Studies on process optimization for production of liquid fuels from waste plastics

A Thesis Submitted in Partial Fulfillment for the Award of the Degree

Of

DOCTERATE OF PHILOPHY
In
CHEMICAL ENGINEERING

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July 2011

DEDICATED TO

All my family members

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CERTIFICATE

This is to certify that the thesis entitled "**Studies on process optimization for production of liquid fuels from waste plastics**", being submitted by **Achyut Kumar Panda** for the award of Ph.D. degree is a record of bonafide research carried out by him at the Chemical Engineering Department, National Institute of Technology, Rourkela, under our guidance and supervision. The work documented in this thesis has not been submitted to any other University or Institute for the award of any other degree or diploma.

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ACKNOWLEDGEMENT

I would like to express my appreciation to all those people who have contributed to make this work possible through their help and support along the way.

My deepest gratitude goes to my thesis supervisor Prof. (Dr.) R. K. Singh and co-supervisor Dr. Dhanada K. Mishra for giving me the opportunity to work on this interesting project and for their valuable guidance, inspiration, constant encouragement, heartfelt good wishes and support through all the phases of the project. I feel indebted to both my supervisors for giving abundant freedom to me for pursuing new ideas. I am indebted to Prof. R. K. Singh for some of his remarkable qualities, such as his depth of perception and patience, perhaps the best I have come across so far, will always continue to inspire me. The experience of working with them, I strongly believe, will have far-reaching influence in my future life.

I take this opportunity to express my deep sense of gratitude to the members of my Doctoral Scrutiny Committee Prof. K. C. Biswal of Chemical Engineering Department, Prof. S. Bhattacharyya of Ceramic Engineering Department and Prof. R. K. Patel of Chemistry Department for thoughtful advice during discussion sessions. I express my immense gratitude to Prof. G. K. Roy of the Department of Chemical Engineering for his valuable suggestions and encouragement. I express my gratitude and indebtedness to Prof. P. Rath, Dr. Madhusree Kundu, Dr. Susmita Mishra, Dr. Basudeb Munshi, Dr. Santanu Paria, Dr. S. Khanam, Dr. Arvind Kumar, of the Department of Chemical Engineering, for their valuable suggestions and instructions at various stages of the work. My special thanks to Mr. Samarandu Mohanty and other supporting staffs for their constant help through out the work.

This work also would not have been possible without the help of all the research group members. I would like to express my gratitude to my research colleague Mr. Sachin Kumar for his assistance in my research work. I am also thankful to my other research colleagues Mr. Gaurav, Mr. Ramakrishna, Mr. Nihar, Mr. Rajiv, Ms. Debalakshmi and Mr. Ratnakar, Mr.Bibhudedra, Mr.Trilochan for their support and good wishes.

Finally, I express my humble regards to my parents and other family members, for their immense support, sacrifice and their unfettered encouragement at all stages.

(Achyut Kumar Panda)

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ABSTRACT

The present work involves the study of process optimization for the production of liquid fuel by the catalytic pyrolysis of different plastics waste such as polypropylene, low density polyethylene and polystyrene using kaolin and acid treated kaolin as catalyst in a laboratory batch reactor. The effect of silica alumina, which has been extensively studied by different investigators for the pyrolysis of different plastics was also studied and compared with that of the catalytic performance of kaolin. From the experimental results, it is found that kaolin is found to be suitable as a catalyst for the degradation of plastics waste to liquid fuel and valuable chemicals. However, silica alumina show superior performance compared to kaolin in terms of yield and reaction time.

From the optimization study it is found that, the maximum oil yield in thermal pyrolysis of polypropylene, low density polyethylene and polystyrene waste was 82.5wt.%, 71.5wt.% and 93wt.% at optimum condition of temperature, which is improved to 87.5wt.%, 79.5wt.% and 94.5wt.% respectively in kaolin catalysed degradation under optimum condition of temperature and feed ratio. The rate of reaction, oil yield and quality of oil obtained in the catalytic pyrolysis are significantly improved compared to thermal pyrolysis.

The catalytic activity of kaolin is further enhanced by treating it with sulphuric acid of different concentrations. Acid treatment increased the surface area, acidity and also altered the pore volume distribution of kaolin, which support the cracking reaction. The maximum yield of oil in the acid treated kaolin catalysed pyrolysis of polypropylene was 92% under optimum conditions.

The composition of the oil was analyzed by FTIR and GC/MS or DHA. The oil obtained from the catalytic pyrolysis of waste polypropylene and low density polyethylene mostly contains aliphatic hydrocarbons where as that from waste polystyrene mostly aromatic hydrocarbons. The product distribution in kaolin and acid treated kaolin catalysed pyrolysis oil is narrowed as compared to the oil obtained in thermal pyrolysis of polypropylene. The presence of kaolin and silica alumina catalysts greatly alters the product distribution in polystyrene pyrolysis. The fuel properties of the oil obtained from the catalytic pyrolysis of polypropylene and low density polyethylene are similar with that of petro-fuels. So they can directly be used as an engine fuel after fractionation or as a feedstock to petroleum refineries. Similarly, the oil obtained from the pyrolysis of waste polystyrene can be used to recover styrene monomer as well as some other components like ethyl benzene, toluene etc as well as a feedstock to petroleum refineries. The diesel blended plastic oil obtained by the catalytic pyrolysis of polypropylene has been tested for its performance and emission in a CI diesel engine. Engine was able to run with maximum 50% waste plastic oil- diesel blends. The engine vibrates at and above this blend. The brake thermal efficiency of the blend is found better compared to diesel up to 80% load. The brake specific fuel consumption is less compared to diesel. The NOx, CO, HC and smoke emissions are higher in case of blend. Thus the oil produced can be used after fractionation or some suitable modification in the engine design and engine conditions.

Taguchi method is used to optimize the process parameters involved in decomposition of waste polypropylene. With this method we upgraded our existing knowledge about the influence of the different process parameters on the yield of liquid fuel in a batch process and thus contributed to improving the process's reliability. The level of importance of the process's parameters is determined by using ANOVA. Moreover, regression modeling has helped us generate an equation to describe the statistical relationship between the process's parameters and the response variable (yield of liquid fuel) and to predict new observations.

Key words: Waste plastics, polypropylene, low density polyethylene, polystyrene, process optimization, pyrolysis, liquid fuel, batch reactor, kaolin, silica alumina, acid treatment, FTIR, GC/MS, DHA, aliphatic hydrocarbons, petro-fuels, styrene monomer, ethyl benzene, toluene, fractionation, diesel blended plastic oil, DI diesel engine, brake thermal efficiency, brake specific fuel consumption, emission, Optimization,Taguchi method, ANOVA

CHAPTER 1

Introduction

INTRODUCTION

1.1 General background

Economic growth and changing consumption and production patterns are resulting into rapid increase in generation of waste plastics in the world. Due to the increase in generation, waste plastics are becoming a major stream in solid waste. After food waste and paper waste, plastic waste is the major constitute of municipal and industrial waste in cities. Even the cities with low economic growth have started producing more plastic waste due to plastic packaging, plastic shopping bags, PET bottles and other goods/appliances which uses plastic as the major component. This increase has turned into a major challenge for local authorities, responsible for solid waste management and sanitation. Due to lack of integrated solid waste management, most of the plastic waste is neither collected properly nor disposed of in appropriate manner to avoid its negative impacts on environment and public health and waste plastics are causing littering and chocking of sewerage system.

On the other hand, plastic waste recycling can provide an opportunity to collect and dispose of plastic waste in the most environmental friendly way and it can be converted into a resource. In most of the situations, plastic waste recycling could also be economically viable, as it generates resources, which are in high demand. Plastic waste recycling also has a great potential for resource conservation and GHG emissions reduction, such as producing diesel fuel from plastic waste. This resource conservation goal is very important for most of the national and local governments, where rapid industrialization and economic development is putting a lot of pressure on natural resources. Some of the developed countries have already established commercial level resource recovery from waste plastics.

Waste plastics are one of the most promising resources for fuel production because of its high heat of combustion and due to the increasing availability in local communities. Unlike paper and wood, plastics do not absorb much moisture and the water content of plastics is far lower than the water content of biomass such as crops and kitchen wastes.

The conversion methods of waste plastics into fuel depend on the types of plastics to be targeted and the properties of other wastes that might be used in the process. Additionally the effective conversion requires appropriate technologies to be selected according to local economic, environmental, social and technical characteristics.

In general, the conversion of waste plastic into fuel requires feedstocks which are non-hazardous and combustible. In particular each type of waste plastic conversion method has its own suitable feedstock. The composition of the plastics used as feedstock may be very different and some plastic articles might contain undesirable substances (e.g. additives such as flame-retardants containing bromine and antimony compounds or plastics containing nitrogen, halogens, sulfur or any other hazardous substances) which pose potential risks to humans and to the environment.

The types of plastics and their composition will condition the conversion process and will determine the pretreatment requirements, the temperature for the conversion and therefore the energy consumption required, the fuel quality output, the flue gas composition (e.g. formation of hazardous flue gases such as NO_x and HCl), the fly ash and bottom ash composition, and the potential of chemical corrosion of the equipment.

The production method for the conversion of plastics to liquid fuel is based on the pyrolysis of the plastics and the condensation of the resulting hydrocarbons. Pyrolysis refers to the thermal decomposition of the matter under an inert gas like nitrogen. For the production process of liquid fuel, the plastics that are suitable for the conversion are introduced into a reactor where they will decompose at 450°C to 550°C. The major product of the pyrolysis being the oil (mixture of liquid hydrocarbons) is obtained continuously through the condenser, once the waste plastics inside the reactor are decomposed enough to evaporate upon reaching the reaction temperature. The evaporated oil may also be further cracked with a catalyst. The boiling point of the produced oil is controlled by the operation conditions of the reactor, the type of reactor, and presence of catalyst. In some cases, distillation equipment is installed to perform fractional distillation to meet the user’s requirements. Hydrocarbons with high boiling points such as diesel, kerosene and gasoline are fractionated. In addition, gaseous hydrocarbons such as methane, ethane, propylene and butanes cannot be condensed and are therefore used otherwise or for carrying out the pyrolysis process.

1.2 Origin of the problem

1.2.1 Scarcity of fossil fuels

The present rate of economic growth is unsustainable without saving of fossil energy like crude oil, natural gas or coal. International Energy Outlook 2010 reports the world consumption of liquid and petroleum products grows from 86.1 million barrels per day in 2007 to 92.1 million barrels per day in 2020, 103.9 million barrels per day in 2030, and 110.6 million barrels per day in 2035 and natural gas consumption increases from 108 trillion cubic feet in 2007 to 156 trillion cubic feet in 2035. This way, the oil and gas reserve available can meet only 43 and 167 years further. Thus mankind has to rely on the alternate/renewable energy sources like biomass, hydropower, geothermal energy, wind energy, solar energy, nuclear energy, etc. Waste plastic to liquid fuel is also an alternate energy source path, which can contribute to depletion of fossil fuel as in this process liquid. Fuel with similar fuel properties as that of petro fuels are obtained.

1.2.2 Solid waste management

On the other hand, suitable waste management strategy is another important aspect of sustainable development. The growth of welfare levels in modern society during the past decades has brought about a huge increase in the production of all kinds of commodities, which indirectly generate waste. Plastics have been one of the materials with the fastest growth because of their wide range of applications due to versatility and relatively low cost. Since the duration of life of plastic products is relatively small, there is a vast plastics waste stream that reaches each year to the final recipients creating a serious environmental problem. Again, because disposal of post consumer plastics is increasingly being constrained by legislation and escalating costs, there is considerable demand for alternatives to disposal or land filling. Advanced research in the field of green chemistry could yield biodegradable/green polymers but is too limited at this point of time to substitute the non-biodegradable plastics in different applications. Once standards are developed for degradable plastics they can be used to evaluate the specific formulations of materials which will find best application in this state as regards their performance and use characteristics. Among the alternatives available are source reduction, reuse, recycling, and recovery of the inherent energy value through waste-to-energy incineration and processed fuel applications. Production of liquid fuel would be a better alternative as the calorific value of the plastics is comparable to that of fuels, around 40 MJ/kg and is carried out by pyrolysis process, occur in absence of oxygen at high temperatures. As a complementary recycling technology to combustion this technique is really attractive from ecological view point.

1.3 Objective of present work

The overall objective of the project is to study the thermal and catalytic pyrolysis of three types of waste plastics i.e. low density polyethylene, polypropylene, and polystyrene in a batch reactor with an objective to optimize the liquid product yield by changing different parameters such as temperature, catalyst and catalyst to plastic ratio. The specific objectives of this study are:

- To study the thermal and catalytic pyrolysis of waste plastics [Polypropylene (PP), Low Density Polyethylene (LDPE) and Polystyrene (PS)] to liquid fuel/chemicals using kaolin and silica alumina catalyst.
- To study the effect of sulphuric acid treatment on the physicochemical characteristics of kaolin and its catalytic behavior in the waste polypropylene.
- To optimize the process experimentally for production of liquid fuel from different waste plastics.
- To characterize the liquid fuel for its composition and fuel properties for its suitability as fossil fuel substitute.
- To study the engine performance and emission analysis of waste plastic oil obtained by the catalytic pyrolysis.
- To optimize the process variables of catalytic degradation of waste polypropylene by Taguchi method.

1.4 Organization of Thesis

The thesis has been organized in ten chapters. The present chapter, chapter-1 is an introductory chapter. Chapter-2 contains pertinent literature review plastic pyrolysis along with some statistics of plastic production and generation of plastic waste and the different methods of recycling of waste plastics. Chapter-3 presents the materials selection for the experiment and their characterization techniques, methods of pyrolysis experiments, and analysis of liquid product obtained in the process. In chapter-4 the effect of sulphuric acid treatment of different concentrations on the physico-chemical characteristic of kaolin is summarized. Chapter–5, 6 and 7 presents the results of thermal and catalytic pyrolysis of waste polypropylene, low density polyethylene and polystyrene respectively. Importance is given to optimize the experimental conditions for the production of maximum oil by varying temperature, catalyst and feed ratio. The compositional analysis and fuel properties of oil produced in the process are also included in these chapters. Chapter-8 presents the study of engine performance and emission analysis of the diesel blended plastic oil obtained in kaolin catalysed pyrolysis of polypropylene, in a CI diesel engine. In chapter-9, the optimization of process variables of catalytic degradation of waste polypropylene is carried out by Taguchi method. Finally, chapter-10 presents the summary of the work and some suggestions for further study.

Chapter 2

Literature review

LITERATURE REVIEW

2.1 Plastics, types, properties and their uses

2.1.1 Definition of plastics

Plastics are ‘‘one of the greatest innovations of the millennium’’ and have certainly proved their reputation to be true. There are a numerous ways that plastic is and will be used in the years to come. The fact that plastic is lightweight, does not rust or rot, low cost, reusable and conserves natural resources is the reason for which plastic has gained this much popularity. Again, Plastics save energy and CO_2 emissions during their use phase. If we were to substitute all plastics in all applications with the prevailing mix of alternative materials, and look from a life cycle perspective, then 22.4 million additional tons of crude oil per year would be required [1].

Plastic covers a range of synthetic or semi synthetic polymerization products which can be moulded into any desired shape when subjected to heat and pressure. They composed of organic condensation or addition polymers and may contain other substances to improve performance or economics. A finished high-polymer article not only consists solely of high polymeric material (polymer or resin) but is mixed with 4 to 6 ingredients, such as lubricant, filler, plasticizer, stabilizer, catalysts, and colouring material, each of which either discharges a useful function during moulding or imparts some useful property to the finished artifact.

Polymerization is the process by which individual units of similar or different molecules ("mers/monomers") combine together by chemical reactions to form large or macromolecules in the form of long chain structures, having altogether different properties than those of starting molecules. Several hundreds and even thousands of "mers" combine together to form the macromolecules, polymers [2].

2.1.2 Physical Properties of Plastics

Plastics have some physical characteristics, which need to be considered when processing any Product. The following Table 2.1 contains physical data for several commercially available plastics.

Table 2.1 Important physical properties of Plastics [3]

Plastic No.	**Plastic**	**Thermal Properties**		**Strength Properties**		**Density Kg/m^3**
		T_m °C	**T_g °C**	**Tensile (Pa)**	**Compressive (Pa)**	
1	PET (polyethylene terephthalate	245 265	73 80	48263301 72394951.5	75842330.2 103421359.3	1290 1400
2	HDPE (high density polyethylene)	130 137		22063223.3 31026407.8	18615844.6 24821126.2	952 965
3	PVC (polyvinyl chloride)		75 105	40679068 51710679.6	55158058.3 89631844.8	1300 1580
4	LDPE (low density polyethylene)	98 115	-25	8273708.7 31371145.6	9652660.2	917 932
5	PP (polypropylene)	168 175	-20	31026407.8 41368543.7	37921165.1 55158058.3	900 910
6	PS (polystyrene)		74 105	35852737.9 51710679.6	82737087.5 89631844.8	1040 1050

2.1.3 Types of Waste Plastics and Their Recyclability [4]

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

Thermoplastics are those, which once shaped or formed, can be softened by the application of heat and can be reshaped repeatedly, till it loses its property. Example: Polyethylene, Polypropylene, Nylon, Polycarbonate etc. Applications are: Polyethylene Buckets, Polystyrene cups, Nylon ropes etc.

Thermosetting Plastics are those, which once shaped or formed, cannot be softened by the application of heat. Excess heat will char the material. Example: Phenol formaldehyde, Urea Formaldehyde, Melamine Formaldehyde, Thermosetting Polyester etc. Applications are: Bakelite Electrical switches, Formica / sermica table tops, melamine Cutlery etc.

The following Table 2.2 shows different types thermoplastics plastics and their recyclability with standard identification mark to identify easily.

Table 2.2 Types of waste plastics and their recyclables [4]

Mark	**Type**	**Recyclable**	**Abbreviation**	**Description & Common uses**
♳	Type 1	Yes	PET	Polyethylene Terephthalate Beverages.
♴	Type 2	Yes	HDPE	High-Density Polyethylene Milk, detergent & oil bottles, toys, containers used outside, parts and plastic bags.
♵	Type 3	Yes, But not common	PVC	Vinyl/Polyvinyl Chloride Food wrap, vegetable oil bottles, blister packages or automotive parts.
♶	Type 4	Yes	LDPE	Low Density Polyethylene, Many plastic bags, shrink-wraps, garment bags or containers.
♷	Type 5	Yes	PP	Poly Propylene. Refrigerated containers, some bags, most bottle tops, some carpets, and some food wrap.
♸	Type 6	Yes, but not common	PS	Polystyrenes. Through away utensils, meatpacking, protective packing.
♹	Type 7	Some	------------	Other. Usually layered or mixed plastic.

Table 2.3 classifies various plastics according to the types of fuel they can produce. It can be observed that thermoplastics consisting of carbon and hydrogen are the most important feedstock for fuel production either in solid or liquid form. As shown in Table 2.4 PE, PP and PS thermoplastics are preferable as feedstock in the production of liquid hydrocarbons. The addition of thermosetting plastics, wood, and paper to the feedstock leads to the formation of carbonaceous substances and lowers the rate and yield of liquid products.

Table 2.3 Classification of various plastics according to the types of fuel they produce

Types of polymer	**Descriptions**	**Examples**
Polymers consisting of carbon and hydrogen	Typical feedstock for fuel production due to high heat value and clean exhaust gas.	Polyethylene, polypropylene, polystyrene. Thermoplastics melt to form solid fuel mixed with other combustible wastes and decompose to produce liquid fuel.
Polymers containing Oxygen	Lower heat value than above plastics	PET, phenolic resin, polyvinyl alcohol, polyoxymethylene
Polymers containing nitrogen or sulfur	Fuel from this type of plastic is a source of hazardous components such as NO_x or SO_x in flue gas. Flue gas cleaning is required to avoid emission of hazardous components in exhaust gas.	Nitrogen: polyamide, polyurethane Sulfur: polyphenylene sulfide
Polymers containing halogens of chlorine, bromine and fluorine.	Source of hazardous and corrosive flue gas upon thermal treatment and combustion.	Polyvinyl chloride, polyvinylidene chloride, bromine-containing flame retardants and fluorocarbon polymers.

Table 2.4 Different thermoplastics preferred as feedstock in the production of liquid hydrocarbons

Type of plastics	**As a feedstock of liquid fuel**
Polyethylene (PE) Polypropylene (PP) Polystyrene (PS) Polymethyl metacrylate (PMMA)	Allowed. Allowed. Allowed. Allowed.
Acrylonitrile-Butadiene-Styrene copolymer (ABS)	Allowed. But not suitable. Nitrogen-containing fuel is obtained. Special attention required to cyanide in oil.
Polyvinyl alcohol (PVA) Polyoxymethylene (POM)	Not suitable. Formation of water and alcohol. Not suitable. Formation of formaldehyde.
Polyethylene terephthalate (PET)	Not suitable. Formation of terephthalic acid and benzoic acid.
Polyurethane (PUR) Phenol resin (PF)	Not suitable. Not suitable.
Polyvinyl chloride (PVC) Polyvinylidene chloride (PVDC)	Not allowed. Not allowed.

2.2 Statistics of consumption of plastics and generation of plastics waste

Constant developments in polymer technology, processing machineries, know-how and cost effective production is fast replacing conventional materials in every segment with plastics. Continuous innovation explains that, plastics production has increased by an average of almost 10% every year on a global basis since 1950. The total global production of plastics has grown from around 1.3 million tonnes (MT) in 1950 to 245 MT in 2006. Plastics continue to be a global success story with Europe (EU25 + Norway (NO) and Switzerland (CH) remaining a major manufacturing region, producing about 25% of the total estimated worldwide plastics production of 245 million tonnes during 2006. An analysis of plastics consumption on a per capita basis shows that this has now grown to over 100 kg/year in North America and Western Europe, with the potential to grow to up to 130 kg/year per capita by 2010 [1]. The highest consumption of plastics among different countries is found in USA which is equal to 27.3 MT against 170 MT world consumption in 2000 and is expected to reach to 39 MT by 2010 [5]. The plastic consumption in some countries are summarised in Figure 2.1. The highest potential for growth can be found in the rapidly developing parts of Asia (excluding Japan), where currently the per capita consumption is only around 20 kg/year. In the European context, it is the new member states such as Poland, Czech Republic and Hungary which are expected to see the biggest increase as their economies development. Their current average per capita consumption of 55 kg is a little more than half of that of the old Member State. Significant growth rate in Asia and Eastern Europe expected, however in 2010 demand per capita in Asia and Eastern Europe is still much below the rate of the ‘‘traditional markets’’ like America and Western Europe. The average Indian consumption of virgin plastics per capita reached 3.2 kg in 2000/ 2001 (5 kg if recycled material is included) from a mere 0.8 kg in 1990/1991 and 1.8 kg in 1998/1999. However, this is only one fourth of the consumption in China (12 kg/capita, 1998) and one sixth of the world average (18 kg/capita) [6,7]. The growth of the Indian plastic industry has been phenomenal equal to17% is higher than for the plastic industry elsewhere in the world [8]. India has a plastic consumption of 3.2 MT during 2000 and is expected to reach nearly 12.5 MT by 2010 [5,6]. Hindu Business line, January 21, 2006 reveals India will be the third largest plastics consumer by 2010 after USA and China. The reason of highest growth rate in last few year in India is due to the fact that, one third of the population is destitute and may not have the disposable income to consume much in the way of plastics or other goods. The virgin industry does not target this population to expand its markets. However, one third of the population is the middle class whose aspirations could be moulded to increase consumption. Plastic manufacturers create needs for this segment of population. The rising needs of the middle class, and abilities of plastics to satisfy them at a cheaper price as compared to other materials like glass and metal, has contributed to an increase in the consumption of plastics in the last few years [8].

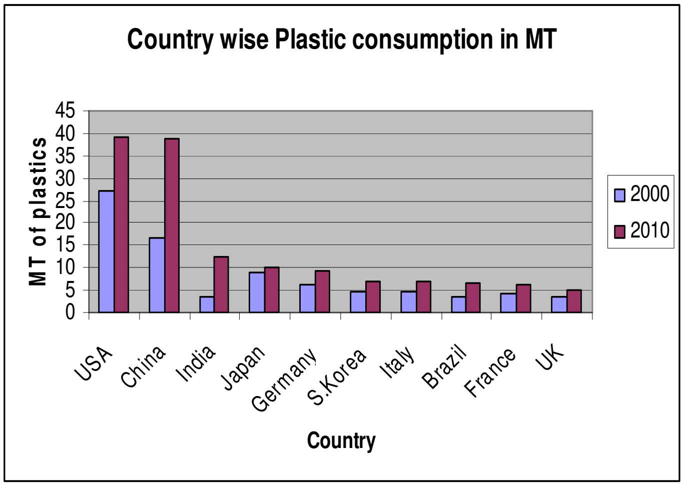


Figure 2.1 Plastic consumption in some important country

(Source: Indian plastics industry Review and Outlook by Plastindia, www.plastindia.org)

The rapid rate of plastic consumption throughout the world has led to the creation of increasing amounts of waste and this in turn poses greater difficulties for disposal. This is due to the fact that duration of life of plastic wastes is very small (roughly 40% have duration of life smaller than 1 month) [9] and depending on the area of application, the service life of plastic products ranges from 1 to 35 years [6]. The weighted average service life of all plastics products is different in different countries and in India it is 8 years; this is much less than the weighted average service life for Germany which is estimated at 14 years. This difference in service life reflects the fact that a particularly high share of plastics is used for short life products in India (e.g. share of plastics packaging: 42% in India versus 27% in Germany [6]. Plastics in municipal solid waste streams make up only 7–9% of the weight of the total waste stream; by volume they may represent 20–30%. Of the organic waste stream, that is, after removal of glass, metals, etc., plastics are about 9–12% by weight [10]. In addition to the presence of plastics in municipal waste streams, many wastes collected from manufacturing or service industries may contain much higher proportions of plastics. According to estimates, in Europe plastic wastes represent 15– 25% of municipal waste. The amount of plastic materials in Europe was 30 MT during 2000 and it will reach 35 MT by 2010 [11]. In USA, the amount of plastic waste was 24.8 MT in 2000 and 29.7 MT in 2006. The amount of plastic consumed as a percentage of total waste has increased from less than 1% in 1960 to 11.7% in 2006 (Environmental Protection Agency (EPA) report 2000 and 2006). In Japan, 15 MT of plastics are produced annually and 10 MT of plastics are discarded [12]. Similarly in India the amount of plastic waste during 2000/2001 was 2.38 MT and is estimated to rise to more than 8 MT by 2010 and 20 MT by 2030 [6]. Plastics have become a major threat due to their non-biodegradability and high visibility in the waste stream. Littering also results in secondary problems such as clogging of drains and animal health problems. Their presence in the waste stream poses a serious problem when there is lack of efficient end of life management of plastic waste. Some countries have too much of plastic rubbish for them to dispose of that, due to the high cost of the disposal of the plastic rubbish, many resort to indiscriminate dumping of plastics. Plastic waste has attracted widespread attention in India, particularly in the last five years, due to the widespread littering of plastics on the landscape of India. The environmental issues due to plastic waste arise predominantly due to the throwaway culture that plastics propagate, and also the lack of an efficient waste management system [8].

2.3 Sources and properties of plastic wastes

Plastic wastes can be classified as industrial and municipal plastic wastes according to their origins; these groups have different qualities and properties and are subjected to different management strategies [13]. Plastic wastes represent a considerable part of municipal wastes; furthermore huge amounts of plastic waste arise as a by-product or faulty product in industry and agriculture [14, 15]. Of the total plastic waste, over 78wt% of this total corresponds to thermoplastics and the remaining to thermosets [12]. Thermoplastics are composed of polyolefins such as polyethylene, polypropylene, polystyrene and polyvinyl chloride [16] and can be recycled. On the other hand thermosets mainly include epoxy resins and polyurethanes and cannot be recycled [12].

2.3.1 Municipal plastic wastes

Municipal plastic wastes (MSW) normally remain a part of municipal solid wastes as they are discarded and collected as household wastes. The various sources of MSW plastics includes domestic items (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.), agricultural (mulch films, feed bags, fertilizer bags, and in temporary tarpaulin-like uses such as covers for hay, silage, etc.), wire and cable, automobile wrecking, etc. Thus, the MSW collected plastics waste is mixed one with major components of polyethylene, polypropylene, polystyrene, polyvinyl chloride, polyethylene terephthalate, etc. The percentage of plastics in MSW has increased significantly [10]. Waste plastics amount to around 20% of the volume and 8% of the weight of all MSW in USA during 2000 which increased to 11.7% by 2006 (Environmental Protection Agency (EPA) 2006 reports) and in Europe it is 15–25% (2004) [8]. In China (2000) and Japan (2001) plastics constitute 13% and 7% respectively in MSW [17]. Similarly in India, of the total MSW, plastic waste increased from 0.7% in 1971 to 4% in 1995 and 9% in 2003 [6,7].

In order to recycle municipal plastic wastes, separation of plastics from other household wastes is required. For mixed plastics some mechanical separation equipment is currently available [18]. For example, using a wet separation process mixed plastics can be separated into two groups: those with a density greater than water such as polystyrene and polyvinyl chloride, and those with a density lower than that of water such as polyethylene, polypropylene, and expanded polystyrene. The latter group is much larger than the first group. Consequently, recycling of municipal plastic wastes should deal with plastic mixtures of polyethylene, polypropylene and polystyrene, provided that the above separation procedures are practiced. Although MSW separation technologies have been studied extensively, it is still not possible to classify MSW mechanically and obtain marketable fractions. So waste separation at the household would be a better option with where household wastes are separately disposed into three parts: (i) combustibles such as paper, kitchen waste, textiles, and wood, (ii) incombustibles such as metals, glass, ceramics, and (iii) plastics.

2.3.2 Industrial plastic wastes

Industrial plastic wastes (so-called primary Waste) are those arising from the large plastics manufacturing, processing and packaging industry. The industrial waste plastic mainly constitute plastics 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 have relatively good physical characteristics i.e. they are sufficiently clean and free of contamination and are available in fairly large quantities. It has been exposed to high temperatures during the manufacturing process which may have decreased its characteristics, but it has not been used in any product applications.

Municipal plastic wastes are heterogeneous, where as industrial plastics wastes are homogeneous in nature. For homogeneous plastic wastes, repelletization and remolding seem to be a simple and effective means of recycling. But when plastic wastes are heterogeneous or consist of mixed resins, they are unsuitable for reclamation. In this case thermal cracking into hydrocarbons may provide a suitable means of recycling, which is termed chemical recycling [13].

2.4 Different methods of plastic waste management

Due to population increase, the demand for plastic products has steadily increased over the last 40 years. Since plastics are non-biodegradable, they cannot be easily returned to the natural carbon cycle; hence the life cycle of plastic materials ends at waste disposal facilities [19]. There are several methods for disposal of municipal and industrial plastic waste, i.e. landfill, incineration (energy recovery), true material recycling (similar recycled product or monomer recovery), and chemical recovery [20]. The suitable treatment of plastic wastes is one of the key questions of the waste management and is important from energetic, environmental, economical and political aspects [21]. In most developed societies domestic organic waste, including plastics packaging, is disposed of in sanitary land filled or by incineration [22]. During early 2000, the largest amount of plastic wastes is disposed of by land filling (65–70%), and incineration (20–25%). Recycling is only about 10% [13]. This figure varies from country to country, however they are approximately nearer to it with some exception. In Japan, the percentage of municipal plastic wastes, as a fraction of MSW, that was land filled in the early 1980s was estimated to be 45%, incineration was 50%, and the other 5% was subjected to separation and recycling. In the USA, more than 15% of the total MSW was incinerated in 1990; only about 1% of post-consumer plastics were recycled. In India, during 1998 around 800,000 tonnes representing 60% of plastic wastes generated in India was recycled involving 2000 units. This level of recycling is the highest in the world. The corresponding figure for Europe is 7%, Japan 12%, China 10%, and South Africa 16%. In Europe 2006 marks a milestone as the first year when recovery and disposal rates of used plastic were equal. The recovery rate of post-consumer end of life plastics now stands at 50% and disposal stands at 50%. The recycling rate for post-consumer plastics has increased to 19.7% up from 18% in 2005 and energy recovery has increased to 30.3% up from 29% in 2005. Of the 11.5 million tonnes recovered 4.5 million tonnes were recycled as material and feedstock and 7.0 million tonnes were recovered as energy. The overall material recycling rate of post-consumer plastics in 2006 was 19.7%, with mechanical recycling at 19.1% (up 2.5% point over 2005) and feedstock recycling at 0.6% (down 1%

from 2005). The energy recovery rate was up by 1.5% from 2005 to 30.3%, reflecting the stricter legislation on landfill in several Member States [1]. From the above recent data it is clear that there is increase in the recycling operation (material and energy) compared land filling due to strict regulations and growing awareness. The Figure 2.2 represents the different routes for plastic waste management being followed.

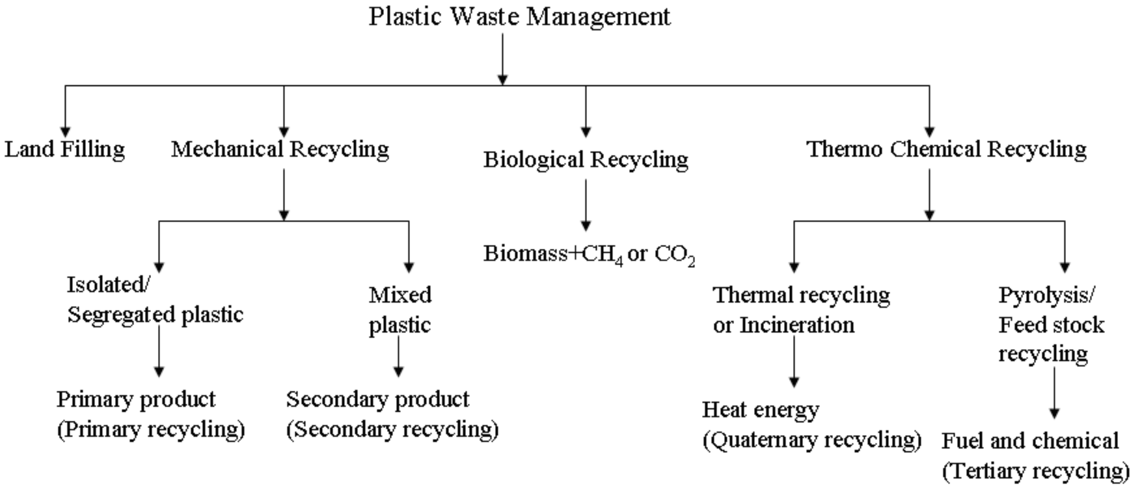


Figure 2.2 Different routes for plastic waste management

2.4.1 Land filling

Highest portion of the solid waste including plastics have been subjected to landfill. However, disposing of the waste to landfill is becoming undesirable due to legislative pressures (where waste to landfill must be reduced by 35% over the period from 1995 to 2020), rising costs, the generation of explosive greenhouse gases (such as methane) and the poor biodegradability of commonly used packaging polymers [23]. In light of these hazards, the Environmental Protection Agency of USA has improved federal regulations for land filling by normalizing the use of liners in the landfill bed, ground water testing for waste leaks, and post landfill closure care; however, since waste plastics have a high volume to weight ratio, appropriate landfill space is becoming both scare and expensive. So, the other methods outlined in Scheme 1 should be preferred as an alternative waste management procedure to replace land filling.

