence of acid modified and variously impregnated BCs on overall conversion was studied. The yields as a function of catalyst type and concentration are provided in Table 3.36. The results indicated that the overall yields did not change significantly in most of the catalyzed runs when compared with un-catalyzed run in case of both polyolefins except Co/BC and Zn/BC. In case of PP, Co/BC caused the total yield to increase and attained a value of 99.32 wt% when used in 1 % concentration and in case of HDPE, Zn/BC gave maximum total yield of 99.84 wt% when used in 2.5 wt% concentration. The rest of the catalysts caused the overall yield to decrease. This decrease went up to 97 and 70 wt% in Ni/BC catalyzed runs in case of PP and HDPE, respectively.

From the results, it can be observed that the yields did not affect to a greater extent with the increase in concentration.

3.6.1.2. Liquid yields

The influence of catalysts under study on liquid yields was also studied. The data is provided in Table 3.36. The results indicated that metal oxide impregnated catalysts exhibited a pronounced effect on the product spectrum in terms of formation of liquid products. It can be observed from the compiled results that among the catalysts used, Co/BC and Zn/BC produced a much greater amount of liquid products compared to other catalysts under study. The liquid yields derived from PP and HDPE in thermal runs were found to be 69.82 and 80.88 %, respectively. In case of pyrolysis of PP, the increase went up to a maximum of 92 % in Co/BC catalyzed run when used in 1% concentration. Similarly, in case of HDPE, the liquid yield enhanced to 91 wt% in Zn/BC catalyzed run when used in 2.5 % concentration.

It can be concluded from the compiled results that the use of catalysts particularly Co/BC and Zn/BC caused a significant increase in the liquid yields when compared with the un-catalyzed run. The results indicated negligible and insignificant effect of increase in their concentration. The reason can be thought is catalytic sites must co-exist within



appropriate molecular distances in case of bi functional catalysts. In higher concentration, the metal ions may disperse in such a fashion that causes inappropriate location of the active sites on surface and within the matrix which in turn can prevent concerted interactions leading to the desired products [93].

It is well established that pyrolysis is initiated by the abstraction of the hydride ion (by Lewis acid sites of the catalyst) from the polymer macromolecule or the addition of a proton (by Brönsted acid sites of the catalyst) to the C–C bonds. Successive scissions of the main chain occur to produce fragments having lower molecular weight liquid products. The resulting decomposed fragments are further cracked in the subsequent steps to yield gas products. The high liquid yields indicated the suppression of overcracking reactions by the catalysts under test to yield small molecules (gas). Such over cracking reactions are responsible for the formation of gas as earlier reported [50].

Variation in liquid yield derived from PP and HDPE can be explained on the basis that the catalysts under study particularly Zn/BC and Co/BC might have facilitated reactions initiated by abstraction of the hydride ion or the addition of a proton due to the inherent acidity or acidity variations incorporated into BC upon impregnation of the metal ions. In addition to acidities, the role of the surface properties of the catalysts can also be thought the solid reason. Hence, the acidity and pore characteristic appeared to be mainly responsible for the catalytic performance shown by Co/BC and Zn/BC in terms of producing maximum liquid yields. It is also apparent from the results indicated that the liquid yields are more significant in case of PP compared to HDPE. The reason can be thought is the onset of overcracking reactions favored in case of HDPE. The acidic sites present in the catalysts play a vital role in the formation of liquid, gas and solid residue as reported earlier. The attack by the acidic sites on the main polymer chains, yield oligomers, which undergo β -scission of chain-end carbonium ions thereby forming gas along with a liquid fraction [94]. Hence, next to acidity of the catalyst, the main polymer chains also have to play a role, thereby giving diversity in product yields.



3.6.1.3. Gas yields

Considerable variations in gas yields as a function of catalyst type and concentration can be observed from the data compiled in Table 3.36. However, the general trend of increase with the increase in concentration can be observed. The gas yields in case of PP and HDPE (thermal run) were found to be 28.84 and 17.24 wt %, respectively. The maximum gas yield of 28.24 wt % was attained in run catalyzed with Fe/BC when used in 10% concentration in case of PP, whereas 39.91 wt% was achieved in run catalyzed with Co/BC when used in 10 % concentration in case of HDPE. It can be observed that most of the catalysts produced insignificant gas yields in case of PP compared with the thermal run, among which Co/BC gave the lowest yield of 6 wt% when used in 1% concentration. However, in case of HDPE, the gas yields obtained in most of the catalyzed runs were higher than achieved in case of thermal run, except Zn/BC which produced the lowest yield of gas (8.89 %) when used in 5 % concentration. In general, the formation of gas is favored with the increase in concentration of the catalyst. This indicated that when used in higher concentration, the catalysts under study might have favored the over cracking reactions leading to formation of predominantly gaseous products.

3.6.1.4. Residue yields

The residue amount as a function of catalyst type and concentration is provided in Table 3.36. It can be observed that in case of some catalyzed runs, the yields remained unaffected and were similar to the ones obtained in case of thermal pyrolysis of both PP and HDPE. However, in some of the catalyzed runs, the amount was considerably reduced even to < 1 wt% i.e. For instance, Co/BC and Zn/BC yielded 0.68 and 0.11 wt % residues in case of PP and HDPE, respectively. In general, the formation of residue decreased with the increase in concentration of the catalysts used.

It is concluded that among the impregnated catalysts, Co/BC and Zn/BC exhibited high activities in terms of maximum liquid yields in cases of PP and HDPE, respectively. On the basis of the maximum yields attained, these catalysts are reported to be the highly active catalysts for pyrolysis of PP and HDPE. The effect of increase in concentration



Table 3.36. Yields of pyrolysates (over all yields and yields of liquid, gas and coke) derived from catalytic pyrolysis of PP and HDPE over original and metal oxides impregnated BCs as a function of catalyst type and concentration.

Catalyst	Catalyst quantity (wt %)	Product yield of PP (%)				Product yield of HDPE (%)			
		Total yield	Liquid	Gases	Solid residue	Total yield	Liquid	Gases	Solid residue
No Cat.	0	98.66	69.82	28.84	1.34	98.12	80.88	17.24	1.88
BC	0.5	80.9	60.91	19.99	19.1	79.87	57.46	22.41	20.13
	1.0	83.13	62.38	20.75	16.87	86.09	67.51	18.58	13.91
	2.5	84.39	65.76	18.63	15.61	86.93	70.19	16.74	13.07
	5.0	84.63	68.77	15.86	15.37	79.38	56.63	22.75	20.62
	10	79.72	59.35	20.37	20.28	78.93	55.97	22.96	21.07
Ni/BC	0.5	98.12	80.36	17.76	1.6	74.39	46.82	27.57	25.61
	1.0	99.09	82.91	16.18	0.91	73.61	49.07	24.54	26.39
	2.5	99.33	83.07	16.26	0.67	75.81	58.48	17.33	24.19
	5.0	99.46	84.97	14.49	0.54	75.77	56.50	19.27	24.23
	10	97.20	77.65	19.55	2.80	70.92	45.89	25.03	29.08
Co/BC	0.5	98.21	84.36	13.85	1.79	87.5	49.98	37.52	12.5
	1.0	99.32	92.76	6.56	0.68	87.55	62.07	25.48	12.45
	2.5	97.70	81.75	15.95	2.30	88.64	69.31	19.33	11.36
	5.0	96.46	75.66	20.80	3.54	88.33	52.09	36.24	11.67
	10	94.94	73.95	20.99	5.06	87.97	48.06	39.91	12.03
Fe/BC	0.5	96.02	71.46	24.56	3.98	92.14	60.86	31.28	7.86
	1.0	96.84	82.8	14.04	3.16	92.46	63.05	29.41	7.54
	2.5	96.89	82.78	14.11	3.11	93.68	66.36	27.32	6.32
	5.0	94.61	68.39	26.22	5.39	93.82	71.34	22.48	6.18
	10	92.96	64.64	28.32	7.04	90.56	52.89	37.67	9.44
Mn/BC	0.5	97.99	71.54	26.45	2.01	68.5	42.00	26.50	31.5
	1.0	98.92	79.23	19.69	1.08	68.5	42.16	26.34	31.50
	2.5	99.24	80.4	18.84	0.76	71.76	46.35	25.41	28.24
	5.0	96.39	69.91	26.48	3.61	73.9	52.71	21.19	26.10
	10	96.21	66.36	29.85	3.79	71.47	43.9	27.57	28.53
Zn/BC	0.5	95.24	75.34	19.9	4.76	97.83	78.6	19.23	2.17
	1.0	96.91	77.13	19.78	3.09	98.64	81.07	17.57	1.36
	2.5	98.40	82.50	15.90	1.60	99.89	91.00	8.89	0.11
	5.0	94.60	72.89	21.71	5.40	97.50	76.54	20.96	2.50
	10	90.67	68.13	22.54	9.33	94.91	63.11	31.80	5.09



was observed only in case of gas yields particularly during pyrolysis of HDPE, which indicated that HDPE is more susceptible to degradation to give gas compared with PP at high catalyst polymer ratios. Based on the results, it is suggested that BC in impregnated forms can be used as active catalysts for pyrolysis of polyolefins under study into useful products.

3.6.2. Liquid Products Composition

The liquid products obtained in case of catalyzed runs (Co/BC and Zn/BC) were submitted to further compositional analysis by FTIR and GC-MS.

3.4.2.2. FTIR Analysis

FT-IR analysis of the pyrolysis oils derived from PP and HDPE in thermal as well as catalytic runs was carried out in order to know about the nature of the hydrocarbons produced in terms of various functional groups present in the liquid fractions. The results are given in Table 3.37 and Fig. 3.22 (a-d) which indicated that the pyrolysis liquid products contained almost same chemical configurations.

The spectrum of PP thermally derived liquid product is provided in Fig. 3.22 (a) which shows a number of major and minor absorption peaks having different intensities (weak and strong) in the selected scanned wave number range of $4000\text{--}400\text{ cm}^{-1}$. The spectrum features several strong peaks in the wave number range of 2922 , 2852 , and 1456 cm^{-1} which can be corresponded to methyl, methylene, and CH_2 bending vibrations, respectively. The spectrum of catalytically derived liquid fraction (Fig. 3.22 b) exhibits several peaks mostly appearing at 2920 , 1545 and 1456 cm^{-1} . Comparing results obtained in case of thermal and catalytically derived liquids, it is evident that the catalyst used did not cause the two bands to shift. However, the band in case of thermal run at 2852 cm^{-1} was disappeared and a new band of weak intensity appeared at 1545 cm^{-1} , which can be confidently corresponded to $\text{C}=\text{C}$.

The spectrum of the thermally derived liquid fraction in case of HDPE features several strong peaks in the wave number range of 2920 , 2853 and 1454 cm^{-1} (Fig. 3.22 c). It is evident from the spectrum that no major changes occurred compared with the



thermally derived liquid fraction. The FT-IR spectrum (Fig 3.22 d) of the catalytically derived liquid product from HDPE shows pronounced peaks appearing at 2954, 2912, 1510, 1550, and 1456 cm^{-1} , which indicated CH_3 (aliphatic), CH_2 (aliphatic), $\text{C}=\text{C}$ (olefinic) and CH_2 bending vibrations. Upon comparing the spectra, it is evident that some new peaks were appeared mostly positioned 1510, and 1550 cm^{-1} , which can be corresponded to $\text{C}=\text{C}$ (olefinic). No peaks in the wave number range corresponded to OH stretching vibration can be observed in all spectra which indicated the absence of water and oxygenates.

The results confirmed the presence of $\text{C}-\text{CH}_3$, CH_3 , $\text{CH}=\text{CH}$, and $\text{C}-\text{C}$ (ring) groups in all of the derived liquids. Hence, it is concluded that the liquid oils were mostly consisted of paraffinic, olefinic and naphthenic hydrocarbons, whereas aromatics and oxygenates were absent. As far as the catalytic effects are concerned, they were found beneficial in terms of producing olefins in case of both polyolefins.

3.4.2.3. GC-MS Analysis

Individual component analysis

The main components of the liquid products obtained by pyrolysis were identified by GC-MS (Fig.3.23). The results are presented in Table 3.38 & Table 3.39. Among the naphthenes identified in the liquid product derived from PP included 1,3,5-trimethyl cyclohexane, 2, 4, 6- trimethylcyclohexane and 1,1-bicyclohexyl, 2-(1-methylethyl)-trans, whereas among olefins; 2, 4-dimethyl-heptene, 7-methyl I-undecene, 4, 5-dimethyl 2-undecene, 5-ethyl-2,4-dimethyl 2-heptene, 2, 4, 6-trimethyl dodecene, 4-2, 3, 4-trimethyl tetradecene, etc. were the most abundant components. It can be seen that in case of PP, out of different paraffins; heptane, 4-methylheptane, 2, 6-dimethyl nonane, dodecane, 2-isopropyl-5-methyl-1-heptane, 2,4-diethyl-I-heptane, and 1-hentetracontane

Similarly, in case of HDPE (Fig. 3.24), the most occurring compounds among naphthenes were; 1-heptyl-2-methyl cyclopropane, methyl cyclohexane, and out of olefins were; 1-nonene, 3-hexadecene 1-dodecene, 1-pentadecene, 1-tetradecene, 1-hexadecene



and 9-tricosene. Among paraffins, the different compound identified were; heptane, octane, nonane, undecane, pentadecane, hexadecane, nonadecane, 2, 6, 10, 1 4-tetramethyl adecane, and 8-hexyl pentadecane.

C-number distribution

The carbon number distributions of the liquid products derived from PP and HDPE were studied by GC-MS analysis. The results obtained are provided in Table 3.40.

In case of un-catalyzed run of PP, the yields of different hydrocarbon range products i.e. C₆-C₁₂, C₁₃-C₁₆, C₁₇-C₂₀, C₂₁-C₃₀ and > C₃₀ were found to be 15.16, 33.04, 18.77, 24.97 and 8.05 %, respectively. In case of Co/AWBC catalyzed run, the yield of lighter range hydrocarbons i.e. C₆-C₁₂ was increased significantly i.e. all most four folds (60.18 %). Similarly, the yield of heavy C-range products i.e. > C₃₀ was also increased and attained a value of 12 %. On contrary, the yield of middle C-range products was decreased significantly. This increase in yield of light products and corresponding decrease in the middle range products can be explained on the basis of successive scissions occurred in heavy oligomers which produced fragments having low molecular weight.

In case of liquid fraction derived from HDPE thermal run, the yields of different C-range products i.e. C₆-C₁₂, C₁₃-C₁₆, C₁₇-C₂₀, C₂₁-C₃₀ and > C₃₀ in thermally derived liquid were found to be 32.56, 30.08, 14.19, 12.35, and 10.95 %, respectively. In case of Zn/AWBC catalyzed run, the yield of lighter products i.e. C₆-C₁₂, C₁₃-C₁₆, and C₁₇-C₂₀ were decreased whereas the yield of middle as well high C-range products (C₂₀-C₃₀ and ≥ C₃₀) were increased. This can be attributed to the acidic properties of the catalyst used. As earlier reported, the acidic sites present in the catalyst usually attack the main polymer chains thereby yielding an oligomer fraction having carbon range distribution of approximately C₃₀-C₈₀. These oligomers further undergo β-scissions of chain-end carbonium ions giving rise to the formation of gas products along with a liquid fraction having carbon distribution range of approximately C₁₀-C₂₅ [94] in the present study, the catalyst used might have favored the formation of the heavy hydrocarbons due to assistance in oligomers formation. The reduction in light products and increase in yield of



middle range products can be corresponded to the inactivity shown by the catalyst under study towards successive scissions of the high molecular weight oligomers initially which resulted to produce fragments having high weight liquid products.

Hydrocarbon group types

The hydrocarbon group type distribution of the catalytically derived liquids was also studied. The data is compiled in Table 3.41. It can be observed that both of the polyolefins (PP and HDPE) produced diverse product spectrum in terms of paraffins, olefins and naphthenes.

In case of PP thermally derived liquid, the yields of paraffins, olefins and naphthenes were found to be 66.55, 25.87 and 7.58 %, respectively. While in case of catalytic run, the yield of paraffins was found to be 62.07 % which slightly decreased, whereas the yields of olefins and naphthenes were found to be 28.29 and 9.64 % respectively. Upon comparing the results with the thermal run, an increase in olefins and naphthenes can be observed. This can be attributed to the fact that the catalyst used is said to be bi-functional (Zn as active ingredient and bentonite as support). Supported transition metals have been reported to be highly effective reforming catalysts. [95, 96] owing to their bi-functional nature. These catalysts contain two kinds of active sites playing different roles. The active metals facilitate the hydrogenation reactions and the acidic sites in the support facilitate reforming reactions. A combination of the two functions may convert plastics into products having diverse spectrum in terms of paraffins, olefins, naphthenes, and aromatics. [97]. The results indicated that the active site (Co) has played some role in dehydrogenation and reforming reactions in addition to the active acidic sites present in the support (bentonite).