2.4.2 Mechanical recycling

Mechanical recycling is reprocessing of the used plastics to form new similar products. This is a type of primary and secondary recycling of plastic where the homogeneous waste plastics are converted into products with nearly same or less performance level than the original product. Efforts were made by the polymer technologists in the 1970s to recover materials from waste plastics suitable for second use but practical experience has shown that reprocessing of mixed contaminated plastics produces polymer polyblends that are inferior mechanically and lacking in durability (which is explained due to peroxidation) compared with those produced from virgin polymers [22]. Although at first sight, mechanical recycling of plastic wastes appears to be a 'green' operation, the re-processing operation is not cost effective as it needs high energy for cleaning, sorting, transportation and processing in addition to the additives used to provide a serviceable product [24]. Again, materials recycling of household waste plastics is particularly difficult when they are contaminated with biological residues or, as is usually the case, when they are a mixture of different kinds of plastics. Technology is being introduced to sort plastics automatically, using various techniques such as X-ray fluorescence, infrared and near infrared spectroscopy, electrostatics and flotation. However the economic viability and practicability of such process in industrial application is not apparent [25]. Entrepreneurial effort has gone into the development of special processing equipment to convert mixed plastics wastes to wood or concrete substitutes in the manufacture of fence posts, benches, boat docks, etc., but there are serious doubts about the ecological benefits of doing this. Some limited success has been achieved with mixed plastics wastes in the manufacture of plastics-based underground chambers by increasing wall dimensions to match the load-bearing strength of concrete. In this application, there is no significant long term deterioration due to exposure to the weather but this procedure could never utilize more than a small fraction of the mixed polymer wastes available [26]. Considerable academic interest has centered round the use of 'compatibilizers' (more correctly, solid phase dispersants to upgrade the mechanical performance of mixed plastics poly blends but in general this is an expensive and energy-intensive procedure which cannot be justified for domestic mixed plastics wastes [22,24]. In this way, it is apparent that mechanical recycling, although employed widely, is not a suitable method when the quality of secondary produce and ecological aspects are considered.

2.4.3 Biological recycling

Both natural and synthetic cis-poly (isoprene) becomes highly resistant to bio-degradation when made into industrial products (e.g. tyres) which is a direct consequence of the presence of highly effective antioxidants added during their manufacture [27]. This has led to intensive research both in industry and in universities to develop polymeric materials that conform to user requirements but are also returned to the biological cycle after use. This resulted in development of biodegradable polymers which can be converted back to the biomass in a realistic time period [28–30]. Biodegradable plastics are already being used successfully in different countries. Mostly they are introduced in food/catering industry which photo-degrades in six weeks. There is also potential to use such plastics in non-packaging applications such as computer or car components. However, there are a number of concerns over the use of degradable plastics. First, these plastics will only degrade if disposed of in appropriate conditions. For example, a photodegradable plastic product will not degrade if it is buried in a landfill site where there is no light. Second, they may cause an increase in emissions of the greenhouse gas methane, as methane is released when materials biodegrade anaerobically. Third, the mixture of degradable and non-degradable plastics may complicate plastics sorting systems. Last but not least, the use of these materials may lead to an increase in plastics waste and litter if people believe that discarded plastics will simply disappear [25]. Due to all these problems at present the biodegraded plastics cannot substitute all the application areas of synthetic plastics.

2.4.4 Thermal recycling/Incineration

Energy generation by incineration of plastics waste is in principle a viable use for recovered waste polymers since hydrocarbon polymers replace fossil fuels and thus reduce the CO_2 burden on the environment. Table 2.5 [22] shows that, the calorific value of polyethylene is similar to that of fuel oil and the thermal energy produced by incineration of polyethylene is of the same order as that used in its manufacture. Incineration is the preferred energy recovery option of local authorities because there is financial gain by selling waste plastics as fuel [26]. Co-incineration of plastic wastes with other municipal solid wastes may be increasingly practiced, because the high caloric value of plastics can enhance the heating value of MSW and facilitate an efficient incineration, while their energy content can also be recovered. However, in most developed countries public distrust of incineration at present limits the potential of waste-to-energy technologies as it produce greenhouse gases and some highly toxic pollutants such as polychlorinated dibenzo para dioxins (PCDD) and polychlorinated dibenzo furans (PCDF). The potential relationship between plastics fed into an incinerator and the formation of dioxins and furans is still unclear and has been suggested that the chlorine content in PVC and other plastics is related to the formation of dioxins and furans [31].

Table 2.5 Calorific values of plastics compared with conventional fuels

Fuel	**Calorific value (MJ/kg)**
Methane	53
Gasoline	46
Fuel oil	43
Coal	30
Polyethylene	43
Mixed plastics	30-40
Municipal solid waste	10

2.4.5 Chemical Recycling

Current state of the art feedstock recycling, also known as chemical recycling or tertiary recycling, aims to convert waste polymer into original monomers or other valuable chemicals. These products are useful as feedstock for a variety of downstream industrial processes or as transportation fuels. There are three main approaches: depolymerisation, partial oxidation and cracking (thermal, catalytic and hydrocracking).

2.4.5.1 De-polymerization

Condensation polymers which include materials such as polyamides, polyesters, nylons and polyethylene terephthalate can be depolymerised via reversible synthesis reactions to initial diacids and diols or diamines. Typical depolymerisation reactions such as alcoholysis, glycolysis and hydrolysis yield high conversion to their raw monomers. However, addition polymers which include materials such as polyolefins, typically making up 60–70% of municipal solid waste plastics, cannot be easily depolymerised into the original monomers by reverse synthesis reaction.

2.4.5.2 Partial oxidation

The direct combustion of polymer waste, which has a good calorific value, may be detrimental to the environment because of the production of noxious substances such as light hydrocarbons, NO_x, sulfur oxides and dioxins. Partial oxidation (using oxygen and/or steam), however, could generate a mixture of hydrocarbons and synthesis gas (CO and H_2), the quantity and quality being dependent on the type of polymer used. A new type of waste gasification and smelting system using iron-making and steelmaking technologies has been described by Yamamoto et al. [32], reportedly to produce a dioxin-free and high-calorie purified gas. Hydrogen production efficiency of 60–70% from polymer waste has been reported for a two-stage pyrolysis and partial oxidation process. Co-gasification of biomass with polymer waste has also been shown to increase the amount of hydrogen produced while the CO content reduced. The production of bulk chemicals, such as acetic acid, from polyolefins via oxidation using NO and/or O_2, is also possible.

2.4.5.3 Cracking/Pyrolysis

Cracking process break down polymer chains into useful lower molecular weight compounds. The products of plastic pyrolysis process could be utilized as fuels or chemicals. Three different cracking processes such as hydrocracking, thermal cracking and catalytic cracking are reported.

2.4.5.3.1 Hydro-cracking

Hydro-cracking of polymer waste typically involves reaction with hydrogen over a catalyst in a stirred batch autoclave at moderate temperatures and pressures (typically

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

2.4.5.3.2 Thermal cracking

Thermal cracking or Pyrolysis, involves the degradation of the polymeric materials by heating in the absence of oxygen. The process is usually conducted at temperatures between 350 °C and 900 °C and results in the formation of a carbonized char (solid residues) and a volatile fraction that may be separated into condensable hydrocarbon oil consisting of paraffins, isoparaffins, olefins, naphthenes and aromatics, and a non-condensable high calorific value gas. The proportion of each fraction and their precise composition depends primarily on the nature of the plastic waste but also on process conditions. The extent and the nature of these reactions depend both on the reaction temperature and also on the residence of the products in the reaction zone, an aspect that is primarily affected by the reactor design. However, the thermal degradation of polymers to low molecular weight materials requires high temperatures and has a major drawback in that a very broad product range is obtained. Catalytic pyrolysis provides a means to address these problems.

2.4.5.3.3 Catalytic Cracking

In this method a suitable catalyst is used to carry out the cracking reaction. The presence of catalyst lowers the reaction temperature and time. In addition, catalytic degradation yields a much narrower product distribution of carbon atom number with a peak at lighter hydrocarbons and occurs at considerably lower temperatures. From an economic perspective, reducing the cost even further will make this process an even more attractive option. This option can be optimized by reuse of catalysts and the use of effective catalysts in lesser quantities. This method seem to be the most promising to be developed into a cost-effective commercial polymer recycling process to solve the acute environmental problem of plastic waste disposal.

2.5 Pyrolysis of plastic waste to liquid fuel —The Process

Pyrolysis is generally defined as the controlled heating of a material in the absence of oxygen. In plastics pyrolysis, the macromolecular structures of polymers are broken down into smaller molecules or oligomers and sometimes monomeric units. Further degradation of these subsequent molecules depends on a number of different conditions including (and not limited to) temperature, residence time, presence of catalysts and other process conditions. The pyrolysis reaction can be carried out with or without the presence of catalyst. Accordingly, the reaction will be thermal and catalytic pyrolysis. Since majority of plastic used are polyolefins, so extensive research has been done on this polymer which is summarised as below.

2.5.1 Thermal pyrolysis of polyolefins

The non-catalytic or thermal pyrolysis of polyolefins is a high energy, endothermic process requiring temperatures of at least 350–500 °C [33–35]. In some studies, high temperature as 700–900 °C is essential in achieving decent product yields [36–38]. The extent and the nature of these reactions depend both on the reaction temperature and also on the residence of the products in the reaction zone, an aspect that is primarily affected by the reactor design.

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

Characteristics of thermal degradation of heavy hydrocarbons can be described with the following points;

1. High production of C_1s and C_2s in the gas product.
2. Olefins are less branched.
3. Some diolefins made at high temperature.
4. Gasoline selectivity is poor; i.e. oil products are a wide distribution of molecular weight.
5. Gas and coke products are high.
6. Reactions are slow compared with catalytic reactions.

Thermal pyrolysis of both virgin and waste plastics as well as other hydro-carbonaceous sources has been studied extensively in the past. A good number of these thermal cracking studies are on polyethylene [33,40,59], polypropylene [34,40,41,44–58] and polystyrene [35,39–43]. On the other hand, only a few have worked on the thermal decomposition of other common plastics such as polyvinylchloride [59,60], polymethyl methacrylate [48], polyurethane [61] and polyethylene terephthalate [60].

Generally, thermal cracking results in liquids with low octane value and higher residue contents at moderate temperatures, thus an inefficient process for producing gasoline range fuels [41,55]. The gaseous products obtained by thermal pyrolysis are not suitable for use as fuel products, requiring further refining to be upgraded to useable fuel products [62,63].

A few researchers have sought to improve thermal pyrolysis of waste polyolefins without employing the use of catalysts; however these changes either yielded insignificant improvements or added another level of complexity and costs to the system [55,64].

2.5.2 Catalytic cracking of polyolefins

Addition of catalyst enhances the conversion and fuel quality. As compared to the purely thermal pyrolysis, the addition of catalyst in polyolefin pyrolysis.

(1) Significantly lowers pyrolysis temperatures and time. A significant reduction in the degradation temperature and reaction time [65] under catalytic conditions results in an

increase in the conversion rates for a wide range of polymers at much lower temperatures than with thermal pyrolysis [66–68].

(2) Narrows and provides better control over the hydrocarbon products distribution in Low density polyethylene (LDPE) [69,70], High density polyethylene (HDPE), polypropylene [71,72] and polystyrene [73,74] pyrolysis. While thermal pyrolysis, results in a broad range of hydrocarbons ranging from C_5 to C_{28} [61], the selectivity of products in the gasoline range (C_5–C_{12}) are much more enhanced by the presence of catalysts [58,67,75]. Again, oils obtained by catalytic pyrolysis contain less olefins and more branched hydrocarbon and aromatic content [65,76].

(3) Increases the gaseous product yields. Under similar temperatures and reaction times, a much higher gaseous product yield is observed in the presence of a catalyst for polyethylene [67,77].

The dramatic effect of catalyzed decomposition of polymers has spurred a wave of research in the area of catalysis and polymer degradation. And thus, Catalytic degradation of plastics is found to have greatest potential to be developed into a commercialized process [78]. One of the most successful examples being the Alka Zadgaonkar's Unique Waste Plastic Management & Research Company plant in India which could produce fuel oil from waste plastics at par with the regular gasoline. The Table 2.6 gives the comparison of different fuel properties for the fuel produced from waste plastics in Zadgaonkar's process with regular gasoline. From the table, it is clear that the oil produced in this process resembles the regular petrol in all respects and reported to give better mileage as compared to commercial petrol. In addition, the cost of production is also reported to be very less [79].

2.5.3 Process design

Many have demonstrated that plastics waste can indeed be converted to useful chemical feedstock by both non-catalytic and catalytic pyrolysis. Literature shows that the distribution can also be affected by different process parameters such as feed composition (plastic type), catalyst loading, catalyst size, the means of polymer and catalyst contact during degradation, reactor type, and degradation process conditions such as temperature, pressure, residence time. The effect of various process variables are described below.

Table 2.6 Comparison of waste plastics fuel to regular gasoline

Properties	**Regular gasoline**	**Plastic waste fuel**
Colour, visual	Orange	Pale yellow
Specific gravity at 28 °C	0.7423	0.7254
Specific gravity at15 °C	0.7528	0.7365
Gross calorific value	11210	11262
Net calorific value	10460	10498
API gravity	56.46	60.65
Sulphur content(by mass)	0.1	<0.002
Flash point (Abel) °C	23	22
Pour point °C	<-20	<-20
Cloud point	<-20	<-20
Reactivity with SS	Nil	Nil
Reactivity with MS	Nil	Nil
Reactivity with Cl	Nil	Nil
Reactivity with Al	Nil	Nil
Reactivity with Cu	Nil	

2.5.3.1 Effect of feed composition (Type of Polymer)

The primary pyrolysis products relates directly to the chemical structure and decomposition of the resin, and also to the mechanism of its decomposition (Purely thermal or catalytic). In general, the decomposition of polyolefin mixtures occurs roughly in the same range as their virgin counterparts (350–500 °C). However, waste polyolefins may degrade at slightly lower temperatures and achieve higher conversions than the respective virgin polyolefins [80–84]. As with virgin plastics, the addition of catalysts in waste pyrolysis greatly influence product yields and conversion rates; however, the disparities between waste and virgin polyolefin pyrolysis lie mainly in the resulting product compositions [85–87]. It is clear that during pyrolysis, interactions between the different materials in a waste feed have a significant effect on the selectivity of specific liquid and gaseous product components [88]. Pyrolysis of plastics yields liquid, gas and solid residue products. Liquid product yields greater than 82.5% and as high as 96% have been found for polyethylene and polypropylene pyrolysis [52,61]; however, these are obtained at high temperatures and within a reaction time of approximately one hour. Polyethylene and polypropylene decomposes in to a range of paraffin and olefins and the paraffin to olefin ratio decreases with increase temperature and time [89]. PONA distributions of FCC catalyzed decompositions show that the olefin yield far exceeds the yield of paraffins, naphthenes, or aromatics (PNAs) in the pyrolysis of polypropylene and HDPE [90,91]. K.H. Lee [92] also showed that the catalytic degradation of waste LDPE produced more paraffins and aromatics than those of waste HDPE and polypropylene. The pyrolysis of polyethylene and polypropylene is characterized by low monomer yield [59,86], where as polystyrene mostly gives monomeric units as the main product. Polystyrene pyrolysis exhibits high yields of aromatics, as high as 97 wt% of liquid product [48,91,93,94]. This is attributed to the polycyclic nature of polystyrene and the thermodynamic challenge posed in converting cyclic compounds to aliphatic chains or alkene compounds [93]. A closer look at the aromatic yield in many of these catalyzed reactions reveals that, the product selectivity is higher for benzene, toluene and ethyl benzene unlike in thermal pyrolysis, where the main product is styrene [36,48,93–95]. Again, the results obtained in the thermal depolymerisation of polymethylmethacrylate are noteworthy since at 723 K, a 98% yield to the monomer has been reported [24]. Mixture of polyethylene and polystyrene decomposes as usual in the case of polystyrene, with the pyrolysis yield somewhat more saturated, the polyethylene providing the required hydrogen. The decomposition of the polyethylene is somewhat accelerated by the presence of polystyrene [89]. This has been explained due to the radicals formed during polystyrene decomposition. The conversions of polyethylene and polypropylene are improved by polystyrene addition [74,84,94]. Conversely, polystyrene decomposition seems to be immune to effects by either of the other polyolefins. Typically, polyethylene pyrolysis favors mostly the formation of paraffins; however, upon increasing its polystyrene or polypropylene content, the yield of aromatic and alkenic products is greatly enhanced, thus improving its octane value [87,96]. This clearly indicates the similarity and variance in the cracking mechanisms in different polyolefins.

The results of the pyrolysis of three different types of plastics such as LDPE, Polypropylene and polystyrene carried out by the different researchers are summarised below.

2.5.3.1.1 Low density polyethylene pyrolysis

Considerable research has been carried out to convert solid waste polyolefinic plastics to useful fuel and chemicals, such as the recovery of fuel and chemicals. Among the different commonly used polyolefins, polyethylene (High density polyethylene and Low density polyethylene) constitute the major share. Generally, studies have involved liquefaction and gasification by catalytic degradation using a suitable catalyst due to lowering of cost and time, and also improving of quality of oil.

Catalytic decomposition of polyethylene (PE) was carried out with a flow reactor and a batch reactor, and the results were compared to clarify the polymer decomposition process during gasification. The decomposition of PE to gas was not found to occur directly from polymer and oligomer chain ends but from the liquid fraction. In the presence of a catalyst, conversion to gas at 430 °C in the flow reactor was 72.0 wt%, while in non-catalytic thermal degradation, it was 7.0 wt%. The presence of a gasification precursor (liquid fraction, MW: 20-400) is particularly important for catalytic decomposition of PE to gas. The gasification of PE does not start directly from the chain ends of a polymer or oligomer, but from branched low molecular weight components. The catalytic decomposition of PE proceeds as follows: polymer- thermally decomposed oligomer-catalytically decomposed low molecular weight components (gasification precursor, liquid fraction) - gas [97].

The combination of two modification techniques developed for the ZSM-5 zeolite, i.e., desilication and incorporation of lanthanum under microwave irradiation, has produced a highly efficient catalyst, DeLaZSM-5, for catalytic degradation of low-density polyethylene (LDPE). Its performance on the degradation was studied at 390^0C and compared with the parent ZSM-5 and the modified intermediate products desilicated ZSM-5 (DeZSM-5) and LaZSM-5. Among the catalysts tested, DeLaZSM-5 showed the highest catalytic degradation rate. In addition, on DeLaZSM-5 the liquid yield was slightly increased and the iso-paraffin index of the liquid was almost doubled, which indicated higher liquid quality compared with the parent ZSM-5 zeolite. The high catalytic activity of DeLaZSM-5 could be explained by its unique acidic properties with a sharp increase of the number and strength of weak acid sites and a decrease of strong acid sites. In the catalytic degradation of LDPE over ZSM-5 catalysts, the degradation rate and product compositions were greatly altered with desilication and introducing La^{3+} sequential modification. The degradation rate was dramatically increased and no over cracking of LDPE was detected. Instead, liquid yield was slightly increased (49.8%) on DeLaZSM-5 than that on parent ZSM-5 zeolite (45.3%). For liquid products, the olefin content was increased and the aromatic content decreased. Especially, the content of isoparaffins almost doubled, which indicated higher liquid quality. The unique acid properties of DeLaZSM-5, which has increased weak acid sites and decreased strong acid sites accounts for the enhanced catalytic degradation of LDPE [98].

Shah et al. carried out the catalytic pyrolysis of LDPE with lead sulfide catalyst. Decomposition of LDPE to derived gas, oil and wax has been studied in terms of the temperature, time and amount of catalyst. The catalytic pyrolysis enables polyethylene to be converted into liquid, gas and wax with nearly 100% efficiency. As the char formation with lead sulfide is negligible therefore the catalyst can be used several times without treatment. No side products are associated with the method. The pyrolysis products mainly consisted of paraffinic and olefinic compounds. Distillation data and other physicochemical tests for fuel oil show that, these oils are suitable to be used as fuel oil for different energy purposes. More than 70% yield of gas and liquid fraction with boiling point up to 350 °C was obtained. So, Lead sulfide was found to be an effective catalyst for conversion of polyethylene into fuel oil [99].

Fly ash-derived amorphous silica–alumina catalysts for LDPE pyrolysis were synthesized easily and inexpensively by the fusion of fly ash with NaOH, followed by activation by co-precipitation. Synthesis parameters such as the NaOH/fly ash weight ratio and activation time had effects on the performance achieved by the catalysts. FSA (1.2-8) synthesized with a NaOH/fly ash weight ratio of 1.2 and an activation time of 8h showed the best performance in terms of catalytic activity and production cost. The catalytic performance of FSA (1.2-8) was comparable with that of commercial catalysts and it was concluded that FSA could be a good candidate for catalytic use in the recycling of waste plastics [100].

Low-density polyethylene was decomposed thermally and catalytically in a Pyrex continuous reactor in an oxidative media at the temperature range of 400–500 °C with a raw material feeding rate of 0.7 gmin^{-1}. Increase of air flow rate and temperature increased the yield of products and also affected the acid number, and the peroxide number. Considerable differences were observed between yields, and composition of products which decreases with increasing temperature. Thermal and catalytic oxidative decomposition is a promising technique to degrade low-density polyethylene waste and provide chemical feedstocks for lubricants, surfactants, and other valuable commodities as this process renders linear low-carbon compounds which are largely alcohols, paraffins and carbonyl compounds both for thermal and catalytic oxidative pyrolysis [101].

Catalytic cracking of low density polyethylene (LDPE) has been investigated using different samples of mordenite zeolite (as catalyst) with different textural properties, which were synthesized by a new synthesis method based on the functionalization of the zeolite seeds with an organosilane. Mordenite samples with BET and external surface areas in the range 385–485 and 9–57 m^2/g respectively were used in LDPE catalytic cracking reactions performed at 420 °C for 2h in a batch reactor provided with a screw stirrer under a continuous nitrogen flow. Thermal cracking of LDPE leads to plastic conversion lower than 30%, while values of 40% are reached when traditional mordenite is used as catalyst. In contrast, when mordenite samples with enhanced textural properties were employed, a plastic conversion of 60% is attained, both gas (C_1–C_5) and gasoline (C_6–C_{12}) fractions being obtained as main products. On the contrary, gasoline fraction is not observed and a heavier hydrocarbon fraction in the range C_{13}–C_{35} is detected when thermal cracking or even catalytic cracking over traditional mordenite samples are carried out. The formation of lighter hydrocarbon products (C_6–C_{12}) over mordenite samples with enhanced textural properties is assigned to the higher activity and accessibility of their acid sites, which promotes both end-chain and random scission cracking reactions of the polymer molecules [102].

Used low density polyethylenes (LDPE) were catalytically pyrolysed by Shah et al. with a wide range of acidic and basic catalysts like silica, calcium carbide, alumina, magnesium oxide, zinc oxide and homogeneous mixture of silica and alumina in batch reactor under atmospheric pressure. Though CaC_2 was better on the basis of reaction time, however the efficiency of conversion into liquid for SiO_2 was found to be maximum at optimum conditions. These two catalysts could be picked up as suitable catalysts for catalytic pyrolysis of polyethylene. The liquid product obtained from catalytic pyrolysis was also characterized for the fuel properties and it was observed that the results for the liquid fractions are comparable with the standard results of physical tests for gasoline, kerosene and diesel fuel oil. The interpretation of FTIR spectra shows that catalytic pyrolysis of LDPE leads to the formation of a complex mixture of alkanes, alkenes, carbonyl group containing compounds like aldehydes, ketones, aromatic compounds and substituted aromatic compounds like phenols [103].

Nanosized ZSM-2 zeolite with crystal size of approx. 100nm was synthesized and ion exchanged in order to characterize its behavior in the catalytic degradation of polyethylene (PE) in a semi-batch reactor. The starting ZSM-2 allowed a reduction in the PE degradation temperature of more than 80 °C as quantified by dynamic thermogravimetric analysis (TGA). By either proton or Lanthanum exchanges, the nano zeolite increased the acidity improving even more these degradation processes. The starting nano metric catalyst was dramatically more active than micro metric Y-zeolite displaying lower onset temperatures of PE degradation due to its higher external surface area. These differences nevertheless were reduced by ion-exchanging the Y-catalysts. The results confirm the relevance of both the zeolite acidity and other parameters, such as crystal size and crystallinity of the zeolite framework, on the catalytic efficiency. Regarding the degradation products during the catalytic process, both zeolites increased the production of low boiling compounds being more efficient the ZSM-2 based catalysts reaching a yield about 90%. Higher amount of accessible sites active for cracking on the external surface of the nanosized crystals would be responsible of this high gas yield. Furthermore, ZSM-2-based zeolites were highly selective to propylene and C_4 compounds compared with Y-based zeolites [104].

Two series of hierarchical nanocrystalline ZSM-5 zeolites prepared by different synthesis strategies (at low temperature and from silanized seeds) and with external surface areas ranging from 150 to 250 m^2/g were tested in the cracking of pure LDPE and HDPE at 340 °C and of waste polyethylene at 360 °C. Hierarchical zeolites showed quite higher activity, with values even six times higher than a standard nanocrystalline sample used as reference (n-HZSM-5). The activity values decreased from LDPE to HDPE due to the occurrence of some degree of branching in the former polymer, which act as preferential cracking sites. The major products were C_1–C_4 hydrocarbons (in the range 30–70%, mostly C_3–C_4 olefins) and C_5–C_{12} hydrocarbons (20–60%), whose share depends on both the polyolefin and the catalyst. The amount of C_{13}–C_{40} hydrocarbons was practically negligible (<1%) due to the high acid strength of the zeolites which promotes end-chain cracking reactions. Likewise, hierarchical nanocrystalline HZSM-5 zeolites prepared from silanized protozeolitic units showed higher activities than the hierarchical nanocrystalline HZSM-5 samples synthesized at low temperature and atmospheric pressure. The differences were especially remarkable in the case of waste polyethylene cracking. These results were ascribed to the stronger acidity of the hierarchical zeolite samples prepared from silanized seeds [105].

Polyethylene wastes (polyethylene bags used in super markets) were pyrolysed using different catalysts such as silica gel, 5A molecular sieve and activated carbon in a batch reactor at 450 °C, 500 °C and 700 °C for 2h using catalyst to PE ratio 10%w/w. The solid and gaseous products were analyzed by gas chromatography and mass spectrometry. The optimum operation temperature and the influence of the three catalysts are discussed with regards to the products formed. The suitable temperature for degradation with silica gel and activated carbon as catalysts was 450 °C and with 5A molecular sieve was700 °C. Degradation products of PE are depending on temperature and catalyst used. All products from different degradations could be used as feed stocks in chemical industry or in energy production based on the value of heat of combustion for solid fraction (45000J/g), similar to the heat of combustion of commercial fuels [106].

2.5.3.1.2 Polypropylene pyrolysis

Durmus et al. [107] investigated the thermal degradation of polypropylene powder by thermogravimetric analysis (TGA) employing four different heating rates over different type of zeolite catalysts such as BEA, ZSM-5 and MOR with different surface areas, pore structures, acidities and Si/Al molar ratios and calculated the apparent activation energies of the processes by the Kissinger equation. The performance of several differently treated clinoptilolite zeolites (dealuminated clinoptilolite catalysts) in the degradation of polypropylene was investigated in a semi-batch reactor at 400 °C by Kim et al. [108]. Zhao et al. [109] have studied the effects of different zeolites as H-Y, Na-Y, H-mordenite and Na-mordenite on the catalytic degradation of polypropylene by thermogravimetry under nitrogen flow. Negelein et al. [110] have investigated the catalytic cracking of polypropylene by silica–alumina and H-ZSM-5 at temperatures between 350 °C and 420 °C and sulfated zirconia at temperatures below 300 °C, also by means of thermogravimetry under helium flow. Audisio et al. [58] have reported the catalytic degradation of polypropylene under vacuum in a semi batch reactor, using catalysts as Al_2O_3, SiO_2, SiO_2–Al_2O_3, and Na-Y, H-Y and REY zeolites, at temperatures between 200 °C and 600 °C. Meanwhile Sakata et al. [111] studied the catalytic cracking of polypropylene with silica–alumina catalyst at 380 °C in a semi batch reactor without external gas flow. Ishihara et al. [112] investigated the catalytic degradation of polypropylene by silica–alumina at temperatures between 180 °C and 300 °C in a semi batch reactor under a nitrogen flow.

Aguado et al. [113,114] have studied the catalytic cracking of LDPE, HDPE and polypropylene in a semi batch reactor at 400 °C under a nitrogen flow using MCM-41, H-ZSM-5 zeolite and silica–alumina as solid acid catalysts. Lin et al. [115] have investigated the catalytic cracking of HDPE and polypropylene in a fluidized bed reactor using H-ZSM-5, H-USY, H-mordenite, silica–alumina and MCM-41, with nitrogen as fluidizing gas. Mordi et al. [116,117] have reported the catalytic degradation of LDPE and PP at 350 °C in a batch reactor under vacuum, using zeolite catalysts as H-ZSM-5, H-Theta-1 and H-mordenite. Uddin et al. [118,119] have studied the catalytic cracking of PE and PP at 430 °C and 380 °C with silica–alumina, H-ZSM-5, silicalite and a non-acidic mesoporous silica catalyst (FSM) in a semi batch reactor without external gas flow. Catalytic cracking of polypropylene has been carried out in a semi batch stirred reactor using spent equilibrium catalyst from FCC units, large pore zeolites as well as amorphous and ordered silica–alumina in order to study extensively the influence of pore size (micro and meso), crystallite size and the number and strength of the active acid sites [120].

Lin et al. used a laboratory catalytic fluidised-bed reactor to obtain a range of volatile hydrocarbons by degradation of polypropylene in the temperature range 290-430 °C using different zeolitic and non zeolitic catalysts such as HZSM-5, HMOR and HUSY, MCM-41 and SAHA and found product streams varied markedly depending on catalysts type and structure [121]. The thermogravimetric study of the thermal and catalytic decomposition (with MCM-41, ZSM-5 and an FCC as a catalyst) of polypropylene shows that the addition of MCM-41 produces a remarkable decrease of almost 110 °C in the temperature of maximum decomposition rate [122]. Zhao et al. found that the degradation temperature of polypropylene strongly depended on the type of zeolite used and the amount added and one type of HY zeolite (320HOA) was shown to be a very effective catalyst [123]. The catalytic degradation of polypropylene has been investigated using solid acid catalysts, such as silica-alumina and zeolites (HZSM-5, natural zeolite, Mordenite etc.), in the range of 350-450 °C. The natural zeolite catalyst (clinoptilolite structure, occurring in Youngil area of Korea) was an efficient catalyst for the polypropylene degradation. The acidity and characteristic pore structure of this zeolite appear to be responsible for the good performance [71].

Achilias et al. carried out the catalytic pyrolysis of low-density polyethylene (LDPE), high-density polyethylene (HDPE) and polypropylene (PP) in a laboratory fixed bed reactor with an FCC catalyst. Analysis of the derived gases and oils showed that pyrolysis gave a mainly aliphatic composition consisting of a series of hydrocarbons (alkanes and alkenes), with a great potential to be recycled back into the petrochemical industry as a feedstock for the production of new plastics or refined fuels [9].

Pyrolysis of polyolefin wastes (PP and PE fractions) was carried out in a fluidized bed reactor equipped with a char removal system, under various reaction conditions (temperature, feed rate, and fluidizing medium). The oil that was obtained in the experiments consisted of aliphatic and mono- and polyaromatic compounds. The content of BTX aromatics in the oil was 53wt% at 746 °C for the PP fraction, and 32wt.% at 728 °C for the PE fraction. For both feed materials, it was found that the concentration of BTX aromatics in the oil increased along with the reaction temperature. In a study that was conducted on the influence of the feed rate and the kind of fluidizing medium used on the oil production, it was found that a higher feed rate and the use of a product gas as the fluidizing medium are more effective for the production of oil. The oils that were obtained in the experiments almost had no metal content and low amount of chlorine (below 10 ppm) for both the PP and PE fractions. Due to the lower metal and chlorine contents of the oil, it seems that the environmental problems caused by the burning of the oil would not be serious. The char and distillation residue produced in the experiments consisted mainly of inorganics, whose utilization remains a challenge, however, has potential for use in road surfacing and as a building material [124].

Degradations of polypropylene (PP) and polyethylene (PE) over pure hexagonal mesoporous silica and aluminum-containing hexagonal mesoporous silica catalysts were studied in a fixed bed catalytic reactor at 380 °C and 430 °C, respectively. The thermal and catalytic degradations of both PP and PE in liquid-phase-contact and vapor-phase-contact modes over pure hexagonal mesoporous silica had no significant effect on the product yields. The liquid products were widely distributed in hydrocarbons with boiling point ranges of 36–405 °C. By adding a small amount of aluminum to the hexagonal mesoporous material, aluminum-containing hexagonal mesoporous silica exhibited good performance in cracking heavy molecular weight hydrocarbons into light hydrocarbons. High liquid yields and less coke deposits were obtained in liquid-phase-contact reaction with increasing aluminum content. The liquid products were mainly composed of C_5–C_{10}

hydrocarbons with boiling points of 36–174 °C, and propene, butene, and butane were main components in gaseous products. The effect of degradation temperature was not observed on product yields though degradation rate of polyolefin into liquid products was faster. Conversely, in vapor-phase-contact reaction, an increase in gaseous yield was observed when increasing the amount of aluminum and temperature of the cracking reactor, while the residue yield remained constant [125].
The kinetics of the thermal and catalytic decomposition of polypropylene (PP) using different contents of an acid catalyst such as MCM-41 has been studied using dynamic thermogravimetry (TG) at a heating rate of 10 K/min, under atmospheric pressure and inert atmosphere (N_2). The thermal and catalytic decomposition of PP shows that the addition of MCM-41 produces a remarkable decrease of almost 110 °C in the temperature of maximum decomposition rate. The effect of the catalyst loading has a saturating effect up to a limit of around 16 wt.% of MCM-41. A quantitative kinetic model has been developed and applied, and the corresponding kinetic constants have been obtained by correlating the experimental thermogravimetric data. The kinetic parameters obtained have revealed a reduction in the activation energy of the catalytic decomposition as compared to the thermal process. The comparison of the results obtained for the catalytic pyrolysis of PP with MCM-41, ZSM-5 and an E-cat of FCC as a catalyst shows the importance of the structural characteristics of polymers as well as those of the catalyst, showing that the more restricted the access to the pores of the catalyst, the lower is the corresponding effect [122].

Catalytic cracking of polypropylene has been investigated over MCM-41 modified by Zr and Mo. The relationship among structure, acidity and catalytic activity of Zr–Mo-MCM-41 was studied. The results showed that Zr–Mo-MCM-41 exhibited high activity for the cracking of PP and good selectivity for producing liquid hydrocarbons of higher carbon numbers. The results were compared with those obtained over HZSM-5, SiO_2–Al_2O_3 and other MCM-41 mesoporous molecular sieves. Moreover, the effect of different Zr sources on the reaction was examined [126].

The catalytic cracking of polyolefin pyrolysis waxes has been studied under conditions that mimic the operation of a catalytic cracking unit (FCC). Two commercial catalysts of different properties were used. Yields and compositions of the lumps (dry gases, LPG, gasoline and coke) were compared with those corresponding to the actual feed in the refinery (vacuum gas-oil). The effect of process operating conditions (temperature and contact time) is significant. Catalyst acidity has a significant effect on conversion (at a temperature around 525 °C) and on yields and compositions of lumps (in the 500–550 °C range). The main effect of increasing catalyst acidity is an increase in coke content on the catalyst by decreasing the yield to dry gases. Due to the higher hydrogen transfer capacity, the gasoline obtained using the catalyst with higher acidity has a higher aromatic (especially C_6–C_8) and paraffinic content, and lower olefin content, being these two latter fractions less branched. An increase in catalyst acidity leads to a lower yield of light olefins and to an increase in the yield of paraffins [127].

The catalytic performance of mesoporous MCM-48 materials in the degradation of polypropylene (PP) was evaluated using a thermogravimetric analyzer and batch reactor. The activation energy of PP degradation was significantly lowered by the addition of Al-MCM-48. The catalytic conversion was also higher over Al-MCM-48 than over Si-MCM-48. Al-MCM-48 mainly generated C_7–C_{10} hydrocarbons, while Si-MCM-48 exhibited a relatively broader distribution of oil products (C_7–C_{14}). Al-MCM-48 showed high catalytic stability for the PP degradation [128].

The activation energy and the reaction model of the pyrolysis of high density polyethylene (HDPE), low density polyethylene (LDPE) and polypropylene (PP) have been estimated from non-isothermal kinetic results. Firstly, the activation energy values obtained by Friedman, Kissinger– Akahira–Sunose and Flynn–Wall–Ozawa iso-conversional methods, are 238–247 kJ/mol for HDPE, 215–221 kJ/mol for LDPE and 179–188 kJ/mol for PP. Secondly, the appropriate conversion model of the process was determined by Coats–Redfern and Criado methods. The pyrolysis reaction models of HDPE and LDPE are accounted for by ‘‘Contracting Sphere” model, whereas that of PP by ‘‘Contracting Cylinder” model [129].

2.5.3.1.3 Polystyrene pyrolysis

Recycling of waste plastics to fuel oil has been attractive and also commercially operated. In contrast to Polyethylene and Polypropylene, Polystyrene can be thermally depolymerised to obtain the monomer styrene with a high selectivity. The oil thus recovered produces lot of carbon dioxide when burnt as fuels. Thus, several investigations have been focused on the recovery of monomer when recycling of Polystyrene is a question [130].

Pyrolysis being an endothermic process, proper heat transfer and a uniform temperature inside the reactor is required for better pyrolysis. Technology has been developed for better pyrolysis with different reactors to achieve better yield of liquid product and monomers. Several pyrolysis processes were developed using fluidized bed and bubble fluidized bed reactors. Although these reactors performed well with heat transfer, they have a major disadvantage due to stickiness of sand particles coated with melted plastics which results in defluidisation and agglomeration. Conical spouted bed reactor (CSB), internally circulating fluidized bed reactor (ICFB), swirling fluidized bed reactor (SFB) are proposed to overcome the above stated problem including maintaining a uniform temperature inside the reactor. The CSB reactor enables vigorous gas-solid contact and, thus, reduces the segregation of particulates observed in the fluidized bed. However, this reactor suffers from the plastic particles after melting, which clogs and blocks particle circulation [131, 132]. The performance of different reactors used by different investigators is summarized below.

Liu et al. developed a specially designed laboratory fluidized-bed reactor for the pyrolysis of polystyrene (PS) waste in the range 450–700 °C with nitrogen as the carrier gas and 20–40 mesh quartz sand as the fluidization medium, operating isothermally at atmospheric pressure. The yield of styrene monomer reached a maximum of 78.7 wt.% at a pyrolysis temperature of 600 °C. Some mono-aromatics with boiling point lower than 200 °C is also obtained as high-octane gasoline fraction. Styrene monomer with 99.6

wt.% purity was obtained after vacuum distillation of the liquid products, which could be used as the raw material to produce high-quality Polystyrene circulation [131].

Lee et al. used a swirling fluidized-bed reactor to recover the styrene monomer and valuable chemicals effectively from the polystyrene waste, since it can control the residence time of the feed materials and enhance the uniformity of the temperature distribution. To increase the selectivity and yield of styrene monomer in the product, catalysts such as Fe_2O_3, BaO or HZSM-5 (Si/Al=30) were used. Effects of temperature, volume flow rate of gas, pyrolysis time and the ratio of swirling gas to the amount of primary fluidizing gas on the yields of oil product as well as styrene monomer are determined. It is found that the reaction time and temperature can be reduced profoundly by adding the solid catalyst. The swirling fluidization mode makes the temperature fluctuations more periodic and persistent, which can increase the uniformity of temperature distribution by reducing the temperature gradient in the reactor. The yields of styrene monomer as well as oil products were increased with increasing the ratio of swirling gas, but exhibited their maximum values with increasing the total volume flow rate of gas [130].

Aguado et al. (2003) used a conical spouted bed reactor (CSBR) for studying the degradation kinetics of polystyrene in the 500-600 °C range. It is found that heat and mass transfer limitations within the particles are important in the temperature range required for maximizing the yield of styrene, when polystyrene particles of 1 mm are fed into the reactor. A high yield of styrene is obtained (64.5 wt.%) in the 723–773 K range. A comparison with other reactor proves the advantages of the gas–solid contact of this reactor for the kinetic study of pyrolysis of plastics at high temperature, which stems from the high heat transfer rate between gas and solid and again from the fact that particle agglomeration is avoided [133].

Polystyrene wastes were degraded in a free-fall reactor under vacuum to regain the monomer at varied temperature between 700 °C and 875 °C and determined its effects on the phase yields, the benzene, styrene, toluene, and naphthalene distribution of the liquid output and C_1–C_4 content of the gaseous output. The liquid yield maximized at around 750 °C and the styrene yield, at 825 °C. In general, operating at higher temperatures lessened the solid residue and increased the gaseous yield and total conversion. Employing waste particles in four different size ranges, it was observed that, the finer the waste particles fed the higher the gaseous yield and total conversion [134].

Different catalysts used in the catalytic pyrolysis of polystyrene are HY zeolites (Protonated Y zeolite) or REY zeolites (Rare earth Y zeolite), silica alumina, HMCM-41 (Protonated MCM-41), natural clinoptilolite, ZSM-5 (Zeolite Sieve of Molecular porosity or Zeolite Socony Mobil–5), mordenite, BaO, MgO, Fe_2O_3.

Audisio et al. reported very low selectivity of the styrene in polystyrene degradation with solid acids such as silica–alumina and HY or REY zeolites at 350 °C. The main products in their study were benzene, ethyl benzene and cumene [135]. Polystyrene catalytic cracking over amorphous silica alumina (SA) and HZSM-5 zeolite results in a lower conversion than the thermal degradation under the same reaction conditions. Decreasing the plastic/catalyst mass ratio over HZSM-5 leads to a reduced cracking activity. In contrast to HZSM-5 and amorphous silica alumina, HMCM-41 has shown enhanced polystyrene conversion compared to the thermal degradation. The main products resulting from the catalytic cracking over HMCM-41 and SiO_2–Al_2O_3 are benzene, ethyl benzene and cumene but in proportions lower than 20 wt. % [136].

The natural clinoptilolite zeolite (HNZ) shows good catalytic performance for the catalytic degradation of polystyrene, without much formation of residues or cokes at 400^0C for 2 h. All the catalysts tested (HNZ, HZSM-5, SA) produced aromatic liquid oils with over 99% of selectivity. While styrene is the major product in both thermal and catalytic degradation over the solid acid catalysts, significant differences are observed in the aromatic products distribution in presence of each catalyst. HNZ and HZSM-5 show a decrease of styrene and an increased selectivity towards ethyl benzene and propyl benzene compared to thermal degradation [137].

The application of basic catalyst to degrade polystyrene is an attractive alternative to acid catalysis. In the presence of acid catalysts, polystyrene affords low-valued indane derivatives, other polycyclic compounds, benzene, and only minor yields of styrene monomer. In contrast, studies suggested that basic catalysts enhanced the yield of styrene monomer from polystyrene compared to thermal and acid-catalyzed degradation [42]. Ukei et al. (2000) reported that solid bases, especially BaO, were more effective catalysts than solid acids for the degradation of polystyrene to styrene monomer and dimer at 350 °C [138].

Solvent addition helps in better heat and mass transfer and lowers operating temperatures. Further advantages of this approach are higher liquid yields and easier control. Sato et al. studied thermal degradation of polystyrene using two different solvent groups at temperatures between 300 °C and 450 °C. The first solvent group comprised of tetralin and 9,10 dihydroanthracene, which are both hydrogen donors. The solvents in the second group were phenol, 2-naphtol and diphenylamine, all with easily removable hydrogen atom. Higher styrene yield was claimed in the second group. Heavy oil was the medium used in another thermal degradation research on polystyrene, the temperature ranging from 370 °C to 415 °C. Nitrogen was employed to carry the products which were mainly styrene, toluene, methyl styrene, ethyl benzene and cumene [139]. Ali Karaduman studied the thermal degradation of Polystyrene with various organic compounds, such as phenol, quinone, naphthalene, and diphenylamine at varied temperature range from 350°C to 450°C. The main products of Polystyrene waste pyrolysis were mainly styrene monomer, ethyl benzene, toluene, and methyl styrene. The product spectrum can be described as a function of pyrolysis temperature and used organic compounds. The yield of styrene in liquid products at various temperatures with different organic compounds varies from 60 to 74%. The optimum pyrolysis temperature to maximize styrene monomer yield (about 60%) was 400°C, and the maximum styrene yield was obtained with naphthalene, 74% as found in this study. The amount of styrene was found to increase in the order: diphenylamine < thermal < phenol < quinone < naphthalene [140].

2.5.3.2. Effect of catalyst loading The use of catalyst in pyrolysis of plastics influences upon kinetics and mechanism, and hence, the product distribution. Conversion increases with catalyst loading [141–143]. The most commonly researched solid acid catalysts in plastic waste pyrolysis include molecular sieves, such as silica alumina [41,78,144,145], zeolites [146–148,116], and MCM-41 [122, 149–150]. Amongst the numerous kinds of zeolites investigated in polyolefin pyrolysis, Beta [151], USY [152], ZSM-11 [150], REY [62,153], Mordenite [116,154], ZSM-5 [155,156] are the most commonly used. Reports on the FCC process are also found in literature [157–159]. Other catalytic materials such as clays (montmorillonite, saponite) [160], reforming catalysts, activated carbon, metal oxides, metal complexes of the type MCl_n–$AlCl_3$ or $M(AlCl_4)_n$ (M = Li, Na, K, Mg, Ca, Ba; n = 1–2), and alkali metal carbonates or alkaline metal carbonates have also been tested for polymer degradation [13]. The common features shared by the different zeolite catalysts are proper acid strength, pore size and pore structure. Generally, the level of the catalyst activity in polyolefin pyrolysis increases with increasing number of acid sites [65]. Thus, zeolite based catalysts achieve higher conversion than non-zeolitic catalysts [76,78,85].The effect of some specific zeolitic and other catalysts used by the different researchers for plastic pyrolysis is as summarized below. The product distribution of the catalytic degradation of high density polyethylene on different zeolites yields hydrocarbons from C_3 to C_{15}. The structure of the zeolitic framework has shown a significant influence on the product distribution. Alkanes are the major products with US-Y, Y, and β-zeolites, whereas alkenes are the major products with mordenite and ZSM-5. The majority of alkanes are reported to be isoparaffins, having a high octane number; this speaks for an increased fuel quality. A small amount of cycloproducts and aromatics are formed on all samples. This is an important advantage of the catalytic degradation, as environmental concern about aromatics grows and strict legislation for low levels of aromatics in fuels is under discussion [148].

Songip et al. studied the conversion of polyethylene to transportation fuel using REY (Rare earth Y) catalyst (7.8A° pore size and 11.8A° supercage) in addition to other acid and non-acid catalysts. REY is reported to be best for oil conversion, gasoline yield, and research octane number of gasoline. It is concluded that the performance of REY zeolite is attributable to its stability, adequate acidity, and relatively large pores into which oil molecules are allowed to penetrate [153].

Clinoptilolite zeolites (with pore structure of a monoclinic framework consisting of a 10-membered ring (7.6A°-3.0A°) and an 8-membered ring (3.3A°- 4.6A°), and is a silica-rich member of the heulandite family either proton-exchanged or further treated by hydrochloric acid are efficient catalysts for the conversion of polypropylene to gasoline-range liquid chemicals. In the degradation of polypropylene, the acidic sites of medium acid strength seem necessary for the formation of carbenium ion and cracking of carbon chains. Pore volume is another important character for the further cracking of initially degraded fragments. High degradation temperature offered lighter hydrocarbons by accelerating the cracking reactions. When it is dealuminated by the HCl treatment, the gaseous products (mainly ethane, propane, propylene and butene) increased greatly. Even though the dealuminated catalysts possess lower acid amount, they have relatively larger pore size, therefore, the degraded liquid components over these catalysts will have more chance to stay in the pore for further cracking to lighter gaseous products. Thermal degradation on clinoptilolite showed high amount of residues, but the proton exchanged clinoptilolite showed practically no formation of residue [108].

Mordenite is reported to enhance the rate of pyrolysis reaction, but it produce much greater fraction of C_{11}–C_{13} paraffins and greatest amount of coke explained due to its bottleneck crystalline structure [155].

ZSM-5 showed the greatest catalytic activity on cracking of heavy hydrocarbons to small gaseous hydrocarbons and formation of aromatics [155,156]. Pyrolysis of polyethylene using ZSM-5 yields greater percentage of gaseous products than oil. This extraordinary yield is explained due to a strongly acidic property and a unique larger intra crystalline pore channel structure of ZSM-5 which helps in excellent catalytic efficiency on cracking, isomerization and aromatization. The larger intra crystalline pore channel structure allows more cracking of the heavy petroleum chemicals. In addition, ZSM-5 possesses a smaller pore diameter (5.4–5.6A°) among zeolites. Since the initially degraded materials on the external surface of catalyst can be dispersed into the smaller internal cavities of catalyst, they can be further degraded to the smaller size of gaseous hydrocarbons, leading to the remarkably high yield production of gaseous material [156].

The use of nanocrystalline HZSM-5 allows greater yields of gas fractions at mild temperatures and a higher selectivity to the products obtained than those achieved by thermal cracking. First, polyethylene is cracked over the acid sites on the external surface of the zeolite; a part of the compounds produced can then diffuse into the internal active surface through the zig-zag pores and over crack giving lighter compounds. Due to the size restriction of the pores, gases are produced mainly in the pores while waxes are the result of external cracking. The temperature affects the gas and wax yields. Gas production increases as the temperature rises. However, when the temperature exceeds 500 °C, some HDPE is cracked thermally, increasing the wax yield and varying the wax and gas compositions. If the catalytic pyrolysis temperature is too low (350–400 °C), the polymer is not fully cracked and a solid residue is produced in the reaction bed. The gases are mainly composed of olefins. Cracking reactions (β-scission) control the reaction mechanism inside the pores. Due to their small dimensions, HZSM-5 pores inhibit bimolecular reactions, which are a source for paraffin production. Terminal olefins are not produced in significant quantities because of the strong effect of isomerization reactions [156].

Grieken et al. [163] using batch type reactors also reported that ZSM-5 accelerated the degradation of plastics, especially polyethylene, giving a large production of gaseous materials and a low oil yield. Similarly, HZSM-5 also reportedly yields more gas fraction and aromatic hydrocarbons in the catalytic degradation of polyethylene. Also this catalyst increases the ratio of branched hydrocarbon to normal hydrocarbon and decreases the formation of straight chain paraffins and olefins.

The catalytic degradation of high-density polyethylene on ultrastable-Y zeolite has significantly reduced the degradation temperature compared with pure thermal degradation in the absence of a catalyst. The products of the catalytic degradation were hydrocarbons in the gasoline range (C_3–C_{15}) were the heaviest detected product. The majority of the products are isoparaffins, suggesting high octane number, speaks for a high quality fuel as a product of a catalytic degradation process [162].

Sharratt et al. [164] reported that the gaseous material rich in C_3 –C_5 olefins is obtained in high yield from the catalytic degradation of high-density polyethylene (HDPE) over HZSM-5 in a fluidized bed reactor. All zeolites increased olefin content in oil product, particularly ZSM-5 and zeolite-Y enhanced the formation of both aromatics and branched hydrocarbons simultaneously.

With silica-alumina (SA), all of the polyethylene is found to be converted to liquid products with high yields (77–83 wt%) and without any wax production. The liquid products were distributed in the range of n-C_5, to n-C_{20} and mostly C_5–C_{15}[165]. The effects of silica-alumina SA-1 (have SiO_2/Al_2O_3 ratios of 83.3/16.7) and silica-alumina SA-2 (have SiO_2/Al_2O_3 ratios 21.1/78.9) catalysts with different SiO_2/Al_2O_3 ratio is studied by Md Azhar et al. [165] in order to investigate the effects of acidity of silica-alumina on liquid product composition. The yield of liquid products was 68 wt% for SA-1 compared to 77 wt% for SA-2. With SA-1, liquid products were distributed in the range of equivalent carbon numbers of n-C_5 to n-C_{15} (boiling point range 36–216 °C), very similar to those of commercial gasoline. Therefore, the SA-1 catalyst degraded the polyethylene sample into much lighter hydrocarbon fuel oil than the SA-2 catalyst. So it can be concluded that the yield and composition of the liquid products can be controlled by altering the SiO_2/Al_2O_3 ratio i.e. the acidity of the catalyst. As the SiO_2/Al_2O_3 ratio of the SA-1 and SA-2 catalysts is different, both the acid strength and acid content of these catalysts may differ. Amorphous silica-alumina also shows a great activity on cracking polyethylene and polypropylene to lighter hydrocarbons. Since amorphous silica-alumina appears to have a higher fraction of total acidity in the strong acid range, it might tend to favor tight binding of carbenium ions to the surface and to carry out continuous cracking. It generated a pronouncedly high yield of lighter olefins due to strong acidity, but was far inferior to zeolites in the formation of aromatics and branched hydrocarbons because of amorphous structure [165].

Mesoporous silica (FSM) with no acid sites is found to have faster rate of polymer degradation than that of non-catalytic thermal degradation and comparable to that over solid acid catalysts. This result is attributed due to the fact that mesoporous silica FSM, having arrays of uniform hexagonal pores of 2.7nm accelerates the degradation of polymers, even though the FSM catalyst does not contain any significant acid sites. Again, when compared with non-catalytic thermal degradation, FSM not only accelerates the rate of degradation of polymers but also degrades the heavier waxy compounds into lighter liquid hydrocarbons [166].

Studies employing mesoporous aluminosilicate such as MCM-41 (Mobile Crystalline Material) suggest that it increases the product character and also reduces the reaction temperature [145]. HMCM-41 also leads to a high conversion of the plastic mixture because of its large pore size, which promotes the access of the polymer molecules to the acid sites [167]. Catalytic reforming over Al-MCM-41 generated a lower proportion of gaseous hydrocarbons and a higher yield of gasoline type condensable products, which was attributed to its weaker acid properties and larger pore dimensions. Catalytic conversion over this meso structured material showed a lower selectivity towards the formation of aromatic products but yield higher proportions of liquid isoparaffins and olefins. The composition of this oil fraction is comparable to commercial gasoline fuel [168].

Two smectites such as saponite and a montmorillonite, as well as their Al-pillared derivatives, are tested for their performance in the catalytic cracking of polyethylene. Below about 600 K, those catalysts proved to be less active than zeolites. However, this picture is drastically changed with temperature, as the clay catalysts were able to completely decompose polyethylene after a small increase in the process temperature. Moreover, they proved superior to zeolites with respect to the formation of liquid hydrocarbon fuel. The yield to liquid products was around 70%. This higher liquid yield of clay-based catalysts is attributed to their weaker acidity, which does not sustain over cracking to small molecules and is also reflected in the liquid product distribution. Clay catalysts furnish hydrocarbon liquid products that are considerably heavier than those from zeolite catalysts. In addition, the clay catalysts furnish products that, in the overwhelming majority, are in the gasoline range. Furthermore, the predominance of alkenes as products over the clay catalysts is due to the significantly lower occurrence of hydrogen-transfer secondary reactions because of the milder acidity of clays. This differentiation probably also explains the lower coke formation over the clay based catalysts [160].

FCC (Fluid catalytic cracking) catalysts usually have faujasite structure with a ratio of Si/Al greater than 1.5. It is formed by the arrangement of truncated octahedra forming cages of 13A° diameter, and the pore opening to these cages are 12-membered rings approximately 7.4A°. The equilibrium FCC catalyst had good catalytic activity for producing light hydrocarbon liquids with carbon number C_6–C_{15}. It is stated that C_2 and C_4 fractions are dominating mainly in gases on the cracking of polyethylene [169].

Activated carbon catalyzed plastics cracking yield normal alkanes and the amount of isoalkanes is very small. When Pt impregnated on activated carbon was tested, the aromatic yield is reported to reach as high as 50% of the plastic sample; it was suggested that this is due to a good combination of cracking and dehydrocyclization activities of the catalyst [14].

Synthesized fly ash catalyst (SFC) is found to decrease the decomposition temperature and the initiation time for pyrolysis and is more effective than some zeolite catalysts or no catalyst. For the pyrolysis of polyethylene, but the pyrolysis oil produced by SFC appeared to be creamy phase and is not in the full boiling point range of diesel. In case of paralyzing polypropylene by SFC, better oil is made for the alternative fuel oil which can be used without problem as commercial diesel oil [170].

The lead sulfide catalytic pyrolysis enables polyethylene to be converted into liquid, gas and wax with nearly 100% efficiency. As the char formation with lead sulfide is negligible therefore the catalyst can be used several times without treatment. No side products are associated with the method. The pyrolysis products mainly consisted of paraffinic and olefinic compounds. Distillation data and other physicochemical tests for fuel oil show that, these oils are suitable to be used as fuel oil for different energy purposes [171].

Catalysts such as metal oxides, metal complexes, and alkali metal carbonates or alkaline metal carbonates have appeared to be used mainly for enhancement of monomer recovery [13].

Degradation of polyethylene on solid bases (ZnO, MgO, TiO_2) yield more oils than on solid acids, though the time required to complete the degradation on solid bases is much longer than on solid acids. The composition of oil on solid bases is reported to be rich in 1-olefins and is poor in aromatics and branched isomers. So, that oils mainly consisting of olefins are not expected for fuel oils because of their polymerization during preservation and/or transportation. Moreover, a low octane number is expected for the oils produced on solid bases, since the oils mainly consisted of straight chain hydrocarbons; n-paraffins and 1-olefins. Similarly, more amount of styrene was yielded from waste polystyrene degraded on solid bases rather than on solid acids. Productions of benzene and indan are one of the features of the polystyrene degradation on solid acids. The solid bases such as BaO and K_2O yields more than 80 wt% both styrene monomer and dimer. Again, thermal degradation of polystyrene films dispersing BaO powders produce around 90 wt% of both styrene monomer and dimer at 623 K. These styrene monomer and dimer could be reused for the production of polystyrene. In this sense, the polystyrene films dispersing BaO catalyst can be considered as one of the models of the recyclable polymer, which has been extensively studied from the view point of the technology for saving carbon resources as well as for environmental issues [172].

2.5.3.3 Effect of catalyst contact mode

One may investigate the catalytic steps involved in polymer degradation by considering different modes of catalyst introduction to the polymer feed. Sakata et al. [78] investigated two modes of contact in the batch pyrolysis of polypropylene using various solid acids: ‘‘liquid phase contact’’ and ‘‘vapor phase contact’’. For the catalytic degradation in the liquid phase contact, both catalyst and polymer are placed in the reactor and heated to the operating temperature. Whereas, with the vapor phase contact mode, the polymer is first thermally degraded into hydrocarbon vapors and then contacted with the catalyst. It has been observed that liquid phase pyrolysis retards the escape of evolving products, thus enhancing interactions and hydrocarbon vapors undergo further cracking in the vapor phase whereas the product yield in the liquid or melt phase contact is reported not to be differ significantly from that obtained by purely thermal degradation of polypropylene [89].

2.5.3.4 Effect of particle/crystallite size of catalyst on product distribution

The effect of catalyst particle size has only been sparsely studied in literature. You et al. [173] investigated the effect of particle size of zeolites on the catalytic degradation of polyethylene wax and found that whereas conversion decreased with particle size, product quality increased. Furthermore, particle sizes in the nano range have been investigated. Serrano et al. [174] reported conversions as high as 90%, temperatures less than 350 °C for the cracking of polypropylene, LDPE and HDPE using nanocrystalline ZSM-5. Aguado et al. [141] observed similar results in the batch pyrolysis of polypropylene an LDPE mixtures using nano-HZSM-5. Based on these results, it can also be deduced that nano-ZSM-5 catalyzed reactions result in very high gas yields in the range of C_3–C_6 products, and apparently in much higher concentrations than is observed with micron-sized ZSM-5. These nano-sized particles are so effective because of their increased surface area. Conversely, high surface area combined with a very small pore system poses great difficulty in achieving decent amounts of gasoline range products in the C_5–C_{12} range. So, the nano-catalyst selectivity to liquid products is also very limited [154,174]. This could be resolved by investigating the particle size effect with catalysts that are selective to gasoline range liquid products such as FCC catalysts.

2.5.3.5 Effect of reactor type

The type of reactor used determines mainly the quality of heat transfer, mixing, gas and liquid phase residence times, and the escape of primary products. A wide range of reactors have been used on a lab-scale in polyolefin pyrolysis. The reactor set-ups investigated so far fall under one of the following categories: Batch reactor, semi-batch reactor, Continuous flow reactor (CFR), modifications or combinations of either of these. A common variable in batch and semi-batch operations is nitrogen which is used for the continuous removal of volatiles from the reactor vessel. The products are then collected by passing the vapors through a condensation system. Most are made out of pyrex or stainless steel. A key disadvantage with this is the high reaction times observed. Furthermore, under batch operation, it seems that the potential of a catalyst is minimized with similar product yields to thermal at similar conditions. From an industrial viewpoint, continuous reaction systems are preferred to batch set-ups for operational reasons [65,67]. In fixed bed semi-batch reactor, polymer and catalysts samples are heated separately and reacted by vapor phase contact. Degraded polymer fragments are carried to the catalyst bed/mesh by a carrier gas, in most cases N_2. Typically the catalyst bed is heated to a higher temperature than the polymer bed [67,175]. More recently, researchers have moved focus towards reactors with greater feasibility in the industrial arena such as fluidized bed reactors. Riser simulator reactors are fluidized batch reactors, specifically designed to simulate similar conditions found in a catalytic riser reactor used in the FCC process. It is adapted for liquid phase catalytic reaction, in which heat from the catalysts could vaporize the melt polymer feed while simultaneously cracking the resulting hydrocarbons [176–181]. The University of Hamburg, in particular, has done a lot of research in feedstock recycling from waste plastics using FCCs, and has subsequently developed the ‘Hamburg process’ which makes use of an indirectly heated fluidized bed [63,93]. During catalytic cracking, quartz sand is replaced by the respective FCC catalyst as packing material. Amongst the various catalysts investigated, FCCs produced the most decent liquid yields in polyethylene pyrolysis. Unlike a batch reactor, a fluidized bed reactor is suited for pyrolysis because it provides very good heat and material transfer rates hence generating largely uniform products. However, the disadvantages are many and include: broad residence time distribution of solids due to intense mixing, attrition of bed internals and catalyst particles, difficulty in scale-up, defluidization problems, requires large amounts of catalysts, low liquid yields due to ‘over cracking’. On the other hand, other continuous systems, such as the three-step continuous flow pyrolysis process involving a preheat, cracking reactor and separation zones, have been investigated by a few [11,52,64,69]. In this method the polymer is first pre-heated to a molten state in a CFR such as an extruder and driven into the 'reactor' where it is further 'cracked' at elevated temperatures.

2.5.3.6 Effect of other process parameters

The effect of other process parameters such as reaction temperature, pressure, reaction time and catalyst loading has been investigated. These are summarized in Table 2.7.

Table 2.7 Effect of different process parameters like pyrolysis temperature and heating rate, operating pressure, residence time, presence of gases, such as N_2, Ar, O_2 or H_2 on pyrolysis.

Process parameter	**Results**
Pyrolysis temperature and heating rate	• Higher operating temperature and high heating rates both enhance bond breaking and favour the production of small molecules [77] • Conversion increases with increase of temperature resulting in decrease of aliphatic content. • Dermibas *et. al.* [33] observed that gaseous products (C_2-C_4) increases and liquid products (C_5-C_9) decreases with increase in temperature. • Effect of the catalysts on the yields and structure of products becomes less significant with increasing temperature [186, 118].
Operating pressure	• Low pressure reduces the condensation of reactive fragments forming coke and heavies [77]. • Murata *et. al*. [30] demonstrates the inverse relation of pressure to temperature in the pyrolysis of polyethylene. With the higher pressure, the carbon number distribution of gaseous and liquid products, and the molecular weight distribution of reactor

	contents shifted to the lower molecular weight side.
Residence time *[34, 149, 152,118,182]*.	• Key parameter in fluidized bed reactors. Generally conversion increases with residence time. • Longer residence time favour a secondary conversion of primary products, yielding more coke, tar, as well as thermally stable products, thus gradually obscuring the effect of original polymer structure [77]. • Miskolczi *et. al [179]* observed that the catalyst activity of HZSM-5 and an FCC catalyst decreased with increasing cracking time in the pyrolysis of HDPE waste. • Effect of residence time on product yield is more pronounced at lower than higher temperatures
Presence of gases, such as N_2, Ar, O_2 or H_2.[77]	Such presence internally generates heat, dilutes the products and influences upon equilibrium, kinetics, and mechanism.

2.6 Reaction mechanism and kinetics of plastics pyrolysis

The degradation of polymer may be considerably different based on the way in which reaction is carried out: heat (thermal degradation), heat and catalyst (thermo catalytic degradation), oxygen (oxidative degradation), heat and oxygen (thermo-oxidative degradation), radiation (photochemical degradation), radiation and oxygen (photo-oxidative degradation), chemicals (chemical degradation), etc. The common characteristic of these methods is that they cause irreversible changes in the structure of polymers. The decomposition of the framework of polymers results in decreasing molecular weight and significant changes of physical and chemical properties. The widely known and thoroughly studied methods are thermal and thermo catalytic degradation, which are referred as chemical recycling in the literature. Chemical recycling and chemical degradation are not the same, because chemical degradation means degradations caused by chemicals (acids, solvents, alkalis, etc.) Several reports have described the thermal and catalytic cracking of waste polymers. Two types of polymers have been widely investigated: polyethylene and polypropylene, because they represent 60–65% of all plastic wastes. The degradation of plastics means heating to high temperatures where macromolecules break into smaller fragments in which valuable mixtures of hydrocarbons (gas, liquid and residue) are obtained [183-187]. The structure of the hydrocarbons produced can be modified by the use of catalyst. Catalytic cracking consumes less energy than the non catalytic process and results in formation of more branch-chain hydrocarbons. On the other hand the addition of the catalyst can be troublesome, and the catalyst accumulates in the residue or coke. There are two ways to contact the melted polymer and catalysts: the polymer and catalyst can be mixed first, and then melted, or the molten plastics can be fed continuously over a fluidized catalyst bed. The usually employed catalysts are US-Y, and HZSM-5. It was found that the HZSM-5 and FCC catalysts provided the best possibility to yield hydrocarbons in the boiling range of gasoline [187-191].

The kinetics and mechanism of these reactions have been elucidated by several physical and chemical methods using different analytical techniques.

2.6.1 Investigative methods for polymer degradation

It must be said at the onset that no single method of investigation is appropriate to cover all pyrolysis phenomena. This is because three extreme categories of pyrolysis behavior can be defined, and each presents a different investigative problem:

(1) Cross linking or other reactions within the polymer leading to the formation of infusible resins, or coke/char precursors.

(2) Chain scissions and other processes leading to decrease in the average molecular weight of the sample.

(3) The formation of significant yields of small molecular weight materials, which may be monomeric, oligomeric, or which may originate from substituents on the chain backbone.

It is very likely that more than one of these categories of behavior will be occurring simultaneously, in which case it will be desirable to pursue several experimental approaches, and to coordinate the results [192].

Categories (1) require the study of changes in the original polymer or the residue from it. This behavior is generally studied by the methods of thermal analysis (thermogravimetric analysis, differential thermal analysis, and differential scanning calorimetry); which may indicate the overall energetics of the processes occurring, but cannot give direct details of the chemistry of the processes involved [192]. Thermogravimetry (TG) is a thermal analysis method in which the mass change of a sample subjected to a controlled temperature programme is measured. The use of isothermal and dynamic TG for the determination of kinetic parameters in polymeric materials has raised broad interest during recent years. Although TG cannot be used to elucidate a clear mechanism of thermal degradation, dynamic TG has frequently been used to study the overall thermal degradation kinetics of polymers because it gives reliable information on the activation energy, the exponential factor and the overall reaction order. Consequently, the corresponding differential TG (DTG) curves exhibit multiple peaks or asymmetric peaks with more or less pronounced shoulders. Except when the mass losses corresponding to each decomposition step occur in different temperature ranges, TG does not provide clear information on thermal degradation mechanisms because of its insufficient ability to analyse the evolved gas mixture. In general, any changes in physical properties may be used to assess category (1) behavior, but again this approach does not directly provide any information about the molecular behavior. The capacity to obtain such molecular information with any reliability depends upon the extent to which spectroscopic methods can be applied to study the polymer residue. Any possibility of using such methods should be explored. If all else fails, an attempt may be made to further degrade the infusible residue under conditions so drastic that fragmentation of the structure occurs; it may then be assumed optimistically that the fragments obtained are sufficiently characteristic of the original residue to permit proposals about its structure. The simplest way to achieve such drastic degradation is to heat the sample to temperatures exceeding

1000 °C, but unfortunately most of the products obtained in this way are small molecules or radicals which are not helpfully characteristic of the overall structure. The best way to obtain large characteristic fragments is to use a technique such as fast ion bombardment or fast atom bombardment; if this is carried out in the source region of a mass spectrometer, mass analysis of the resulting fragments can be performed in situ [193].

Category (2) behavior is more amenable to study; in particular, viscometry and any of the recognised techniques of polymer molecular weight measurement can be considered, and liquid chromatographic methods, especially gel-permeation chromatography are now widely used. The latter technique is especially useful since the results provide information about changes in molecular weight distribution; such changes may provide mechanistic clues [192].

However, the study of polymeric residues and partially degraded solid polymers [i.e. categories (1) and (2)] presents numerous experimental problems. The sensitivity of the available techniques is also very less for the accurate assessment. This means that mechanistic information derived from measurements on solid samples or residues is generally less reliable than that derived from measurements on volatiles, as discussed in the following paragraphs [192].

Behavior leading to the formation of small molecular-weight materials [category (3)] will be evidenced by the fact that such materials are generally volatile at the elevated temperatures used for pyrolysis. They may be condensed on a cold surface or in a cold trap, and subsequently analysed, though this approach is not recommended because of the high probability of secondary reactions occurring when the frozen condensate is heated to recover the products for analysis. When this occurs it can give a very misleading idea of degradation processes occurring within the sample. Another method of estimating the yield of volatiles is in terms of the pressure they create in a continuously pumped system (“thermal volatilization analysis”) but this method is of only moderate sensitivity, and becomes cumbersome when there are several pyrolysis products [192].

The techniques of gas-liquid chromatography (GLC) and mass spectrometry (MS), either individually or in combination (GLC-MS) have been used on the assessment of volatiles. In either case the pyrolysis (Py) may be performed in situ, and the resulting techniques of Py-GLC and Py-MS both have the distinct advantage that pyrolysis products are not only analysed, but removed from the pyrolysis zone as they are formed, so that secondary reactions are minimized. In Py-MS the pyrolysis zone is within or close to the continuously- pumped source of the mass spectrometer; in Py-GLC the pyrolysis products are swept away by the inert carrier gas as they are formed. In many respects these two techniques are complementary. Py-MS is rather less sensitive, and the results may be difficult to interpret if there are several pyrolysis products, because their MS cracking patterns will be superimposed. However, mass spectra are much more specific for characterizing volatiles than are chromatographic peaks. Py-GLC is extremely sensitive when detectors such as flame ionization detectors are used, and chromatograms of pyrolysis products are much simpler than mass spectra. The combined technique of Py-GLC-MS uses a suitable interface to pass the gas chromatographic effluent into a mass spectrometer so that each GLC peak is mass analysed. This is the most useful approach for initially characterizing the products from the pyrolysis [192].