In case of HDPE, the distributions of various hydrocarbon group types in the liquid product derived from thermal run were as: paraffins; 59.70 %, olefins; 31.90 % and naphthenes; 8.40 %. The yields pattern of paraffinic, olefinic and naphthenic hydrocarbons obtained during the catalyzed run was 62.15, 33.34 and 4.48 %, respectively. Comparing the results with thermal run, the use of Zn/AWBC caused an increase in the formation of paraffinic and olefinic hydrocarbons compared to thermal



run. The yield of naphthenes showed a decrease. The results indicated that in case of HDPE, the distributions were also affected in the presence of the catalyst. The olefinic intermediates resulted in case of HDPE in the form of the primary cracking products in the catalyzed run were not easily changed to paraffins by the hydrogenation. In addition, the adverse effect on the formation of naphthenes indicated the poor reforming ability of the catalyst used probably due to the nature of the support. As reported elsewhere, polymer cracking is well known to proceed by carbocation mechanisms, where the initially formed ions undergo chain reactions via processes, such as isomerization, β -scission, hydrogen transfer and oligomerization to yield typically light paraffins and olefins [94]. Hence, the catalysts used in current study might have facilitated such reactions there by giving a product with high paraffins and olefins. Olefinic hydrocarbons can influence the properties of fuels including increase in the reactivity of gasoline fuels in combustion processes[98] and also improve fuel octane number & anti-knock performance [99]. Hence, the high olefinic contents indicated that the derived liquids could be considered as substitute fuel or as feed stock for obtaining racing fuels.

It can be observed from the compiled results that the yields of both paraffins and olefins in PP and HDPE derived liquids were significant in catalyzed runs and showed preponderance of paraffins and olefins compared to thermal run. The results indicated the effectiveness of the catalysts used in terms of enhancement in olefins and naphthenes in case of PP and paraffins and olefins in case of HDPE.

From the above discussion, it can be concluded that polyolefins (both PP and HDPE) can be converted more meaningfully into useful liquid products through catalytic route. Impregnated bentonites (BCs) particularly Co/BC and Zn/BC can be used for the process as catalysts for conversion of PP and HDPE into value added products. Polypropylene can be converted catalytically to produce significant amount of oilified liquid with the yield as high as 92 % (wt basis). HDPE can be converted catalytically to produce significant amount of oilified liquid with the yield as high as 91 % (wt basis). The catalytically derived liquids were enriched in terms of heavy hydrocarbons in case of PP while in light and middle range products in case of HDPE as



confirmed from FTIR and GC-MS analyses. The catalytically derived liquid derived from PP was enriched in olefins & paraffins while in case of HDPE in paraffins and olefins.

Table 3.37. Major absorption peaks observed and assigned configurations in the FT-IR spectra of the liquid products derived from catalytic pyrolysis of PP and HDPE over BCs

Liquid product	Position (cm ⁻¹)	Intensity	Assigned configuration
Thermal run PP	2922	strong	CH ₃ (aliphatic)
	2852	strong	CH ₂ (aliphatic)
	1456	strong	CH ₂ bending vibrations
Co/BC catalyzed run	2920	strong	CH ₃ (aliphatic)
	1554	weak	C=C (olefinic)
	1456	strong	CH ₂ bending vibrations
Thermal run HDPE	2920	strong	CH ₃ (aliphatic)
	2853	strong	CH ₂ (aliphatic)
	1454	strong	CH ₂ bending vibrations
Zn/BC catalyzed run	2954	strong	CH ₃ (aliphatic)
	2912	strong	CH ₂ (aliphatic)
	1510 & 1550	medium	C=C (olefinic)
	1456	strong	CH ₂ bending vibrations

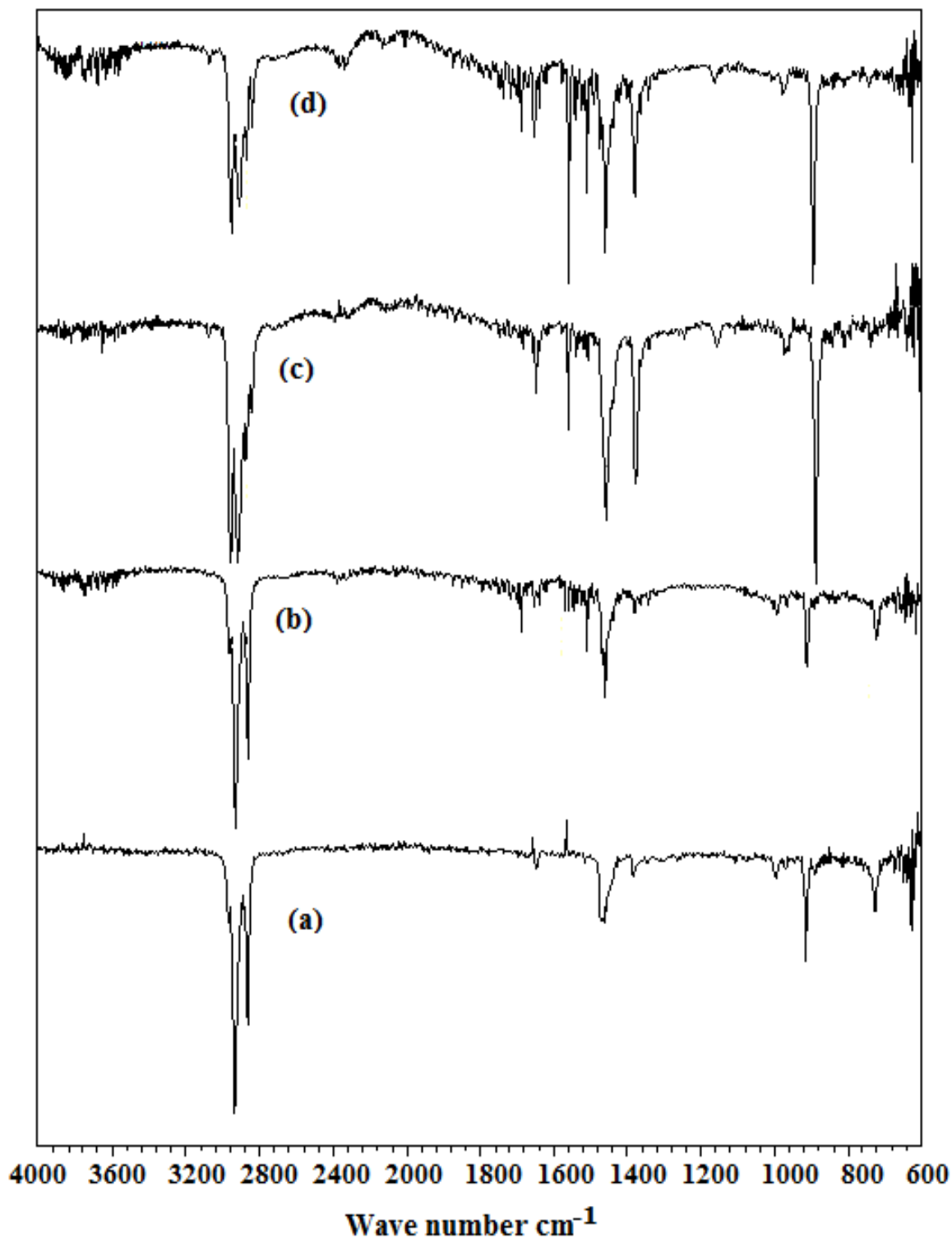


Figure 3.22. FT-IR spectra of the liquid products derived from catalytic pyrolysis of polyolefins over BCs (a) PP thermal run (b) PP catalyzed run (c) HDPE thermal run (d) HDPE catalyzed run.

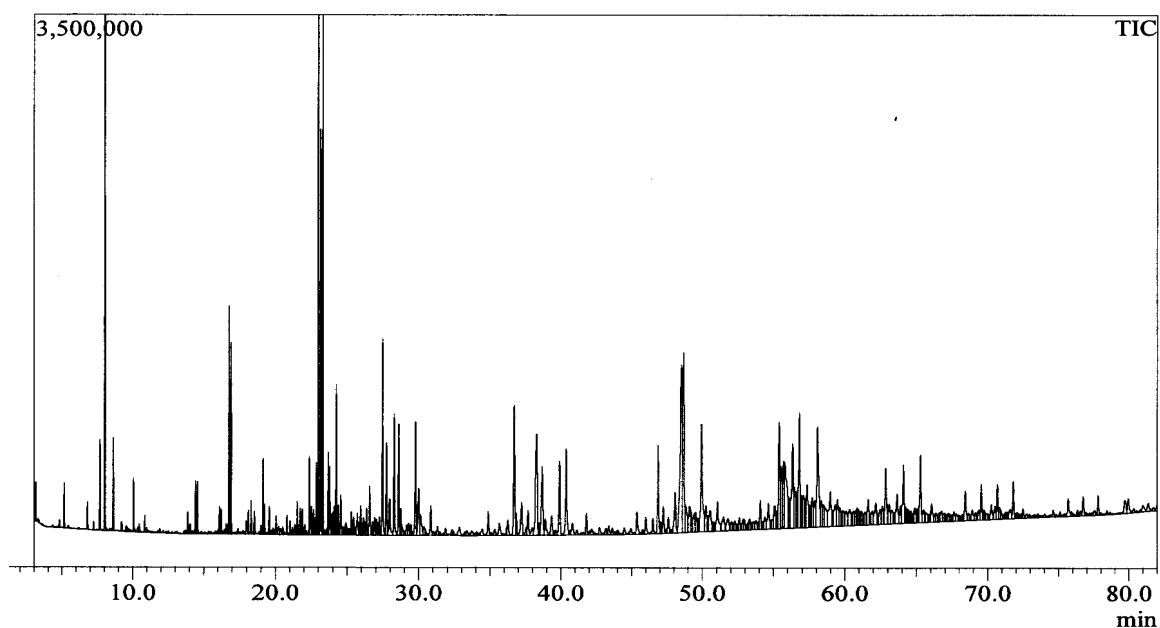


Figure 3.23. GC-MS spectrum of liquid product derived from PP by pyrolysis in the presence of Co/BC

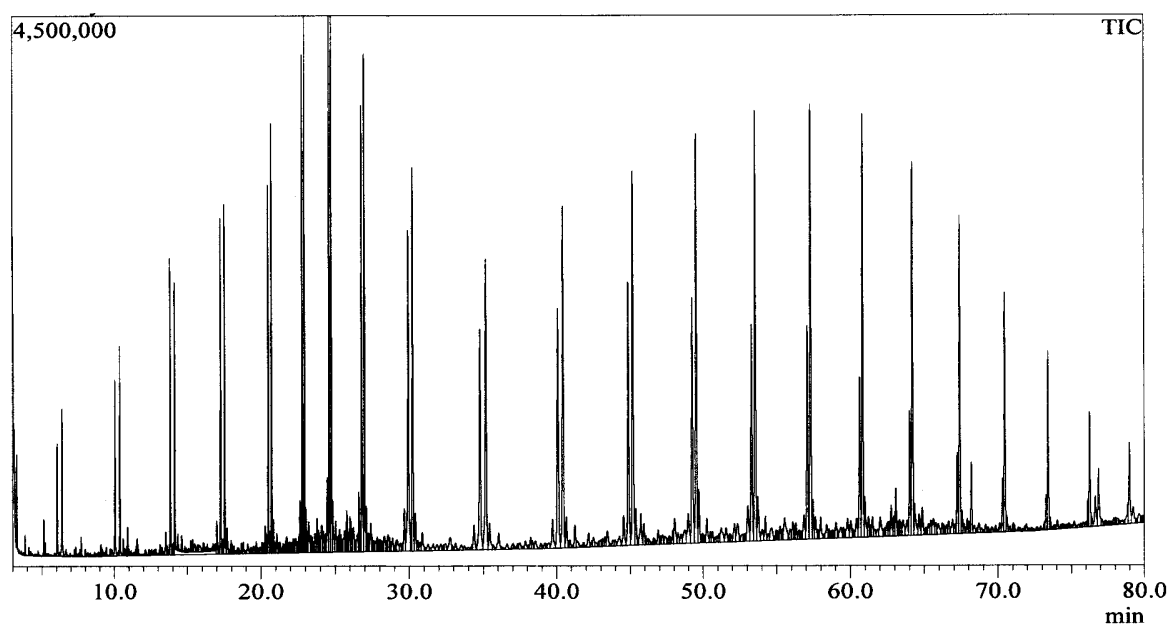


Figure 3.24. GC-MS spectrum of liquid product derived from HDPE by pyrolysis in the presence of Zn/BC

**Table 3.38.** Hydrocarbons identified in the liquid product derived from catalytic pyrolysis over Co/BC

ID #	Compoun	t _R	% peak area/ relative conc.
Naphthenes			
1.	1,3- Dimethylcyclopentane	3.033	0.38
2.	Cyclopentane, 1,2-dimethyl- cis	3.083	0.19
3.	Cyclopentane, 1,2-dimethyl- trans	3.133	0.37
4.	Cyclohexane, methyl -	3.861	0.01
5.	Cyclopentane, 1,1 ,3,4-tetramethyl-, cis	6.806	0.43
6.	Cyclohexane, 1,3,5-trimethyl -	7.682	1.46
7.	Cyclohexane, 1,3,5-trimethyl -	8.638	1.90
8.	Cyclohexene, 3,5,5-trimethyl -	9.229	0.11
9.	1-Isopropyl-1,4,5-trimethyleyclohexane	16.58	0.21
10.	2,4,6- Trimethylcyclohexane	19.155	1.36
11.	Cyclohexane, 2,4-diethyl-1-methyl -	19.584	0.59
12.	Cyclohexane, 1,2-diethyl-3-methyl -	20.07	0.35
13.	2,4,6- Trimethylcyclohexane	22.562	0.25
14.	1,1-Bicyclohexyl, 2-(1-methylethyl) -	23.678	1.25
15.	Cyclohexane, 1,1-(1 ,5-pentanediy)bis	24.1	0.37
16.	Cyclopentane, 1,2-dibutyl-	40.82	0.41
Total yield			9.64
Olefins			
17.	2,4- Dimethyl-heptene	8.045	8.58
18.	I-Nonene	10.073	1.00
19.	1,6-Octadiene, 2,6-dimethyl-, (Z) -	10.861	0.27
20.	2-Decene, 4-methyl-(Z)	14.053	0.17
21.	2-Decene, 2,4-dimethyl -	16.119	0.71
22.	I-Undecene,7-methyl -	16.782	2.42
23.	2-Undecene, 4,5-dimethyl-, R,S-(Z)	16.923	1.96
24.	I-Undecene, 8-methyl -	18.323	0.39
25.	2-Undecene, 8-methyl, (Z)	18.542	0.26
26.	1,7-Nonadiene,4,8-dimethyl -	19.242	0.52
27.	1-Dodecene	21.03	0.06
28.	2-Undecene, 4,5-dimethyl-, R, R-(E)	21.03	0.22
29.	2-Heptene, 5-ethyl-2,4-dimethyl -	22.369	1.45
30.	9-Eicosene, (E) -	24.025	0.15
31.	5-Eicosene, (E) -	23.932	0.13
32.	3-Eicosene, (E) -	24.176	0.32



33.	1,19-Eicosadiene	24.251	1.37
34.	7- Tetradecene, (E) -	24.993	0.02
35.	2-Methyl-2-docosene	25.463	0.19
36.	4- Tetradecene, 2,3,4-trimethyl -	41.813	0.66
37.	1,15-Hexadecadiene	44.488	0.05
38.	1- Tricosene	45.783	0.05
39.	Dodecene-2,4,6-trimethyl -	49.955	3.22
40.	4- Tetradecene, 2,3,4-trimethyl-cis	51.073	1.54
41.	4- Tetradecene, 2,3,4-trimethyl	65.284	1.70
42.	1,37 -Octatriacontadiene	65.653	0.07
43.	11-Dodecene, 2,4,6-trimethyl -	71.809	0.81
Total yield			28.29
Paraffins			
44.	Heptane	3.293	3.06
45.	Heptane, 4-methyl -	5.15	3.57
46.	Heptane, 2,4-dimethyl -	7.253	0.21
47.	Nonane, 2,6-dimethyl -	14.416	3.89
48.	Decane,4-methyl -	14.565	2.73
49.	Undecane	17.588	0.03
50.	Dodecane	20.616	3.01
51.	Hexane, 5-methyl-2-(1-methylethyl) -	21.533	0.35
52.	Dodecane, 4,6-dimethyl -	21.73	0.34
53.	Decane, 2,3,5,8-tetramethyl -	21.883	0.27
54.	Pentadecane	22.563	0.11
55.	2-Isopropyl-5-methyl heptane	23	5.78
56.	Decane, 2-methyl -	23.16	3.43
57.	heptane, 2,4-diethyl -	23.317	5.08
58.	Decane, 2-hexyl -	23.788	1.57
59.	Isotridecane	25.295	1.36
60.	Dodecane, 4,6-dimethyl -	25.946	0.35
61.	Decane, 3,3,6-trimethyl -	26.136	0.24
62.	Dodecane, 6,8-dimethyl -	26.37	0.35
63.	Octane, 2-butyl -	27.032	0.07
64.	Tetradecane	27.042	0.30
65.	Decane, 4-hexyl -	27.473	2.57
66.	2-Hexyl octane	27.756	1.4
67.	Decane, 2-methyl -	27.963	0.72
68.	Hexadecane, 3,7,11,15-tetramethyl -	28.765	0.38
69.	Dodecane, 2, 6, 11-trimethyl -	30.37	0.11