Recently, the development of a TG-MS and TG-FTIR interface design has made a significant breakthrough in thermal degradation investigations. The combination of TG and FTIR provides a very useful tool for the determination of the degradation pathways of a polymer, copolymer or the combination of one of these with an additive. The TG is normally coupled to the FTIR spectrometer *via* a glass-coated transfer line. This transports the volatile products evolved during the decomposition of the sample to the gas cell of the FTIR spectrometer. Both the transfer line and the gas cell are heated to prevent condensation of the decomposition products. The FTIR spectrometer measures the spectra of the gases in the cell rapidly at frequent intervals. TG-FTIR makes it possible to assign the volatile components under investigation to the decomposition stages detected by TG during an experiment. Based on the measurements conducted, it is possible to achieve a simultaneous quantitative and qualitative characterisation of the materials investigated. TG-MS is a useful ‘hyphenated’ technique combining the direct measurement of weight loss as a function of temperature with the use of a sensitive spectroscopic detector. The TG is coupled to the MS *via* a heated metal or quartz glass capillary tube. One end of the capillary is positioned close to the sample in the thermo balance. Part of the evolved gases is sucked into the capillary by the vacuum in the MS. The MS repeatedly measures the entire mass spectrum or monitors the intensity of characteristic fragment ions (*m*/*z*, the mass-to-charge ratio). TG-MS features are high sensitivity and high resolution, which allow extremely low concentrations of evolved gases to be identified, together with overlapping weight losses that can be interpreted qualitatively. In addition to the weight-loss information, MS permits temporal resolution of the gases that are evolved during thermal or thermo oxidative degradation of a polymer in controlled atmospheric conditions. The characteristics of a broad variety of TG-MS instrumental solutions that depend partly on the sample characteristics and the desired conditions of thermal degradation are normally considered in relation to polymer characterization [193].

Py-GC is mainly employed in structure analysis that includes the exploration of monomer arrangement in the (co)polymer system, such as the number-average sequence length and stereo regular distributions. In addition to the traditional post-pyrolysis derivatisation, pre-pyrolysis derivatisation has been developed in order to reselect degradation pathways effectively.

Pyrolysis is carried out either outside or inside the identification instrument. In the outside mode, the thermal degradation is carried out by a pyroprobe connected to the injection port of a GC using a selected technique–time-programmed or flash pyrolysis. GC-separated individual pyrolysates can be identified with different equipment connected to the GC, e.g., Py-GC-MS, Py-GC-FTIR or Py-GC-AED (atomic emission detector) [193].

Direct pyrolysis–mass spectrometry (Py-MS) is applied to determine the primary structure of macromolecules and to investigate selective thermal degradation mechanisms. This technique allows the thermal decomposition products of the polymer sample to be observed directly in the ion source of the mass spectrometer, so that the evolving products are ionised and continuously detected by repetitive mass scans almost simultaneously with their formation. Since pyrolysis is accomplished under high vacuum, the thermal fragments are readily removed from the hot zone, and because of the low probability of molecular collisions and fast detection the occurrence of secondary reactions are reduced. Therefore, primary pyrolysis products bearing the structure of the decomposing materials are mainly detected [193].

In recent years pyrolysis–gas chromatography–mass spectrometry (Py-GC-MS) has been widely used for the separation and identification of the volatile pyrolysis products of polymers and can be considered as the most convenient method to detect simultaneously the presence of decomposition products qualitatively and quantitatively. Evolved gas analysis (EGA) performed by using a GC coupled with a mass-selective detector offers a number of advantages for the decomposition study. The number of peaks seen in the total ion chromatogram (TIC) represents the number of compounds detected by GC-MS. The relative intensity of each peak corresponds to the relative concentration of each compound. The identification of each decomposition product can also be confirmed either by using model compounds and/or by comparing the spectrum with those in a GC-MS library [193].

2.6.2 Reaction mechanism of polymer degradation

As a rule, the plastic pyrolysis follows complex routes that cannot be described by one or more chemical reactions, but still rather imperfectly by either empirical formulas featuring fractional stoichiometric coefficients or compressive systems of elementary reaction, i.e. reaction that really occur as written [89].

A detail study on the mechanism for the thermal decomposition of polymers is proposed by Cullis and Hirschler [194]. The four different mechanisms proposed are: (1) End-chain scission or unzipping, (2) Random-chain scission/fragmentation, (3) Chain-stripping/elimination of side chain, (4) Cross-linking. The decomposition mode mainly depends on the type of polymer (the molecular structure).The following Table 2.8 describes the reaction pattern of different thermoplastics where first three types of mechanism is being followed [89]. This has been shown as below [195].

$M_n^* \rightarrow M_{n-1}^* + M$ ---------------------------- 2.1

$M_{n-1}^* \rightarrow M_{n-2}^* + M$ -----------------------------2.2

$M_n \rightarrow M_x + M_y$ ----------------------------- 2.3

Reactions 2.1 and 2.2 represent the thermal degradation and reaction 2.3 represents the random degradation route of the polymers pyrolysis. The fourth type of mechanism i.e. cross linking often occurs in thermosetting plastics upon heating at high temperature in which two adjacent ‘stripped’ polymer chains can form a bond resulting in a chain network (a higher MW species). An example is char formation.

A diagram of the most probable reactions involved in thermal degradation of polymers is given in Figure 2.3. It must be emphasized, however, that the instability of macromolecules under heat treatment is often due to the presence of anomalous weak links in the polymer. In these cases, low molecular weight models of the normal chain unit are much more stable than the polymer.

As a matter of fact the cracking of C–C bonds takes place as the result of competition between reactions initiated by thermal and catalytic effects of thermo catalytic degradation. It means that thermal and catalytic reactions do not separate from each other, therefore in discussing thermo catalytic cracking of polymers one has to touch upon both the thermal and catalytic degradation reactions. It is well known that, the thermal (non catalytic) cracking of plastics occurs by a radical mechanism, wherein the initiating radicals are formed by the effect of heat.

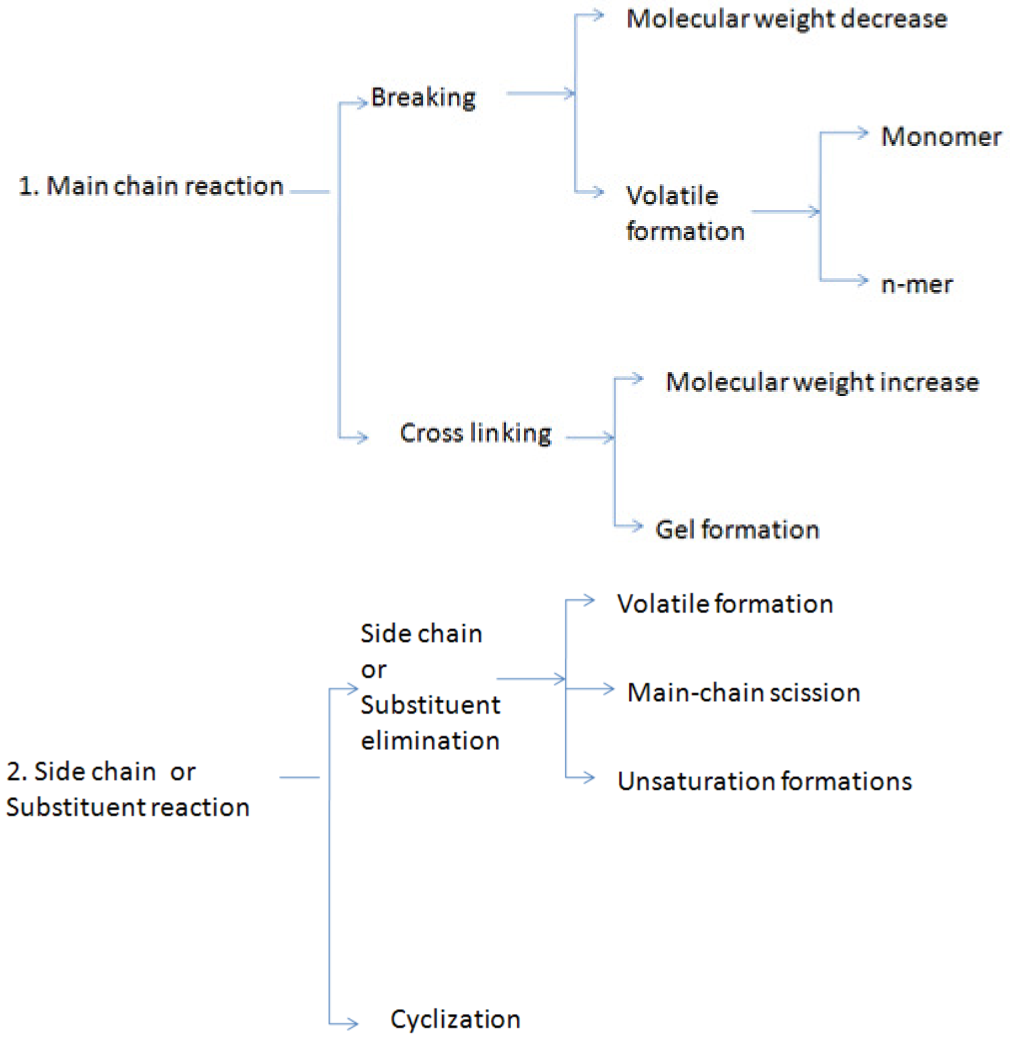


Figure 2.3 Most probable reactions involved in thermal degradation of polymers

On the other hand, catalytic cracking generally proceeds though carbenium ions, which are considered to be produced by the abstraction of hydride ion from the polymer (when the catalyst acts as Lewis acid) or the addition of proton to the polymer (when the catalyst acts as Bronsted acid) macromolecule in the initial reaction step. Fragments formed in the first cracking reactions cracked further into lower molecular weight hydrocarbons on the active sites of the catalyst. Unstable primary fragments are cracked in further decomposition reactions.

Table 2.8 Mode of thermal decomposition of different thermoplastics and products

Resin	**Mode of thermal decomposition**	**Low temperature products**	**High temperature products**
Polyethylene	Random chain rupture (involves random fragmentation of polymer along polymer length, results in both monomers and oligomers).	Waxes, paraffin oil, α-olefins.	Gases and light oils.
Polypropylene	Random chain rupture	Vaseline, olefins	Gases and light oils
Polyvinyl chloride	Chain-stripping, (Side chain reactions involving substituents on the polymer chain i.e. elimination of reactive substitutes or side groups (HCl) on the polymer chain, chain dehydrogenation and cyclization).	HCl (< 300^0C), Benzene.	Toluene (>300^0C).
Polystyrene	Combination of unzipping and chain rupture, forming oligomers	Styrene and its oligomers.	Styrene and its oligomers.
Polymethyl methacralate	Unzipping (Cracking is targeted at chain ends first, and then successively proceeds down the polymeric length, results in monomer formation).	Monomer Methyl methacralate	Less Methyl methacralate, More decomposition.
Polytetrafluoro ethylene	Unzipping	Monomer tetrafluoro ethylene	
Polyethylene terephthalate	β-Hydrogen transfer, rearrangement and decarboxylation	Benzoic acid and vinyl terephthalate	
Polyamide 6	Unzipping	Caprolactum	

The following elemental reactions take place both in thermal and thermo-catalytic cases:

(a) Initiation

(b) Formation of secondary radicals

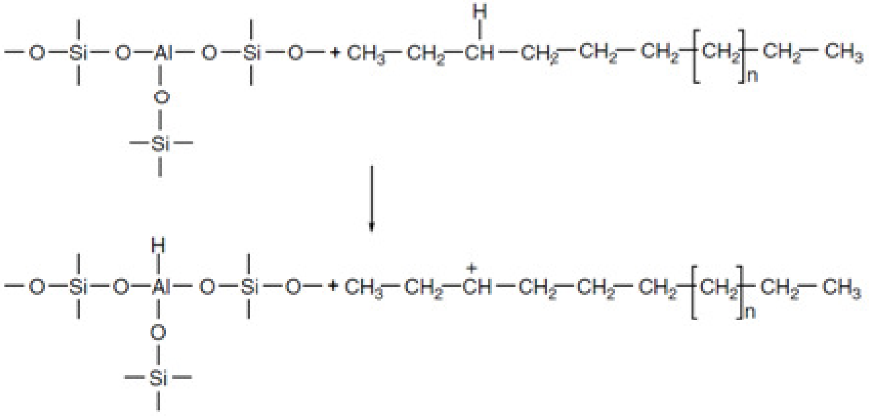
- Depolymerization, formation of monomers;
- Favorable and unfavorable hydrogen transfer reactions;
- Intermolecular hydrogen transfer (formation of paraffins and dienes);
- Isomerization via vinyl groups;

(c) Termination by disproportionation or recombination of radicals

In the presence of catalysts, heterogeneous catalytic cracking occurs on the surface interface of the melted polymer and solid catalysts. The main steps of reactions are as follows: diffusion on the surface of catalyst, adsorption on the catalyst, chemical reaction, desorption from the catalyst, diffusion to the liquid phase. The reaction rate of catalytic reactions is always determined by the slowest elementary reaction. The dominant rate controlled elementary reactions are the linking of the polymer to the active site of catalyst. But the selectivity of catalysts on raw materials and products might be important. The selectivity is affected by molecular size and shape of raw materials, intermediates and products [196].

(a) Initiation

The mechanism of initiation is partly radical in thermo catalytic degradation. The cracking of C–C bonds occurs by homolytic cracking of C–C bonds, at regions with structural faults or distortion of the electron cloud. Thermal decomposition of polyethylene initially proceeds essentially by random scission mechanism. But, catalytic cracking generally proceeds through a carbenium ion, which is considered to occur by the abstraction of hydride ion from polymer or the addition of proton on the polymer macromolecule in the initial step of the reaction [197] which is shown in reaction 2.4.



-----------------2.4

Bond dissociation energy of C-C and C-H bonds is 347 kJ/mol and 413 kJ/mol, respectively. The cracking of C–C bonds has lower energy consumption, than that of C–H, because it has lower bond energy, by 40–60 kJ/mol, than the C–H bond. Thus, C-C bond dissociation is the more probable initiation step, since it is weaker of the two. The framework of waste polymers might be cracked at C–C bonds at low temperature and both at C–C and C–H bonds at high temperature. Hence, random scission to unstable hydrocarbon radicals is the initiation step in thermal degradation. [198].

Table 2.9 shows the activation energies of elemental reactions in the case of polymer degradation. It is noticeable the initiating reactions have the highest potential barrier. This potential barrier can be decreased by the use of catalysts and it results a decrease of 50–100 kJ/mol in activation energy [199].

Table 2.9 Energies of elementary steps in polymer degradation [199]

Elementary steps	**Activation energy (kj/mol)**
Initiation	284-336
Depropagation	21-77
Termination by disproportionation or recombination	4-10
Diffusion in molten state	27
Diffusion in solid state	41

In the presence of catalysts the beginning of cracking of C–C bonds of macromolecules of polymer occurs at a lower temperature than in the absence of catalysts. This phenomenon could be explained by the acidic sites of the catalysts which assist the formation of greater number of unstable molecular fragments at lower temperature.

Volatile products are formed from polymers with suitable yields only above 450 °C without catalysts, but at 300–400 °C using catalysts. On the other hand, some noncatalytic cracking takes place at 400–450 °C [196, 198, 199], because the preferred compounds are aliphatic ones. It is well known that above 450–460 °C the possibility of reactions of cyclization, aromatization and polycondensation increases considerably and these results growing concentrations of naphthenes and aromatics. If waste polyolefins (LDPE, HDPE, PP) have to be converted into aliphatic olefins and paraffins the low temperature is a key parameter.

Another important parameter is the catalyst concentration. Thermo catalytic cracking of HDPE and MDPE over HZSM-5 and Y-zeolite catalysts was carried out in a cycled spheres reactor. It was found that the required temperature of cracking could be decreased by 2% using a low concentration of catalysts, and by 16–20% in the case of greater catalyst concentration because the reaction rate increased with increasing catalyst concentration [200].

Smaller differences were found between thermal and thermo catalytic degradations in respect to yields and structure of products at higher temperatures (450–500 °C), than at lower temperatures (400–420 °C).

(b) Formation of secondary unstable compounds

Unstable molecular fragments (radicals and ions) formed in the initiating reaction take part in further decomposition reactions with uncracked macromolecules of polymer or radicals and ions, resulting, among others, in secondary instable compounds of lower molecular weight.

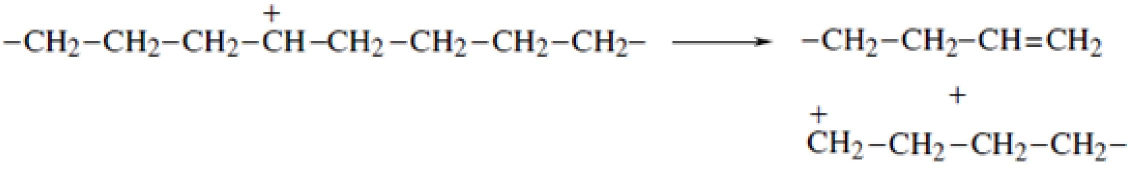
In thermal pyrolysis, the different radicals thus formed from random scission are capable of stabilizing themselves either by hydrogen abstraction or β-scission, all of which form a stable molecule. The reaction that would be favored for stabilization depends on temperature. At (200–300 °C), where sufficient energy is not available for termination of radicals, abstraction is the preferred route for radical stabilization leading to higher hydrocarbons at these low temperatures. However as temperature increases, the increase in H^+ radicals somewhat slows down this reaction. Therefore, abstraction is probably not favored at high temperature. At high temperatures (300°C), other reactions viz., intermolecular and intramolecular H-transfer, β-scission, etc. become important. Mostly, at higher temperature intermolecular hydrogen transfer takes place followed by β-scission, which justifies the formation of more amounts of lighter hydrocarbons beyond 300 °C. Again, 1,5-hydrogen transfer is important in producing products such as dimers, trimers, tetramers, pentamers etc. At 400–500 °C, β–scission and/or depolymerization is responsible to produce lower molecule [201].

Although, the thermal degradation of PE has been generally classified as “random scission” from the analysis of the degradation products [202, 203], not all the degradation pathways are random scissions. For example, Murata et al. measured the scission products of PE and PS at various temperatures and pressures and reported that there were two scission pathways from a macroscopic viewpoint. One is the random scission, and other is the chain-end scission [204, 205]. From a microscopic viewpoint, the chain end radicals are active, which causes a depolymerization reaction and abstraction of hydrogen from the main chain. Other researchers have reported that six-membered ring formation was the most stable for the radical transfer process [206].

Uno et al. have studied the degradation pattern of PE at higher temperature to quantify the different session at different temperatures. They found, the amount of scission products does not depend on the carbon number at 590 °C, while the amount of smaller compounds was larger than that of larger chemicals at 800 °C. This indicates that polyethylene decomposes only by primary decomposition at 590 °C while it decomposes through secondary decomposition at 800 °C. The characteristic distribution observed in lower molecular weight could be explained by direct scission and one to five-step radical transfer scission. These results showed that chain-end scission increased along with the temperature. In particular, the direct scission and one-step-radical transfer increased along with the temperature, which indicate that β-scission occurs on the chain end before the radical transfer because the rate of β-scission become faster as the temperature rises [207].

In addition, at higher temperature the polymer chain cracked to a greater degree; therefore the primary unstable fragments react with alkanes. It is important to note that the probability of formation of aromatics by Diels–Alder reactions is greater. In these reactions, e.g. polyenes might be the precursors of benzene at higher temperature. In the olefins it is found that the double bond moves toward the end of the framework in the case of non branched structures, and that of tertiary carbons of branched structures. Terminal double bonds turn into internal ones in the case of catalytic cracking, but this is not typical in thermal cracking. The different reactions that occur in second step are given in reactions 2.5 to 2.10.

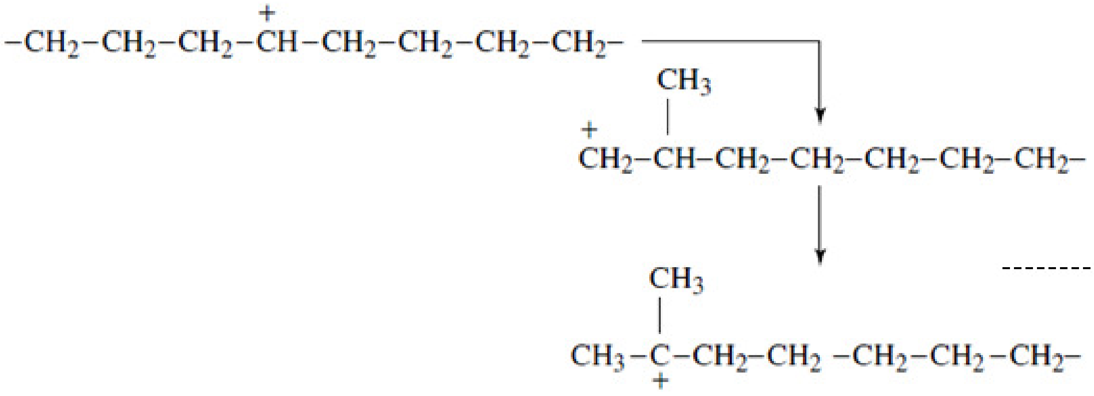
(A) β-scission



$$-CH_2-CH_2-CH_2-\overset{+}{C}H-CH_2-CH_2-CH_2-CH_2- \longrightarrow -CH_2-CH_2-CH=CH_2 + \overset{+}{C}H_2-CH_2-CH_2-CH_2-$$

----------------------------2.5

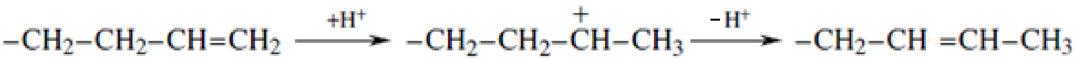
(B) Isomerization of carbon framework



$$-CH_2-CH_2-CH_2-\overset{+}{C}H-CH_2-CH_2-CH_2-CH_2- \longrightarrow \overset{+}{C}H_2-\overset{\overset{CH_3}{|}}{C}H-CH_2-CH_2-CH_2-CH_2-CH_2- \longrightarrow CH_3-\underset{+}{\overset{\overset{CH_3}{|}}{C}}-CH_2-CH_2-CH_2-CH_2-CH_2-$$

---------2.6

Isomerization of double bond



$$-CH_2-CH_2-CH=CH_2 \xrightarrow{+H^+} -CH_2-CH_2-\overset{+}{C}H-CH_3 \xrightarrow{-H^+} -CH_2-CH=CH-CH_3$$

----------------------2.7

(C) Hydrogen transfer reactions

Intermolecular hydrogen transfer reactions

$$-CH_2-CH_2-CH_2^+ + -CH_2-CH_2-CH_2-CH_2- \longrightarrow -CH_2-CH_2-CH_2- + -CH_2-CH_2-CH_2-CH_2^+$$

-------------------2.8

Intramolecular hydrogen transfer reactions

$$-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2^+ \longrightarrow -CH_2-CH_2-CH_2-CH_2^+-CH_2-CH_2-CH_2-$$

----------------------- 2.9

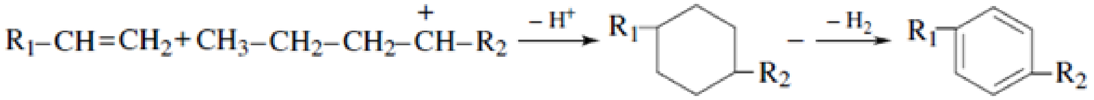
Generally the concentration of iso-paraffins and olefins increased with decreasing temperature because the increase in further degradation of branched hydrocarbons is greater, than that of non-branched with increasing temperature. A similar phenomenon could be observed in the case of catalysts possessing a weak hydrogenation property accompanied by considerable acidity, because the olefin intermediates formed are isomerized in greater ratio on the acidic sites of catalysts. On the other hand not only the probability of isomerization, but catalyst activity is decreases with decreasing of the acidity of catalysts.

(c) Termination with recombination or disproportionation

Primary and secondary unstable molecular fragments formed in the cracking reactions could be stabilized in several ways. Recombination or disproportionation of unstable fragments is one simple way. As a result of recombination the molecular weight and branching of products might be significantly increased. It is important to note that both recombination and disproportionation are second-order reactions according to reaction kinetics.

Cyclization, aromatization or polycondensation are other ways of termination. Basically cyclic alkenes, alkenes, mono and polynuclear arenes or coke are formed in these reactions. Termination reactions are principally controlled by the properties of polymers and the temperature.

Cyclization and aromatization



----------------------2.10

Sekine and Fujimoto [208] have proposed a free radical mechanism for the catalytic degradation of PP using Fe/activated carbon catalyst. During degradation, methyl, primary and secondary alkyl radicals are formed, and by hydrogen abstractions and recombination of radical units, methane, olefins and monomers are produced [50]. The various steps in catalytic degradation are shown in reactions 2.11 to 2.18. In initiation step, random breakage of the C-C bond of the main chain occurs with heat to produce hydrocarbon radicals. In propagation, the hydrocarbon radical decomposes to produce lower hydrocarbons such as propylene, followed by β-scission and abstraction of H radicals from other hydrocarbons to produce a new hydrocarbon radical. Disproportionation or recombination of two radicals is termination reaction. During catalytic degradation with Fe/activated charcoal in a H_2 atmosphere, hydrogenation of hydrocarbon radical (olefin) and the abstraction of the H radical from hydrocarbon or hydrocarbon radical generate radicals, enhancing degradation rate. In a reaction temperature lower than 400 °C or a reaction time shorter than 1h, many macromolecular hydrocarbon radicals exist in the reactor, and recombination occurs readily because these radicals cannot move fast. However, with Fe/Activated Carbon in a H_2 atmosphere, these radicals are hydrogenated and therefore recombination may be suppressed. Consequently, it seems as if the decomposition of the solid product is promoted, including low polymers whose molecular diameter is larger than the pore size of the catalysts.

(a) Initiation

(1) $R_1\text{-}R_2 \longrightarrow R_1^{\cdot} + R_2^{\cdot}$ -------------2.11

(b) Chain reaction

(2) $R_1^{\cdot} \longrightarrow R_3^{\cdot} + C_2$ or C_3 -----------2.12

(3) $R_2^{\cdot} + R_4 \longrightarrow R_2 + R_4^{\cdot}$ ------------2.13

(c) **Termination**

(4) $R_5^{\cdot} + R_6^{\cdot} \longrightarrow R_5 + R_6^{\cdot}$ --------------2.14

(5) $R_7^{\cdot} + R_8^{\cdot} \longrightarrow R_7\text{-}R_8$ -----------------2.15

(d) In presence of Fe/Activated Carbon + H_2

(6) $R_9^{\cdot} + H^{\cdot} \longrightarrow R_9$ ------------2.16

(7) $R_{10}\text{-}H \longrightarrow R_{10}^{\cdot} + H^{\cdot}$ -------------2.17

(8) $R_{11}^{\cdot} \longrightarrow R_{11} + H^{\cdot}$ ------------2.18

Wall et al. [209] have studied the catalytic degradation of waste plastics and have found that when these polymers have been heated above 380 °C, they undergo depolymerization and degradation by a free radical chain reaction.

Plastic degradation in presence of a reforming catalyst is explained differently. The reforming catalysts are said to be bifunctional, in view of the two kinds of active sites playing different roles. The metallic sites catalyze hydrogenation and dehydrogenation reactions, while the acidic sites on the support catalyze isomerization reactions. A proper combination of these two functions can promote a variety of reforming reactions such as isomerization where straight-chain paraffins are isomerized to branched-chain molecules, dehydrocyclization where straight-chain paraffins are converted to cycloparaffins, and dehydrogenation in which naphthenes are dehydrogenated to aromatics; the octane numbers of gasoline-range hydrocarbons are improved without changing their carbon numbers. The most commonly used reforming catalyst is $Pt/SiO_2-Al_2O_3$ with about 0.5 wt. % Pt only. The reactions 2,19 to 2.21 for n-pentane isomerization illustrates the reforming reactions [155].

$$\text{n-C}_5 \overset{\text{Pt}}{\Leftrightarrow} \text{n-C}_5\ (\text{olefin}) + H_2 \quad \text{--------------------2.19}$$

$$\text{n-C}_5\ (\text{olefin}) \xrightarrow{\text{acid site}} \text{i-C}_5\ (\text{olefin}) \quad \text{-------------------2.20}$$

$$H_2 + \text{i-C}_5\ (\text{olefin}) \overset{\text{Pt}}{\Leftrightarrow} \text{i-C}_5\ (\text{paraffin}) \quad \text{-----------------2.21}$$

2.6.3 Reaction kinetics of polymer degradation

The description of decomposition reactions during degradation of polymer is quite difficult, because they are very complex in chemical structure. And there are considerable differences between thermal degradation of waste plastics in the absence and presence of catalysts, but the type of reactor or the amount of plastics used for degradation is also important. Degradation in presence of catalysts is called thermo-catalytic degradation. Cracking experiments are done in batch reactors in 95% of polymer degradation studies [210-219] and within it the thermogravimetric analysis connected with different techniques (e.g. TG, DTG, DSC, TG-MS, etc.) is predominant [220-225]. Only a few researchers have investigated the cracking of waste polymers under continuous or semi-continuous conditions [226-229]. One reason for this is that considerable amounts of wastes are needed for continuous cracking and difficulties emerge caused by the geometry of the reactor and greater amounts of materials (e.g. Circulation, heat transfer, coking fouling, etc.) or the feeding of catalysts, their separation from products and regeneration.

Some kinetic models for thermal or catalytic polymer degradation have been proposed. The commonly used approach is first-order kinetics to investigate the characteristics of degradation (Equation 2.1). In this approach, first the weight loss curve of polymers during the decomposition is determined and overall rate constants are calculated [220, 222-224, 230-233]. The objectives of experiments are the determination of the apparent activation energies and other reaction kinetic parameters (reaction rate, pre-exponential constant, etc.) of degradation resulting volatile products (gases and liquids). Besides the development of kinetic models the prediction of the yields or main properties of products in the knowledge of properties of the raw material are also important. The principal problem in this case is the derivation of reaction rate constant because some factors significantly affect the conversion of degradation (physical, geometrical, steric, etc.). Usually a constant value of reaction rate is postulated and first-order kinetic equation together with the Arrhenius equation is used. Relations become more difficult when considering autocatalytic reactions. Some correlations exist to calculate reaction kinetic parameters under dynamic circumstances [234, 235]. The activation energy and the pre-exponential constant are determined from the logarithmic form of the Arrhenius equation (Equation 2.2).

$$-\frac{dm}{dt} = km^{n} \text{------------------------} (2.1)$$

$$k = Ae^{-\frac{E}{RT}} \text{------------------------} (2.2)$$

Where n is the reaction order, *k* is the reaction rate coefficient, m is the weight of residue, *t* is the time of degradation, E is the activation energy and A is the pre-exponential constant.

Relations can be simplified by using thermogravimetric and connected methods, but a new parameter i.e. the heating rate is to be introduced. Table 2.10 shows some of the approaches used for the determination of kinetic parameters [235-239].

When comparing the equations in Table 2.10, it is found that the equations of Flynn–Wall, Horowitz–Metger and Friedmann gave excellent correlation in the case of degradation of polypropylene [236, 237]. Others created software to calculate the reaction kinetic parameters using the first-order kinetic equation based on these equations. Key parameters were calculated with the minimization of differences between calculated and experimental results obtained directly by a thermogravimetric apparatus [234].

Table 2.10 Summery of approaches for the determination of kinetic parameters [235-238]

Method	Equation	Nomenclature
Flynn-Wall	$\Delta\ln\beta = -1052\left(\frac{E}{R}\right)\Delta\left(\frac{1}{T}\right)$	E Thermal decomposition activation energy (kj/mol) R Gas constant (8.314 j/mol k) T Temperature β Heating rate (^{0}C/min) α Conversion (extent of reaction) dα/dt Rates of weight loss n Order of reaction T_m Temperature corresponding to the maximum reaction rate A Pre-exponential factor T_s is the temparature at which 1-α=1/exp=0.368 $\theta = T - T_s$
Friedmann	$\ln\left(\frac{d\alpha}{dt}\right) = \ln\left\{A(1-\alpha)^{n}\right\} - \frac{E}{RT}$	
Kissinger	$\ln\left(\frac{\beta}{T_m^{\ 2}}\right) = \ln\frac{AR}{E} + \ln\left[n(1-\alpha)^{n-1}\right] - \frac{E}{RT}$	
Ozawa	$\ln\beta = -0.4567\frac{E}{RT} + \left(\log\frac{AE}{R} - \log F(\alpha) - 2.315\right)$ Where, $F(\alpha) = \int_{0}^{\alpha}\frac{d\alpha}{(1-\alpha)^{n}} = \frac{A}{\beta}\int_{T_\alpha}^{T}\exp\left(\frac{-E}{RT}\right)dT$	
Horowitz-Metger	$\ln\ln\left\{\frac{1}{(1-\alpha)}\right\} = \frac{E\theta}{RT_s^{\ 2}}$	

Good correlation between data was observed in case of HDPE and PS by using this software.The main problem in case of thermo-catalytic cracking of polymers is the activity loss of catalysts; therefore first-order kinetics is applicable only with some simplifications in thermo-catalytic cases. On the other hand there is a relation modeling the fluid catalytic cracking taking into consideration the catalyst deactivation in refineries [239]:

$$\eta = \exp[-\alpha C(c)] \qquad ---------- \; (2.3)$$

Where η is the activation loss of catalyst, $C(c)$ is the coking of catalyst and α is a constant depending on the type of catalyst.

Equation (2.3) was used to model the thermo-catalytic degradation of waste polyethylene and polypropylene [230]. In this case researchers had to calculate η for each catalyst. On the other hand it is complicated; therefore researchers disregard the change of reaction rate and order caused by deactivation of catalysts in most experiments. The reaction rates and other reaction kinetic parameters are given in Table 2.11 [240].

Table 2.11 The reaction rates and other reaction kinetic parameters of degradation of waste polyethylene and polypropylene [240]

Kinetic Model	**Equation**	**E_a(kj/mol)**	**n**	**A (min^{-1})**
$HDPE \xrightarrow{k_1} V + R$ V: volatile products; R: Residue products	$\frac{d[HDPE]}{dt} = -Ae^{\frac{-E}{RT}}[HDPE]^n$, E =Thermal decomposition activation energy (kj/mol), R= Gas constant (8.314 j/mol k), T =Temperature, n= Order of reaction	250	0.65	1.71×10^{17}
$PP \xrightarrow{k_1} V + R$	$\frac{d[PP]}{dt} = -Ae^{\frac{-E}{RT}}[PP]^{n_1}$ n_1= Order of reaction	125	0.40	2.04×10^{8}

There are also some empirical equations for describing the yields of products formed in the cracking reactions of polymers. One of them is the Atkinson and McCaffrey kinetic model, which derives the weight loss of polymer for their initial degree of polymerization, weight of sample and reaction rate. As a matter of fact the reaction rate constant is calculated by using a first-order kinetic equation [241, 242].

The temperature significantly affects the conversion of thermo-catalytic degradation besides the characteristic of catalysts. The time–temperature superposition describes the dependence of reaction rate from temperature. The conversion can be increased both with degradation temperature and time. It means that the cracking time which is needed to achieve the same degree of conversion decreases with increasing temperature. The shift factor is the quotient of cracking times at different temperatures or the quotient of temperatures at different cracking times. The value of the shift factor is affected by the characteristics of the polymer and by the cracking conditions. There are two methods to derive the shift factors: the Arrhenius equation and the Williams–Landel–Ferry (WLF) equation. Chan et al. calculated the value of shift factors in case of polypropylene degradation [243]. It was found that the product of reaction rate coefficients and cracking times at different temperatures is nearly constant. The shift factors and constants of the WLF equations can be calculated by the use of these similarities.

2.7 Economic and ecological aspects of catalytic pyrolysis of plastics

The new technologies and economics have come to play an important role in plastics recycling. As described in previous section, plastic recycling principally refers to recovery, which is divided into material recycling and energy recovery. Material recycling is again divided into mechanical and feedstock recycling. The choice between these methods will depend on the types of plastics waste, the relative ease / difficulty in total or partial segregation from other plastics and / or other waste materials, ecological and cost aspect involved in the process. While determining economic boundary conditions of plastics recycling, it is necessary to make a distinction between: (i) mechanical recycling to the same or similar applications (ii) mechanical recycling to new areas of applications (iii) incineration and energy recovery, cement kilns, incineration for power generation (iv) feedstock recycling to form different products like conversion to monomer, fuel, reducing agent in blast furnace for the production of iron, gasification and liquefaction.