70.	Hexadecane	35.367	0.13
71.	Pentacotane	36.715	3.15
72.	Heptane 2,4-diethyl -	38.294	3.46
73.	Nonadecane	40.672	0.11
74.	Heneicosane	45.37	0.34
75.	Octane, 2-butyl	47.248	0.53
76.	Hexadecane, 3,7,11,15-tetramethyl -	47.607	0.28
77.	Heptane, 2,4-diethyl -	48.083	1.36
78.	Heptadecane	49.739	0.08
79.	Hexadecane, 2,6, 10, 14-tetramethyl -	53.74	0.10
80.	Pentatriacontane	55.399	1.73
81.	Tetrapentacontan	56.336	1.24
82.	Hentetracontane	56.806	5.86
83.	Docosane	57.514	0.05
84.	Octadecane	61.165	0.07
85.	Octane, 2-butyl	62.854	1.46
86.	Octacosane, 2,4,6,8-tetramethyl -	63.649	0.43
87.	Tetratetracontane	64.361	0.05
88.	Tetratriacontane	67.629	0.06
89.	Octacosane	70.69	0.22
90.	Pentadecane, 8-hexyl -	73.543	0.02
91.	Hexatriacontane	76.553	0.06
Total yield			62.07

Co/BC: 1 %

Table 3.39. Hydrocarbons identified in the liquid products derived from catalytic pyrolysis of HDPE over Zn/BC

ID #	Compound	t _R	% peak area/ relative conc.
Naphthenes			
1.	1,3-Dimethylcyclopentane	3.026	0.22
2.	Cyclopentane, 1,2-dimethyl-, cis -	3.073	0.18
3.	Cyclopentane, 1,2-dimethyl -	3.128	0.8
4.	Cyclohexane, methyl -	3.851	0.32
5.	Cyclopentane, 1,1,3,4-tetramethyl -	6.957	0.01
6.	Cyclohexane 1,3,5 trimethyl -	7.336	0.07
7.	Cyclopropane, 1-heptyl-2-methyl -	13.843	2.27
8.	Cyclohexane, ecosyl	16.069	0.03
9.	1-isopropyl-1,4,5-trimethylcyclohexane	16.28	0.04



10.	2,4,6-Trimethylcyclohexane	19.077	0.11
11.	Cyclohexane, 2,4-diethyl-1-methyl -	19.509	0.03
12.	1,1-Bicyclohexyl, 2-(1-methylethyl) trans	29.657	0.40
Total yield		4.48	
Olefins			
13.	1-Octene	6.065	1.73
14.	2,4-Dimethyl-1-heptene	7.988	0.16
15.	1-Nonene	10.062	2.38
16.	2-Decene, 4-methyl-	14.148	0.31
17.	2-Decene, 2,4-dimethyl-	16.069	0.02
18.	1 -Undecene, 8-methyl -	18.384	0.01
19.	1,7-Nonadiene, 4,8-dimethyl -	19.077	0.11
20.	1-Dodecene	20.508	3.52
21.	5-Tetradecene, (E)	20.933	0.05
22.	E-10-Pentadecene	22.643	0.66
23.	5-Eicosene, (E)	23.957	0.05
24.	3-Eicosene, (E)	23.957	0.02
25.	1,19-Eicosadiene	23.957	0.02
26.	1-Nonadecene	23.957	0.02
27.	3-Hexadecene, (Z)	24.614	4.03
28.	2-Methyl-2-docosene	25.54	0.04
29.	1, 9-Tetradecadiene	26.597	0.73
30.	1-Pentadecene	26.791	3.42
31.	18-Nonadecene	34.369	0.61
32.	1-Tetradecene	34.788	3.95
33.	1-Hexadecene	40.086	4.26
34.	1,1-Dodecene-2,4,6-trimethyl -	40.445	1.50
35.	5-Octadecene (E)	41.483	0.02
36.	15-Hexadecadiene	44.562	0.79
37.	1-Tricosene	45.402	0.46
38.	1-Heptadecene	53.725	0.87
39.	Z-5-Nonadecene	64.348	1.56
40.	11, 37-Octatriacontadiene	65.626	0.26
41.	4-Tetradecene, 2,3,4-trimethyl-	65.308	0.01
42.	9-Hexacosene	67.537	0.2
43.	9-Tricosene, (Z)	73.281	1.56
44.	11-Dodecene-2,4,6-trimethyl -	71.642	0.01
Total yield		33.34	
Paraffins			



45.	Heptane	3.284	2.65
46.	Heptane,4-methyl -	5.125	0.07
47.	Octane	6.399	4.31
48.	Heptane-2,4-dimethyl -	7.176	0.06
49.	Nonane	10.395	5.20
50.	Nonane, 2,6-dimethyl -	14.612	0.11
51.	Decane, 4-methyl -	14.612	0.11
52.	Undecane	17.541	4.2
53.	Dodecane	20.858	0.19
54.	Dodecane, 4,6-dimethyl -	22.1	0.05
55.	Decane, 2,3,5,8-tetramethyl -	22.1	0.05
56.	2-Isopropyl-5-methyl heptane	23.045	0.48
57.	Decane, 2-methyl -	23.22	0.19
58.	Heptane, 2,4-diethyl -	23.22	0.19
59.	Decane, 2-hexyl -	23.957	0.35
60.	Pentadecane	24.843	2.37
61.	Isotridecane	25.291	0.07
62.	Dodecane, 4,6-dimethyl -	25.932	0.08
63.	Decane, 3,3,6-trimethyl -	25.932	0.07
64.	Dodecane, 4,6-dimethyl -	25.932	0.03
65.	Tetradecane	27.101	0.33
66.	2-Hexyl octane	27.827	0.06
67.	Tricosene	28.726	3.04
68.	Hexadecane, 3,7, 11,15-tetramethyl -	28.614	0.13
69.	Dodecane, 1,2,6-trimethyl -	30.403	0.32
70.	Hexadecane	35.425	4.23
71.	Pentacontane	36.619	0.07
72.	Hentetracontane	37.004	0.17
73.	Heptane, 2,4-diethyl -	38.212	0.37
74.	Nonadecane	40.659	2.67
75.	Heneicosane	45.402	3.6
76.	Hexadecane, 1,3, 7, 11,-tetramethyl -	47.911	0.15
77.	Heptadecane	49.724	2.73
78.	Hexadecane, 2,6, 10,1 4-tetramethyl -	53.725	3.65
79.	Pentatriacontane	55.228	0.15
80.	Heneicosane	57.471	2.55
81.	Docosane	57.628	0.17
82.	Tetradecene, 2,3,4-trimethyl -	58.778	0.06
83.	Octadecane	61.225	0.23



84.	Octane, 2-butyl -	63.315	0.11
85.	Octacosane, 2,4,6,8-tetramethyl	63.542	0.01
86.	Tetratetracontane	64.348	0.19
87.	Tetratriacontane	67.679	0.04
88.	Pentacosane	70.315	2.79
89.	Octacosane	70.814	0.04
90.	Pentadecane, 8-hexyl -	73.413	6.05
91.	Hexatriacontane	76.251	4.57
92.	Triacontane	78.991	2.84
Total yield		62.15	

Zn/BC: 2.5 %

Table 3.40. Carbon range distributions in liquid products derived from catalytic pyrolysis of PP and HDPE over BCs

Polyolefin	Catalyst	Distribution (%)				
		C ₆ -C ₁₂	C ₁₃ -C ₁₆	C ₁₇ -C ₂₀	C ₂₁ -C ₃₀	> C ₃₀
PP	No catalyst	15.16	33.04	18.77	24.97	8.05
	Co/BC*	60.18	16.01	5.06	5.44	12.65
HDPE	No catalyst	32.56	30.80	14.19	12.35	10.95
	Zn/BC**	30.34	17.46	12.70	22.28	14.64

Catalyst loading: *1 % and **2.5 %

Table 3.41. Hydrocarbon group types distributions in liquid products derived from catalytic pyrolysis of PP and HDPE over BCs

Polyolefin	Catalyst*	Distribution (%)			
		Paraffins	Olefins	Naphthenes	Aromatics
PP	No catalyst	66.55	25.87	7.58	0.00
	Co/BC*	62.07	28.29	9.64	0.00
HDPE	No catalyst	59.70	31.90	8.40	0.00
	Zn/BC**	62.15	33.34	4.48	0.00

Catalyst loading: *1 % and **2.5 %



3.7 CATALYTIC PYROLYSIS OVER TYPE D CATALYSTS (METAL IMPREGNATED CARBON- DARCO)

Pyrolysis reactions of PP and HDPE were carried out in a fixed bed reactor in the presence of original and metal impregnated porous carbons as catalysts under optimized conditions. The catalysts used were original (Darco (20-40 mesh) and transition metal impregnated activated carbons (Zn/AC, Cr/AC, Ni/AC, Co/AC, Fe/AC, and Mn/AC). The performance of each catalyst and its concentration in terms of overall yields of pyrolysates and yields of liquid, gas and coke/solid residue was evaluated.

Having large surface area, pore volume and pore diameter as well as mild acidity, meso porous carbons are reported to be potential candidates in catalytic pyrolysis of waste plastics [94, 100-103]. To further enhance catalytic properties, metal dispersed meso porous carbons are currently researched due to their excellent catalytic activities in a variety of organic reactions [104].

In the present study, original and various metal impregnated carbons as catalysts were employed in pyrolysis of PP and HDPE to get useful fuel products. The activity and selectivity of individual catalysts in term of overall yield and yields of liquid, gas, and residue/coke products were evaluated. Influence of each catalyst on product composition in term of carbon range products and hydrocarbon group type distributions in the derived liquid products is also reported.

3.7.1. Activity Tests

Pyrolysis reactions of both polyolefins (PP and HDPE) over original and metal impregnated ACs were carried out. Catalysts under study were used with the objectives to yield mostly liquid (oil) as principle product and gases and coke as by products. The overall yields and yields of liquid, gas, and coke as a function of catalyst type and concentration were determined and compared with un-catalyzed run. The results are provided in Table 3.42.



3.7.1.1. Overall product yields

From the data compiled in Table 3.42, it can be seen that the overall yield pattern achieved in case of thermal run was all most same i.e. about 98 %, in case of both PP and HDPE. However, in case of catalyzed runs, the yields varied greatly with type of the catalyst and fall within the range of 80 to 99 wt%. The yield pattern obtained in case of PP indicated that maximum yield of 99.64 wt% was attained in case of reaction carried over Fe/AC (1%). The yield pattern achieved in case of HDPE indicated that Zn/AC (2.5 %) gave the highest yield of 99.85 wt%. This is indicative of the fact that polymers under study are more susceptible toward degradation in the presence of catalysts under study.

3.7.1.2. Liquid yields

The liquid yields obtained in case of thermal and catalytic runs are provided in Table 3.42. Relative to thermal run, the liquid yield increased but differently in case of each catalyst. The difference in the yield patterns in the two cases (thermal and catalytic) can be associated with a difference in the mechanism of degradation: radical without catalyst and essentially ionic in case of catalyst [105].

The effect of polymer to catalysts ratio (catalyst concentration) was also studied. The results indicated synergistic effect and an improvement in liquid yields with the increase in concentration can be observed. However, when used in very high concentration, the liquid yields decreased and the gas yields increased. This is likely due to the activity shown by the catalysts used towards cracking of the resultant liquid products thereby altering the liquid/gas ratio when used in low concentration. In case of PP, the liquid yield in thermal run was about 70 %, whereas maximum liquid yield of about 87 % was attained in the presences of Fe/AC (2.5 %). Similarly, in case of HDPE, the liquid yield in thermal run was about 80 %, however, in the presence of Zn/AC (2.5 %), the yield of liquid was even less than the one achieved in case of thermal run.

3.7.1.3. Gas yields

Gas yields were also studied in un catalyzed and catalyzed runs. A variation in yields as a function of catalyst concentration is provided in Table 3.42. It is evident from



the data that catalysts caused poor gas yields when used in low concentration. Maximum gas yields were obtained when the catalysts under study were used in high concentration. However, the concentration effect in case of both polyolefins was different. In case of PP, most of the catalysts gave poor gas yield compared to thermal run, with the lowest obtained in case of Fe/AC. On the other hand, in case of HDPE, all the catalysts gave higher gas yields, relatively to thermal run.

3.7.1.4. Residue yields

The effect of each catalyst and its concentration on the formation of residue/char was also studied. The yield pattern indicated that the residue amount was unaffected even in case of some catalyzed runs when compared with the thermal run. However, in case of PP and HDPE, the residue amount attained the lowest level in case of some of the runs catalyzed by Fe/AC and Zn/AC, which indicated the superior cracking activities of these catalysts. The variation in results achieved may also be attributed to the different tendency of the two polymers to form char.

It can be concluded from the above discussion that the variation in yields achieved in case of thermal and catalytic runs may be attributed to the variation in acidity of the catalysts used. As earlier reported the internal acidity is responsible for transformations of various hydrocarbons [106]. The acidity of Fe/AC was found to be 5.2 and that of Zn/AC was found to be 4.5 mg KOH/g (Table 3.42), which is quite higher compared to other catalysts used. The variation in yields in current study can also be correlated with the variation in total acidity of the catalysts in addition to other factors like surface properties including surface area, pore volume and pore diameter as shown in surface properties analysis and in the scanning electron microscope (SEM) micrographs.



Table 3.42. Yields of pyrolysates (over all yields and yields of liquid, gas and coke) derived from catalytic pyrolysis of PP and HDPE over original and metal salts impregnated ACs as a function of catalyst type and concentration.

Catalysts	Catalyst quantity (g %)	Product yield of PP (%)				Product yield of HDPE (%)			
		Total yield	Liquid	Gases	Solid residue	Total yield	Liquid	Gases	Solid residue
No Cat.	0	98.66	69.82	28.84	1.34	98.12	80.88	17.24	1.88
AC	0.5	88.87	78.65	10.22	11.13	84.49	69.62	14.87	15.41
	1.0	90.00	80.58	9.42	10.00	84.72	71.57	13.15	15.28
	2.5	86.58	71.69	14.89	13.42	82.99	60.68	22.31	17.01
	5.0	86.01	63.85	22.16	13.99	82.07	56.59	25.48	17.93
	10	83.62	57.11	26.51	16.38	80.6	50.64	29.96	19.40
Fe/AC	0.5	98.8	84.15	14.65	1.20	92.46	50.18	42.28	7.54
	1.0	99.64	86.74	12.90	0.36	95.37	62.74	32.63	4.63
	2.5	99.64	86.82	12.82	0.36	95.01	60.45	34.56	4.99
	5.0	97.81	79.44	18.37	2.19	94.85	59.33	35.52	5.15
	10	94.25	68.26	25.99	5.75	93.89	55.87	38.02	6.11
Ni/AC	0.5	82.67	60.17	22.5	17.33	93.48	75.67	17.81	6.52
	1.0	83.30	66.58	16.72	16.7	92.63	76.83	15.8	7.37
	2.5	85.36	69.63	15.73	14.64	92.41	73.74	18.67	7.59
	5.0	79.62	57.21	22.41	20.38	88.84	58.60	30.24	11.16
	10	74.93	55.86	19.07	25.07	88.46	57.06	31.40	11.54
Zn/AC	0.5	96.30	71.92	24.38	3.70	91.9	47.81	44.09	8.10
	1	96.30	72.81	23.49	3.71	95.77	65.36	30.41	4.23
	2.5	96.87	74.92	21.95	3.13	99.88	80.71	19.17	0.12
	5	94.35	69.34	25.01	5.65	86.32	45.7	40.62	13.68
	10	94.29	60.78	33.51	5.71	83.00	40.37	42.63	17.00
Mn/AC	0.5	94.65	66.29	28.36	5.35	86.42	67.93	18.49	13.58
	1.0	103.25	72.67	30.58	3.25	88.4	70.57	17.83	11.6
	2.5	96.47	71.98	24.49	3.53	90.08	75.88	14.20	9.92
	5.0	95.55	60.12	35.43	4.45	90.46	79.25	11.21	9.54
	10	92.76	56.9	35.86	7.24	89.28	73.48	15.80	10.72
Co/AC	0.5	88.71	48.38	40.33	11.29	80.5	50.53	29.97	19.50
	1.0	90.62	55.65	34.97	9.38	80.82	52.94	27.88	19.18
	2.5	90.55	50.35	40.20	9.45	88.14	69.05	19.09	11.86
	5.0	86.32	47.15	39.17	13.68	86.24	63.67	22.57	13.76
	10	86.21	41.26	44.95	13.79	78.91	49.08	29.83	21.09



3.4.3. Liquid Products Composition

From the point of view of maximum yields of liquid fractions, Fe/AC (2.5 %), and Zn/AC (2.5%) were found to be the highly active catalysts in case of PP, and HDPE, respectively. The liquids obtained with Fe/AC, and Zn/AC catalyzed runs were further submitted to compositional analysis by FTIR and GC-MS.

3.4.3.1. FT-IR Analysis

FT-IR spectroscopy is a useful tool used to examine the hydrocarbon types or functional groups in the pyrolytic oil derived from waste polymers. The liquid pyrolysates derived from PP and HDPE in thermal and selected catalytic runs were characterized by FT-IR spectroscopy. The spectra obtained are displayed in Fig.3.25 (a-e). The corresponding peaks data and possible assignments have been assembled in Table 3.43.

The spectrum of the liquid product derived from PP in thermal run (Fig.3.25) indicates two strong absorption peaks centered at around 2953 and 2868 cm^{-1} , a weak absorption peak at 1620 cm^{-1} , and two medium peaks at 1456, 1377 cm^{-1} . These peaks can be corresponded to aliphatic C-H stretching (for CH_3 and CH_2), olefinic C=C stretching, and CH_2 bending vibrations and C-H scissoring and bending vibrations of alkanes, respectively. An ill developed peak centered at 887 cm^{-1} shows olefinic C-H. It can be observed that the liquid under study mostly consisted of aliphatic and some olefinic hydrocarbons.

The spectrum of the pyrolysate derived from PP using Fe/AC as catalyst (Fig.3.25 b) features some additional peaks as compared to thermal run. Peaks appearing at 2954, 2912 and 2870 cm^{-1} can be corresponded to methyl and methylene C-H. Two new peaks centered at 1625 and 1570 cm^{-1} indicate olefinic C=C. A medium intensity peak at 1456 shows CH_2 bending vibrations and a strong intensity peak positioned at 1375 shows olefinic C-H scissoring and bending vibrations. It may be noted that the spectrum of the catalytically derived liquid product has pronounced peaks corresponding to olefinic C=C, which indicated the enrichment of the liquid fraction in terms of olefins.



The spectrum of the liquid product obtained in case of HPE thermal run is provided in Fig.3.25 (c). Several absorption peaks mostly positioned at 2920 and 2852 cm^{-1} corresponded to aliphatic C-H for CH_3 and CH_2 groups, respectively can be observed. A weak intensity absorption peak positioned at 1525 cm^{-1} shows olefinic $\text{C}=\text{C}$, and a medium intensity peak centered at 1456 cm^{-1} indicates CH_2 bending vibrations. A strong peak observed at 908 cm^{-1} can be corresponded to C-H of olefins.

The FT-IR spectrum of the catalytic pyrolysate obtained from HDPE in the presence of Zn/AC catalyst is provided in Fig.3.25 (d). Peaks corresponded to aliphatic C-H, olefinic $\text{C}=\text{C}$, and C-H olefinic configurations can be observed. Upon comparing both spectra, no new peak was observed. However, the peaks appeared in different intensities, for instance strong intensity peaks corresponded to olefin in thermal run, was converted to weak in case of catalytic run. Similarly, strong intensity peak at 2912 cm^{-1} in thermally derived liquid was shifted to weak intensity peak in case of catalytically derived liquid product.

3.4.3.2. GC-MS Analysis

Individual component analysis

The main chemical components of the liquid products obtained by pyrolysis of PP and HDPE, were identified by GC-MS (Fig. 3.26 and Fig. 3.27). It can be seen that in case of catalytic pyrolysis of PP, among the naphthenes, major compounds were found to be 1,3,5-trimethyl cyclohexane, and 1,1-bicyclohexyl, 2-(1-methyl ethyl), whereas main olefinic compounds included 2,4-dimethyl-1-heptene, 2-methyl-1-decene, 2,4-diethyl-1-heptene, 5-eicosene and 2,4,6-trimethyl-11-dodecene. Among the paraffins, the most abundant compounds were found to be heptane, 4-methyl heptane, octane, 2,4-dimethyl heptane, 2,6-dimethyl nonane, 2-Isopropyl-5-methyl-1-heptane, 2-hexyl dodecane, and pentacontane. Out of

In case of catalytic pyrolysis of HDPE, the main compounds among naphthenes were; 1, 2-dimethyl cyclopentane, and 1, 1 -bicyclohexyl, 2-(1-methylethyl). The major olefins included 2, 4-dimethyl-1-heptene, 1-dodecene, 1- tridecene, 3-hexadecene, 3-



tricosene, 1- heptadecene and Z-5-nonadecene, whereas the major. Among paraffins were found to be ; heptane, octane, nonane, undecane, dodecane, 2,3,5,8-tetramethyl decane, 2-butyl 1-octane, , tetradecane, 2-methyl I-decane, , docosane, ootaeosane and 8-hexyl pentadecane.

Upon comparing the results, the derived liquid is enriched in paraffins and olefins and lean in naphthenes. High combustion efficiency of these compounds (paraffinic and olefinic) has been reported elsewhere, hence confirming the selectivity of the catalyst under study in formation of components having fuel value.

C-number distribution

The compounds identified by GC-MS in the pyrolytic oils were grouped into five categories according to their carbon number distribution i.e. C₆-C₁₂, C₁₃-C₁₆, C₁₇-C₂₀, C₂₁-C₃₀ and >C₃₀. The results are provided in Table 3.46 which indicated that the concentrations of light and middle C-range products in case of catalyzed run were significantly high compared to the thermal run. In case of PP pyrolysis, the thermal run gave liquid product mostly consisted of products having carbon number distributions as C₆-C₁₂; 15 %, C₁₃-C₁₆; 33.04 %, C₁₇-C₂₀; 18.77, C₂₀-C₃₀; 24.97 and > C₃₀; 8.05 %, while in case of catalyzed run, the distributions were found to be C₆-C₁₂; 59.79 %, C₁₃-C₁₆; 14.53 %, C₁₇-C₂₀; 10.64 %, C₂₀-C₃₀; 7.16 %, and > C₃₀; 12.65%. The results indicated the synergistic effect exhibited by the catalyst under study on the C-number distribution particularly on the formation of C₆-C₁₂ products which was found to be increased from 15 to 59 %. A pronounced decline can be observed in case of C₁₃-C₁₆ hydrocarbons. It can be seen that the catalyst altered the product distribution and caused enrichment in terms of light products at the expense of middle range hydrocarbons i.e. C₁₃-C₁₆.

The results obtained in case of HDPE are provided in Table 3.46. The yield pattern obtained in case of thermal run indicated the enrichment of the derived liquid in products having carbon number distributions of C₆-C₁₂ and C₁₃-C₁₆.

The results achieved in case of catalyzed run indicated that the catalysts used did not cause a significant effect on the yield pattern. A slight increase can be observed in



case of C₆-C₁₂ and C₁₃-C₁₆ products. The decline in the yield of C₂₀-C₃₀ was also observed, which indicated that the catalyst under study facilitated the cracking of C₂₀-C₃₀ range hydrocarbons to yield C₆-C₁₂ and C₁₃-C₁₆ products.

Hydrocarbon group types distribution

The hydrocarbon group types distribution (paraffinic, olefinic, and naphthenic) of the derived liquids identified by GC-MS are presented in Table 3.47. In case of PP, the catalytic run using Fe/AC, caused the yield of olefins to increase by 16 %, the yield of paraffin's exhibited a decrease of 15 % as compared to thermal run, whereas the yield of naphthenes was almost comparable (Table 3.47). As reported elsewhere, cracking is well known to proceed by carbocation mechanisms, where the initially formed ions undergo chain reactions via processes, such as isomerisation and β -scission (monomolecular) and hydrogen transfer and oligomerisation (bimolecular), to yield typically light paraffins and olefins [107]. Hence, the Fe-catalyst might have assisted both monomolecular and bimolecular transformations via oligomerization giving a product spectrum dominated by olefins [108]. The high oligomerization ability of the Fe-based catalysts has already been reported [109].

In contrast, catalytically derived liquid of HDPE using Zn/AC, the yield of paraffins was increased from 59 to 64 % as compared to the thermal run. The yield of olefins remained the same, while a small decrease in naphthenes can be observed. The reason can be thought is the occurrence of several reactions like hydrogenolysis and ethene (olefins) hydrogenation simultaneously [110]. The catalysts under study might have facilitated these reactions which lead to a marginal increase in paraffins with corresponding decrease in naphthenes. No aromatics were observed in case of thermal as well as catalytic runs. As metals like Fe and Zn have been found to assist mostly in the hydrogenation reactions which can be thought one of the reasons for absence of aromatics in the product.

The widespread distribution of the products in case of pyrolysates derived from both PP and HDPE in terms of paraffins, olefins, and naphthenes can be observed which in turn can be explained on the basis of differences in the mechanism in case of thermal



and catalytic runs. As reported earlier, the thermal degradation of polymers is initiated through two reaction steps. A depolymerization reaction step which yield an olefin and hydrogen transfer from the tertiary carbon atom along the polymer chain to the radical site and β -scission which give rise to the formation of many oligomers. Tetramers and the higher oligomers can exist in more diastereomeric forms. In case of catalytic run, the degradation takes place through ionic mechanism, which generally undergoes through (a) abstraction of a hydride ion from the feed polymer assisted by the Lewis acid sites of the catalyst or addition of a proton to the olefins formed during the thermal step via action of the Bronsted acid sites and (b) isomerization of the secondary & tertiary ions and β -scission. The latter step accounts for the widespread distribution of the products in terms of paraffins, olefins, and naphthenes [111].

It can be concluded that among the various ACs used, Fe/AC and Zn/AC were found to be more active and selective in terms of high liquid yields and the enrichment of the derived liquids in term of C-range products and hydrocarbon group type's distributions particularly when used in low concentration. Fe/AC showed good activity in case of PP and Zn/AC in case of HDPE. Fe/AC caused the formation of light hydrocarbons with preponderance of olefinic hydrocarbons, while Zn/AC gave widespread distribution of the products with slight enrichment in terms of paraffin.



Table 3.43. Major absorption peaks observed and assigned configurations in the FT-IR spectra of the liquid products derived from thermal and catalytic pyrolysis of PP and HDPE over ACs

Sample	Position (cm ⁻¹)	Intensity	Assigned configuration
Thermal pyrolysis of PP	2953	strong	CH ₃ (aliphatic)
	2868	strong	CH ₂ (aliphatic)
	1620	weak	C=C (Olefinic)
	1456	strong	CH ₂ bending
	1375	medium	C-H scissoring/bending
	887	strong	C-H (olefinic)
Catalytic pyrolysis of PP using Fe/AC	2954	strong	CH ₃ (aliphatic)
	2912	strong	CH ₃ (aliphatic)
	2870	weak	CH ₂ (aliphatic)
	1625	medium	C=C (Olefinic)
	1570	strong	C=C (Olefinic)
	1456	medium	CH ₂ bending
	1375	strong	C-H scissoring/bending
Thermal pyrolysis of HDPE	887	strong	C-H (olefinic)
	2920	strong	CH ₃ (aliphatic)
	2852	strong	CH ₂ (aliphatic)
	1525	weak	C=C (olefinic)
	1456	medium	CH ₂ bending
	908	strong	C-H (olefinic)
Catalytic pyrolysis of HDPE using Zn/AC	2953	strong	CH ₃ (aliphatic)
	2921	medium	CH ₂ (aliphatic)
	2850	weak	C=C (olefinic)
	1460	medium	CH ₂ bending
	1377	medium	C-H scissoring/bending
	908	weak	C-H (olefinic)

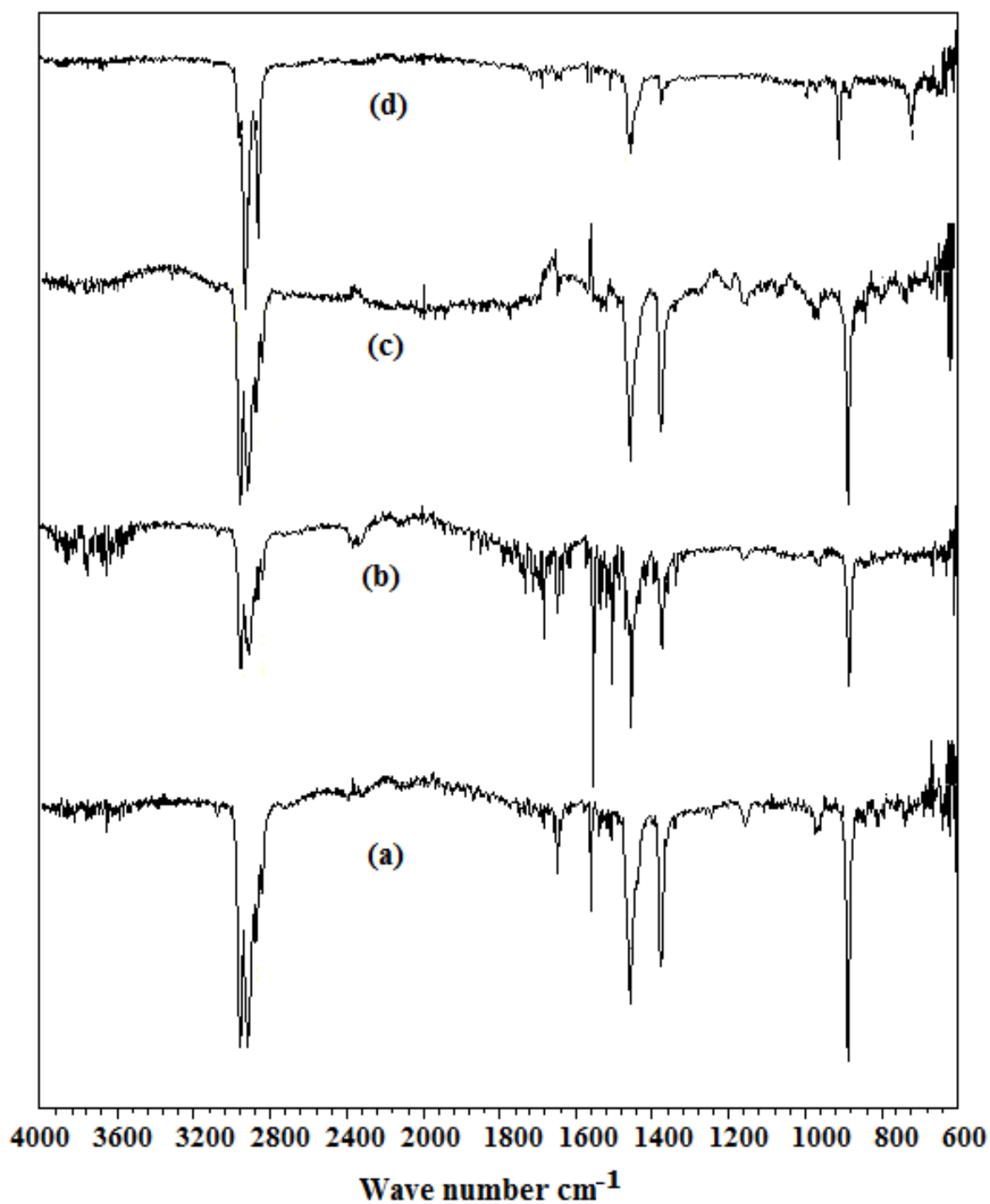


Figure 3.25. FT-IR spectra of the liquid products derived from thermal and catalytic pyrolysis of polyolefins (a) PP thermal run (b) PP catalyzed run (c) HDPE thermal run (d) HDPE catalyzed run.