Worldwide, mechanical recycling is the most preferred and accepted method of plastics recycling. However, it includes a wide variety of processing techniques and a broad range of processing methods requires lot of energy, which increase the cost depending on the degree of contamination. After collection of the portions that can be recycled by mechanical recycling, there remain numerous very small, heavily contaminated articles or cross-linked products or products contaminated with hazardous substances. Heavily contaminated plastics waste collected from domestic waste stream can be utilized by energy recovery from waste incineration plants. Cost of this system of recovery is considered highest among all the alternatives. Again, incinerator design and operation depends upon the type of waste to be incinerated and another important factor to carry out this process is to minimize the harmful emissions. Non adherence to these two basic principles caused serious failures of various incineration activities in the 80's raising doubt about the effectiveness of this process itself. Feedstock recycling would be a better alternative from cost and ecological aspects. As the cost of feedstock recycling even in the best case of large-scale plants may be similar (as high as) to the cost for incineration and energy recovery and doesn't produce harmful emission if designed properly. Again this process is complementary to mechanical recycling since it is less sensitive to unsorted or uncontaminated plastic waste and enlarges the overall recycling capacities for large waste quantities to be supplies in future. This is also important today from the global warming point of view and the operator in a developing country is able to cash on the carbon credit as there is reduction in dependence on fossil fuels [244].

Extensive research has been carried out on catalytic pyrolysis of plastics using different catalysts and the process has also been materialized in different countries.

In the early 1990s BP Chemicals, first tested technology for feedstock recycling, using a fluid bed cracking process. Research on a laboratory scale was followed (1994) by demonstration at a continuous pilot plant scale (nominal 50 kg/hr) at BP's Grangemouth site, using mixed waste packaging plastics. The technology was further developed with some support from a Consortium of European companies (Elf Atochem, EniChem, DSM, CREED) and from APME. In 1998, BP Chemicals, VALPAK and Shanks & McEwan, set up a joint project (POLSCO), to study the feasibility of a 25000 tonnes/yr plant, including logistics infrastructure for supplying mixed plastics from Scotland. The process involves initial cleaning of waste plastics to remove the non plastic impurities and heating them in a fluidised bed reactor operating as 500 °C, in absence of oxygen. Lime absorber is used to remove the HCl produced due to the presence of polyvinyl chloride. The different type plastic that has been used includes polyethylene, polypropylene, polyvinyl chloride, polyethylene terephthalate and styrenic polymers. The hydrocarbon products (85% yield) can be fed directly to petrochemical plants or to gasoline without further purification [89].

Veba oil developed a commercial process, operating in a temperature range of 350–450 °C and requiring a high hydrogen partial pressure (50–100 bar) using a liquid phase reactor. The technology was realized in the coal-to-oil plant at Bottrop, with a capacity of 40, 000 tonnes annually doubled at the end of 1995 [89].

A large pilot plant, with a substantial capacity of 15,000 tonne/yr, was started up in Ludwigshafen in 1994 by the BASF in which plastic waste is converted into petrochemical products using a tubular cracker reactor [89].

A plant operating according to the Hamburg University pyrolysis process was built at Ebenhausen, Germany with a capacity of 5000 tonnes per year. This process was developed by W. Kaminski in 1883 in which Pyrolysis is carried out in an externally heated fluidised bed reactor containing sand [89].

The first report of turning plastic wastes into oil came in 2001 from the People's Daily, China's English language newspaper. An oil refinery in Hunan province had succeeded in processing 30, 000 tonnes of plastic wastes into 20,000 tonnes of gasoline and diesel oil that satisfied the provincial standards. Wang Xu, who built the refinery in 1999, started experimenting with waste plastic processing in the 1980s, and later teamed up with Hunan University doctoral tutor Zeng Guangming who gave him scientific advice on decomposing plastic wastes. In the 1980s, Illinois microbiologist Paul Baskis in the United States modified the process to produce lighter, cleaner oil, but failed to convince investors until 1996, when a company called Changing World Technologies began development with Baskis to make the process commercially viable [205]. Again, the plants with a capacity of 1000 tonnes/annum have been running nearby many cities in China [246].

Environmental Technology Systems Ltd is a U.K. company, incorporated in 2003, which now has the rights to acquire a proven Chinese technology to convert waste plastics into gasoline and diesel fuels produce 2,000 tonnes per annum of fuel oil (roughly, half petrol and half diesel) from 2,740 tonnes of waste plastics. The balance is 410 tonnes of combustible gas which is used to provide heat for the process. The sole by-product is 330 tonnes of 'slag'. The process is continuous and can handle all plastics including polyvinyl chloride and no pre-sorting is required. The plastic is shredded prior to being passed into the feed-hopper and the process uses non-pressurised modular catalytic reactor running at moderate temperatures of 350 °C to 400 °C [247] converts plastic feed into 73% fuel oil, 15% gas and 12% inert ash residue (mainly dirt introduced with the waste). The fuel oil can be burned immediately to produce heat or electricity or it can be fractionated into roughly equal parts transport grade diesel and high-octane gasoline that is lead and sulphur-free. The Technology is "clean". There is no odour. There are no gaseous emissions or liquid effluents beyond modern petrochemicals practice. The eco friendly processing plants produce high quality fuels, which meet or exceed current industry standards for transport grade fuels [248].

In India, a zero-pollution industrial process to convert non-biodegradable and mostly non-recyclable plastic waste into liquid hydrocarbons has been set up at Butibori industrial estate, Nagpur in 2005 by Prof. Alka Zadgaonkar. The Zadgaonkar's Unique Waste Plastic Management & Research Company plant devours a whole range of plastic waste from discarded carry bags to mineral water bottles and broken buckets to polyvinyl chloride pipes, polyethylene terephthalate bottles, even acrylonitrile butadiene styrene plastic material used in the making of computer monitors and TV sets, keyboards etc and converts it 100 percent into liquid hydrocarbon fuels (85 percent) and gases (15 percent). This is the World's first continuous process for plastic recycling to liquid fuel [249, 250].

Enviro-Hub the waste management and recycling firm announced the construction of Singapore's first $50 million plastic-to-fuel plant which converts waste plastic into useable fuels and gases. It is building the world's first large-scale, commercial plastic-to-fuel plant. This process is based on patented technology imported from India, for which Enviro-Hub now holds an exclusive license, heats waste plastic with a special catalyst that breaks it down into 85 percent diesel, 10 percent liquid petroleum gas and 5 per cent coke [251].

Most recently the projects operating at a full scale includes liquefaction units using continuous stirred tank reactors, at Niigata and Sapporo, Mikasa works, Coke oven pyrolysis by Nippon Steel Corp, high-pressure gasification by EBARA-UBE, ASR gasification at Aomori (Ebara Co.), Glycolysis of polyethylene terephthalate bottles by Teijin [89].

Dumfries Plastics Recycling (DPR), a subsidiary of British Polythene Industries, is a SEPA (Scottish Environment Protection Act) accredited recycling plant. DPR can recycle 5,000 tonnes/annum of post-use agricultural stretch film, the only unit in the world capable of doing so. The DPR Washing Plant can also recycle other post-use polyethylene films and is designed to handle heavily contaminated films, (some films contain over 50% sand/soil/water) [252]

Chapter 3

Experimental

EXPERIMENTAL

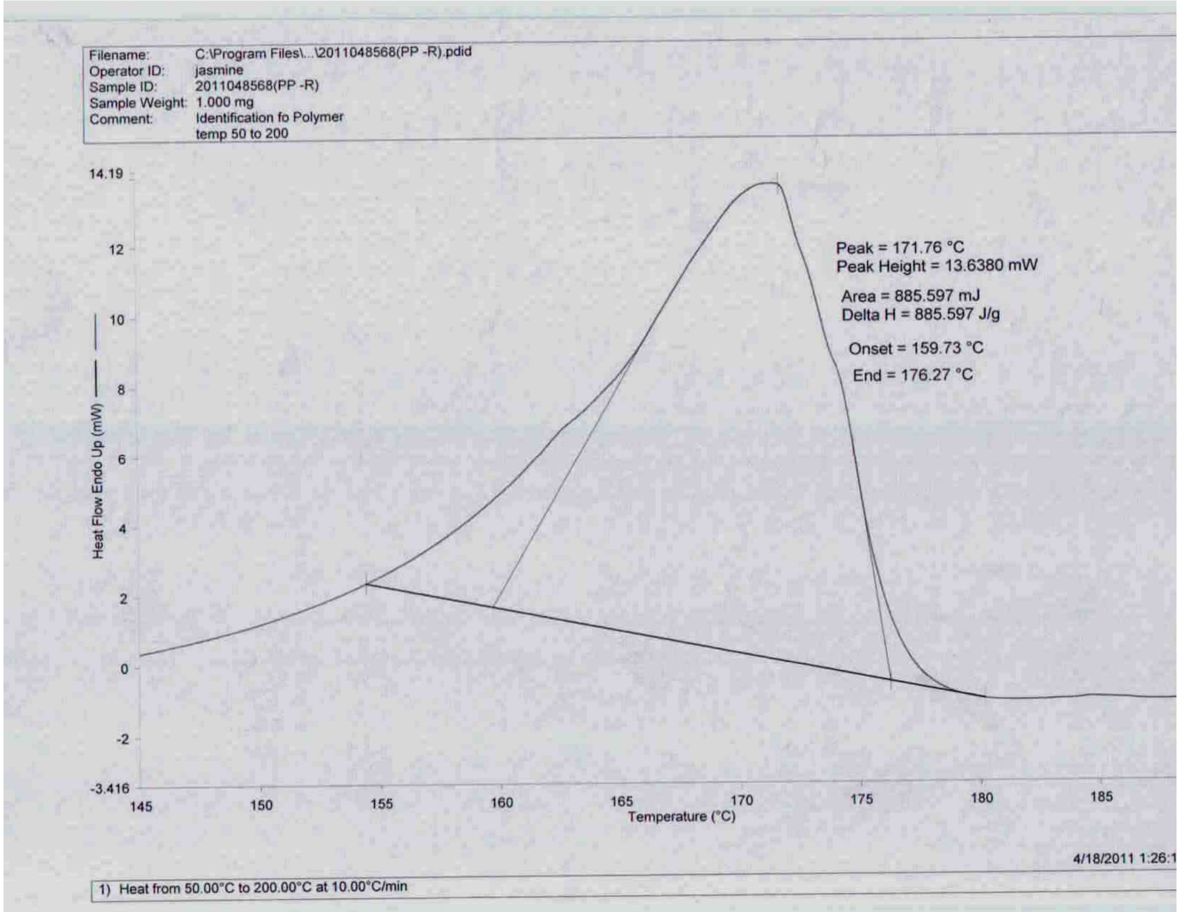
3.1 Materials

3.1.1 Plastics: Three different types of waste plastics have been considered for the experiments. They are polypropylene (PP), low density polyethylene (LDPE), and polystyrene (PS). The waste samples are identified by determining melting temperature and glass transition temperature from DSC curve. The decomposition pattern of plastic samples were carried out in a DTG-60/60H of SHIMADZU in a silica crucible with temperature ranging from 35^{0}C to 600^{0}C at a heating rate of 10^{0}C/min.

3.1.1.1 Virgin and Waste polypropylene: Polypropylene pellet (2.5 mm in size) obtained from Reliance industries limited, India with density and MFI value found as 0.905 g cc and 8-9 g/10 min^{-1} (at 230 °C and 2.16 kg load), respectively were used for experiments. Waste Polypropylene (used plastic disposable glasses) was collected from the National Institute of Technology Rourkela campus. The waste plastic disposable glasses were cut into flakes by a shredder and the flakes were used in the pyrolysis experiments (Figure 3.1). The waste polypropylene is identified by the DSC of the sample (Figure 3.2). The melting point of the waste sample is found to be 171 °C which ensures the samples to be polypropylene.

Figure 3.1 Virgin polypropylene, disposable glass, and sheredised glass

3.1.1.2 Waste Polystyrene (thermocol): The waste Thermocol (Figure 3.3) in form of disposed off packaging material was collected from the waste yard of the National Institute of Technology campus.



Filename: C:\Program Files\...\2011048568(PP -R).pdid
Operator ID: jasmine
Sample ID: 2011048568(PP -R)
Sample Weight: 1.000 mg
Comment: Identification fo Polymer
temp 50 to 200

Peak = 171.76 °C
Peak Height = 13.6380 mW
Area = 885.597 mJ
Delta H = 885.597 J/g
Onset = 159.73 °C
End = 176.27 °C

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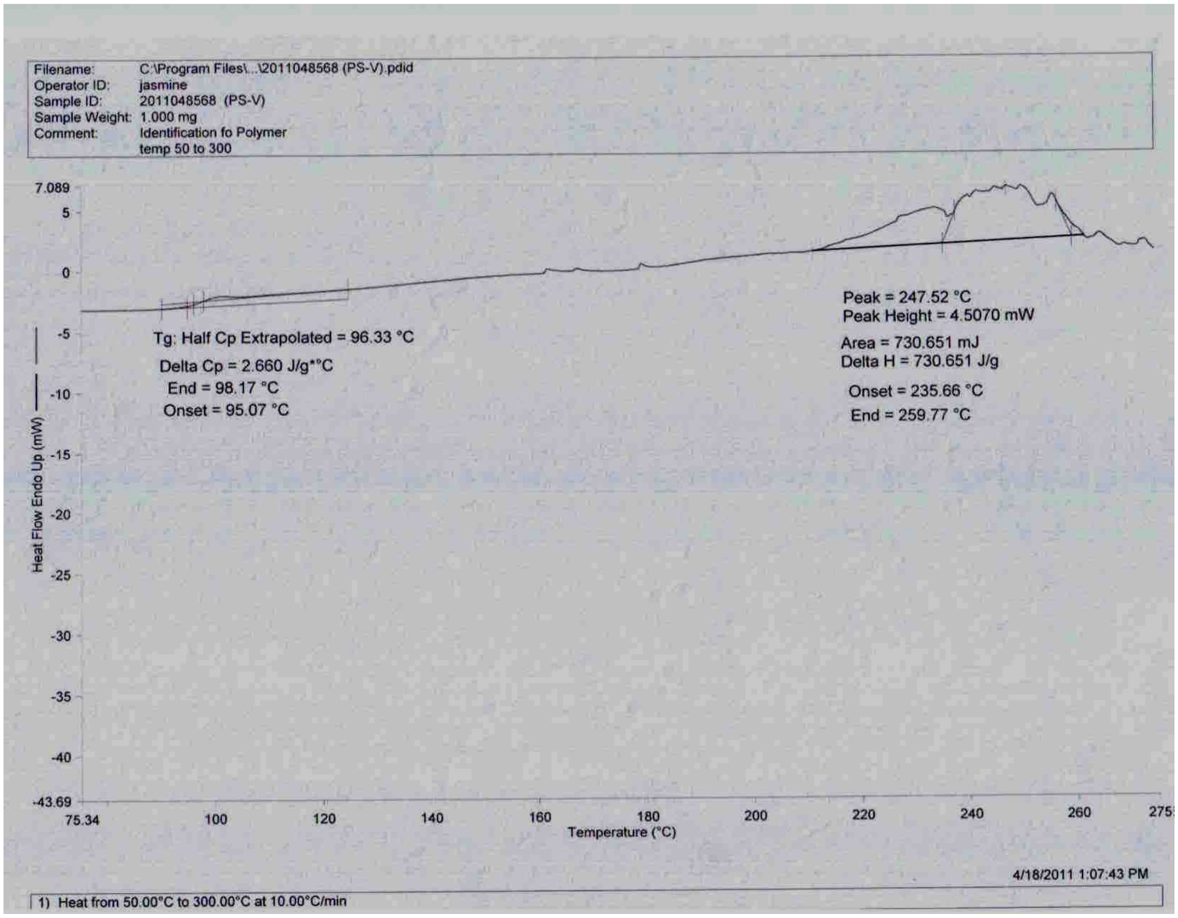
1) Heat from 50.00°C to 200.00°C at 10.00°C/min

Figure 3.2 DSC of waste polypropylene

Figure 3.3 Waste thermocol

The soft and high volume thermocol samples were first kept inside the oven at 80 °C for one hour resulting in a low volume hard brittle mass which was then ground to powder. The powdered sample was subjected to pyrolysis. The DSC of the waste sample is shown in Figure 3.4. From the figure, the melting point and the glass transition temperature (T_g)

of the waste sample is found to be 247 °C and 96 °C respectively, which ensures the samples to be polystyrene.



Filename: C:\Program Files\...\2011048568 (PS-V).pdid
Operator ID: jasmine
Sample ID: 2011048568 (PS-V)
Sample Weight: 1.000 mg
Comment: Identification fo Polymer
temp 50 to 300

Figure 3.4 DSC of thermocol

3.1.1.3 Waste low density polyethylene (polyethylene bag): The fine cuttings of waste polyethylene shopping bags (made of LDPE) of 2 cm^2 area were used for the pyrolysis experiments. The DSC of this waste sample is shown in Figure 3.5. From the figure, the melting point of the waste sample is found to be 110 °C respectively, which ensures the samples to be low density polyethylene.

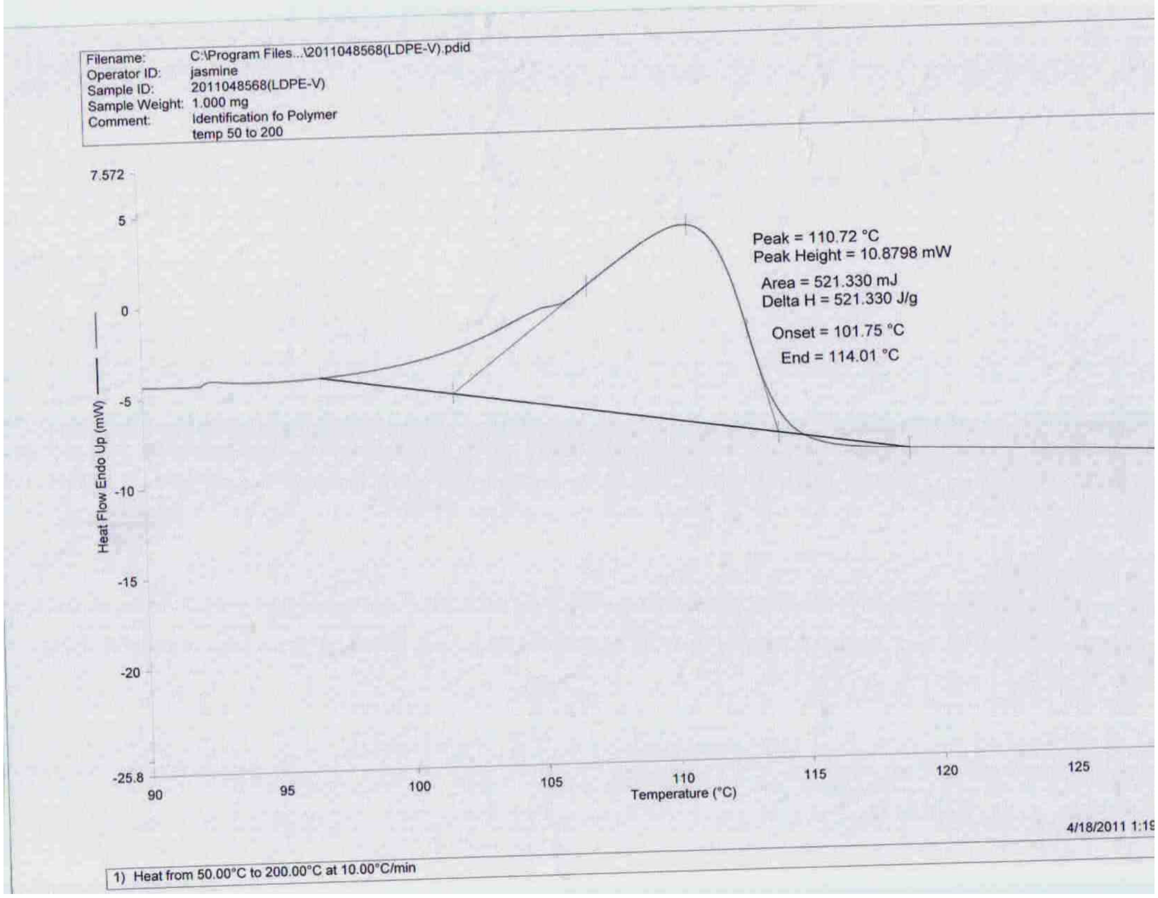


Figure 3.5 DSC of waste low density polyethylene

3.1.2 Catalyst: Two types of catalysts were used in this experiment. They are kaolin and silica alumina.

3.1.2.1 Kaolin: Commercial grade kaolin clay procured from Chemtex Corporation, Kolkata, India was used as catalyst in the pyrolysis reaction. The chemical composition of the kaolin sample was found to be SiO_2 43.12 %, Al_2O_3 46.07 %, Fe_2O_3 nil, MgO 0.027 %, CaO 0.030 %, ZnO 0.0064%, K_2O 0.01%, TiO_2 0.74, LOI at 1000 °C 9.9%. The XRD of the sample (Figure 3.6) showed well defined reflections at 2 theta value of 12° and 25° corresponding to the d values of 7.154 Å. These peaks correspond to the reflections from [001], which are typical characteristic peaks of kaolinite. Again the peaks corresponding to the 2θ value 34–36°, 38–42°, 45–50°, and 54–63° may vary for kaolinites from different origin [26]. From the proximate analysis and XRD report it could be concluded that the major component of the sample was kaolinite with Hinckley index of 0.4.

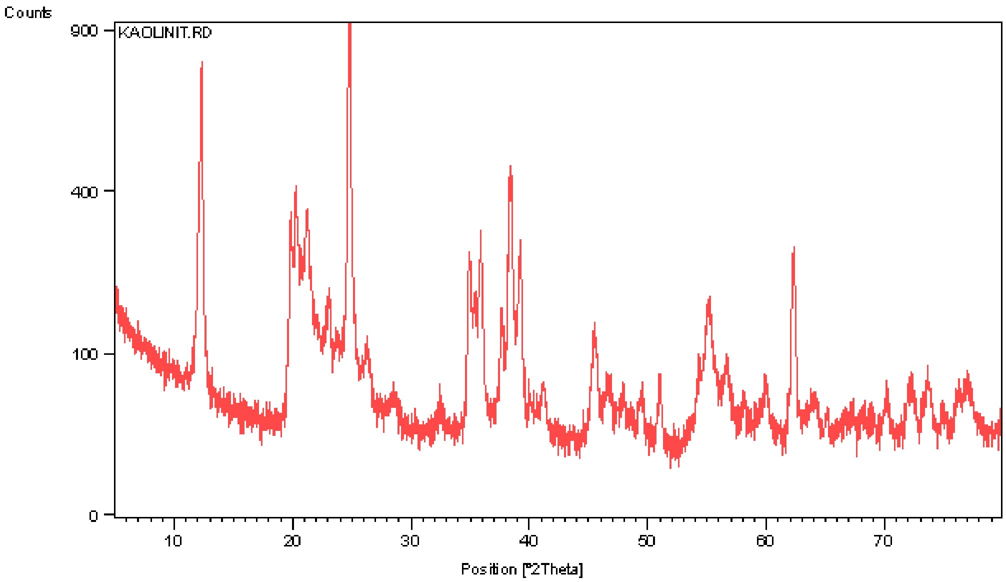


Figure 3.6 XRD of kaolin

Some traces of impurities (may be mica, quartz and feldspar which could not be traced in the XRD report) were also present which contribute the components other than SiO_2 and Al_2O_3. The BET surface area of kaolin was found to be 23m^2/g. The pore size distributions of kaolinite samples showed a sharp peak at a radius of 3.5nm, thus it is mesoporous. The acidity of the kaolin determined using ammonia-temperature programmed desorption method was 0.04 mmol NH_3/g.

3.1.2.2 Silica Alumina: Commercial grade Silica Alumina was procured from Chemtex Corporation, Kolkata, India. The chemical composition of the Silica Alumina sample was found to be SiO_2 42.45%, Al_2O_3 35.1300%, Fe_2O_3 1.3100%, MgO 1.1060%, CaO 2.1430%, ZnO 0.0064%, K_2O 0.4410%, TiO_2 0.5600%, LOI at 1000 °C 16.82%. The XRD (Figure 3.7) of the sample showed well defined reflections at 2 theta value of 12°, 20°, 25°, 27°, 35°, 38°,and 62°. The surface area and acidity of the sample was found to be 29 m^2/g and 0.214mmol NH_3/g respectively.

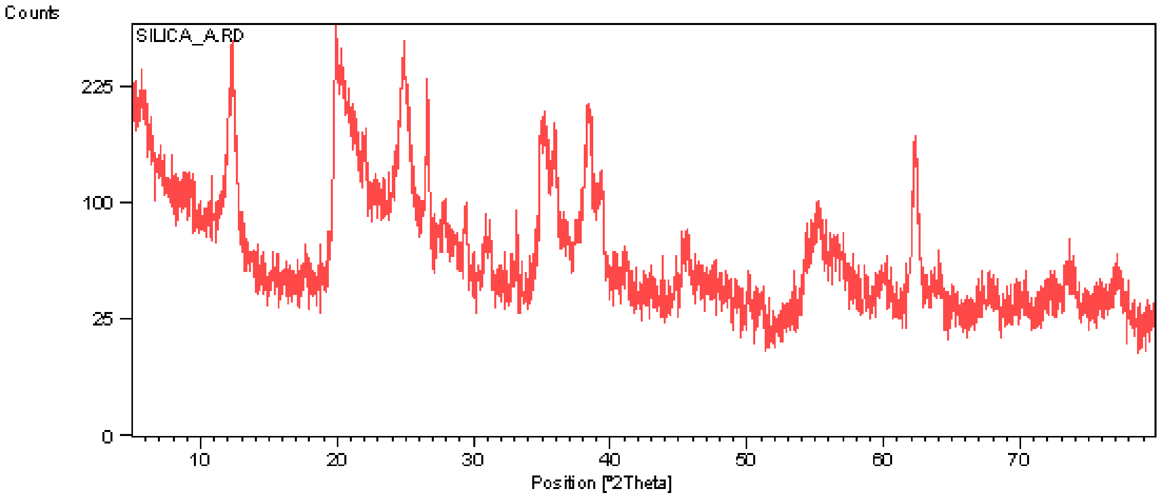


Figure 3.7 XRD of Silica Alumina

3.2 Methods

3.2.1 Catalyst modification: The chemical activation/modification of kaolin was carried out by adding 50g of the clay to 500ml of sulphuric acid solution of different concentrations (1M, 3M, 5M, 10M) and refluxing at 110°C under the atmospheric pressure in a round bottomed flask equipped with a reflux condenser for 4 hours. The resulting clay suspension was then rapidly quenched by adding 500ml ice cold water. The content was then filtered, repeatedly washed with distilled water to remove any unspent acid, dried in an oven, calcined at 500°C for one hour and ground in a mortar pastel to powder form. The untreated sample is referred to as KC and treated samples are referred to as KC1M, KC3M, KC5M and KC10M in the subsequent text where the numbers refers to the different concentration of acid used. Another sample named KC5M750 is obtained by calcining at 750°C after 5M acid treatment in the same process. The clay samples were characterized by using XRD, XRF, TGA, SEM, Nitrogen adsorption desorption isotherm technique, FTIR to understand the affect of acid treatments.

3.2.2 Catalyst characterization technique: The different kaolinite clay materials were characterized by X-Ray Fluorescence spectroscopy (XRF), X-Ray Diffraction (XRD), Fourier Transformed Infrared Spectroscopy (FTIR), Thermogravimetric Analysis (TGA), Differential Thermal Analysis (DTA), sorptometric studies, Scanning Electron Microscope (SEM) and by temperature programme desorption ammonia methods.

3.2.2.1 X-Ray Fluorescence (XRF): XRF analyses of the samples were done using a Model-PW2400 of Phillips make, with X-ray tube of rhodium anode and scintillation detector with a current 40mA and voltage 40mV.

3.2.2.2 X-Ray Diffraction (XRD): The X-ray diffraction data was collected using a Philips Analytical X-ray Instrument, X'Pert-MPD (PW 3020 vertical goniometer and PW 3710 MPD control unit) employing Bragg–Brentano parafocusing optics. The XRD patterns were recorded in the range of 5–70° with a scanning rate of 2°/min.

3.2.2.3 Fourier Transformed Infrared Spectroscopy (FTIR): FTIR spectra were recorded on a Perkin-Elmer infrared spectrophotometer as KBr pellets with resolution of 4 cm^{-1}, in the range of 400-4000 cm^{-1}. The sample and analytical grade KBr were dried at 100 °C over-night prior to the FTIR analysis.

3.2.2.4 Thermogravimetric/Differential Thermal Analysis (TG/DTA): Thermogravimetric analyses were carried out with a SHIMADZU DTG-60/60H instrument. A known weight of the sample was heated in a silica crucible at a constant heating rate of 10 °C/min operating in a stream of N_2 atmosphere with a flow rate of 40ml/min from 35 °C to 600 °C.

3.2.2.5 Sorptometric studies: Nitrogen adsorption–desorption measurements (BET method) were performed at liquid nitrogen temperature (−196 °C) with an autosorb BET apparatus from Quantachrome Corporation The analysis procedure is automated and operates with the static volumetric technique. Before each measurement, the samples were outgassed first at 200 °C for 2 hours, at 5×10^{-3} torr and then at room temperature for 2 hours, at 0.75×10^{-6} torr. The isotherms were used to determine the specific surface areas using the BET equation.

3.2.2.6 Scanning Electron Microscope (SEM): Scanning electron micrographs were taken on a JEOL-JSM 5600 LV microscope, equipped with a 6587 EDS (energy dispersive X-ray spectrometry) detector, using an accelerating voltage of 15 kV. The samples were deposited on a sample holder with an adhesive carbon foil and sputtered with gold.

3.2.2.7 Temperature programmed desorption of ammonia method (NH_3-TPD): The acid properties of the catalysts were probed by ammonia TPD measurements in Micromeritics 2900 TPD equipment. Previously, the samples were outgassed under He flow (50Nml/min) by heating with a rate of 15 °C/min up to 560 °C and remaining at this temperature for 30 min. After cooling to 180 °C, the samples were treated with a 30Nml/min ammonia flow for 30 min. The physisorbed ammonia was removed by passing a He flow at 180 °C for 90 min. The chemically adsorbed ammonia was determined by increasing the temperature up to 550 °C with a heating rate of 15 °C/min, remaining at this temperature for 30 min, and monitoring the ammonia concentration in the effluent He stream with a thermal conductivity detector.

3.2.3 Pyrolysis experimental set up: The pyrolysis setup used in this experiment is a batch reactor shown in the Figure 3.8 and 3.9. It consists of a reactor made of stainless steel tube (length- 145 mm, internal diameter- 37 mm and outer diameter- 41 mm) sealed at one end and an outlet tube at other end for obtaining the volatile/gas/oil products of the reaction.

Figure 3.8 Experimental set up and stainless steel reactor

The SS tube is heated externally by an electric furnace, with the temperature being measured by a Cr-Al: K type thermocouple fixed inside the reactor and temperature is controlled by external PID controller. Shimaden PID controller SR1 was used to control the temperature of the furnace. The accuracy of this PID controller is ± 0.3% FS (FS = 1200ºC) . So the temperature can be measured with ±3.6ºC.

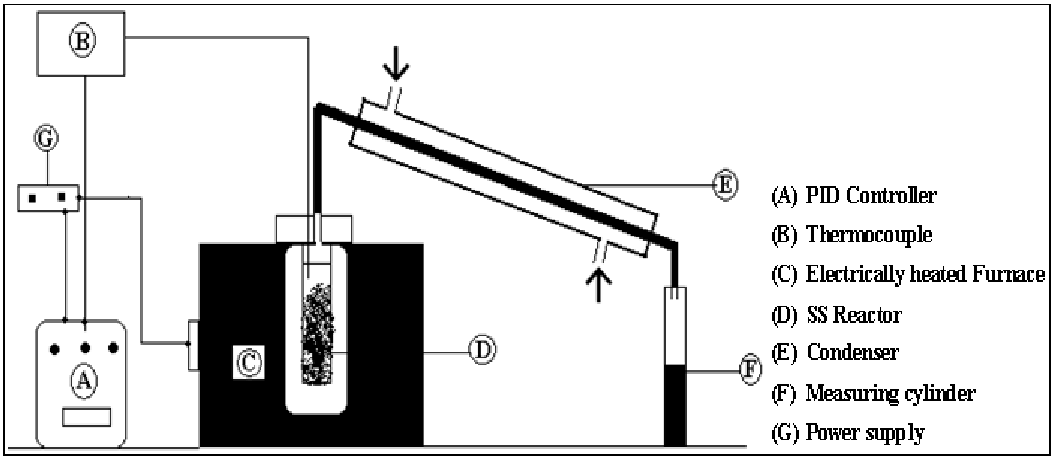


Figure 3.9 Schematic representation of pyrolysis set up

3.2.4 Pyrolysis experimental procedure: 20g. of plastics samples (polypropylene pallets/ polypropylene disposable glass flakes/waste LDPE bag/ waste thermocol polystyrene) were loaded in each pyrolysis reaction. Precision balance of SHINKO DENSHI Co. LTD, JAPAN, Model: DJ 300S was used to measure the weight of the samples. This machine capacity is 200 gram and accuracy is 0.0001 gram and so the weight can be measured within ±0.0001g.

In the catalytic pyrolysis, a mixture of catalyst and the plastics samples in different catalyst to plastics proportion (1:2, 1:3, 1:4, 1:6, 1:10, 1:20, 1:40) was subjected to pyrolysis in the reactor set up and heated at a rate of 20 °C/min. up to the desired temperature. The condensable liquid products were collected through the condenser and weighed. After pyrolysis, the solid residue left out inside the reactor was weighed. Then the weight of gaseous product was calculated from the material balance. Reactions were carried out at different temperatures ranging from 400-550 °C.

3.2.5 Analysis of oil: The composition of the oil has been determined by GC/MS and Detail hydrocarbon analyzer.

3.2.5.1 Fourier transformation infrared spectroscopy (FTIR): FTIR of the pyrolysis oil obtained at different temperatures were taken in a Perkin-Elmer Fourier transformed infrared spectrophotometer with resolution of 4 cm^{-1}, in the range of 400-4000 cm^{-1} using Nujol mull as reference to know the functional group composition.

3.2.5.2 Gas chromatography and mass spectroscopy (GC/MS): The GC/MS of the oil sample was carried out in Sargam laboratory, Chennai. The specification of GC/MS is summarized below.

Instrument: GC-MS-QP 2010 [SHIMADZU]

GC Condition

Column Oven Temperature: 70°C, Injector Temperature: 200°C, Injection Mode: Split
Split Ratio: 10, Flow Control Mode: Linear Velocity, Column Flow: 1.51ml/min,
Carrier Gas-Helium: 99.9995% purity

Column Oven Temperature Program

Rate	Temperature (°C)	Hold Time (min)
-	70.0	2.0
10	300.0	7.0 (32 mins total)

Column : DB-5

Length: 30.0m
Diameter: 0.25mm
Film Thickness: 0.25µm

MS Condition

Ion Source Temperature : 200 °C
Interface Temperature : 240 °C
Start m/z : 40
End m/z : 1000

3.2.5.3 Detailed hydrocarbon analyzer (DHA)

The detail composition of liquid product was analyzed using Detailed Hydrocarbon Analyzer (DHA) of Perkin Elmer Model Arnel 4050 DHA (Figure 3.10). This analyzer is an engineered chromatography system based on the Perkin Elmer Clarus 500 Gas Chromatograph (GC) with programmable pneumatic control (PPC) which comes standard with DHA software completely integrated with Perkin Elmer's Total Chrom Workstation used to characterize hydrocarbon samples through high-efficiency capillary gas chromatography and Flame Ionisation Detector (FID). The column consists of tuned

100m x 0.25mm x 0.5µm polydimethylsiloxane and the carrier gas used in this process was Helium. The oven programme starts with initial temperature 5.0 °C/min (cryogenics: LN_2), initial hold for 10.00min, (maximum temperature 350 °C and equilibration time 5.0 min) then, 5.0 °C/min to 48 °C , hold for 53.4 min, then 1.4 °C/min to 200 °C hold for 18.0 min.