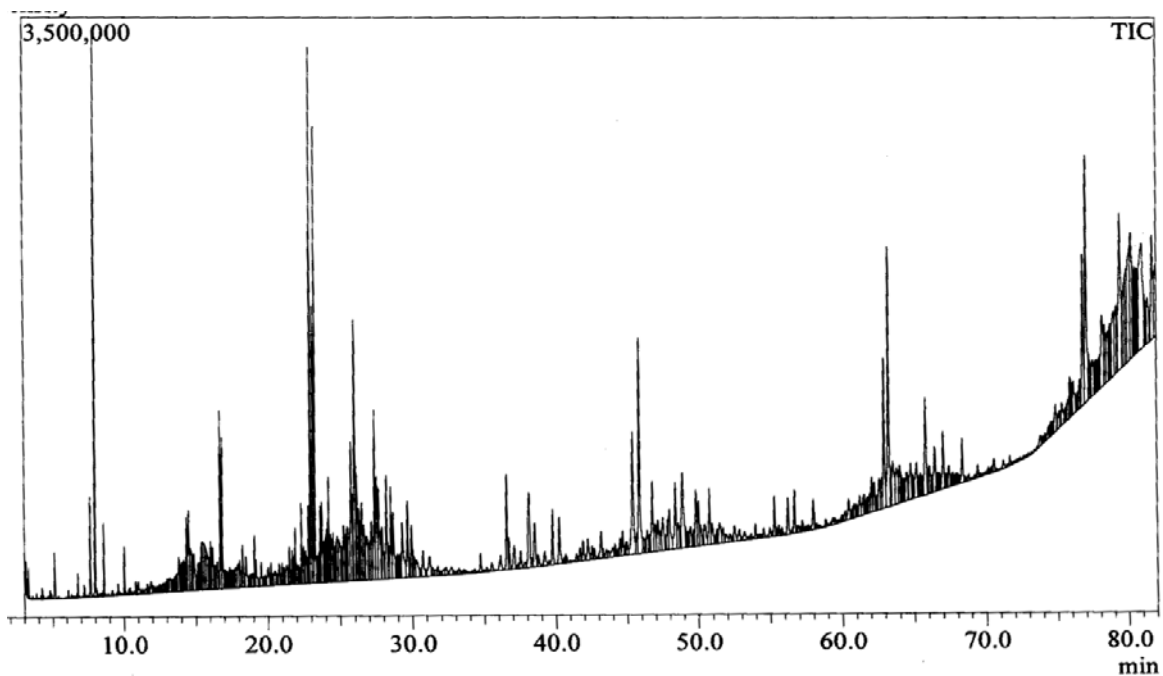


Figure 3.26. GC-MS spectrum of liquid product derived from PP by pyrolysis in the presence of Fe/AC

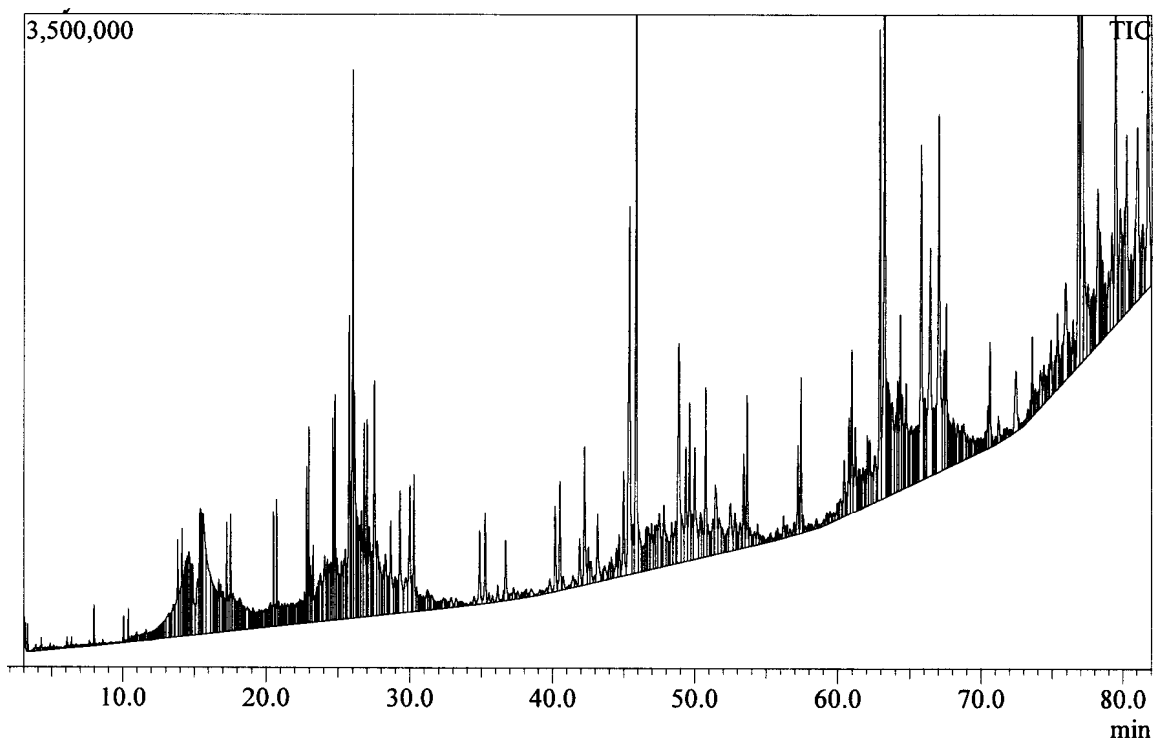


Figure 3.27. GC-MS spectrum of liquid product derived from HDPE by pyrolysis in the presence of Zn/AC

**Table 3.44.** Hydrocarbons identified in liquid product derived from catalytic pyrolysis of PP over Fe/AC

S. #	Compound	t _R	% peak area/ relative conc.
Naphthenes			
1.	Cyclopentane, 1,2-dimethyl -	3.115	0.57
2.	Cyclohexane, methyl -	3.843	0.11
3.	Cyclopentane, 1,1 ,3,4-tetramethyl-, cis	6.765	0.60
4.	Cyclohexane, 1,3,5-trimethyl -	7.862	0.06
5.	Cyclohexane, 1,3,5-trimethyl -	8.598	2.75
6.	1-Isopropyl-1,4,5-trimethyl cyclohexane	16.529	0.27
7.	Cyclohexane,2,4-diethyl-1-methyl -	19.533	0.67
8.	Cyclohexane, 1,2-diethyl-3-methyl -	20.022	0.44
9.	1,1-Bicyclohexyl, 2-(1-methylethyl), trans	23.633	1.31
10.	Cyclohexane, 1, 1-(1,5-pentanediy) -	24.058	0.36
11.	Cyclopentane, 1,2-dibutyl -	40.689	0.59
Total yield			7.73
Olefins			
12.	2,4-Dimethyl-1-heptene	7.985	5.41
13.	1-Nonene	10.024	1.79
14.	1,6-Octadiene, 2,6-dimethyl-, (Z)	10.813	0.31
15.	2-Decene, 2,4-dimethyl -	16.177	0.74
16.	1-Undecene,7-methyl-	16.725	3.39
17.	2-Undecene, 4,5-dimethyl -	16.866	2.74
18.	1-Undecene, 8-methyl -	18.264	0.66
19.	2-Undecene, 8-methyl-(Z)	18.48	0.42
20.	1,7-Nonadiene,4,8-dimethy-	19.34	0.01
21.	1-Dodecene	20.225	1.09
22.	5- Tetradecene, (E)	21.29	0.06
23.	2- Undecene, 4,5-dimethyl-	20.983	0.31
24.	2-Heptene, 5-ethyl-2,4-dimethy-	22.325	2.17
25.	1-Decene, 2-methyl -	23.113	4.34
26.	1-Heptene 2,4-diethyl -	23.269	6.73
27.	1- Decene, 2-hexyl -	23.745	0.98
28.	3-Eicosene, (E)	24.132	0.44
29.	1,19-Eicosadiene	24.205	1.50
30.	18- Nonadecene	24.344	0.27
31.	1- Tetradecene	35.159	0.07
32.	5-Eicosene, (E)	39.779	2.09



33.	1- Hexadecene	40.244	0.71
34.	4- Tetradecene, 2,3,4-trimethyl -	41.907	0.43
35.	11-Dodecene, 2,4,6-trimethyl, (R,R,R)	49.836	2.74
36.	4- Tetradecene, 2,3,4-trimethyl -	50.954	0.83
37.	4- Tetradecene, 2,3,4-trimethyl -	65.18	0.93
38.	1,37-Octatriacontadiene	65.6	0.05
Total yield			41.21
Paraffins			
39.	Heptane	3.273	2.84
40.	Heptane, 4-methyl-	5.111	2.24
41.	Octane	6.386	2.09
42.	Heptane, 2,4-dimethyl -	7.208	2.52
43.	Nonane, 2,6-dimethyl -	14.368	7.44
44.	Decane, 4-methyl-	14.518	1.50
45.	Hexane, 5-methyl-2-(1-methylethyl)	21.488	0.54
46.	Dodecane, 2,4-dimethyl -	21.686	2.51
47.	Decane, 2,3,5,8-tetramethyl -	21.841	0.38
48.	2-Isopropyl-5-methyl heptane	22.95	7.77
49.	Isotridecane	25.236	0.96
50.	2-Methyl-2-docosene	25.41	0.21
51.	Dodecane, 4,6-dimethyl-cis	25.888	0.62
52.	Dodecane, 4,6-dimethyl-trans	26.307	0.51
53.	Dodecane, 2-hexyl -	27.393	3.5
54.	Pentacontane	36.706	2.97
55.	Hentetraeontane	46.952	0.34
56.	Hexadecane, 3,7,11,15-tetramethyl -	47.98	1.37
57.	Pentatriacontane	55.594	0.38
58.	Tetrapentacontane	56.542	1.15
59.	Hentetraeontane	56.696	2.33
60.	Docosane	57.439	3.21
61.	Octadecane	61.092	1.03
62.	Octacosane	70.573	2.11
63.	Triacontane	79.183	0.06
Total yield			50.58

Fe/AC: 2.5 %

**Table 3.45.** Hydrocarbons identified in liquid derived from catalytic pyrolysis of HDPE over Zn/AC

S. #	Compound	t _R	% peak area/ relative conc.
Naphthenes			
1.	1,3-Dimethylcyclopentane	3.063	0.31
2.	Cyclopentane, 1,2-dimethyl-, cis	3.112	0.56
3.	Cyclopentane, 1,2-dimethyl-	3.12	0.56
4.	Cyclohexane, methyl-	3.839	0.23
5.	Cyclopentane, 1,1,3,4-tetramethyl, cis-	6.761	0.17
6.	Cyclohexane, 1,3,5-trimethyl -	7.637	0.25
7.	Cyclohexane, 1,3,5-trimethyl -	8.595	0.28
8.	Cyclohexane, eicosyl	16.176	0.18
9.	1- Isopropyl-1,4,5-trimethylcyclohexane	16.722	0.41
10.	Cyclohexane, 2,4-diethyl-1-methyl -	19.532	0.23
11.	Cyclohexane, 1,2-diethyl-3-methyl -	20.024	0.19
12.	2,4,6- Trimethylcyclohexane	22.517	0.19
13.	1,1 -Bicyclohexyl, 2-(1-methylethyl)- trans	57.975	1.03
Total yield			4.59
Olefins			
14.	2,4-Dimethyl-1-heptene	7.977	1.18
15.	1-Nonene	10.055	0.64
16.	1,6-Octadiene, 2,6-dimethyl, (Z)	10.812	0.18
17.	2-Decene, 4-methyl	14.033	0.23
18.	2-Decene, 2,4-dimethyl -	16.068	0.20
19.	1-Undecene, 7-methyl -	16.865	0.37
20.	2-Undecene, 4,5-dimethyl -	16.865	0.37
21.	1-Undecene, 8-methyl -	17.977	0.18
22.	1,7-Nonadiene, 4,8-dimethyl -	19.173	0.21
23.	1-Dodecene	20.518	1.29
24.	5-Tetradecene, (E)	20.875	0.29
25.	2-Undecene, 4,5-dimethyl -	20.983	0.19
26.	2-Heptene, 5-ethyl-2,4-dimethyl -	22.324	0.24
27.	Pentadecene	22.656	0.36
28.	1- Tridecene	22.812	1.49
29.	5-Eicosene, (E)	23.744	0.35
30.	3-Eicosene, (E)	24.628	1.33
31.	1, 19-Eicosadiene	24.204	0.34
32.	18- Nonadecene	24.204	0.34



33.	3-Hexadecene, (Z) -	24.628	1.75
34.	1,9- Tetradecadiene	26.631	0.85
35.	1- Pentadecene	26.816	2.73
36.	1- Tricosene	28.196	0.24
37.	1- Pentadecene	29.989	3.71
38.	18- Nonadecene	34.458	0.31
39.	1-Tetradecene	34.86	1.82
40.	5-Eicosene, (E) -	39.781	0.43
41.	1- Hexadecene	40.174	1.85
42.	5-Octadecene, (E) -	41.351	0.33
43.	1- Heptadecene	44.986	1.85
44.	1- Tricosene	46.058	0.25
45.	3- Tricosene	49.379	1.99
46.	1- Heptadecene	53.421	1.87
47.	Z-5- Nonadecene	64.161	1.26
Total yield			31.02
Paraffins			
48.	Heptane	3.27	3.75
49.	Heptane, 4-methyl -	5.103	0.23
50.	Octane	6.385	2.47
51.	Heptane, 2,4-dimethyl -	7.204	0.16
52.	Nonane	10.387	3.15
53.	Nonane, 2,6-dimethyl -	14.515	1.27
54.	Decane, 2-methyl -	14.515	0.26
55.	Undecane	17.545	2.49
56.	Dodecane	20.738	3.97
57.	Hexane, 5-methyl-2-(1-methylethyl)-	21.486	0.18
58.	Dodecane, 4,6-dimethyl -	21.684	0.19
59.	Decane,2,3,5,8-tetramethyl -	21.839	3.19
60.	2-Isopropyl-5-methyl heptane	23.06	0.24
61.	Decane, 2-methyl -	23.109	0.56
62.	Heptane, 2,4-diethyl -	23.264	0.81
63.	Decane, 2-hexyl -	23.744	0.38
64.	Pentadecane	24.862	0.28
65.	Dodecane,4,6-dimethyl -	25.666	0.18
66.	Octane, 2-butyl-	26.508	3.23
67.	Tetradecane	27.009	4.78
68.	Decane, 2-hexyl -	27.393	0.35
69.	7-methyl tridecane	27.393	0.35



70.	Decane,2-methyl -	28.196	3.42
71.	2-Isopropyl-5-methyl heptane	28.196	2.42
72.	Dodecane, 2,6,11-trimethyl -	30.462	0.25
73.	Hexadecane	35.51	0.32
74.	Isotridecane	35.883	0.16
75.	Pentacontane	36.552	0.41
76.	Heptane, 2,4-diethyl -	38.508	0.25
77.	Nonadecane	40.757	0.34
78.	Heptadecane	49.842	0.41
79.	Hexadecane, 2,6,10, 14-tetramethyl -	53.846	0.42
80.	Hentetracontane	56.68	0.25
81.	Heneicosane	57.208	1.80
82.	Docosane	57.422	6.25
83.	Tricosane	60.779	1.57
84.	Octadecane	61.129	0.37
85.	Tetratetracontane	64.484	0.35
86.	Tetradecane, 2,3,4-trimethyl	65.133	0.19
87.	Pentacosane	70.473	0.69
88.	Octacosane	70.613	4.25
89.	Pentadecane, 8-hexyl -	73.576	3.35
90.	Hexatriacontane	76.447	2.35
91.	Triacontane	79.182	1.89
Total yield			64.18

Zn/AC: 2.5 %

**Table 3.46.** C-number distributions in liquid products derived from catalytic pyrolysis of PP and HDPE over ACs.

Polyolefin	Catalyst	Distribution (%)				
		C ₆ -C ₁₂	C ₁₃ -C ₁₆	C ₁₇ -C ₂₀	C ₂₁ -C ₃₀	>C ₃₀
PP	No catalyst	15.16	33.04	18.77	24.97	8.05
	Fe/AC *	59.79	14.53	10.64	7.16	12.65
HDPE	No catalyst	32.56	30.80	14.19	12.35	10.95
	Zn/AC **	36.55	27.28	7.50	21.23	7.05

Catalyst loading: *1 % and **2.5 %

Table 3.47. Hydrocarbon group types distributions in liquid fractions derived from catalytic pyrolysis of PP and HDPE over ACs

Polyolefin	Catalyst*	Distribution (%)			
		Paraffins	Olefins	Naphthenes	Aromatics
PP	No catalyst	66.55	25.87	7.58	0.00
	Fe/AC *	50.58	41.21	7.73	0.00
HDPE	No catalyst	59.70	31.90	8.40	0.00
	Zn/AC **	64.18	31.02	4.59	0.00

Catalyst loading: *1 % and **2.5 %



3.8 FUEL PROPERTIES OF LIQUIDS DERIVED FROM THERMAL AND CATALYTIC PYROLYSIS OF POLYPROPYLENE AND HIGH DENSITY POLYETHYLENE

One of the major objectives of the present work was to convert polyolefins under study into liquid products having fuel value to find alternative fuel resources and to see their prospective uses as feed stock to refineries or as blends to the marketable premium fuel products particularly gasoline and diesel fuel oil. The fuel properties were determined in case of crude as well as their distillate fractions. The crude pyrolysates were tested with relevance to fuel oil (light), where as the distillate fractions obtained at $<180^{\circ}\text{C}$ were tested with relevance to gasoline, and the fractions obtained in the b.pt range of $180\text{--}250^{\circ}\text{C}$ were tested relevance to light gas oil. The standard fuel oil analyses developed for petroleum based fuels were applied to all samples. The important properties determined are listed in Table 3.48. The properties determined included:

- I. Physical properties (density, API gravity, Conrad son carbon residue, and ash).
- II. Flow properties (kinematic viscosities and pour point).
- III. Combustion properties (heating value, flash point, aniline point and diesel index).
- IV. Antiknock properties (octane number, cetane number, and anti knock index).

The results were compared with petroleum-derived products to look for their fuel oil qualities desired in chemical and thermal applications.

3.8.1. Distillation Study of Crude Liquid Pyrolysates

The crude liquid pyrolysates obtained from PP and HDPE in thermal as well as catalytic runs were subjected to atmospheric distillation to obtain distillate fractions in gasoline and kerosene/diesel oil boiling range. Each pyrolysate was divided into two straight runs, (a) ranging from initial boiling point (IBP) to 180°C and (b) from 180°C to final boiling point (FBP). These fractions were named as distillate fractions A and fractions B, respectively. The % yields of distillate fractions A and B as well the yields of residue left were also determined.



3.8.1.1. Distillation Study of Liquid Pyrolysates Derived from PP

The distillation behavior of thermal and catalytically derived pyrolysates of PP was studied. The data is provided in Table 3.49.

In case of the thermal pyrolysate derived from PP, the % yield of distillate fraction A was found to be 30.5 %, whereas that of fraction B was 53.85 %. The residue obtained was found to be 15.45 %. The initial boiling point (IBP) was observed to be 68 °C and the final boiling point (FBP) was 250 °C. The results indicated that the thermally derived pyrolysate of PP consisted mostly (> 50 %) of higher hydrocarbons with boiling range of 180 to 250 °C, followed by lighter hydrocarbons (30 %) with boiling range of 68 to 180 °C. The fraction having boiling range above 250 °C was less than 20 %.

The liquid pyrolysate derived from PP in the presence of Pb/BaTiO₃ as catalyst consisted of fractions A and B in almost equal proportion, with minimum quantity of non-distillable residue. The yields of lighter distillate fraction A with b.pt < 180 °C and higher distillate fraction B with b.pt > 180 °C were found to be 43 and 42 %, respectively, and that of residual fraction was 12 %. In comparison to distillation behavior of the thermal run, it can be observed that the catalyst caused an increase in the yield of the distillate fraction B, whereas a decrease in the yield of fraction A was noticed.

The distillation behavior of the pyrolysate derived from PP in Fe/PBC catalyzed run was similar to that of Pb/BaTiO₃ catalyzed run. The yields of distillate fraction A and B were almost the same i.e. 44 and 42 %, respectively, and the yield of residue was about 13 %. It can be seen that Fe/PBC caused an increase the yield of distillate fraction A, and has decreased the yield of fraction B and residue, as compared to thermal run.

In case of pyrolysate obtained in Co/BC catalyzed run, the yields of distillate fraction A and fraction B were 56 and 23 %, respectively whereas that of non-distillable residue was about 21 %. Compared with the yield of distillates obtained in case of thermal run, it can be observed that the catalyst has appreciably enhanced the yield of fraction A as well as the residue, whereas the yield of fraction B decreased to about half.



Similarly, in case of pyrolysate obtained in Fe/AC catalyzed run, the yield of fraction A was enhanced to 50 %, and that of fraction B was decreased to 28 %. The residue yield was about 21 %.

3.8.1.2. Distillation Behavior of the Pyrolysates Derived from HDPE

The distillation study of the thermal and catalytically derived pyrolysates of HDPE was carried out. The data is provided in Table 3.50. The results of thermal run showed that the yield of distillate fraction A (b.pt <180 °C) was less than that of distillate fraction B (b.pt; 180 to 250 °C). The yields of distillate fractions A, B and non distillate residue were found to be 39, 43 and 17 %, respectively.

In case of pyrolysate obtained in Pb/BaTiO₃ catalyzed run, the yields of distillate fraction A and fraction B were found to be 28 and 55 %, respectively, whereas that of residual fraction was about 16 %. This means that the catalyst caused an increase in the yield of the distillate fraction B whereas decreased the yield of fraction A, as compared to thermal run. Moreover, the IBP and FBP of the distillate fraction A and fraction B were reduced compared to thermal run. The catalytic pyrolysate of HDPE obtained in Zn/PBC catalyzed run was found to be consisted of distillate fraction B in major proportion (61.54 %) and fraction A in smaller proportion (22 %), whereas the yield of residue was about 16 %. The results indicated that Zn/PBC has incredibly increased the yield of the fraction B.

The catalytic pyrolysates obtained in Zn/BC and Zn/AC catalyzed runs showed similar behavior. In case of both pyrolysates, the yield of fraction A was about 38 %, that of fraction B was 35 % and residual fraction was 25 %. In comparison to thermal run, the yield of fraction B was decreased and yield of residue was increased in case of both of the catalyzed runs, whereas the yield of distillate fraction A remained unchanged.

From the distillation data of the pyrolysates, particularly from the boiling range, it is concluded that all pyrolysates are comprised of a mixture of different fractions such as gasoline, kerosene, and diesel [112].

**Table 3.48.** Standard test methods used for fuel properties of PP and HDPE derived liquid products

Property	Unit	Test method
Density @ 15 °C	g/cm ³	IP160/87/ ASTM D-2598
API gravity @ 60°F	-	IP160/87/ ASTM D-1298
Kinematic Viscosity @ 40 °C	mm ² /s	IP 71/80/ ASTM D-445-74
Gross heat of combustion	kJ/kg	IP 12/ASTM D-2382
Carbon Residue	% wt	IP13/82/ASTM D-189-88
Ash	% wt	IP 4/81/ ASTM D-482-80
Cetane number	-	IP 41/ ASTM D-613
Octane Number (MON/RON)	-	IP 360 /ASTM D-2885
Pour point	°C	IP 15/67/ ASTM D-97
Flash Point	°C	IP 34/85/ ASTM D-5
Aniline point	°C	IP 2/78/ ASTM D-611
Diesel index	-	IP 21/53/ASTM D-611

**Table 3.49.** Distillation behavior of pyrolysates obtained from PP in thermal and catalytic runs

Liquid pyrolysate	Distillate fraction A		Distillate fraction B		Residue % yield
	% Yield	b.pt range (°C)	% yield	b.pt range (°C)	
No catalyst	30.70	68-180	53.85	180-250	15.45
Pb/BaTiO ₃	43.33	66-180	42.40	180-230	12.27
Fe/PBC	44.17	65-180	42.29	180-270	13.54
Co/BC	55.73	70-180	23.19	180-260	21.08
Fe/AC	50.14	90-180	28.50	180-245	21.36

Table 3.50. Distillation behavior of pyrolysates obtained from HDPE in thermal and catalytic runs

Liquid pyrolysate	Distillate fraction A		Distillate fraction B		Residue % yield
	% Yield	b.pt range (°C)	% yield	b.pt range (°C)	
No catalyst	39.21	70-180	43.59	180-249	17.20
Pb/BaTiO ₃	28.36	67-180	55.61	180-235	16.03
Zn/PBC	22.46	69-180	61.54	180-265	16.01
Zn/BC	38.41	75-180	35.77	180-235	25.82
Zn/AC	38.60	85-180	35.69	180-240	25.71

3.8.2. Fuel Properties of Crude Pyrolysates and Their Distillate Fractions

The fuel properties of raw/crude liquid pyrolysates derived from pyrolysis of PP and HDPE and their distillate fractions A & B were determined and cross analyzed in comparison to commercial existing petroleum based oils to assess their quality. The results are provided in Tables 3.51-3.54.

3.8.1.1. Physical Properties

The physical chemical properties including density, specific gravity, API gravity and ash of the crude liquids derived from thermal and catalytic cracking of PP and HDPE and their distillate fractions A & B were determined. The data of crude pyrolysates derived



from thermal and catalytic pyrolysis of PP is given in Table 3.51 and that of HDPE in Table 3.52 while fuel properties determined in case of their distillate fractions are given in Table 3.53 and Table 3.54, respectively.

The densities (ρ) of crude liquid oil derived from thermal pyrolysis of PP and HDPE were found to be 0.86 and 0.89 g/cm³, respectively. The API gravities were also determined and found to be 33.03 and 27.48, respectively. In case of liquid pyrolysates derived from various catalyzed runs, the values of ρ were found to fall within the range of 0.85 - 0.86 g/cm³. Similarly, API gravities were found to fall within the range of 33.03-34.97. The API gravity of 40 has been reported for light crude oil [113]. The results meet with the values reported for light oil [113, 114].

The ash content of each pyrolysate was also determined. It was found that ash contents were negligible in case of both thermally and catalytically derived liquids. This is indicative of the fact that the crude liquid fractions are free from any detritus contamination and even high molecular weight soot. Similarly, the carbon residue of all the pyrolysates were found to fall within the range 0.02 - 0.08 wt %, which are almost negligible.

The physico-chemical properties including density, specific gravity, API gravity and ash of the distillates obtained from thermal and catalytic pyrolysates of PP were determined. The data showed that the densities of all distillates fractions A obtained in case of pyrolysates of PP were in the range of 0.79 to 0.8 g/cm³, whereas in case of fraction B, were fallen in the range of 0.84 to 0.85 g/cm³. The difference between the nature of both fractions can be more prominently observed from their API gravities. The values of API gravity of distillate fractions A were found to fall in the range of 45 to 54, whereas those of distillate fractions B, in the range of 34 to 37. The results indicated that the densities and API gravities of fractions A are close to gasoline and that of fraction B resembles to gas oil [115].

The ash contents determined in case of both distillates fractions were negligible which showed that the pyrolysates are free from any metallic or inorganic contamination and even high molecular weight soot. The carbon residue of both fractions were found to



fall within the range of 0.02 to 0.04 (%), however, the carbon residues of fractions A were negligible compared to fractions B.

The physical properties included density, specific gravity, API gravity and ash contents were also determined in case of pyrolysates derived from HDPE. The results indicated that the values of the densities of the fractions A were slightly lower than fractions B. In case of distillate fractions A obtained from thermal and catalytic pyrolysates of HDPE, the densities were found to fall within the range of 0.77- 0.80 g/cm³, while in case of distillates fractions B, the values were within the range of 0.85- 0.86 g/cm³. The API gravity showed significant variations in case of the distillate fractions. In case of fractions A, the values were found to be within the range of 45-52, while in case of distillate fractions B, the values were in the range of 33.03- 34.97. Among distillates obtained from different pyrolysates, the distillates of the pyrolysate obtained in Zn/PBC catalyzed run depicted the highest API gravities, followed by thermal pyrolysates, whereas other pyrolysates showed relatively lower API values. The results showed that the API gravity of the distillate fractions A, match well with those of gasoline range fuels, while that of fractions B, meet with gas oil specifications.

Negligible ash contents were observed in all the distillate fractions. The % wt of the carbon residue in case of distillate fractions A was found to be about 0.01 to 0.02 %, whereas in case of fraction B, the % wt of carbon residue was found to fall within the range 0.02- 0.06 %. The results indicated that these hydrocarbons are free from any metallic or inorganic contaminations.

3.8.1.2. Flow Properties

The flow properties including viscosity, and pour point of PP and HDPE derived crude liquids from both thermal and catalytic runs were determined. The viscosity of a fluid whether Newtonian or non Newtonian is a measure of its resistance to shearing forces it offers during flow or resistance to flow under gravity. This property plays an important role in the operation of the fuel injection system. Further, it affects atomization quality and subsequent combustion properties of the fuel. The kinematic viscosities (ν) of PP and HDPE derived crude liquid products from thermal pyrolysis were found to be



4.09 and 5.08 mm²/s, respectively. The ν of PP and HDPE derived liquid products from catalytic pyrolysis were found to fall within the range of 2.45-4.68 mm²/s, and 3.68-5.06 mm²/s, respectively. As per standard kinematic viscosities of fuel oil (3.5–9.7mm²/s), liquids under study are reported to be in accordance with fuel oil [116, 117]. Comparing the results with the viscosities of petroleum fuels, the values meet the specifications of fuel oils.

Pour point of a liquid fuel is the lowest temperature at which a liquid ceases to flow which describes the fluidity of fuels at low temperatures. The loss of fluidity of liquid fuels is usually caused by an increase in viscosity or crystallization of waxy materials. The pour points of the crude liquid products obtained from thermal pyrolysis of PP and HDPE were found to be -9 and -5 °C, respectively, while that derived from catalytic runs were found to be within the range of -6 to -10 °C, and +7 to -10 °C, respectively. The values are in accordance with the standard values of fuel oil [118].

It can be observed from the compiled results that the pour points determined in case of crude liquids derived from catalytic runs were quite low in case of PP, which is indicative of the fact that these liquids are free from crystallites and other impurities which may cause inhibition in flow of liquid fuels under reduced temperatures. Although, the pour point of the light distillates petroleum fractions varies, however, the pour point of the light fractions occur around 6 °C. The values obtained in case of pyrolysates match well with fuel oils.

The flow properties of the distillates obtained from thermal and catalytically derived pyrolysates of PP including viscosity and pour point were determined. The results indicated that the kinematic viscosities of fractions A were lower than fractions B. Kinematic viscosities of the distillate fractions A were in the range of 1.35 to 1.65 mm²/s, which closely match the gasoline range products. Similarly, in case of distillate fractions B, the kinematic viscosities were found to be within the range of 2.11-2.22 mm²/s, which more likely resemble different grades of middle oils. The values of pour points determined in case of distillates fraction A and fraction B obtained from thermal and



catalytic pyrolysates of PP were almost the same, and were found to be less than $> -10^{\circ}\text{C}$. The values meet specifications for fuel oils.

Among the flow properties, kinematic viscosity and pour point were determined in case of distillate fractions obtained from thermal and catalytically derived pyrolysates of HDPE. The values of kinematic viscosity of the distillate fractions A were found to be in the range from 1.39 to 1.63 mm^2/s , except for only one sample where it was found to be 2.01 mm^2/s . The values of kinematic viscosity for distillate fractions B were quite higher than those of fractions A, and were within the range of 2.11-2.61 mm^2/s . The results indicate that the viscosity of the distillate fractions match with the various grades of diesel oil which has been reported to be in the range of 1.3-4.1 cSt (grade No. 1-D and 2-D) at 40°C [119]. On the other hand, the viscosity values of the distillate fractions A are in agreement with the light premium fuels i.e. gasoline and gas oil. It can be observed from the results, that among various fractions A, the one derived from the pyrolysate obtained with Zn/AC catalyst exhibited the highest viscosity (2.01 mm^2/s), followed by thermal pyrolysate (1.61 mm^2/s) and Zn/PBC pyrolysate (1.57 mm^2/s), whereas the pyrolysates of Pb/BaTi₂O₃ and Zn/BC catalyzed runs have lowest viscosities (1.38 and 1.39 mm^2/s , respectively). Similarly, in case of distillate fractions derived from different pyrolysates, the one obtained with Zn/AC catalyst has maximum viscosity (2.61 mm^2/s), followed by that of Zn/BC (2.53 mm^2/s), Pb/BaTi₂O₃ (2.43 mm^2/s), then Zn/PBC (2.23 mm^2/s) whereas the distillate fractions B of thermal pyrolysates showed minimum viscosity (2.11 mm^2/s).

The pour points of the distillates fractions were found to be in the range of $(-1^{\circ}\text{C}) - (-10^{\circ}\text{C})$. In case of distillate fractions A, pour points were found to fall within the range $(-6^{\circ}\text{C}) - (-10^{\circ}\text{C})$. On the other hand, in case of distillate fractions B, pour points were found to fall within the range of $(-1^{\circ}\text{C}) - (-10^{\circ}\text{C})$. In nutshell, the distillate fractions derived from the pyrolysates obtained in Zn/AC catalyzed run showed high pour points than the thermally derived pyrolysates. Results suggested that the values of pour points determined in case of the distillates fractions meet the fuel grade criteria.