Figure 3.10 Detailed hydrocarbon analyzer

3.2.5.3 Fuel properties: All the fuel properties of the oil were tested by prescribed IS-1448 methods and summarized in the Table 3.1

Table 3.1 Test protocol

Properties	Test methods	Properties	Test methods
Specific Gravity	I.S.1448 P.16	Flash Point	I.S.1448: P:20
Density	I.S.1448 P.16	Fire Point	I.S. 1448 P:20
Kinematic Viscosity	I.S,.1448 P: 25	Gross Calorific Value	I.S. 1448: P:6
Pour Point	I.S.1448 P:10	Calculated Cetane Index	I.S.1448 :P:9
Cloud Point	I.S.1448: P:10	Distillation	I.S. 1448: P.18

The density and specific gravity measurement is done with accuracy of ±0.0005g/ml. and the other parameters such as pour point, cloud point, flash point and fire point is measured with ±1ºC accuracy.

Chapter 4

Effect of sulphuric acid treatment on the physico-chemical characteristics of kaolin

EFFECT OF SULPHURIC ACID TREATMENT ON THE PHYSICO-CHEMICAL CHARACTERISTICS OF KAOLIN

4.1 Introduction

Kaolin is one of the clay material widely used for a large number of applications, such as in ceramics, paper coating, paper filling, paint extender, rubber filler, plastic filler, cracking catalysts or cements. Kaolinite is the major mineral component of kaolin, which may usually contains quartz and mica and also, less frequently, feldspar, illite, montmorillonite, ilmenite, anastase, haematite, bauxite, zircon, rutile, kyanite, silliminate, graphite, attapulgite, and halloysite. [253, 254]. Chemically kaolin is a 1:1 layer sheet structured hydrated aluminum silicate with a very fine particle size with one siliconoxygen (SiO_4) tetrahedral layer and one alumina $[Al(O, OH)_6]$octahedral layer (or, expressed in other way, $[Si_2O_5]^{2-}$ sheet and $[Al_2(OH)_4]^{2}$ sheet) with pseudo-hexagonal symmetry, bonded together through sharing of apical oxygens and exist alternately. Its theoretical formula is $Si_2Al_2O_5(OH)_4$ (other formulas are $Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O$ and $Al_2O_7Si_2.2H_2O$), which has a molecular weight of 258.071g/mol.[254, 255, 256].

The use of clay-type aluminosilicates in heterogeneous catalysis as solid acid catalysts is almost as old as the catalysis concept itself. Among the earliest heterogeneous catalysts there were acid-activated bentonites and kaolinites. Despite the actual dominant use of micro porous zeolite acid catalysts in modern petrochemical processes, there is still a wide interest in the use of acid-modified clays, not only because of their low cost but also because the structure and dimension of their pores appear more suitable, compared to zeolites, for the cracking of larger molecules [257].

The industrial utilization of kaolinite is closely related to its reactivity and surface properties, which depend strongly on surface modification. Several methods have been suggested in literature to improve the properties of clay materials which include among others mechano-chemical activation [258-268], intercalation [269-271], thermo-chemical treatment [253, 254, 272-274] and chemical activation [275-277].

Acid activation has been widely studied as a chemical treatment method for the improvement of the surface and catalytic properties of fibrous clays (sepiolite and palygorskite), smectitic clays (saponite and montmorillonite) [253] and amorphized (Calcined/grounded) kaolin [253,255,256,265-268,278,279]. The method involves leaching of the clays with inorganic acids, causing disaggregation of clay particles, elimination of mineral impurities, and dissolution of the external layers, thus altering the chemical composition and the structure of the clays. The solubility of the clay minerals in acids is of fundamental importance because it reveals certain attributes of the clay minerals. From a practical standpoint, solubility characteristics are important in determining the utility of various clays as sources of aluminum and for the production of porous materials. The acid treatment is beneficial in terms of increased surface area, porosity and number of acid centers with respect to the parent clays. The acid treated clays are composed of a mixture of non attacked clay layers and a hydrous, amorphous, and partially protonated silica phase. These high surface area silica gels are competitive in different industrial uses and very promising as sorbents or as catalyst supports [253].

It is found that the solubility of kaolinite in acids varies with the nature and concentration of the acid, the acid-to-kaolinite ratio, the temperature, and the duration of treatment. Grim reviewed some other studies related to acid–kaolinite reactions [280]. Most of these investigations have indicated that the kaolinite is more soluble in sulfuric than in hydrochloric acid. Again, under similar condition of acid treatment, but after amorphization by heating or grinding, all or substantially all the alumina of the kaolinite is soluble. The shielding of aluminum cation by the silicon-oxygen network and the presence of Al-O-Si bonds results in low solubility of kaolinite in acids [268, 281].

Literature reveals a number of works on the systematic examination porous silica prepared from mechanically and thermally amorphized kaolinite by sulfuric acid leaching. However, a systematic analysis of the chemical activation of untreated crystalline kaolin with sulphuric acid of different concentrations, with a wide characterization of the obtained solids and a complete discussion of the phenomena governing this process is sparsely available in the literature. The increasing interest in looking for new applications of clays justifies such a systematic study of this process. So, the objective of this work is to study the behavior of kaolin clay treated with sulphuric acid of different concentrations. The changes in physico-chemical properties are studied by different instrumental techniques such as SEM, XRF, XRD, FTIR, TGA-DTA and BET surface area analyzer.

4.2 Experimental programme

The details about the kaolin clay, the acid activation process and different characterization technique are described in the experimental section 3.

4.3 Results and discussions

4.3.1 XRF characterization

The XRF analysis was carried out to know the chemical compositions of the clay and the subsequent chemical changes that occurred due to acid treatment. Table 4.1 shows the results of chemical analysis of the parent and acid treated kaolinite clay. The parent clay contains alumina and silica which are in major quantities where as other oxides such as magnesium oxide, calcium oxide, potassium oxide, zinc oxide and titanium oxide are present in trace amounts.

According to the literature [268], the reaction between kaolinite and sulfuric acid is described by the chemical equation

$$Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 2SiO_2 + 5H_2O.$$

During the acid treatment it was observed that the composition of the parent clay changes considerably. As the strength of the acid increases the Al_2O_3, MgO, CaO and K_2O contents in the acid treated material decreases progressively. Simultaneously, SiO_2 content increased with increase in the acid strength due to which the Si/Al ratio increased. The decrease in the alumina content in the acid treated sample can be ascribed to the leaching of the Al^{3+} ions from the octahedral layer due to hydrolysis under acidic conditions. During acid treatment, it was observed that even at low acid strength the concentration of CaO, MgO and K_2O reduced, but that of TiO_2 and ZnO remained almost unchanged at low concentration and reduced slightly at very high acid concentration (10M).

Table 4.1 Chemical analysis of clay.

Material	**Chemical content (% weight)**								**Si/Al ratio**
	SiO_2	**Al_2O_3**	**MgO**	**CaO**	**K_2O**	**ZnO**	**TiO_2**	**Fe_2O_3**	
KC	43.12	46.07	0.027	0.030	0.010	0.0064	0.74	Nil	0.65
KC1M	48.48	42.17	0.006	0.004	0.007	0.0062	0.77	Nil	0.81
KC3M	61.81	32.85	Nil	0.008	0.005	0.0062	0.81	Nil	1.3
KC5M	66.15	29.38	Nil	0.011	0.005	0.0062	0.87	Nil	1.63
KC10M	87.46	7.70	Nil	0.004	0.001	0.0056	0.51	Nil	8.09

When the acid strength is in the range of 3-5M, the decrease in the aluminum content in the clay was more rapid. This can be interpreted due to the shielding of aluminum cation by the silicon-oxygen network and the presence of Al-O-Si bonds results in low solubility at low acid strength (up to 3M). As the acid strength increase from 3M to 5M the octahedral layer is attacked to a greater extent leading to rapid solubility. At very high strength such as 10 M most of the Al and other ions are removed due to severe leaching of the clay structure. For example at 10M H_2SO_4 acid treatment, the Al_2O_3 content decreases from 46.07 to 7.70% where as the SiO_2 content increases from 43.12 to 87.46%. The XRF study clearly indicates that leaching occurred in a sequential manner due to attack at octahedral layer as the acid strength increased from 1M to 10M resulting in the de-alumination of clay.

4.3.2 XRD analysis

The structural changes that occurred in the clay material due to acid treatment were studied using X-ray diffraction technique. Figure 4.1 shows the XRD profiles of the untreated and acid treated kaolins. The parent clay shows well defined reflections at 2theta value of 12^0, 25^0 (corresponding to the d values of 7.154 Å. These peaks correspond to the reflections from [001]), which are typical characteristic peaks of kaolinite. Again the peaks corresponding to the 2theta value 34-36^0, 38-42^0, 45-50^0, 54-63^0 may vary for kaolinites from different origin [278]. Upon acid treatment the peak intensity of the clay was found to decrease progressively. This is due to the structural disorder that occurred owing to the acid treatment, which affects the crystalline character of the clay. At low acid strength, the reflections of the original kaolinite phase became narrower (KC1M and KC3M) and the Hinckley index [279] of both kaolinites increased to 0.7. The narrowing of the peak may be related to the increase of crystallite size and/or the decrease of the mean lattice strain [281].

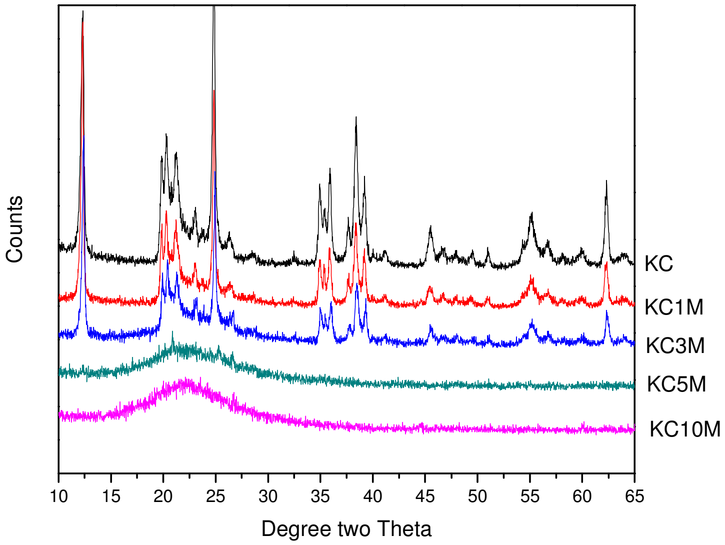


Figure 4.1 XRD of pure and acid treated kaolinite clay

It was observed that the kaolin clay treated with high strength acid i.e. 5M and 10 M does not show any well defined peak in the X-ray diffractograms. This indicates that these materials are amorphous in nature and there is a large degree of structural disorderliness in these samples. Since leaching is quite severe in this acidic strength, the layered structure of clay material disintegrates to give an amorphous phase.

4.3.3 FTIR analysis

The FTIR spectrum of the acid treated kaolinite clay is shown in Figure 4.2 and the corresponding band assignments is shown in Table 4.2. In the O-H stretching region, the parent and acid treated clay shows three prominent bands at 3620, 3653 and 3695 cm^{-1} corresponds to Al-OH stretching (Figure 4.2, panel I). Inner hydroxyl groups, lying between the tetrahedral and octahedral sheets give the absorption at 3620cm^{-1}. A strong band at 3695cm^{-1} is related to the in phase symmetric stretching and a weak absorption at 3653cm^{-1} are assigned to out-of-plane stretching vibrations. The band observed at 3445cm^{-1}, assigned to the high amount of water physisorbed on the surface of the clay [257,278,282]. When the clay was treated with acid there was not much variation in the peak pattern for 1M acid. However with further increase in acid strength the peak intensity was found to decrease progressively.

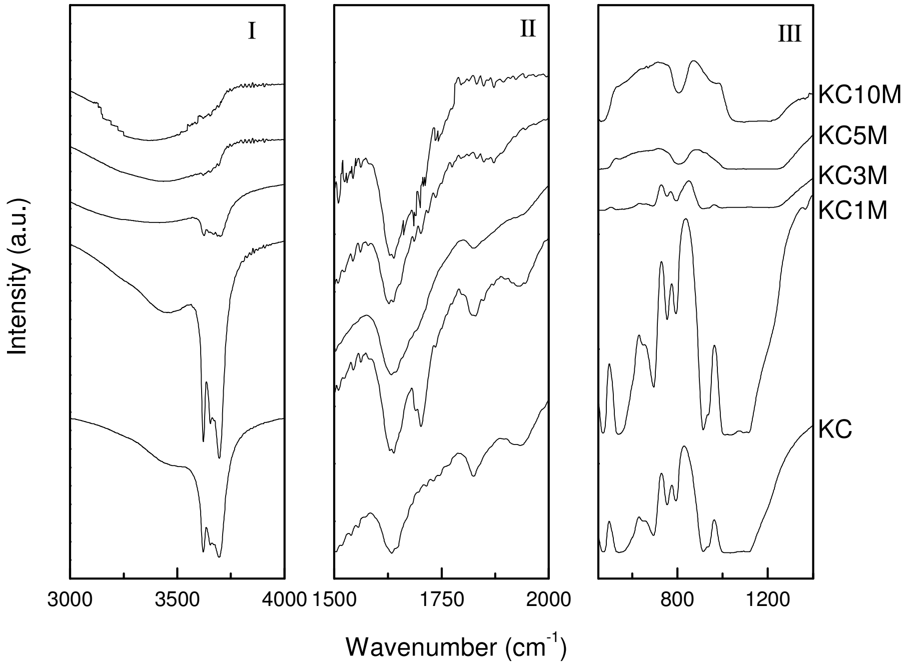


Figure 4.2 FTIR of pure and acid treated kaolinite clay

For the 5M and 10 M treated materials the structural hydroxyl vibration band is extremely weak indicating penetration of protons into the clay mineral layers and attack to the structural hydroxyl groups resulted in the dehydroxylation and a successive leaching of the Al ions from the octahedral layer [257].

In the bending region mode, the clay materials show a series of IR bands with peak maxima at 1634, 914, 795 and 755 cm^{-1} (panel II and III). The peak at 1634 cm^{-1} is quite intense in can be attributed to the bending vibration mode of physisorbed water on the surface of free silica produced due to leaching [282]. This peak was found to be absent in case of the 10M treated clay due to structural disintegration. The IR peaks at 914, 795 and 755 cm^{-1}can be assigned to the Al–Al–OH, Al–Mg–OH and Si-O-Al vibration of the clay sheet. The high intense 914 cm^{-1} peak due to vibrations of inner OH groups was found to be drastically reduced for 3M acid treated clay. This peak was of negligible intensity in case of the 5M and 10 M treated clay. This clearly points to the fact that when the acid concentration is more than 3M the de-alumination process is facilitated rapidly during acid treatment [257].

Table 4.2 Important IR bands of kaolinite clay with their possible assignments [153, 257, 278, 281]

Band cm^{-1}	**Assignments**
3445 3620, 3653 & 3695	Al--O-H_{str} (physisorbed water) Al--O-H_{str} (structural hydroxyl groups, octahedral)
1634	H-O-$H_{bending}$(physisorbed)
912 1032, 1101 & 1114	Al–Al–OH_{str}, Si-O_{str}
795 755	Al–Mg–OH_{str} Si-O-Al_{str}
805	Si-O_{str}
693	Si-O_{str}, Si-O-Al_{str}
541	Si-O_{str}, Si-O-Al_{str}
472	Si-O_{str}

Again well resolved strong bands in the 1120-1000cm^{-1} region (panel II) is due to Si-O stretching in untreated kaolinite which changed in shape and position and finally diminished after 3M acid treatment due to structural changes in the tetrahedral cations. In addition, a new peak was observed at 805 cm^{-1} for the acid treated sample, which gained intensity with increase in the acid strength [253, 257, 278]. This peak is due to the formation of free amorphous silica. The FTIR result is in clear agreement with the XRF study which indicates sequential degradation of the clay sheet upon acid treatment.

4.3.4 TG-DTA

The TGA curves (Figure 4.3a) of the pure and acid treated kaolins show two well-defined weight loss regions due to the loss of physisorbed water (below 200^{0}C) and dehydroxylation of coordinated and structural water (above 450^{0}C).

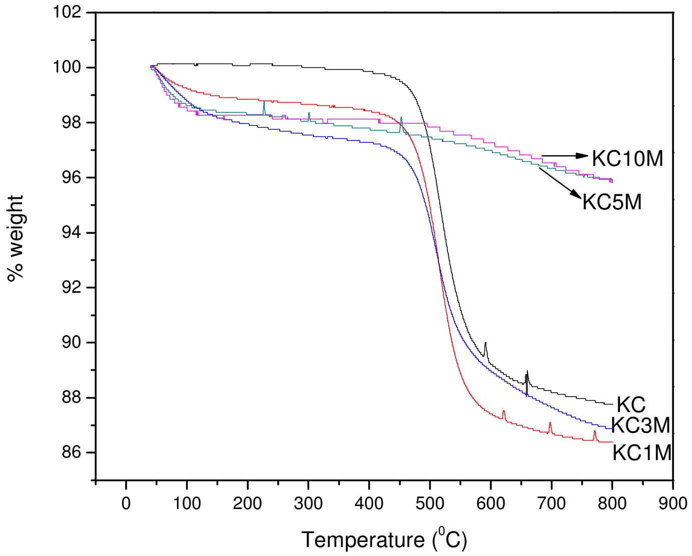


Figure 4.3a TGA of pure and acid treated kaolinite clay

In general, clay materials contain three kinds of water molecules in their structure. The physisorbed and interlayer water is loosely bound and are mobile they can be removed by heat treatment below 200^{0}C. The water molecule present in the first coordination sphere of the interlayer ions are strongly bonded and they require higher temperature in the range of 300-500^{0}C for their removal. Finally the structural hydroxyl groups can condense and dehydrate in the temperature range of 500-800^{0}C. In the present study, the low temperature water loss can be assigned to the physisorbed water, where as the high temperature weight loss is due to the dehydration and dehydroxylation of the clay sheet. Comparing the TGA profile of the parent and the acid treated clay it was observed that acid treatment increased the amount of physisorbed water and it increased with increase in acid concentration. This may be due to the fact that acid treatment increased the amount of amorphous silica and also surface area which made the water adsorption higher. In the high temperature weight loss regions however, the percentage loss is lower for acid treated clay as compared to the parent clay. This is due to the removal of the octahedral Al ions along with the concurrent removal of structural hydroxyl groups due to acid treatment.

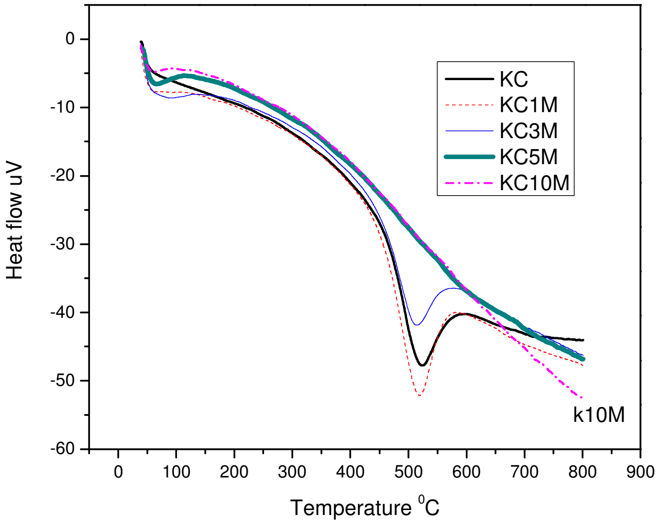


Figure 4.3b DTA of pure and acid treated kaolinite clay

The DTA profiles of the clay and acid treated clay are shown in Figure 4.3b supports the weight loss pattern due to water removal in the TGA study. The DTA curve of untreated kaolin showed two endothermic peaks at 56 and 531^{0}C. The endothermic peak centered at around 56^{0}C may be due to physisorbed water and a large peak at 531^{0}C might be due to the liberation of water caused by dehydroxylation of coordinated and structural water molecule. Increase in acid concentration increased the physisorbed water and decreased the structural and coordinated water leading to change in the endothermic peaks in treated samples.

4.3.5 Adsorption-Desorption isotherm and BET surface area

The N_2 adsorption-desorption isotherms of the pure and acid treated kaolinite presented in Figure 4.4. The isotherms of these samples are classified as type IV on the basis of IUPAC recommendations; this isotherm type is typical of mesoporous structures. The hysteresis loop of these samples is similar to type H3, typical of agglomerates of plate-like particles containing slit-shaped pores [266]. The isotherms also suggest the presence of some micro porosity and macro porosity.

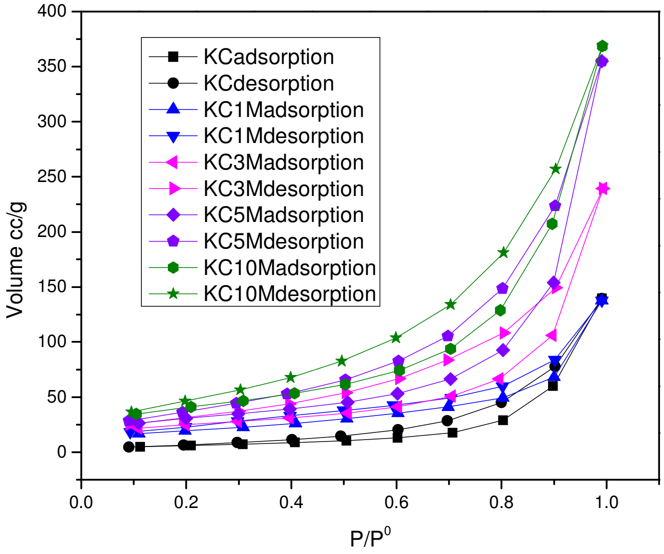


Figure 4.4 N_2 adsorption/desorption isotherm of pure and acid treated kaolinite clay

The pore volume and BET surface area increased with increasing acid strength, which is summarized in the Table 4.3. Upon 1M acid treatment, the new surface area of the original material is three times greater and with 10M acid treatment the surface area increased to 143m^2/g. Increase in acid concentration lead to increase of surface area and pore volume. The increase in surface area and pore volume is due structural de-alumination leading to the change microstructure (mesoporous to microporous) and formation of amorphous phase.

Table 4.3 BET Surface area and pore volume of different clay.

Catalyst	**Surface area m^2/g**	**Pore volume cc/g**	**Acid centers (mmol/g)**
KC	23	0.361	0.049
KC1M	69	0.489	0.108
KC3M	83	0.670	0.116
KC5M	107	0.967	0.210
KC10M	143	1.18	0.007

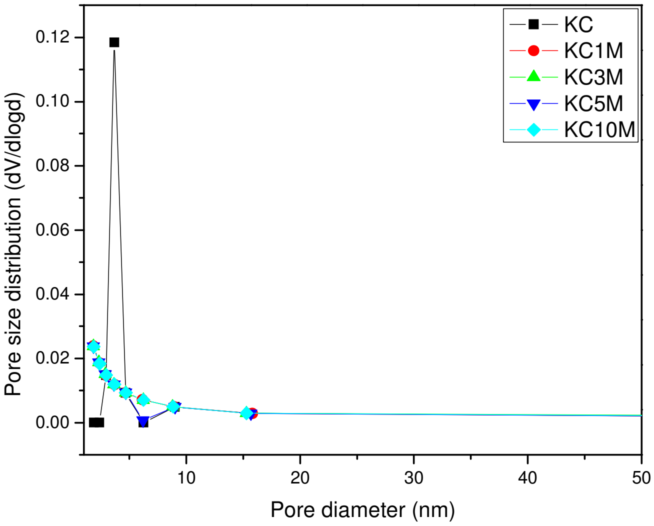


Figure 4.5 Pore size distribution of pure and acid treated kaolinite clay

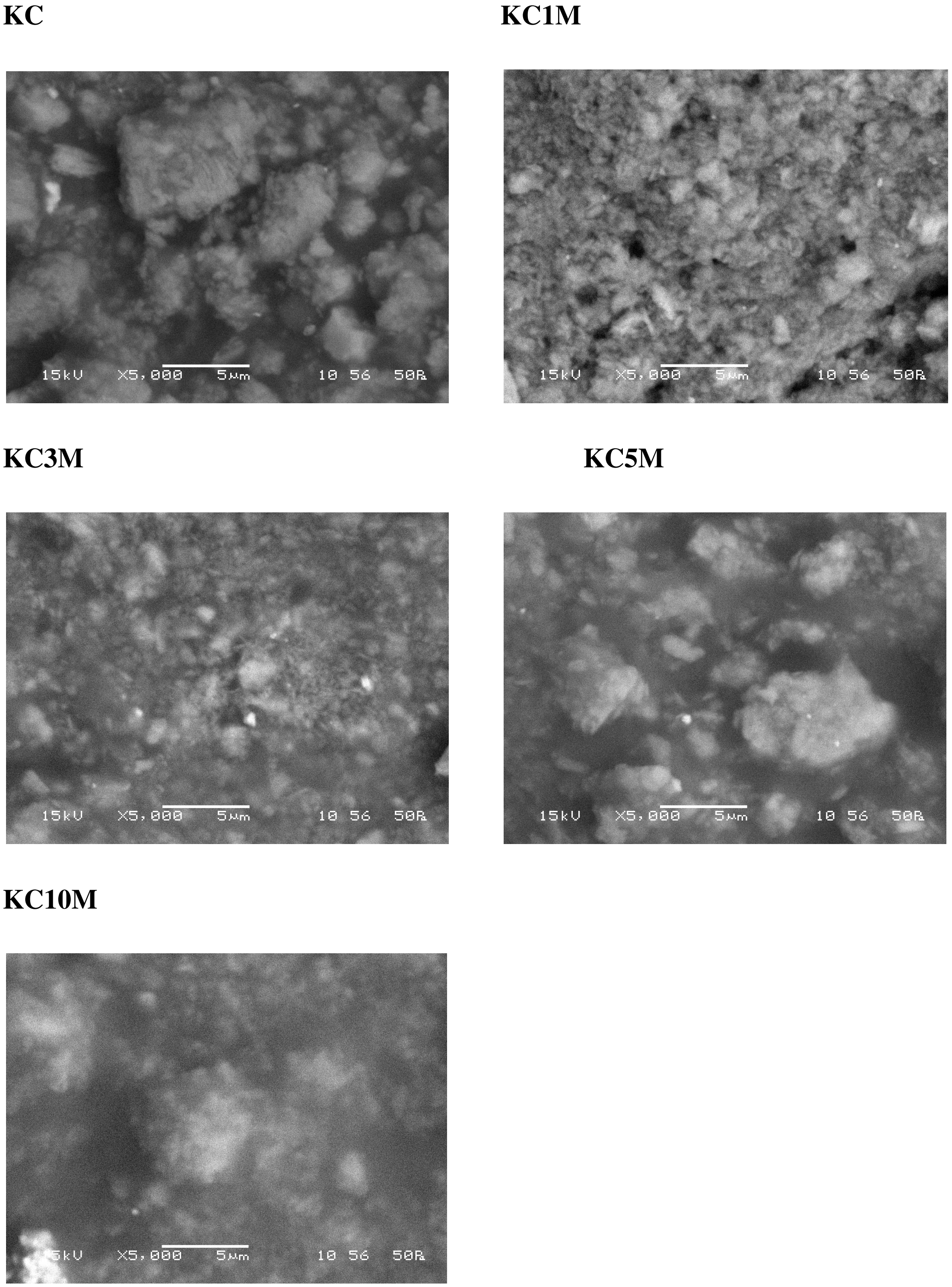
The pore size distribution of untreated kaolinite samples shows a sharp peak at a radius of 3.5nm (Figure 4.5) and thus is mesoporous. The acid treatment changed the pore size distribution where the sharp peak curve vanished indicating the decrease in the number of pores with diameter 3.5nm and increase in the number of pores with diameter <3.5nm. Acid leaching created more number of pores with diameter 1.8nm (<2nm) i.e. micro pores. But the pore size and number of micro pore is independent of acid concentration.

4.3.6 Acidity evaluation

The relative amount of the acid sites of the samples was evaluated by thermal desorption of ammonia. Ammonia is a strong base ($pKb \approx 5$) that reacts even with extremely weak acid sites, which therefore makes NH_3-TPD a useful technique for evaluating the relative amount of acid sites present on a surface. The acidity of the different samples is summarized in Table 4.3. The acidity of the kaolin is 0.049mmol/g which increases to 0.108mmol/g, 0.116mmol/g and 0.210mmol/g by treating it with 1M, 3M, and 5M sulphuric acid respectively followed by calcination at 500^0C. The increase of acidity is due to creation of specific acid sites on the surface of silica generated due to leaching. And this increase is optimum at 5M acid treatment. The acidity is further increased to 0.246mmol/g, when the 5M sulphuric acid treated clay sample is calcined at 750^0C which may be due to rapid hydrolysis of the clay at high temperature leading to the generation of acid sites. Treatment with 10M sulphuric acid, results in the drastic decrease in acidity to 0.007mmol/g due to excessive de-alumination (about 85%).

4.3.7 SEM analysis

The scanning electron micrographs of the different kaolin clay samples are presented in Figure 4.6 which shows the morphological features. The SEM micrograph of KC reveals the presence of large particles that appeared to have been formed by several flaky particles stacked together in form of agglomerates. The SEM images of KC1M, KC3M, KC5M and KC10M show different particle morphology. The micrographs of KC1M and KC3M indicate the disaggregation and decrease in size of clay structure on acid treatment and that of KC5M and KC10M shows well-bonded aggregates rather than detached particles.



KC

KC1M

KC3M

KC5M

KC10M

Figure 4.6 SEM of pure and acid treated kaolinite clay

4.4 Conclusion

In this work we have studied the effect of the acid treatment on the structural and chemical properties of kaolin clay. The XRF and SEM study indicated clearly the leaching and disintegration of the clay sheet upon acid treatment of different concentration. As the strength of the acid increased, Al_2O_3, MgO, CaO, K_2O,TiO_2 and ZnO contents in the acid treated material decreased progressively simultaneously increasing the SiO_2 content. XRD studies of the acid treated clay indicated the structural transformation of the clay sheet upon acid treatment. The pure clay is crystalline, where as the crystallinity and the interlayer structure of the clay material was found to be altered with acid treatment and became amorphous at high acid strength (i.e. at and above 5M). FTIR study of the acid treated clay shows the presence of several kinds of structural OH groups whose peak position and intensity changes with increase in acid concentration. Acid treatment with 1M concentration did not cause much variation in the peak pattern. However with further increase in acid strength the peak intensity was found to decrease progressively and became extremely weak for the 5M and 10M treated materials indicating the dehydroxylation and successive leaching of the Al ions from the octahedral layer. Since the OH groups play a predominant role in clay catalysis, the acid treatment up to 3M concentration may be beneficial in terms of generation of new acidic sites. Again, the N_2 adsorption/desorption analysis of the samples indicated the increase in surface area and pore volume with acid treatment. Thus, this method can be useful for manufacturing a surface active, porous and high surface area material which can be used for catalyst as well as an adsorbent.

Chapter 5

Thermo-catalytic pyrolysis of virgin and waste polypropylene using kaolin and silica alumina catalyst

THERMO-CATALYTIC PYROLYSIS OF VIRGIN AND WASTE POLYPROPYLENE USING KAOLIN AND SILICA ALUMINA CATALYST

5.1 Introduction

Polypropylene (PP) is a crystalline thermoplastic and one of the major and versatile members of the polyolefins family. It serves double duty, both as a plastic and as a fiber. As a plastic it is used to make things like dishwasher-safe food containers and as a fiber, it is used to make indoor-outdoor carpeting. In addition, polypropylene is also used in several markets, for instance, in food packaging, medical bags, computer components, automotive industry, pipes and general containers etc. This versatility of PP is due to its good chemical resistance and its low density.

Structurally, it's a vinyl addition polymer; polypropylene can be made from the monomer propylene by Ziegler-Natta polymerization and by metallocene catalysis polymerization.

Polypropylene, one of the main components of plastic wastes is widely used as industrial and household thermoplastics. Its contribution is 40% of the total global polyolefins demand during 2009. Global polypropylene demand is estimated to have declined by 1.4 percent in 2009, a more moderate figure compared to 2008 which saw a decline of 3.1 percent due to de-stocking of the value chain. North America and Western Europe were especially affected, while the Asian market saw minimal growth in 2009. The growth in the emerging economies of Central and Eastern Europe, Middle East and Africa was ahead of that seen in the more mature markets of North America, Western Europe and

Japan. However, the outlook for polypropylene is much better in the period 2009-2015 as consumption is forecast to grow by 5.7 percent per annum with over half of this volume growth focused in the Asian markets, particularly China and India [283].

Thermal and catalytic pyrolysis of polypropylene was reported in the literature. The performances of different catalysts are studied using different reactors in various reaction conditions in order to obtain a suitable process for the conversion of polypropylene to liquid fuel. The objective of this work is to study the thermal and catalytic degradation of polypropylene in a batch reactor using kaolin, acid treated kaolin and Silica-Alumina catalysts and compare their catalytic performances by varying the temperature, catalyst type and catalyst to plastic ratio with a view to optimize the yield of liquid fraction. The study also includes, the characterization of oil obtained in the optimum conditions, for its composition and fuel properties to know its suitability as a fossil fuel substitute. The reusability of the kaolin catalyst has also been studied to know its catalytic performance when it is used for number of times.

5.2 Experimental programme

The details about the virgin and waste polypropylene, catalysts such as kaolin, silica alumina and acid treated kaolin used in this experiment and also the experimental set up and procedure are summarized in the experimental section 3.

5.3 Results and discussion

5.3.1 TGA of polypropylene samples

The thermal degradation of polypropylene samples (waste and virgin) was carried out using TGA in order to know the thermal properties. Figure 5.1 shows the normalized weight loss for both the samples as a function of temperature. The level of degradation of the virgin and waste plastics is slightly different and the order of temperature levels of waste polypropylene is less than pure polypropylene.

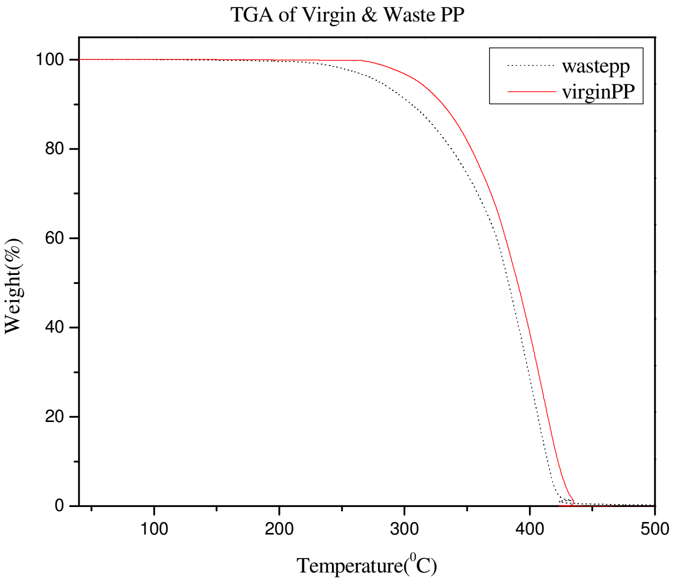


Figure 5.1 TGA of polypropylene samples

The degradation of both virgin and waste polypropylene occurred between 220 °C to 440 °C. Waste plastic starts degrading at low temperature as compared to virgin plastic. Again, the weight loss of 50% (T_{50}) takes place at 382 °C and 391 °C for waste and pure polypropylene respectively. The small difference in the thermal properties of pure and waste may be due to weakening bonding in waste sample during their processing and use.