3.8.1.3. Combustion Properties

The combustion properties i.e. heat of combustion, flash point, aniline point and diesel index were calculated. The heating values determined in case of PP and HDPE derived crude liquid products from thermal runs were found to be 35.50 and 30.60 MJ/kg, and in case of catalytic runs were 34.1- 45.0 MJ/kg (PP), and 34.20- 40 MJ/ kg (HDPE), respectively.. Calorific values of various fuel oils, i.e. diesel, gasoline, petrol and petroleum fuel have been reported to be 44.8, 47.3, 48 and 43MJ/Kg, respectively [113, 116, 117]. The values are quite high particularly in case of catalytically derived liquids which suggests that the pyrolysates meet the fuel grade criteria and can be used for energy generation.

The flash point of a liquid fuel is the lowest temperature at which the vapors above the liquid ignite when an external flame is applied. It is a measure of volatility and considered as an important parameter in fuel handling to prevent fire hazards during storage. The flash points of the crude liquid products derived from thermal pyrolysis of PP and HDPE were found to be 30 °C and 48 °C, and that of catalytically derived liquids were found to fall within the range of 25-40 °C and 37.4-40 °C, respectively. The flash points reported for various fuels are, kerosene; 23 °C, diesel fuel; 55 °C and light fuel oil; 79 °C . Flash point of fuel oil has been reported to be 40 °C. All the above values were found to be in accordance with the standard value of fuel oil [120].

The aniline point is the lowest temperature at which equal volumes of aniline and the sample become completely soluble (ASTM D611) and is a useful tool to find out the presence of aromatics in the fuel samples. The aniline point determined in case of PP and HDPE in thermal runs were found to be 40 and 45 °C and in case of catalytic runs were found to be 30- 75 °C and 42-75 °C, respectively. The aniline point can be used as a parameter for evaluation of the degree of aromaticity of a sample [121].

Combustion properties of diesel oil are described by the diesel index. The diesel index calculated in case of liquids derived from thermal pyrolysis of PP was found to be 34.35 and in case of HDPE was 31.05 while in case of catalytic runs; the values were found to fall within the range 30.07-59.02 in case of PP and 35.54-52 in case of HDPE.



The values are comparable with the petroleum fuels and showed excellent combustion properties.

The combustion properties were also investigated in case of distillate fractions of crude pyrolysates derived from PP. The results indicated that the heating values of the distillate fractions A were found to be higher than distillate fractions B. In case of distillate fractions A, obtained from thermal and variously catalytic pyrolysates, the heating values were found to fall within the range of 38.4-42.1 MJ/kg, while in case of distillate fractions B, their values were in the range of 35.6-40.7 MJ/kg. It could be observed that highest heating values were given by the distillates fractions obtained from the pyrolysates of Fe/PBC catalyzed run followed by thermal pyrolysate followed by Pb/BaTi₂O₃, whereas the distillate fractions from pyrolysate obtained in Co/BC and Fe/AC catalyzed runs showed minimum heating values. The heating values of the fractions A and B were found to be matching more with the gasoline and gas oil, respectively, hence meeting the fuel grade criteria [122, 123].

The flash point of a liquid fuel may be described as the minimum temperature at which the vapors of the fuel ignite in the presence of an external flame, it is actually the measure of volatility of the fuel and is an important quality which is to be considered in storage and handling of fuel. Among the distillates fractions derived from thermal and catalytic pyrolysates of PP, the values for flash points of fractions A were found to be less than those of fractions B. In case of distillate fractions A, the flash points were found to be fallen within the range of 23 to 30 °C, whereas for fractions B, their values were observed within the range 38 to 45 °C. The results indicated that the flash points of all the distillate fractions A were comparable with those of kerosene and gasoline range fuels, respectively. Similarly, the flash points of the fractions B closely match the gas oil. The flash point of kerosene is reported to be 23 °C, diesel fuel; 55 °C and light fuel oil; 79 °C. Among the distillate fractions obtained in case of various pyrolysates, the flash points of the distillates fractions A and B were relatively higher in case of pyrolysates obtained with Fe/AC and Co/BC, than those of thermal and catalytic pyrolysates obtained with Pb/BaTiO₃ and Fe/PBC.



The aniline point of a fuel indicates the minimum temperature at which the sample becomes miscible with equal volume of aniline (ASTM D611). It refers to the relative proportion of aromatics in the fuel, hence it could be used as a parameter for evaluation of the degree of aromaticity of a sample. Like other properties, the values of aniline points also varied greatly for both the distillates fractions. The fractions A showed lower values and fractions B showed high values of aniline points. Results indicated that the aniline points of fractions A were found to fall within the range of 29 - 49 °C, whereas that of distillate fractions B were found within the range of 52-70 °C. Among the distillate fractions of different pyrolysates, the highest aniline points were observed in case of distillate fractions obtained with Co/BC catalysts, followed by Co/AC followed by Fe/PBC, whereas that of Pb/BaTiO₃ and thermal run had the lowest aniline points. Results indicated that the aniline points of the fractions A match well with gasoline range fuels, and those of fractions B match with the gas oil [122, 123].

Diesel index describes the combustion properties of diesel oil. The values of the diesel index of fractions A were mostly found to fall within the range of 41- 48. In case of fractions B, their values were found to fall within the range of 44-55. It could be concluded from these results that distillate fractions B, obtained from the thermal and catalytic pyrolysates have excellent combustion properties matching best with gas oil.

The combustion properties determined in case of the distillates fractions obtained from pyrolysates derived from HDPE included heat of combustion, flash point, aniline point and diesel index. The calorific heat values of the distillate fractions were found within the same range, however, the fractions A showed higher heating values than fractions B. In case of fractions A, the heating values were found to be within the range of 38.4- 41.3 MJ/kg. Similarly, in case of distillates fractions B, the heating values were in the range of 36.5- 38.2 MJ/kg. The values meet with the quality of premium light fuels. Among the distillates fractions A obtained in case of various pyrolysates, the fraction obtained from pyrolysate of HDPE in Pb/BaTiO₃ catalyzed run showed highest heating value (40.2 MJ/kg), followed by Zn/PBC (41.3 MJ/kg), thermal run (40.0 MJ/kg), Zn/AC (39.4 MJ/kg) and Zn/BC (38.4 MJ/kg). However, distillate fractions B, obtained



with Zn/AC catalyst showed heating value (39.7 MJ/kg) followed by thermal run (38.2 MJ/kg), Pb/BaTiO₃ (37.8 MJ/kg), Zn/PBC (36.8 MJ/kg) and Zn/AC (36.5 MJ/kg).

The values of flash points of the distillates fractions A were found to be smaller than those of fractions B. Among different distillate fractions A, the flash points were found to fall within the range of 30 -32 °C. Among distillate fractions B, the flash points were found within the range of 36-43 °C. The flash points of both distillate fractions were found to lie between the gasoline and gas oil.

The results of the aniline points were analogous to that of flash points. In case of distillates A, the aniline points varied between 32 and 40 °C, whereas in case of distillate fractions B, the aniline points were found to be within the range of 50-73 °C. Among different distillate fractions, the highest aniline points were given by pyrolysates obtained in Zn/BC, and Zn/AC catalyzed runs.

The values of diesel index of both distillates fractions were found to be almost in similar range, i.e. 42 -54. In case of fractions A, diesel indexes were found to fall within the range of 42.64- 53.78, while in case of fractions B samples, in the range of 42.66 to 53.97. It could be concluded from these results that both distillate fractions obtained from the thermal and catalytic pyrolysates showed the combustion characteristics in agreement with those of various grades of diesel oil.

3.8.1.4. Antiknock Properties

The antiknock properties like octane number, cetane number and antiknock index of the crude pyrolysates were determined. The anti-knock quality of automotive C₆-C₁₀ rang hydrocarbons is characterized by the octane number. The octane number of gasoline-range products had been reported to fall between 60 and 120, depending on the parameters. The octane number of liquid products derived from PP in thermal runs were; (MON=87.6 & RON= 97.8) and HDPE (MON= 85.3 & RON= 95.3). The octane number determined in case of pyrolystated driven from catalytic runs were; PP (MON=85.4- 105 & RON= 85- 95.4) and HDPE (MON= 85.8-104 & RON= 90.1- 95.8).



The results indicated that the pyrolysates had good antiknock properties. The high octane number of the fractions indicated the presence of paraffins, olefins and branched structures. Alkenes with the same number of carbon atoms in the molecule have higher RON than the respective alkanes and lower RON than the respective iso-alkanes [107]. The pyrolysates obtained from thermal cracking of PP has the best anti knocking characteristics compared to HDPE regarding the RON value. It is generally believed that the aromatic hydrocarbons have the highest octane number in the naphtha fraction [124]. Branched hydrocarbons in naphtha-like fractions have high octane numbers [125]. However, HDPE derived naphtha-like fraction has high octane number, which may be due to the high content of olefins [124]. The RON value is used as an index of the quality of the liquid products. The higher the octane number, the higher is the tendency for the liquid to burn evenly and completely [126].

The cetane numbers of thermally and catalytically derived liquid fractions were also determined which were found to be 49.3 in case of PP and 46.0 in case of HDPE in thermal runs. In case of catalytic runs, the values were found to be fallen with in the range of 46.5-100 (PP) and 46.8-99.9 (HDPE). The high cetane number is due to the presence of linear paraffins and α -olefins. The results indicated that the fractions under study were enriched in these configurations.

The antiknock index (AI) is the average of the research octane number and the motor octane number. The AIs were also calculated in case of liquids derived from both thermal and catalytic runs. The values of AIs were found to be 92.8, and 90.2 in case of PP and HDPE thermal runs while in case of catalytic runs were found to be fallen in the range 90.5-100.3 (PP) and 68.5-100.6 (HDPE). Gasoline has been reported to have AI of more than 90 [127]. The results indicated that the values are comparable to the commercial gasoline.

It may be concluded that the liquid products derived from both thermal and catalytic runs of PP and HDPE met the fuel grade qualities and are suggested to be a blend of gasoline and diesel range hydrocarbons. The products can be used as transportation fuels in energy market for gasoline and diesel production.



The results showed that the derived liquids presented acceptable values for all the studied properties when compared to the specified values for the conventional petroleum-derived fuels. The properties of PP derived liquids were quite comparable to the commercial gasoline and gas oil samples compared to HDPE. Moreover, the catalytically derived liquid showed significant changes in critical properties of the pyrolysates.

The antiknock properties of the distillate fractions of the pyrolysates derived from PP included octane number, and antiknock index were also investigated. The anti-knock quality of gasoline range hydrocarbons is characterized by octane number, which ranges between 60 and 120, depending on the parameters. Hence, this property was only determined for gasoline range distillate fractions. The motor octane numbers (MON) of the distillate fractions A were found to fall within the range of 91-96. Similarly, the research octane numbers (RON) of the fractions A were found to fall within the range of 101 -105. The results indicated that the values of MON and RON of the distillate fractions A resembled with that of gasoline range products. It has been reported that excess of olefinic and iso-paraffinic hydrocarbons impart high octane number to the fuel, hence the fraction A may be considered to be rich in these functionalities.

Like the octane number of gasoline, the cetane number indicates the quality of the gasoil/diesel oil. Hence, this property was determined for distillate fractions of the gas oil range. The cetane numbers of the fractions B were found to fall within the range of 59- 67. The results showed that all the distillate fractions B have high cetane number and thereby exhibited similarity to the gas oil fuels. It has been reported that high cetane number is due to the presence of linear paraffins and α -olefins, which showed that fractions B are rich in these types of hydrocarbons.

The antiknock index (AI) represents the average of the RON and MON, the value of AI for gasoline has been reported to be 90. Although distillate fractions have high AI, however, in case of distillate fractions A, the values of AI were higher (95-101). The results indicated that the values are comparable to commercial gasoline.

It may be concluded from the results that the fuel qualities of the distillate fractions A (b.pt. 65-180 °C) closely matched with gasoline and kerosene range



hydrocarbons. On the other hands, the fuel characteristics of the distillate fractions B (b.pt. 180-250 °C) showed that these fractions behaved more like various grades of diesel oil.

Among the antiknock properties, octane number, cetane number and antiknock index of the distillate fractions of pyrolysates derived from HDPE were also investigated. The MON and RON values for distillate fractions A were found to be higher than those of fractions B. The values of MON among various fractions A, were found to fall within the range of 90.7 - 95, whereas that of fractions B ranged from 80.3 to 87.8. Likewise, the values of RON determined in case of fractions A were found to fall within the range of 100.8- 105, whereas in fractions B, the values were found to fall within the range of 90 to 97.8.

It could be observed from the results, that the values of MON and RON are higher in case of distillate fractions obtained from catalytic pyrolysates than that of thermal pyrolysates. Maximum MON and RON were determined in case of distillate fractions A and fractions B derived from pyrolysate obtained in Zn/PBC and Zn/BC catalyzed runs. The high octane number of these fractions could be attributed to the high contents of olefins, cyclo-paraffins and iso-paraffins.

Cetane number was determined in case of distillate fractions B. The cetane numbers were found to fall within the range of 45.0-61.8. Among different distillates fractions obtained from various crude pyrolysates, high cetane numbers were demonstrated by those derived from the pyrolysates obtained in Zn/AC, Zn/PBC and Zn/BC catalyzed runs. The high cetane numbers of fractions B samples showed that these fractions resemble with the combustion characteristic of gas oil fuel, which are rich in linear paraffins and α -olefins.

Like octane number, the values of anti knock index were also found to be higher for distillates fractions A. For fractions A, the AI values were found to fall within the range of 94.9- 100. As the value of AI for premium gasoline is commonly more than 90, therefore, it may be suggested that distillate fractions A behaved like gasoline range fuel.

**Table 3.51.** Fuel properties of the crude liquid products derived from thermal and catalytic pyrolysis of PP

Property	Unit	No Cat.	Pb/BaTiO ₃	Fe/PBC	Co/BC	Fe/AC
Physical Properties						
Density @ 15 °C	g/cm ³	0.86	0.85	0.85	0.85	0.86
ApI gravity @ 60 °C	-	33.03	34.97	34.97	34.97	33.03
Ash	% wt	0.00	0.00	0.00	0.00	0.00
Carbon Residue	% wt	0.07	0.02	0.04	0.06	0.06
Flow Properties						
Kinematic Viscosity @ 40 °C	mm ² /s	4.09	2.45	3.17	4.68	3.36
Pour Point	°C	-9	-12	-10	-6	-10
Combustion Properties						
Gross heat of combustion	MJ/kg	35.50	45.00	36.4	34.6	34.1
Flash Point	°C	30	25	39.5	38.2	39
Aniline Point	°C	40	30	76	66	75
Diesel Index	-	34.35	30.07	59.02	49.8	55.16
Anti Knock Properties						
Octane Number (MON)	-	87.6	85.4	105.3	105.1	105
Octane Number (RON)	-	97.8	95.4	95.3	95.2	95
Centane Number	-	49.3	46.5	68.7	100.1	68.5
Anti Knock Index	-	92.8	90.5	100.3	68.6	100

**Table 3.52.** Fuel properties of the crude liquid fractions derived from thermal and catalytic pyrolysis of HDPE

Property	Unit	No Cat.	Pb-Co/BaTiO ₃	Fe/PBC	Co/BC	Fe/AC
Physical Properties						
Density @ 15 °C	g/cm ³	0.89	0.89	0.87	0.86	0.87
ApI gravity @ 60 °C	-	27.48	27.48	31.14	33.03	31.14
Ash	% wt	0.00	0.00	0.00	0.00	0.03
Carbon Residue	% wt	0.08	0.04	0.07	0.07	0.07
Flow Properties						
Kinematic Viscosity @ 40 °C	mm ² /s	5.08	3.68	5.06	4.51	4.58
Pour Point	°C	-5	-10	0.00	5	7
Combustion Properties						
Gross heat of combustion	MJ/kg	30.60	34.20	32.2	33.4	32.2
Flash Point	°C	48	40	40	37.4	40
Aniline Point	°C	45	42	70	68	75
Diesel Index	-	31.05	35.54	49.2	51	52
Anti Knock Properties						
Octane Number (MON)	-	85.3	85.8	105.6	104.8	100.1
Octane Number (RON)	-	95.3	95.8	95.6	94.8	90.1
Centane Number	-	46.0	46.8	68.9	99.9	65
Anti Knock Index	-	90.2	90.7	100.6	68.5	95.1



Table 3.53. Fuel properties of the distillate fractions A & B obtained from the thermal and catalytic pyrolysates of PP

Property	Unit	No Catalyst		Pb/BaTiO ₃		Fe/PBC		Co/BC		Fe/AC	
		A	B	A	B	A	B	A	B	A	B
Physical Properties											
Density @ 15 °C	g/cm ³	0.79	0.85	0.78	0.84	0.76	0.84	0.8	0.85	0.8	0.84
API gravity @ 60°F	-	47.6	34.97	49.91	36.95	54.68	36.95	45.37	34.97	45.37	36.95
Ash	% wt	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Carbon residue	% wt	0.01	0.02	0.01	0.01	0.02	0.03	0.02	0.04	0.02	0.03
Flow Properties											
Kinematic Viscosity @ 40 °C	mm ² /s	1.65	2.22	1.35	2.11	1.4	2.13	1.62	2.19	1.51	2.16
Pour point	°C	<-10	<-10	<-10	<-10	<-10	<-10	<-10	<-10	<-10	<-10
Combustion properties											
Gross heat of combustion	MJ/kg	41.3	39.5	40.86	39.2	42.1	40.7	38.4	36.71	38.5	35.6
Flash Point	°C	25	41	25	38	23	39	26	42	30	45
Aniline point	°C	30	52	29	56	35	57	49	70	41	65
Diesel index	-	40.93	43.92	42.02	49.06	45.22	49.73	54.53	55.25	48	55.55
Anti knock properties											
Octane Number (MON)	-	91	-	90.15	-	96.3	-	91.6	-	95	-
Octane Number (RON)	-	101.5	-	100.43	-	106.3	-	101.6	-	105	-
Cetane number	-	-	59	-	62.2	-	61.5	-	66.5	-	67.2
Anti knock index	-	96.25	91.55	95.29	90.65	101.3	97.7	96.6	91.85	100	94.6

A: Fraction <180 °C

B: Fraction >180 °C

**Table 3.54.** Fuel properties of the distillate fractions A & B obtained from the thermal and catalytic pyrolysates of HDPE.