5.3.2 Results of Pyrolysis

5.3.2.1 Effect of temperature on product distribution in thermal pyrolysis: Three different fractions namely condensable low viscous liquid/high viscous liquid/wax like products, non condensable gases/volatiles and solid residue were obtained during pyrolysis. At different temperatures, the yield distribution of different fractions clearly differed and summarized in Figure 5.2. The condensable fraction (oil/wax) obtained at low temperature (400 °C and 450 °C) was less viscous and highly volatile oil, where as that obtained above 475 °C were viscous liquid or wax. The recovery of condensable fraction was low (67.6 wt.% for pure polypropylene and 65.2wt.% for waste polypropylene) at 400 °C and increased to highest yield of 82.85wt.% at 500 °C for pure polypropylene and 82.25 wt.% at 500 °C for waste polypropylene and then gradually decreased with further increase in temperature.

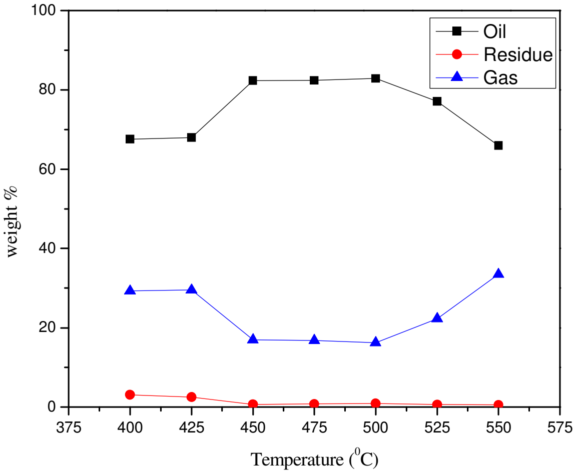


Figure 5.2 Effect of temperature on product distribution of polypropylene thermal pyrolysis.

The vapour/volatile fractions increased at high and low temperatures leading to low condensable. At low temperature, the reaction time was more (Figure 5.3b), due to which secondary cracking of the pyrolysis product occur inside the reactor and resulted in large amount of highly volatile/gaseous product. Similarly, the low liquid and high gaseous yield at higher temperature was due to the formation of more non condensable gaseous/volatile fractions by rigorous cracking. The results of thermal pyrolysis of pure and waste polypropylene are summarized in the Figure 5.3a and 5.3b. From these figures it is observed that, pyrolytic degradation performance of both waste and pure polypropylene in the thermal pyrolysis was almost similar. Thus, further studies were carried out using waste polypropylene.

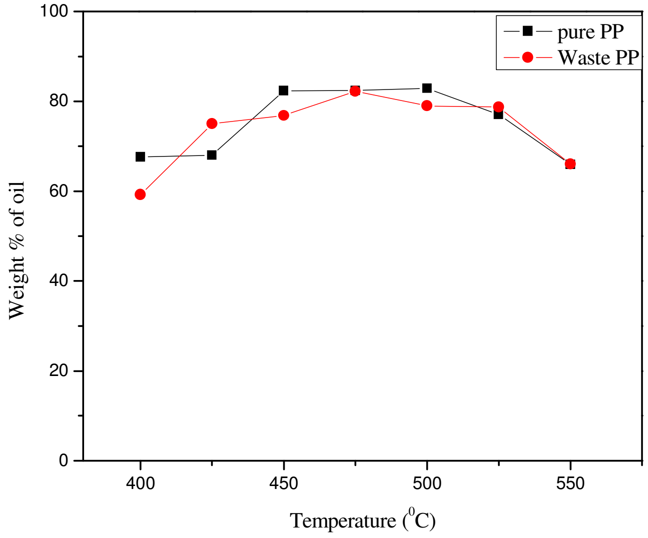


Figure 5.3a Effect of temperature on yield of pyrolysis of PP

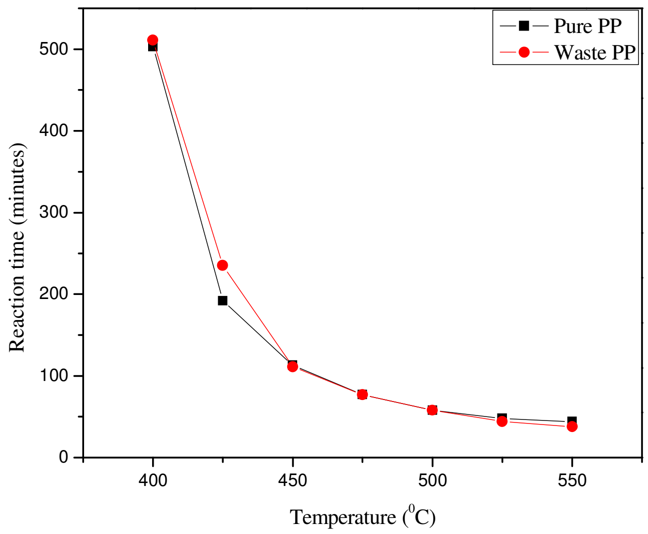


Figure 5.3b Effect of temperature on reaction time of pyrolysis of PP

5.3.2.2 Effect of presence of kaolin catalyst: The thermal decomposition of polypropylene was carried out in presence of kaolin as catalyst with different polypropylene to catalyst ratio. Reaction time decreased and oil yield increased with increase in catalyst amount (Figure 5.4a). Highest yield of oil (87.5wt.%) was obtained at 3:1 plastics to catalyst ratio at 500 °C. The effect of catalyst was not significant at 20:1 polymer to catalyst ratio and it is almost negligible at 40:1 polymer to catalyst ratio. Figure 5.4b shows the effect of presence of catalyst on oil yield at different temperatures. It is observed that the oil yield increased in catalytic pyrolysis compared to thermal reaction. Again, unlike in thermal pyrolysis, the condensable products in catalytic pyrolysis, even at higher temperature are also low viscous liquid and not high viscous liquid or in wax form. All the above changes in the reaction in presence of kaolin can be explained due to its mesoporous surface and acidity, which facilitate the cracking reaction.

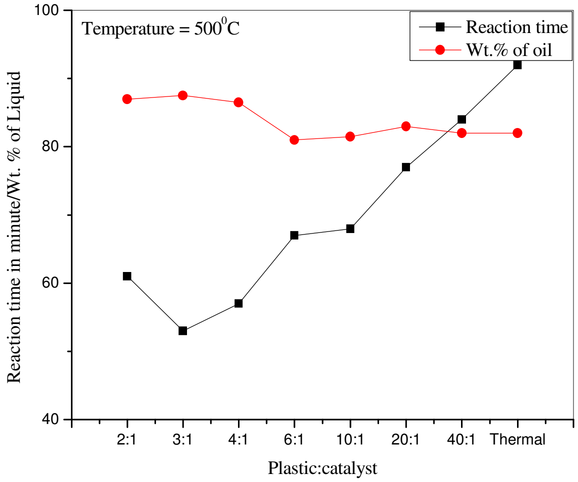


Figure 5.4a Effect of plastic: catalyst ratio on the reaction time and oil yield of pyrolysis of PP

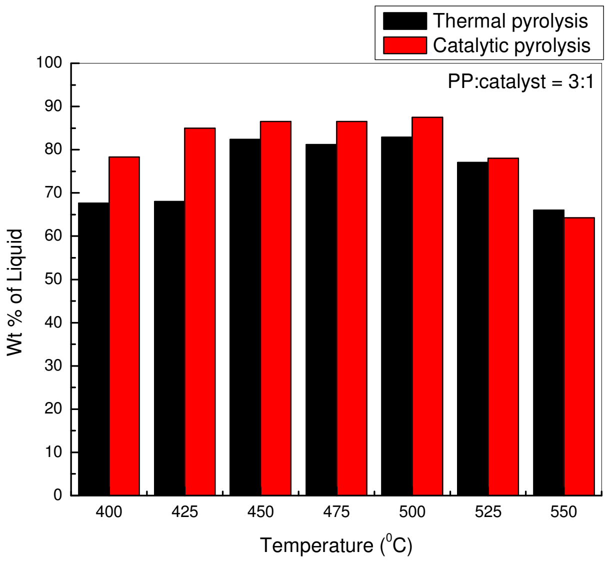


Figure 5.4b Effect of catalyst on oil yield at different temperature of pyrolysis of PP

5.3.2.3 Reusability of kaolin catalyst

The activity of kaolin catalyst was studied by re-using it for a number of times in the degradation of polypropylene and the results are summarized in the Table 5.1. It is observed that the yield and quality of liquid oil product remain almost same up to four times repeated use of the catalyst and yield decreased at 5th time use. The reaction time of the reaction increased gradually for every repeated use. The decrease in the catalytic activity may be due to the deposition of carbon and other plastics impurities over the surface. The SEM EDX (Figure 5.5 a b c d) of the catalyst sample clearly distinguishes the deposition of carbon over the surface of used catalyst. The kaolin after using for 5th run degradation was regenerated by calcinating it inside a muffle furnace at 750 °C for one hour. The catalytic activity of regenerated catalyst was found to be almost same as that of the fresh kaolin. When the used catalysts were regenerated at high temperature, the deposited carbon burnt off and surface of catalyst become free of all depositions.

Table 5.1 Product distribution, reaction time and physical properties of oil obtained in catalytic pyrolysis with Feed- KP: WP-1:3 at temperature- 500 °C

No of times re-used	**Weight of different fractions in weight %**			**Reaction time in minutes**	**Specific gravity of oil @15 °C /15°C**	**Viscosity of oil at 30 °C in Cst**
	Oil	**Gas**	**Solid residue**			
Fresh	87.5	8.9	1.6	44	0.7777	2.27
1st time	87.0	10.6	1.9	58	0.7776	2.27
2nd time	87.0	10.4	2.1	64	0.7645	2.27
3rd time	86.6	10.25	1.75	68	0.7641	2.26
4th time	86	10.4	1.6	68	0.7638	2.26
5th time	84	14.25	1.75	73	0.7630	2.24
Regenerated catalyst	88	10.25	1.75	45	0.7732	2.26

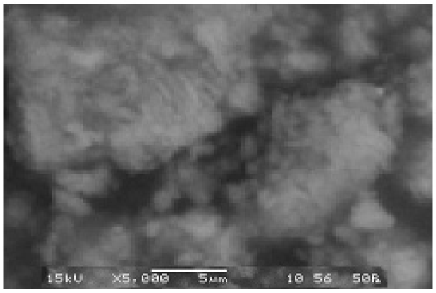


Figure 5.5a SEM of fresh Kaolin

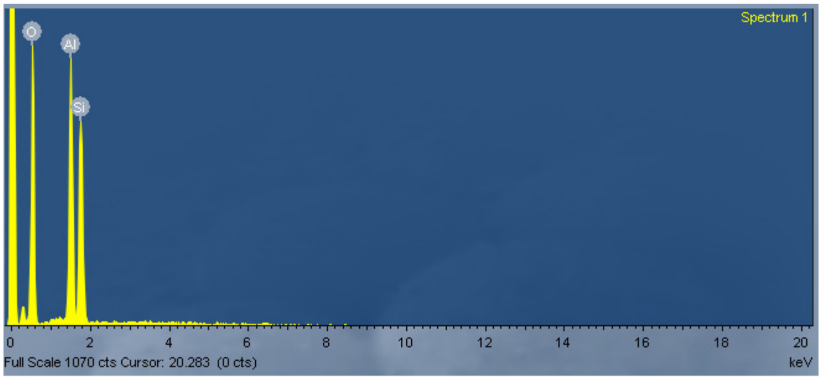


Figure 5.5b EDX of fresh kaolin

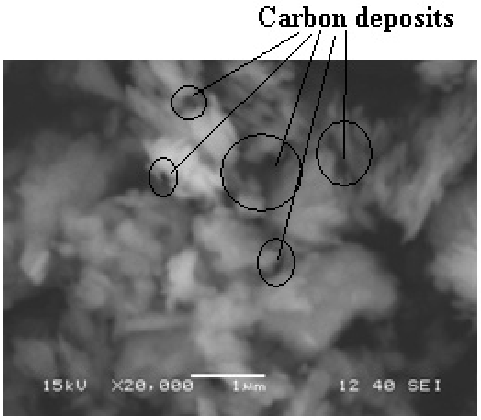


Figure 5.5c SEM of used Kaolin

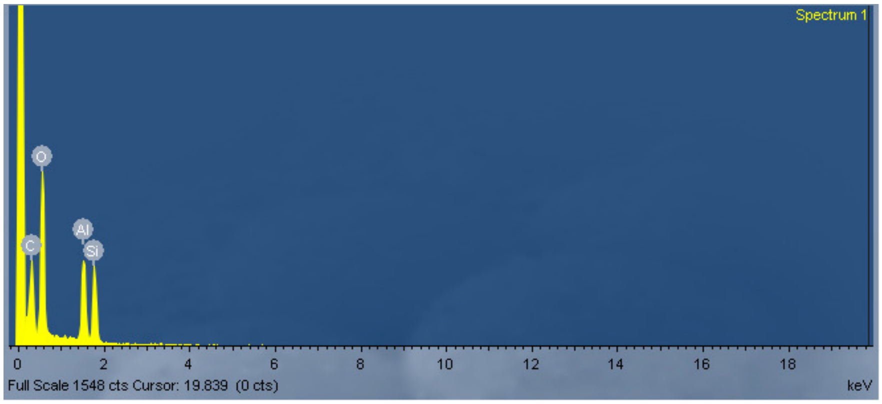


Figure 5.5d EDX of used Kaolin

5.3.2.4 Effect of presence of Silica alumina

The pyrolysis reaction of polypropylene was also carried out in presence of silica alumina catalyst and compared its catalytic performance with kaolin. The catalytic reaction was carried out by taking different feed compositions (catalyst to polypropylene ratio) using both the catalysts. It is observed that, **reaction** time decreased and oil yield increased with decrease in polymer to catalyst ratio up to 3:1 and afterwards with 2:1 feed composition, there was slight decrease in yield. There was almost no effect of catalysts above 20:1 polymer to catalyst ratio.

Figure 5.6a indicates the comparison of yield of liquid fraction in thermal, kaolin catalysed and Si-Al catalysis pyrolysis at different temperatures. Presence of both the catalysts increased the yield of condensable fraction (oil) as compared to thermal pyrolysis at all temperatures except at 550 °C. The highest yield of oil using kaolin catalyst was 87.5wt. % at 500 °C and that of using Si-Al catalyst was 91wt. % at 500 °C with catalyst to polypropylene ratio 1:3. From Figure 5.6b, it is observed that the reaction time of the pyrolysis reaction also decreased with addition of catalyst. Si-Al performed slightly better than kaolin catalyst with respect to decreasing the reaction time and yield of oil fraction which can be explained due to its higher acidity as compared to kaolin.

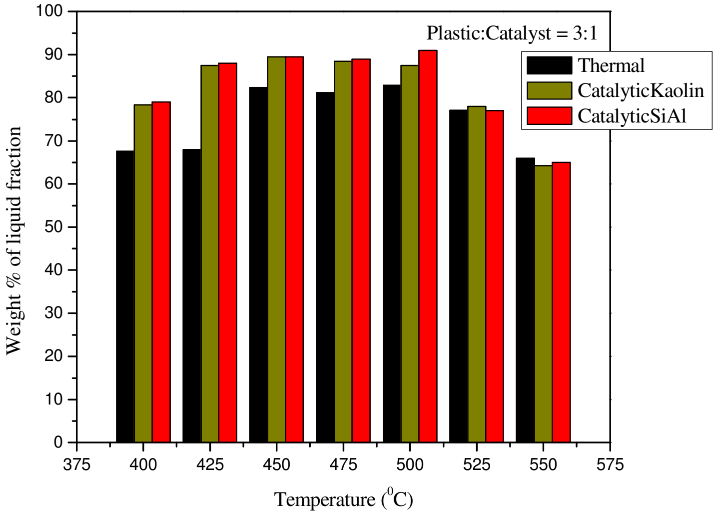


Figure 5.6a Effect of catalyst on yield of liquid yield.

Figure 5.6c provides a comparison of the rate of production of oil in thermal and catalytic pyrolysis. In thermal pyrolysis there was gradual increase in oil production with time. There was sharp increase in oil yield with time observed in presence of both the catalyst. Both the catalyst followed similar trend, but silica alumina performed slightly better in terms of yield of oil and decrease in reaction time. Both the catalysts facilitate the cracking of polypropylene due to the availability of solid surface and acidity.

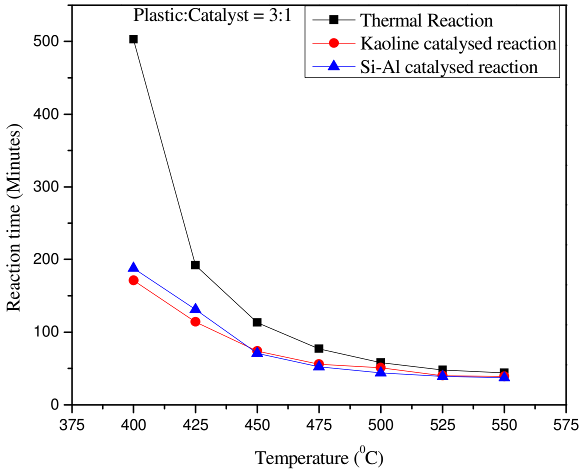


Figure 5.6b Effect of temperature and catalyst on reaction time.

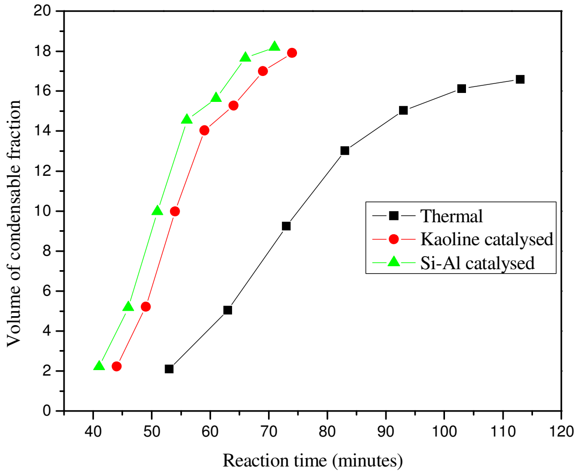


Figure 5.6c Effect of catalyst on rate of production of oil.

The product yield of different fractions, density and viscosity of the liquid products obtained in the thermal and catalytic degradation of polypropylene at specified conditions are reported in Table 5.2.

Table 5.2 Pyrolysis of polypropylene in optimum condition

Parameters	**Type of pyrolysis reaction**		
	Thermal (Temperature = 500 °C)	**Kaolin catalysed (Plastic: catalyst = 3:1 and Temperature = 500 °C)**	**Si-Al catalysed (Plastic: catalyst = 3:1 and Temperature = 500 °C)**
Liquid product (wt. %)	82.85	87.5	91
Gaseous/volatile(wt.%	16.25	11.75	8
Solid residue (wt. %)	0.9	0.75	1
Density of oil at 15 °C (in g/cc)	0.84	0.745	0.7702
Viscosity of oil at 30 °C (in Cst)	4.31	2.18	2.21

5.3.2.5 Effect of use of acid treated kaolin

The pyrolysis of polypropylene was carried out in presence of different acid treated kaolin catalysts and the results were compared with thermal and kaolin catalysed reactions (Figure 5.7a and 5.7b). From the figure it is observed that, the yield of oil fraction increases and reaction time decreases with increase in acid concentration and is optimum for 5MKC.The maximum oil yield obtained using this catalyst is 92%. The increase in catalytic activity of different acid treated kaolins is due to increased surface area, pore volume and acidity with increase in acid concentration [108,191]. Kaolin treated with 10M sulphuric acid i.e. 10MKC doesn't have any catalytic activity due to severe dealumination and amorphization leading to negligible acidity value.

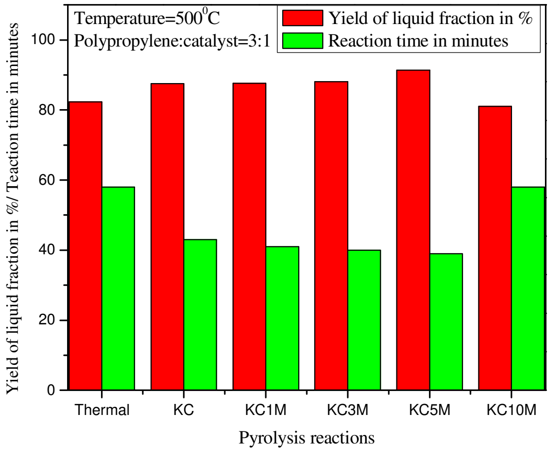


Figure 5.7a Effect of different catalysts on the yield of liquid fraction

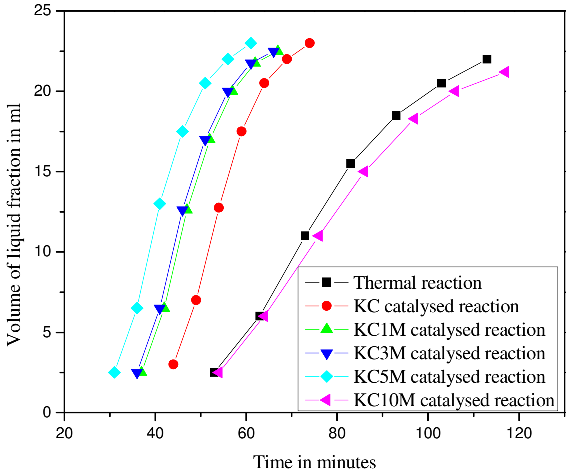


Figure 5.7b Effect of different catalysts on rate of production of oil.

From the Figure 5.7b it is observed that, the rate of production of oil also increases with acid treatment. In thermal pyrolysis there is gradual increase in oil production with time. A sharp increase in oil yield with time is observed in presence of acid treated catalysts up to 5MKC. All the acid treated kaolin catalysts up to 5MKC followed similar trend, and performance of catalysts increases with severity of acid treatment in terms of yield of oil and decrease in reaction time. The rate of oil production in 10MKC catalysed reaction is almost similar to thermal catalysis reaction.

5.3.3 Characterization of liquid products

The oil samples are characterized using FTIR for functional group composition, GC-MS for detail composition and fuel properties to know its usability as an engine fuel.

5.3.3.1 FTIR of oil

The Figure 5.8 indicates the FTIR of thermal and catalytic pyrolysed oil at 500 °C. The important assignments were summarized in the Table 5.3. From the table it is clear that, the oil consists mostly alkanes, alkenes and also some oxygenated hydrocarbons.

Table 5.3 FTIR functional group composition of pyrolysis oil

Wave number (cm^{-1})	**Type of vibration**	**Nature of functional group**
2956/2916	C-H $_{\text{stretching}}$	Alkane
1377	C-H$_{\text{Scissoring and Bending}}$	Alkane
2870	C-H $_{\text{stretching}}$	Alkane
1651	C=C $_{\text{stretching}}$	Alkene
1456	C=C $_{\text{stretching}}$	alkene
970	C-H $_{\text{Bending}}$	Alkene
887	C-H $_{\text{out of plane bending}}$	Alkene
738	C-H $_{\text{Bending}}$	Alkene, Phenyl ring substitution
1110, 1156	C-O $_{\text{stretching}}$	Alcohols, Ethers, Carboxylic acids, Esters
1694, 1710, 1770	C=O $_{\text{stretching}}$	Aldehydes, Ketones, Carboxylic acids, Esters

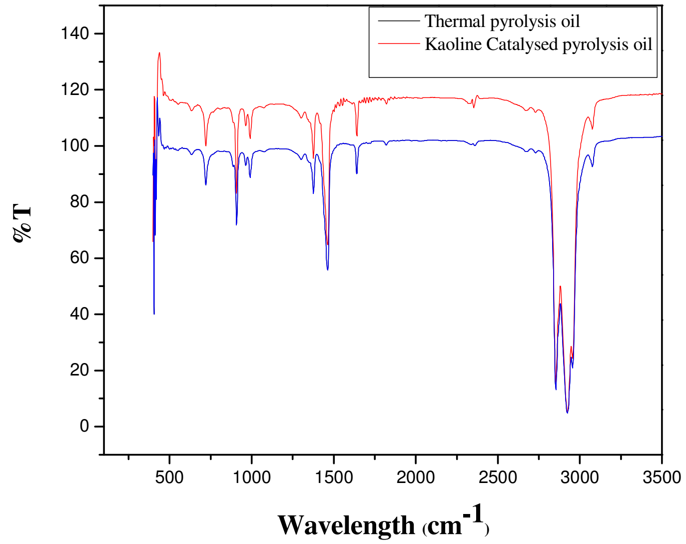


Figure 5.8 FTIR of oil obtained in thermal and kaolin catalysed pyrolysis at 500 °C

4.3.3.2 GC-MS of oil

The GC-MS of the oil obtained in thermal and different catalytic pyrolysis reaction at 500^0C are shown in Figure 5.9a, 5.9b, 5.9c, 5.9d. Different components present in the oil obtained by comparing NIST library are summarized in the Table 5.4a, 5.4b, 5.4c and 5.4d respectively. This result indicates the presence of different hydrocarbons mostly alkanes and alkenes in the oil. In addition, some oxygenated compounds such as alcohol, ketone, etc. are also found in the oil which may be due to oxidative degradation of polypropylene in presence of limited quantity of oxygen inside the reactor as the reaction is not carried out in inert atmosphere. Hayashi J et al. reported, polypropylene is more susceptible to oxidation than others because it contains tertiary carbons and it forms peroxide in the chemical form of –C–O–O–H in presence of oxygen even at 150 °C. Peroxides are further decomposed to more stable oxygen-containing groups such as hydroxyl and carbonyl groups [45].

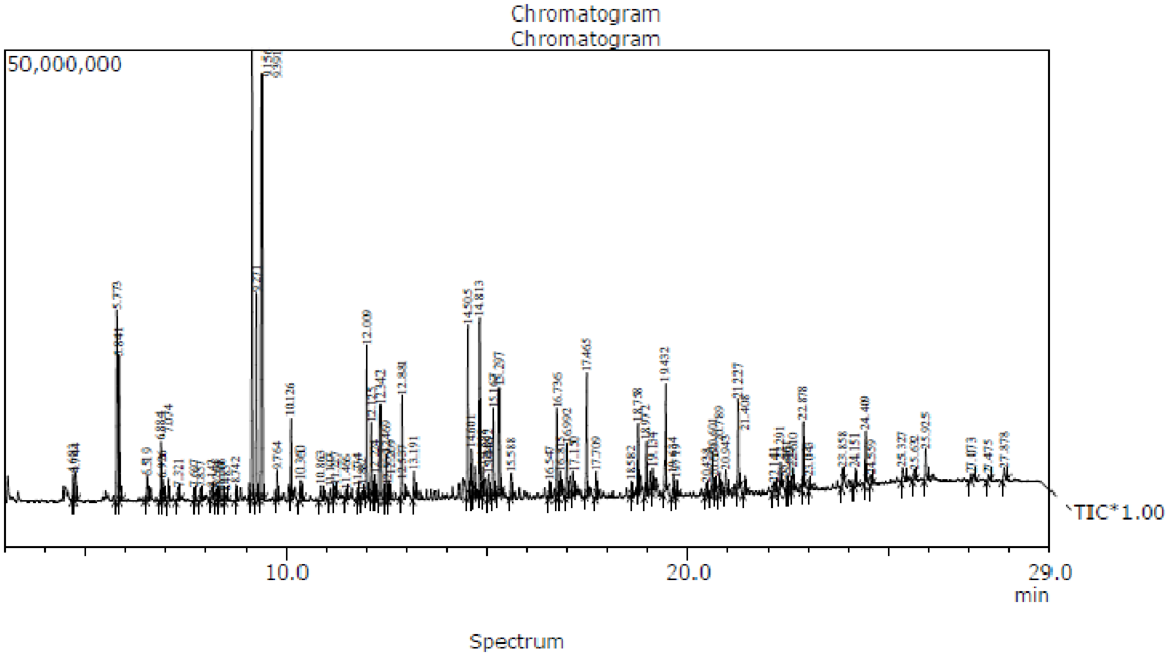


Figure 5.9a GC-MS of oil obtained in the thermal pyrolysis of waste polypropylene at 500 °C

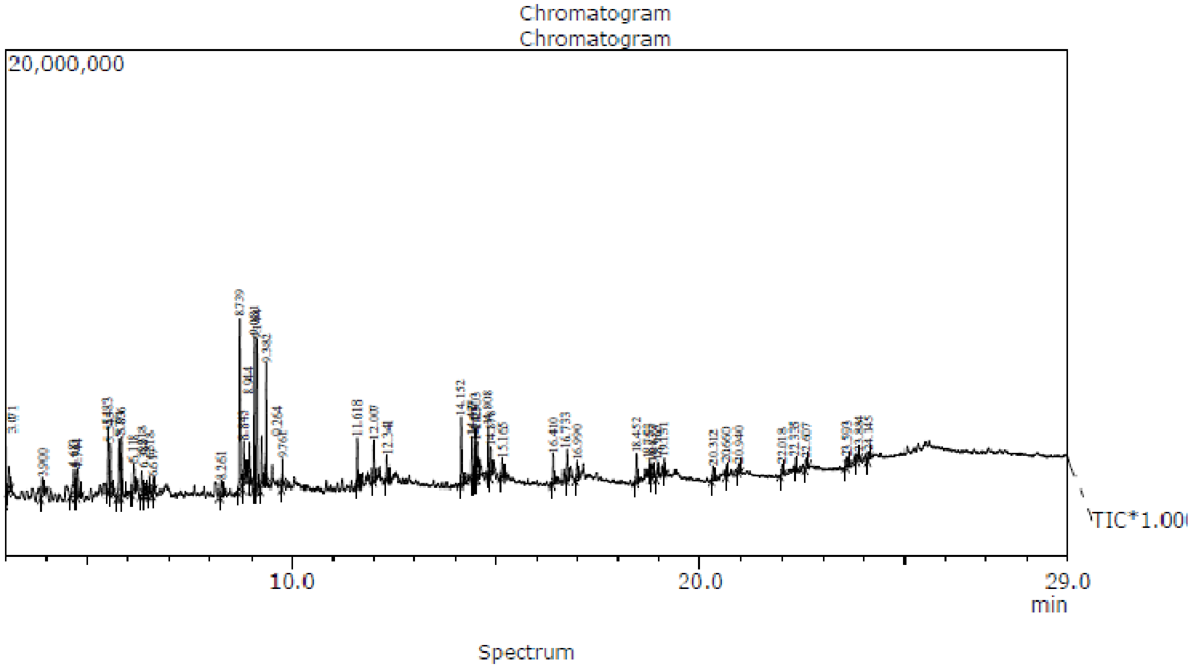


Figure 5.9b GC-MS of oil obtained in the kaolin catalysed pyrolysis of waste polypropylene at 500 °C

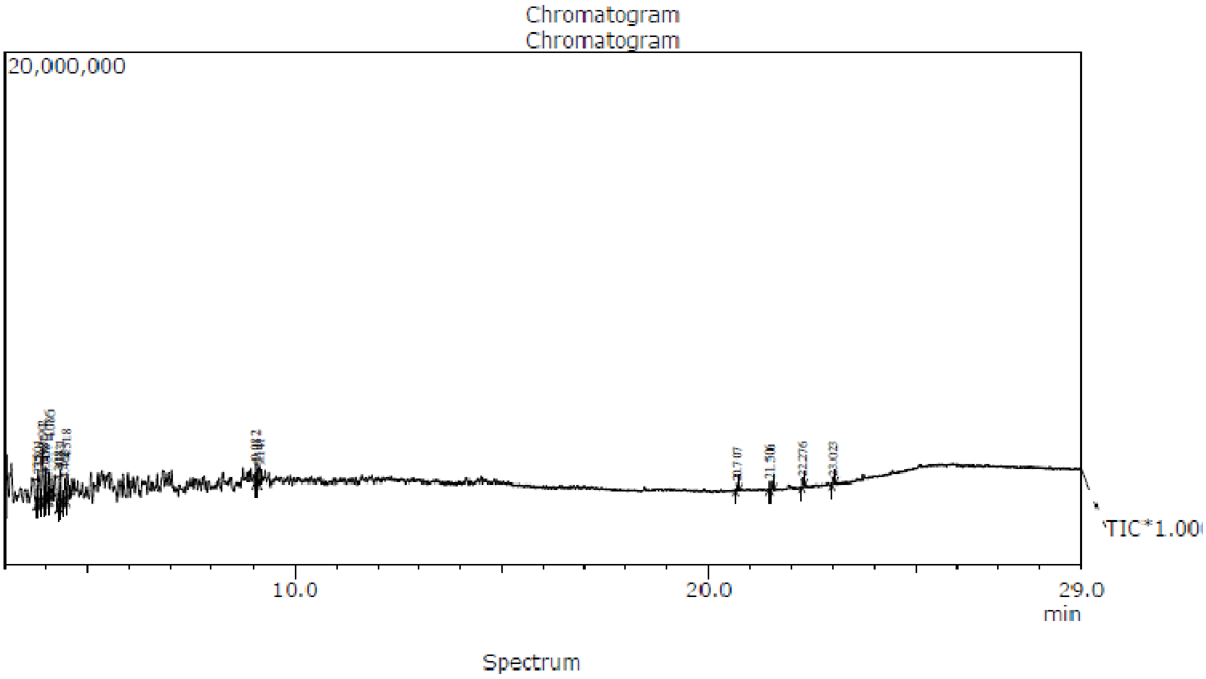


Figure 5.9c GC-MS of oil obtained in the 1MKC catalysed pyrolysis of waste polypropylene at 500 °C

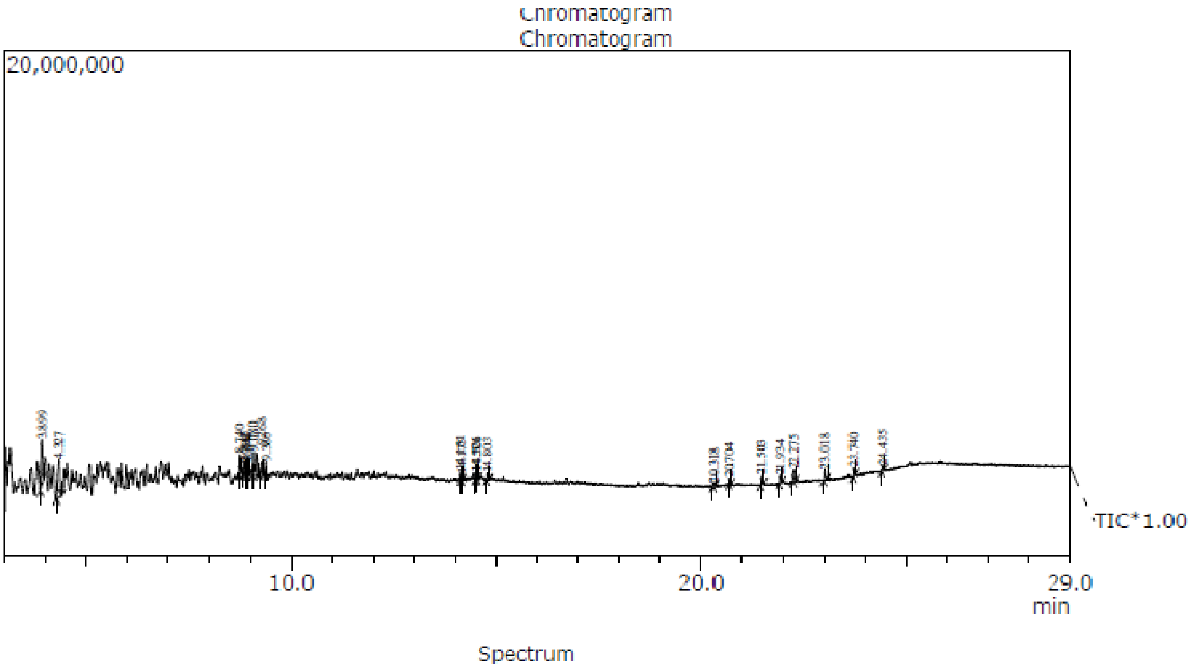


Figure 5.9d GC-MS of oil obtained in the 5MKC catalysed pyrolysis of waste polypropylene at 500 °C.