Property	Unit	No Catalyst		Pb-Co/BaTiO ₃		Zn/PBC		Zn/BC		Zn/AC	
		A	B	A	B	A	B	A	B	A	B
Physical Properties											
Density @ 15 °C	g/cm ³	0.78	0.85	0.79	0.86	0.77	0.85	0.79	0.86	0.8	0.86
API gravity @ 60°F	-	49.9	34.97	47.6	33.03	52.26	34.97	47.6	33.03	45.37	33.03
Ash	% wt	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Carbon residue	% wt	0.02	0.04	0.02	0.02	0.01	0.04	0.01	0.05	0.01	0.06
Flow Properties											
Kinematic Viscosity @ 40 °C	mm ² /s	1.63	2.11	1.38	2.42	1.57	2.23	1.39	2.53	2.01	2.61
Pour point	°C	<-10	<-10	<-10	<-10	<-10	<-10	<-70	-1	-6	-2
Combustion properties											
Gross heat of combustion	MJ/kg	40	38.2	40.2	37.8	41.3	36.8	38.4	36.5	39.4	37.9
Flash Point	°C	30	43	32	37	30	39	31	38	32	36
Aniline point	°C	35	50	32	59	36	56	45	73	40	70
Diesel index	-	47	42.66	42.64	45.64	50.58	46.44	53.78	53.97	47.18	52.18
Anti knock properties											
Octane Number (MON)	-	91.5	-	89.9	-	95	-	94.5	-	90.7	-
Octane Number (RON)	-	101.5	-	99.9	-	105	-	104.5	-	100.8	-
Cetane number	-	-	45	-	45.01	-	58.6	-	61.5	-	61.8
Anti knock index	-	96.5	85.4	94.9	87.4	100	92.8	99.5	88.8	95.75	86.38



3.9 COMPARATIVE STUDY

In the present work, four catalyst systems including original and metal doped BTs, original and metal oxide impregnated PBCs, original and metal oxide impregnated BCs and original and metal salts impregnated carbons ACs were used, separately to evaluate their effectiveness in pyrolysis of two commonly used polyolefins i.e. PP and HDPE into useful fuel like products. Both surface properties and acidity of the catalyst systems were considered in evaluating their activity and selectivity in term of products yields (over all yields and yields of liquids, gases and residues), their influence on the desired liquid products composition, and fuel properties (both crude liquids and their distillate fractions).

In thermal run, total conversion as high as 98.66 % (liquid; 69.82%, gas; 28.84%, and residue; 1.34 %) was achieved at 300 °C in case of PP and 98.12 % (liquid; 80.88 %, gas; 17.24 %, and residue; 1.88 %) in case of HDPE at 350 °C. The results showed that the liquid fractions consisted of a wide range of hydrocarbons mainly distributed within C₆–C₁₆. The liquid product obtained in case of PP was found to be enriched in the naphtha range hydrocarbons. Similarly, the liquid product obtained in case of HDPE was also found to be enriched in naphtha range hydrocarbons with preponderance in gasoline and diesel range hydrocarbons. The % distributions of paraffinic, olefinic, and naphthenic hydrocarbons in liquid product derived from PP were found to be 66.55, 25.7, and 7.58 %, respectively, whereas in case HDPE, their % distributions were 59.70, 31.90, and 8.40 %, respectively. Upon comparing the hydrocarbon group type yields, both PP and HDPE gave high yields of paraffinic hydrocarbons.

The efficacy of original, as well as Pb, Co and Pb & Co co-doped barium titanates in pyrolysis of polypropylene (PP) into useful products was also studied and the results were compared with thermal and other catalyzed runs. The results indicated that the catalyst used did not affect the total conversion. However, all catalysts particularly doped catalysts showed good activities in conversion to liquid products when used in 1 % concentration. The proportions of naphtha range carbon range hydrocarbons i.e. C₆–C₁₂, and C₁₃–C₁₆ were high in runs catalyzed by Pb/BaTiO₃ and Co/BaTiO₃. Further, un doped



BaTiO₃, Pb-BaTiO₃ and Co/BaTiO₃ enhanced the formation of paraffins, olefins and naphthenes. Based on the overall yield of liquid products as well as the proportion of hydrocarbons ranging from C₆ to C₁₆, Pb doped BaTiO₃ was found to be the effective catalyst for conversion of PP to value added products.

The results obtained in case of HDPE catalyzed with titanates as catalysts indicated that the individual catalyst when used in different concentrations exhibited a synergistic effect on product yields particularly liquid products. Among the catalysts used, Pb-Co/BaTiO₃ gave the highest liquid yield (86 %) when used in 1 wt % concentration. The same catalyst gave the highest yield of middle carbon range products i.e. C₁₃-C₁₆, & C₁₇-C₂₀. Inversely, the original BaTiO₃ favored the formation of C₆-C₁₂ and C₁₃-C₁₆ range hydrocarbons, whereas Pb/BaTiO₃ and Co/BaTiO₃ enhanced the yield of C₁₃-C₁₆, and C₂₁-C₃₀ range products. Regarding the hydrocarbon group types, all the catalysts significantly increased the formation of paraffins and reduced the yield of olefins and naphthenes compared to thermal run.

The effect of catalyst types and concentration on total conversion and conversion to liquid, gas and coke/residue was studied in the presence of metal impregnated PBCs. The results indicated that all catalysts when used in different concentrations have greatly affected the yields particularly liquid yields. Among the catalysts used, Fe/PBC (2.5%) and Zn/PBC (1 %) gave highest liquid yields of 96.7 & 91.1 wt% in case of PP and HDPE, respectively.

In case of run catalyzed by Fe/PBC, the yield of C₆-C₁₂ range hydrocarbons in case of PP was increased by 32 %, whereas the yields of C₁₃-C₁₆, C₁₇-C₂₀, C₂₁-C₃₀ and >C₃₀ range hydrocarbons were reduced by 7, 2, 22 and 3 %, respectively when compared with thermal run. The results indicated that the catalyst exhibited high activity in enhancing the formation of light hydrocarbons.

In case of HDPE, Zn/PBC enhanced the yields of middle range hydrocarbons i.e. C₁₃-C₁₆ and C₁₇-C₂₀ by 4 and 16 %, respectively, whereas the yield of low carbon range products (C₆-C₁₂) was decreased by about 19 % while that of high carbon range products (>C₂₁) remained unaffected. The hydrocarbon group types analysis indicated that Fe/PBC



enhanced the formation of naphthenes and reduced the formation of olefins in case of PP, whereas the formation of paraffins remained unaffected. In case of HDPE, Zn/PBC caused significant increase in formation of paraffinic hydrocarbons and decreased the olefinic and naphthenic hydrocarbons.

The effect of BCs and their concentration on overall yields and yields of liquid, gas and residue was studied. The results achieved indicated that among the catalysts used, Co/BC and Zn/BC produced a much greater amount of liquid products compared to other catalysts under study. In case of PP, the increase went up to a maximum of 92 % in Co/BC catalyzed run when used in 1% concentration. Similarly, in case of HDPE, the liquid yield enhanced to 91 wt% in Zn/BC catalyzed run when used in 2.5 % concentration.

The GC-MS results indicated good catalytic role of metal oxide impregnated bentonites with optimum activity and selectivity exhibited by Co/BC and Zn/BC in case of PP and HDPE. In case of PP, Co/BC catalyzed run caused the yield of light C-range products i.e. C₆-C₁₂ to increase significantly all most four folds (60.18 %). Similarly, yield of heavy C-range products i.e. > C₃₀ was also increased and attained a value of 12 %. On contrary, the yield of middle C-range products was decreased significantly. In case of HDPE, Zn/BC catalyzed run caused the yields of lighter products i.e. C₆-C₁₂, C₁₃-C₁₆, and C₁₇-C₂₀ to decrease whereas the yields of middle as well high C-range products (C₂₁-C₃₀ and $\geq$ C₃₀) were increased.

The catalysts also affected the hydrocarbon group types distributions. In case of PP, the catalytic run, caused the yield of paraffins to slightly decrease, whereas the yields of olefins and naphthenes were reduced significantly when compared with thermal run. In case of HDPE, the use of Zn/BC caused a significant increase in the formation of paraffinic and olefinic hydrocarbons.

The results obtained in case of runs catalyzed with original (Darco (20-40 mesh) and transition metal salts impregnated activated carbons (Zn/AC, Cr/AC, Ni/AC, Co/AC, Fe/AC, and Mn/AC) were also compared.



In case of PP, the maximum liquid yield of about 87 % was attained in run catalyzed with Fe/AC (2.5 %). In case of HDPE, none of the catalyst was found to be effective in enhancing the yield and the yield of liquid was even less than the one achieved in case of thermal run. In case of PP run catalyzed with Fe/AC, the distributions were found to be C₆-C₁₂; 59.79 %, C₁₃-C₁₆; 14.53 %, C₁₇-C₂₀; 10.64 %, C₂₁-C₃₀; 7.16 %, and > C₃₀; 12.65%. The results indicated the synergistic effect exhibited by catalyst under study on the C-number distribution particularly on the formation of C₆-C₁₂ products which was found to be increased from 33 to 59 %. A pronounced decline can be observed in case of C₁₃-C₁₆ hydrocarbons. It can be seen that the catalyst altered the product distribution in term light compounds at the expense of middle range hydrocarbons i.e. C₁₃-C₁₆. The results achieved in case of PP catalyzed with Zn/AC indicated that the catalysts did not cause a significant effect on the yield pattern. However, a slight increase can be observed in case of C₆-C₁₂ and C₁₃-C₁₆ products. The decline in yield of C₂₁-C₃₀ was also observed, which indicated that the catalyst under study facilitated the cracking of C₂₁-C₃₀ range hydrocarbons to yield C₆-C₁₂ and C₁₃-C₁₆ products.

The results of hydrocarbon group types distribution in the liquid products indicated that in case of PP, the catalytic run using Fe/AC, caused the yield of olefins to increase by 16 % , the yield of paraffins exhibited a decrease of 15 % as compared to thermal run, whereas the yield of naphthenes was almost comparable with the thermal run. In contrast, catalytically derived liquid of HDPE using Zn/AC, the yield of paraffins was increased from 59 to 64 % as compared to the thermal run. The yield of olefins remained the same, while a small decrease in naphthenes can be observed.

In terms of highest liquid products achieved in case of PP, the order of reactivity of the catalysts was; Fe/PBC > Pb/BaTiO₃ > Co/BC > Fe/AC.

In terms of the C-range distributions; light products (C₆-C₁₂), the order of selectivity was; Co/BC > Fe/AC > Fe/PBC > Pb/BaTiO₃, middle range products (C₁₃-C₁₆), Pb-Co/BaTiO₃ > Fe/PBC > Co/BC > Fe/AC, heavy products (C₁₇-C₂₀), BaTiO₃ > Fe/PBC > Fe/AC > Co/BC, heavy products; (C₂₁-C₃₀), BaTiO₃ > Fe/AC > Co/BC > Fe/PBC, and heavy products (>C₃₀); BaTiO₃ - Fe/AC > Fe/PBC > Co/BC > Fe/PBC.



In terms of formation of paraffins, olefins and naphthenes, the selectivity orders were: $PBC > Pb/BaTiO_3 > BC > AC$, $Pb/TiO_3 > AC > BC > PBC$ and $Pb/TiO_3 > Fe/PBC > Co/BC > Fe/AC$, respectively.

In terms of highest liquid products achieved in case of HDPE, the order of reactivity of the catalysts was; $Co/BaTiO_3 > Zn/PBC > Zn/AC > Zn/BC$. However, none of the catalysts except $Co/BaTiO_3$ appreciably increased the yield of the liquid products and the yields were comparable with the thermal run.

In terms of highest liquid products achieved in case of HDPE, the order of reactivity of the catalysts was; $Zn/PBC > Pb/BaTiO_3 > Zn/BC > Zn/AC$. In terms of the C-range distributions; light products (C_6-C_{12}), the order of selectivity was; $Zn/AC > Zn/BC > Co/BaTiO_3 > Zn/PBC$.

In case of middle range products ($C_{13}-C_{16}$); the order was; $Zn/PBC > Co/BaTiO_3 > Zn/AC > Zn/BC$, and in case of heavy products ($C_{17}-C_{20}$), the order was; $Zn/PBC > Pb-Co/BaTiO_3 > Zn/BC > Zn/AC$. Similarly, in case of heavy products ($C_{21}-C_{30}$), the order was; $Pb/BaTiO_3 > Zn/BC > Zn/AC > Zn/PBC$, and heavy products ($>C_{30}$) ; $Zn/BC > BaTiO_3 > Zn/PBC > Zn/AC$.

In terms of formation of paraffins, olefins and naphthenes, the selectivity orders were: $Co/BaTiO_3 > Zn/PBC > Zn/AC > Zn/BC$, $Zn/BC > un-doped BaTiO_3 > Zn/AC > Zn/PBC$ and $Zn/AC > Zn/BC > Pb-Co/BaTiO_3 > Zn/PBC$, respectively.

The crude and their distillate fractions were also analyzed for fuel properties. The results indicated that the derived pyrolysates and their distillate fractions were fuel-like meeting the fuel grade criteria. The fuel properties of both thermal and catalytically derived pyrolysates were in conformity with fuel oil in case of raw pyrolysates and with gasoline and light gas oil in case of distillate fractions.



CONCLUSIONS

- Optimum temperature and time were decided on the basis of highest liquid yields. Temperature of 300 °C was found to be optimum in case of PP and 350 °C in case of HDPE (Liquid yield PP; 69.82 wt % & HDPE; 80.88 wt %). Reaction time of 30 minutes was found to be optimum.
- A significant improvement in liquid yields, and composition/distribution relative to thermal pyrolysis was achieved in catalyzed runs. Polyolefins (both PP and HDPE) were converted more meaningfully into useful liquid products through catalytic route (In case of PP, optimum liquid yield of 96.7 wt% was achieved in Fe/PBC (2.5 wt % loading) catalyzed run followed by 91.1 wt% over Fe/PBC (1 wt % loading) in case of HDPE).
- The liquid products obtained under optimized conditions in case of thermal as well as catalytic runs were mostly consisted of a wide spectrum of hydrocarbons mainly distributed within the C₆–C₁₆ carbon number range products in case of both polyolefins.
- The catalytic activities of the variously catalysts were toward formation of C₆–C₁₂ in case of PP (In Co/BC catalyzed run, the yield of lighter range hydrocarbons i.e. C₆–C₁₂ was increased significantly all most four folds i.e. 60.18 %) and towards C₁₃–C₁₆, and C₂₁–C₃₀ range hydrocarbons in case of HDPE.
- All pyrolysates contained mostly olefinic hydrocarbons as compared to thermal run with no oxygenates and aromatics.
- All pyrolysates gave gasoline, and light gas oil fractions upon distillation in meaningful amounts.
- The standard fuel oil analyses developed for petroleum based fuels were applied to crude/lump pyrolysates as well as their distillate fractions to look for their fuel oil qualities in chemical and thermal applications. The results showed that the derived liquids presented acceptable values for all the studied properties when compared to the specified values for the conventional petroleum-derived fuels.
- The fuel properties of both of the thermally and catalytically derived pyrolysates were in conformity with fuel oil in case of crude pyrolysates and with gasoline and light gas oil in case of distillate fractions.



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