Table 5.4a GC-MS composition of oil obtained by the thermal pyrolysis of polypropylene at 500 °C.

Peak	**Retention Time in minute**	**Area %**	**Name of the component**	**Molecular Formula**
1	4.683	0.70	4-Methyldecane	$C_{11}H_{24}$
2	4.744	0.72	4-Methyldecane	$C_{11}H_{24}$
3	5.773	6.07	2,4-Dimethyl-1-Decene	$C_{12}H_{24}$
4	5.841	1.83	4-Methoxyphenyl Methyl Carbinol	$C_9H_{12}O_2$
5	6.519	0.49	1-Tridecanol	$C_{13}H_{28}O$
6	6.884	1.24	(2,4,6-Trimethylcyclohexyl)	$C_{10}H_{20}O$
7	6.926	0.43	(2,4,6-Trimethylcyclohexyl)	$C_{10}H_{20}O$
8	7.074	0.48	2,4-Diethyl-1-Methylcyclohexane	$C_{11}H_{22}$
9	7.321	0.29	2,4-Diethyl-1-Methylcyclohexane	$C_{11}H_{22}$
10	7.697	0.25	2,4-Diethyl-1-Methylcyclohexane	$C_{11}H_{22}$
11	7.857	0.25	Isotridecyl Alcohol	$C_{13}H_{28}O$
12	8.143	0.24	4,6-Dimethyldodecane	$C_{14}H_{3}0$
13	8.264	0.25	4,6-Dimethyldodecane	$C_{14}H_{30}$
14	8.368	0.33	3,7,11,15-Tetramethyl-2-Hexadecen-	$C_{20}H_{40}O$
15	8.485	0.16	1,19-Icosadiene	$C_{20}H_{38}$
16	8.742	0.31	2,4-Dimethyl-2-Decene	$C_{12}H_{24}$
17	9.156	10.14	Tridecanol	$C_{13}H_{28}O$
18	9.271	5.17	1-Tridecanol	$C_{13}H_{28}O$
19	9.391	8.44	2-Isopropyl-5-Methyl-1-Heptanol	$C_{11}H_{24}O$
20	10.126	1.46	Cyclododecylmethanol	$C_{13}H_{26}O$
21	10.360	0.40	Cyclododecylmethanol	$C_{13}H_{26}O$
22	10.863	0.44	Isotridecyl Alcohol	$C_{13}H_{28}O$
23	11.107	0.33	2,6,11,15-Tetramethylhexadecane	$C_{20}H_{42}$
24	11.227	0.26	10-Methylnonadecane	$C_{20}H_{42}$
25	11.466	0.18	4,6-Dimethyldodecane	$C_{14}H_{30}$
26	11.774	0.21	7,11-Dimethyl-10-Dodecen-1-Ol	$C_{14}H_{28}O$
27	11.882	0.20	(2,2,6,6-	$C_{11}H_{22}O$
28	12.224	0.34	1-Tridecanol	$C_{13}H_{28}O$
29	12.509	0.30	Beta.-Pinone	$C_9H_{14}O$
30	12.537	0.33	3,7,11,15-Tetramethyl-1-Hexadecanol	$C_{20}H_{42}O$
31	12.881	2.34	7,11-Dimethyl-10-Dodecen-1-Ol	$C_{14}H_{28}O$
32	15.297	2.24	(2,2,6,6-	$C_{11}H_{22}O$
33	15.588	0.54	(2-Cyclohexyl-1-Methylpropyl)	$C_{16}H_{30}$
34	16.547	0.38	1-Methyl-3-Propyl- Cyclooctan	$C_{12}H_{24}$
35	17.150	0.65	1,2,3,4,5,6-Hexaethylcyclohexane	$C_{18}H_{36}$
36	17.465	2.86	1,2,3,5-Tetraisopropylcyclohexane	$C_{18}H_{36}$

37	17.709	0.52	1,2,3,5-Tetraisopropylcyclohexane	$C_{18}H_{36}$
38	18.582	0.31	1-Methyl-3-Propylcyclooctane	$C_{12}H_{24}$
39	19.134	0.61	1,5-Diethyl-2,3-Dimethylcyclohexane	$C_{12}H_{24}$
40	19.432	2.86	1,2,3,5-Tetraisopropylcyclohexane	$C_{18}H_{36}$
41	19.634	0.61	1,2,3,5-Tetraisopropylcyclohexane	$C_{18}H_{36}$
42	20.438	0.29	1,2,3,5-Tetraisopropylcyclohexane	$C_{18}H_{36}$
43	20.659	0.26	1,2,3,4,5,6-Hexaethylcyclohexane	$C_{18}H_{36}$
44	20.943	0.66	1,2,3,4,5,6-Hexaethylcyclohexane	$C_{18}H_{36}$
45	20.943	0.66	1,2,3,4,5,6-Hexaethylcyclohexane	$C_{18}H_{36}$
46	21.227	1.99	1,2,3,5-Tetraisopropylcyclohexane	$C_{18}H_{36}$
47	21.408	0.44	1,2,3,5-Tetraisopropylcyclohexane	$C_{18}H_{36}$
48	22.141	0.22	1,2,3,5-Tetraisopropylcyclohexane	$C_{18}H_{36}$
49	22.610	0.55	1,2,3,4,5,6-Hexaethylcyclohexane	$C_{18}H_{36}$
50	22.878	1.54	1,2,3,5-Tetraisopropylcyclohexane	$C_{18}H_{36}$
51	23.043	0.28	1,2,3,5-Tetraisopropylcyclohexane	$C_{18}H_{36}$
52	24.151	0.44	1,2,3,4,5,6-Hexaethylcyclohexane	$C_{18}H_{36}$
53	24.559	0.20	Methyl Cis-11-Icosenoate	$C_{21}H_{40}O_2$
54	25.632	0.99	Cyclohexane,1,2,3,5-	$C_{18}H_{36}$
55	27.475	0.20	1,2,3,4,5,6-Hexaethylcyclohexane	$C_{18}H_{36}$
56	27.878	0.55	3,7,11,15-Tetramethyl-1-Hexadecanol	$C_{20}H_{42}O$

Table 5.4b GC-MS composition of oil obtained by the kaolin (KC) catalysed pyrolysis of polypropylene at 500 °C

Peak	**Retention Time In Minute**	**Area %**	**Name of The Component**	**Molecular Formula**
1	3.071	1.68	7-Methyl-4-Undecene	$C_{12}H_{24}$
2	3.900	1.30	(2E)-3,7-Dimethyl-2-Octene	$C_{10}H_{20}$
3	4.683	2.58	4-Methyl Decane	$C_{11}H_{24}$
4	4.744	1.81	2,5,5-Trimethylheptane	$C_{10}H_{22}$
5	5.483	3.57	2,4-Dimethyl-2-Decene	$C_{12}H_{24}$
6	5.543	2.90	2,4-Dimethyl-2-Decene	$C_{12}H_{24}$
7	5.771	3.59	2,4-Dimethyl-1-Decene	$C_{12}H_{24}$
8	5.836	3.62	1-Tridecanol	$C_{14}H_{30}O$
9	6.118	1.85	1,5-Diethyl-2,3-	$C_{12}H_{24}$
10	6.318	1.60	1,5-Diethyl-2,3-	$C_{12}H_{24}$
11	6.388	0.64	2-(2,3-Dimethylcyclopentyl)-1-	$C_{10}H_{20}O$
12	6.518	0.83	7-Methyl-1-Undecene	$C_{12}H_{24}$
13	6.617	0.70	1-Tridecanol	$C_{13}H_{28}O$
14	8.261	1.01	2-Isopropyl-5-Methyl-1-Hexanol	$C_{10}H_{22}O$
15	8.739	8.82	2,4-Dimethyl-2-Decene	$C_{12}H_{24}$
16	8.843	1.84	2,3,7-Trimethyl-2-Octene	$C_{11}H_{22}$

17	8.944	1.84	(3E)-2,2-Dimethyl-3-Decene	$C_{12}H_{24}$
18	9.081	7.39	2,3,7-Trimethyl-2-Octene	$C_{11}H_{22}$
19	9.144	7.24	Tridecanol	$C_{13}H_{28}O$
20	9.264	3.11	1-Tridecanol	$C_{13}H_{28}O$
21	9.382	4.98	2-Isopropyl-5-Methyl-1-	$C_{11}H_{24}O$
22	9.761	1.24	(3E)-2,2-Dimethyl-3-Decene	$C_{12}H_{24}$
23	11.618	2.26	2,4-Dimethyl-2-Decene	$C_{12}H_{24}$
24	12.007	1.80	Tridecanol	$C_{13}H_{28}O$
25	14.152	3.42	(3E)-2,2-Dimethyl-3-Decene	$C_{12}H_{24}$
26	14.427	2.24	(3E)-2,2-Dimethyl-3-Decene	$C_{12}H_{24}$
27	14.503	1.69	2-Butyl, 1-Octanol	$C_{12}H_{26}O$
28	14.527	1.72	2,4-Dimethyl-2-Decene	$C_{12}H_{24}$
29	14.878	1.58	1,5-Diethyl-2,3-	$C_{12}H_{24}$
30	16.410	1.65	1,2,3,4,5,6-	$C_{18}H_{36}$
31	18.452	1.53	1,2,3,4,5,6-	$C_{18}H_{36}$
32	18.832	1.01	1,5-Diethyl-2,3-	$C_{12}H_{24}$
33	19.131	0.78	1,5-Diethyl-2,3-	$C_{12}H_{24}$
34	20.312	0.97	1,2,3,4,5,6-	$C_{18}H_{36}$
35	22.607	0.53	1,2,3,5-	$C_{18}H_{36}$
36	24.145	0.41	1,2,3,5-	$C_{18}H_{36}$

Table 5.4c GC-MS composition of oil obtained by the 1M sulphuric acid treated kaolin (1MKC) catalysed pyrolysis of polypropylene at 500 °C

Peak	**Retention Time in minute**	**Area %**	**Name of the component**	**Molecular Formula**
1	3.775	3.49	3,7-Dimethyl-2-Octene	$C_{10}H_{20}$
2	3.801	12.33	2,6-Dimethyl-3-Octene	$C_{10}H_{20}$
3	3.902	15.93	4-Decene	$C_{10}H_{20}$
4	3.981	10.84	(3E)-2-Methyl-3-Nonene	$C_{10}H_{20}$
5	4.008	4.51	4,5-Dimethyloctane	$C_{10}H_{22}$
6	4.086	8.20	1,1,2,3-	$C_{10}H_{20}$
7	4.331	10.26	2,6-Dimethyl-1-Octene	$C_{10}H_{20}$
8	4.463	7.13	(3E)-3-Methyl-3-Nonene	$C_{10}H_{20}$
9	4.518	7.67	(3E)-2-Methyl-3-Nonene	$C_{10}H_{20}$
10	9.082	5.15	(3E)-2,2-Dimethyl-3-Decene	$C_{12}H_{24}$
11	9.141	2.87	Isotridecyl Alcohol	$C_{13}H_{28}O$

Table 5.4d GC-MS composition of oil obtained by the 5M sulphuric acid treated kaolin (5MKC) catalysed pyrolysis of polypropylene at 500 °C

Peak	**Retention Time in minute**	**Area %**	**Name of the component**	**Molecular Formula**
1	3.899	17.44	(3E)-3-Decene	$C_{10}H_{20}$
2	4.327	21.91	(4E)-4-Decene	$C_{10}H_{20}$
3	8.740	4.55	2,4-Dimethyl-2-Decene	$C_{12}H_{24}$
4	8.845	2.92	2,3,7-Trimethyl-2-Octene	$C_{11}H_{22}$
5	8.901	1.89	(2E)-3,7,11,15-Tetramethyl-2-	$C_{20}H_{40}$
6	8.944	3.28	(3E)-2,2-Dimethyl-3-Decene	$C_{12}H_{24}$
7	9.080	12.98	(3E)-2,2-Dimethyl-3-Decene	$C_{12}H_{24}$
8	9.380	4.68	1-Tridecanol	$C_{13}H_{28}O$
9	14.151	2.04	2,3,7-Trimethyl-2-Octene	$C_{11}H_{22}$
10	14.501	2.09	1-Tridecanol	$C_{13}H_{28}O$
11	14.526	1.20	(3E)-2,2-Dimethyl-3-Decene	$C_{12}H_{24}$
12	14.803	2.15	1-Tridecanol	$C_{13}H_{28}O$

4.3.3.3 Fuel properties of oil

All the fuel properties of the oil samples obtained in the catalytic pyrolysis of polypropylene obtained in the kaolin and Si-Al catalysed pyrolysis of polypropylene at optimum conditions are tested by prescribed IS methods are summarized in the Table 5.5. From the distillation report of the oil it is observed that, the boiling point range of the oil is 68-346 °C and 59-341°C using kaolin and Si-Al respectively, which infers the presence of mixture of different oil components such as gasoline, kerosene and diesel in the oil. Again, 30% oil recovery occurs at 160 °C, which is the boiling range of gasoline. Rest 70% must be in the range of kerosene and diesel. All the other fuel properties of the oil obtained using both the catalyst is almost similar and comparable to that of petro fuels. From this result, it can be concluded that the oil produced in the catalytic pyrolysis can be used as a substitute of petro fuels in engine.

Table 5.5 Fuel properties of the oil obtained at 500 °C with 1:3 catalyst to feed ratio

Tests	**Kaolin catalysed oil at 500^0C with plastic to catalyst ratio 3:1**	**Si-Al catalysed oil at 500^0C with plastic to catalyst ratio 3:1**
Colour	Yellow	Yellow
Specific Gravity@ 15 °C /15 °C	0.7777	0.7712
Density @ 15 °C in gm/cc	0.7771	0.7702
Kinematic Viscosity in Cst @ 30	2.27	2.21
Pour Point °C	< - 45	< - 45
Cloud Point °C	< - 45	< - 45
Gross calorific Value in Kcals/kg	11,256	11,262
Flash Point °C	< - 12	< - 12
Fire Point °C	< - 12	< - 12
Boiling point range (°C)	68-346	59-341

5.4 Conclusion

Samples of virgin and waste polypropylene are cracked thermally and catalytically in the presence of kaolin, acid treated kaolin, and silica alumina catalyst in a fixed bed reactor in the temperature range 400-550^0C in order to optimize the suitable conditions for the production of liquid fuel. The dependencies of process temperature, effect of catalyst, feed composition on yield of the fuel fraction were determined. It was observed that up to 450^0C, the major product of thermal pyrolysis was liquid oil and the major products at other higher temperatures (475-550^0C) are either viscous liquid or wax. The highest yield of pyrolysis liquid product was 82.85% by weight at 500^0C. Use of above catalysts decreased the reaction time, increased the yield of liquid fraction and also narrows the product distribution. Again the liquid fraction at all the temperature was low viscous liquid oil. The maximum oil yield using kaolin was 89.5wt.%, 91wt.% using silica alumina and 92wt.% using 5MKC (acid treated kaolin) at 500^0C. Si-Al performed better in this regard compared to kaolin. Both the catalysts have no effect with feed composition above 20:1. The oil obtained in this process was analyzed using FTIR and GC-MS for its composition. Different fuel properties of the oil studied by IS methods are identical with the different petro fuels.

On the basis of the obtained results, hypothetical continuous process of waste polypropylene plastics processing for engine fuel production can be presented. Further detailed kinetic studies would be necessary for a better understanding of the degradation mechanism and design of catalyst for proper uses of degraded products. In addition, natural kaolin being available abundantly could be a good candidate for its commercial application in the degradation of polypropylene.

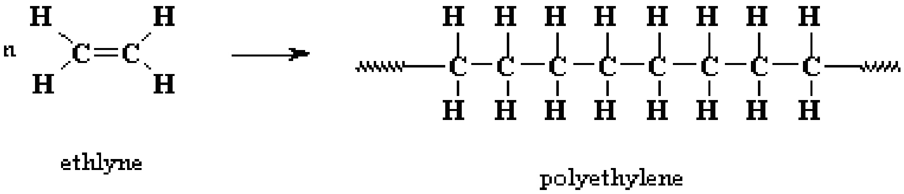
Chapter 6

Catalytic degradation of waste low density polyethylene to liquid fuel

CATALYTIC DEGRADATION OF WASTE LOW DENSITY POLYETHYLENE TO LIQUID FUEL

6.1 Introduction

Low-density polyethylene (**LDPE**) is a thermoplastic made from petroleum. It was the first grade of polyethylene, produced in 1933 by Imperial Chemical Industries (ICI) using a high pressure process via free radical polymerization. Its manufacture employs the same method even today.



LDPE is commonly recycled and has the number "4" as its recycling symbol. Despite competition from more modern polymers, it continues to be an important plastic grade. LDPE contains the chemical elements carbon and hydrogen. It is defined by a density range of 0.910–0.940 g/cm³. It is not reactive at room temperatures, except by strong oxidizing agents, and some solvents which cause swelling. It has good resistance (minor attack) to aldehydes, ketones and vegetable oils, limited resistance (moderate attack suitable for short-term use only) to aliphatic and aromatic hydrocarbons, mineral oils, and oxidizing agents and poor resistance, and not recommended for use with halogenated hydrocarbons. It can withstand temperatures of 80 °C continuously and 95 °C for a short time. LDPE has more branching (on about 2% of the carbon atoms) than HDPE, so its intermolecular forces (instantaneous-dipole induced-dipole attraction) are weaker, its tensile strength is lower, and its resilience is higher. Also, since its molecules are less tightly packed and less crystalline because of the side branches, its density is lower [284].

Global polyolefins demand is estimated at 111 million tons in 2009. The contributions of different polyolefins are LDPE=16%, LLDPE= 17%, PP=40% and HDPE=27%. The demand growth for LDPE in 2009 was negative 1.9 percent due to the effects of the global economic downturn and sustained competition from other polyethylenes like LLDPE and HDPE. In comparison, the demand for LLDPE grew an estimated 2.6 percent in 2009 after experiencing negative 4.2 percent growth in 2008 and it increased its penetration in the combined LLDPE/LDPE market from 50 percent in 2006 to 52 percent in 2009 as a result of competitively priced conventional and second generation grades. LLDPE demand is forecast to grow by 6.2 percent per year over the period to 2015. Global HDPE demand grew by 1.1 percent in 2009 compared to 2008. HDPE growth in the period 2009-2015 is projected to be approximately 5.5 percent, of which Asia and the Middle East are forecast to contribute over 40 percent of total growth. Total polyolefins capacity increased by 47 million tons in the period 1999-2009 with approximately seven million tons of additional capacity being available in 2009. 2010 should also see significant capacity increases as nine million tons of polyethylene is due to come on-stream, pending project delays and closures of existing uncompetitive assets. LDPE capacity additions up to 2009 have been minimal, but the period 2010-2015 is expected to see capacity growth as projects currently under construction come on-stream. This will have a profound effect on operating rates and 250 000 tons of speculative capacity will close in 2010. Up to 2015, closures are forecast of smaller, old and less competitive assets in the more mature markets of Western Europe, North America and Japan. 2009 saw 2.9 million tons of additional HDPE and LLDPE capacity after moderate increases earlier in the same decade. As with LDPE, significant capacity additions are due in the period 2010-2013 with corresponding negative speculative capacity following closures of uncompetitive facilities and unexpected project delays [283].

From the above data it is observed that, due to the widespread use but low life of, a large amount of such plastic wastes accumulate in the waste stream creating a number of environmental problems. Literature survey clearly portrays a number of studies of LDPE degradation using different catalysts for the liquefaction and gasification by catalytic degradation to lower the cost and time, and also improve quality of oil [97-100,103,285,286].

The present work involves the degradation of LDPE into fuel oil thermally and catalytically in presence of kaolin catalyst. The effect of temperature and catalyst on the rate of reaction, product distribution and quality has been studied. The oil produced in catalytic process was analyzed by FTIR and GC-MS for composition and also for the different fuel properties to understand the catalytic efficiency and also to predict the oil quality.

6.2 Experimental programme

The details about the waste LDPE and kaolin catalyst used in this experiment and also the experimental set up and procedure are summarized in the experimental section 3.

6.3 Results and discussion

6.3.1 TGA of LDPE samples

The Thermogravimetric curves for LDPE waste was depicted in figure 6.1. The degradation of LDPE plastics occur between 380-450 °C.

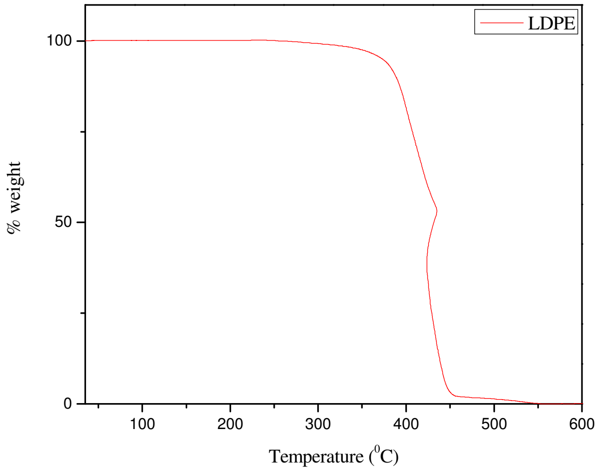


Figure 6.1 TGA of LDPE waste

Also the degradation temperature at which weight loss of 50% (T_{50}) takes place was about 440 °C and total weight loss occurred at 540 °C. So the pyrolysis reaction was carried out in the temperature range 400-500 °C.

6.3.2 Results of pyrolysis

6.3.2.1 Effect of temperature on product distribution in thermal pyrolysis: The degradation products were classified into three groups: condensable liquid and/or wax, gas and carbonaceous solid residue. Figure 6.2 shows the distribution of different fractions produced from thermal degradation of LDPE. The amount of condensable fraction increased with increase of temperature and the nature of the fraction depends on the temperature. At low temperatures (400 °C to 450 °C) this fraction was less viscous liquid oil, where as with increase of temperature the fraction became viscous and waxy (475 °C to 500 °C). The recovery of condensable fraction was low 30.8 wt.% at 400 °C, 71.45% at 450 °C, 78.1% at 475 °C and increased to highest yield of 86.65wt.% at 500 °C.

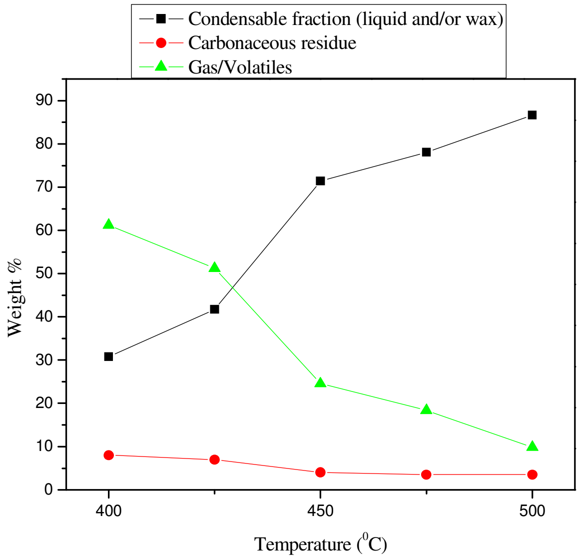


Figure 6.2 Distribution of product at different temperature

The gas/volatile fractions (which could not be collected at room temperature) decreased with increase of temperature. At low temperature the residence time was more (figure 6.3a), due to which secondary cracking of the pyrolysis product occur inside the reactor and resulted in large amount of highly volatile/gaseous product which was not possible at higher temperature due to low residence time of the reaction inside the reactor. Similarly, the low gas/volatile and high condensable fraction at higher temperature was due to improper cracking of the polymer, as the primary pyrolysis product of the reaction come out of the reactor due to high energy prior to further cracking to smaller molecule.

6.3.2.2 Effect of addition of kaolin catalyst: The product distribution completely changed when the same reaction was carried out in presence of kaolin as catalyst in different proportion. The amount of condensable fraction was more and reaction time was less in presence of catalyst at all the temperature range compared to thermal degradation (Figures 6.3a and 6.3b).

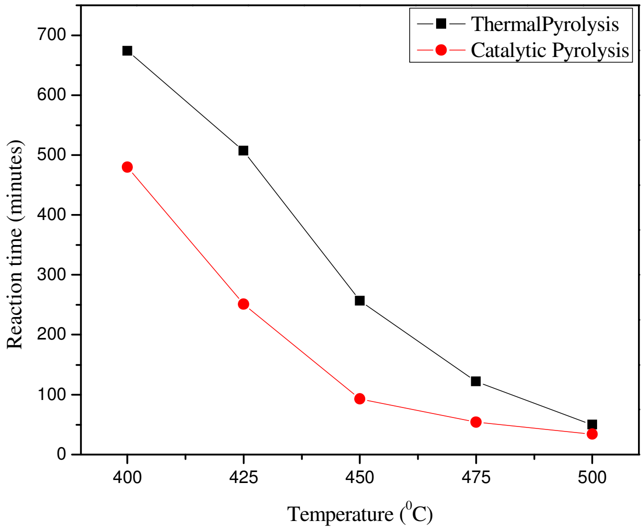


Figure 6.3a Effect of temperature on the reaction time in thermal and catalytic pyrolysis

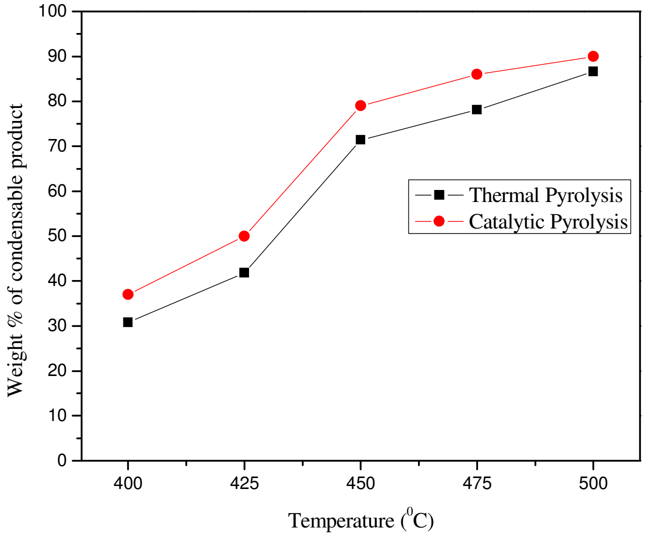


Figure 6.3b Effect of temperature on the yield of condensable fraction in thermal and catalytic pyrolysis

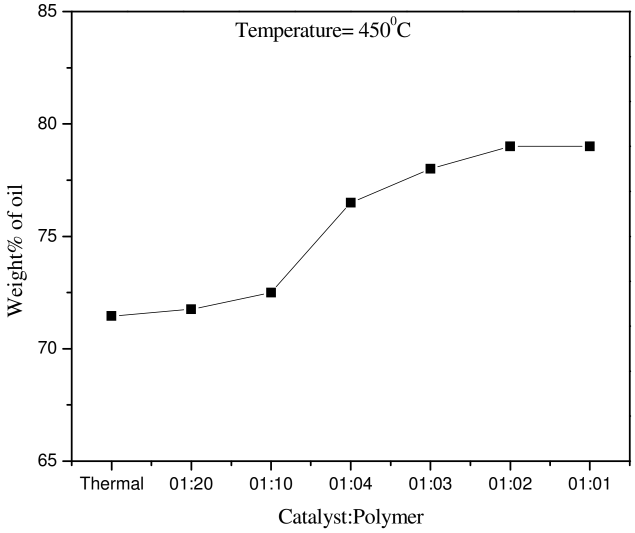


Figure 6.4 Effect of catalyst: polymer ratio on yield of liquid oil

The feed ratio (catalyst: plastic) also affect the yield of condensable fraction up to 1:20 after which no change in kinetics of the reaction was observed (Figure 6.4). The highest yield of liquid fraction at 450 °C was 79.5 wt.% with 1:2 catalyst to plastics ratio. Although the rate of reaction increased with increase in the amount of catalyst, but wax like product obtained even in presence of catalyst at temperature at 475 °C and above. Thus kaolin as a catalyst increased the yield as well as lowered the reaction time. The mesoporous surface of kaolin facilitates the cracking reaction.

6.3.2.3 Reusability of catalyst

The activity of kaolin catalyst was studied by re-using it for a number of times in the degradation of LDPE and the results are summarized in the Table 6.1. It is observed that the yield and quality of liquid oil product remain almost same up to four times repeated use of the catalyst and yield decreased at 5th time use. But the reaction time increased gradually for every repeated use. The decrease in catalytic activity may be explained due to the deposition of carbon over its surface. The kaolin after using for 5th run degradation was regenerated by calcinating it in a muffle furnace at 750 °C for one hour. The catalytic activity of regenerated catalyst was found to be almost same as that of the fresh kaolin. When the used catalysts were regenerated at high temperature, the deposited carbon burnt off and surface of catalyst become free of all the deposition.

6.3.3 Characterization of liquid products

The oil sample was characterized using FTIR and GC-MS for functional group composition and fuel properties to know its usability as a liquid engine fuel.

6.3.3.1 FTIR of oil: The Figure 6.5 indicates the FTIR of catalytic pyrolysed oil at 450 °C. The important assignments were summarized in the Table 6.2. This result indicates the presence of different hydrocarbons in the oil.

Table 6.1 Catalytic pyrolysis Feed (Kaolin: LDPE-1:2), Temperature- 450 °C

No of times re-used	Oil (weight %)	Reaction time in minutes	Specific gravity @15 °C/15 °C	Viscosity at 40 °C in Cst
Fresh	79.5	93	0.7794	1.89
1st time	79.5	94	0.7796	1.89
2nd time	78	99	0.7745	1.88
3rd time	77.5	104	0.7744	1.87
4th time	78	107	0.7712	1.88
5th time	74	112	0.7692	2.82
Regenerated catalyst	79	94	0.7782	2.84

Table 6.2 FTIR composition of LDPE oil obtained at optimum condition of kaolin catalysed pyrolysis

Wave number (cm^{-1})	Type of vibration	Nature of functional group
2956/2863,	C-H $_{\text{stretching}}$	Alkane
1643	C=C $_{\text{stretching}}$	Alkene
1651	C=C $_{\text{stretching}}$	Alkene
1460, 1376, 1302	C-H $_{\text{Scissoring and Bending}}$	Alkane
965, 908, 888, 721	C-H $_{\text{Bending}}$	Alkene
888	C-H $_{\text{out of plane bending}}$	Alkene

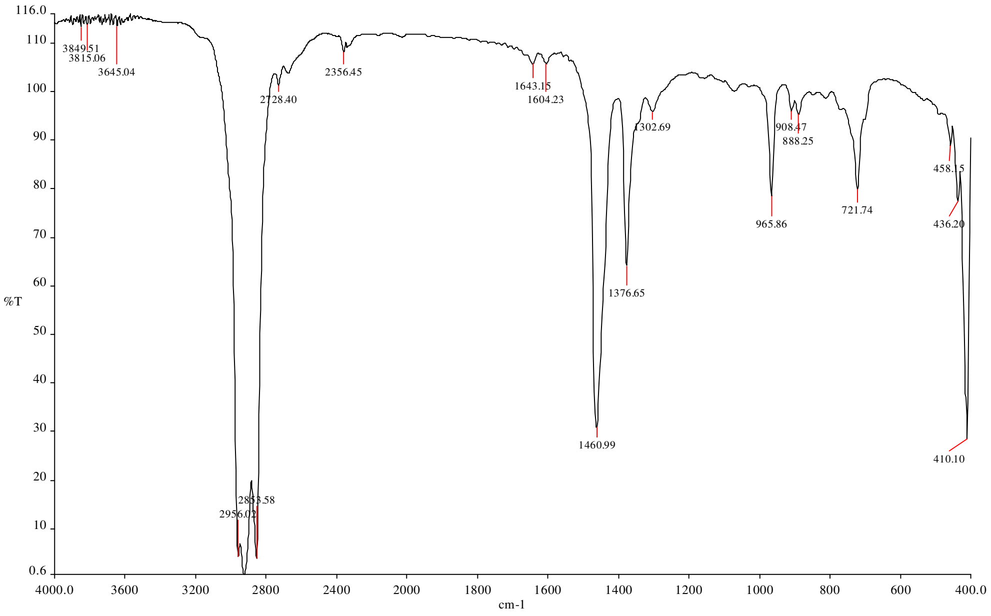


Figure 6.5 FTIR of kaolin catalysed LDPE oil obtained at optimum condition of kaolin catalysed pyrolysis

6.3.3.2 GC/MS of oil: The GC-MS plot of the oil obtained by the catalytic pyrolysis of LDPE at 450 °C with 1:2 catalysts to plastics ratio is given in the Figure 6.6.

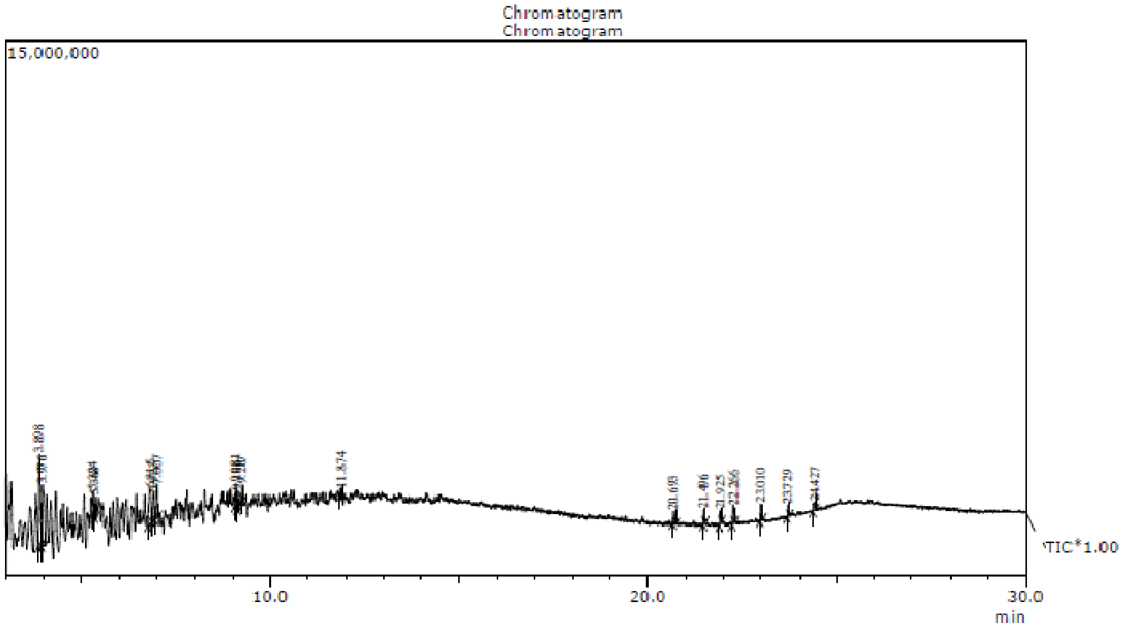


Figure 6.6 GC-MS of LDPE oil obtained at optimum condition of kaolin catalysed pyrolysis

The different components present in the oil are summarized in the Table 6.3. The oil mostly contains alkene and alkanes with carbon number C_{10}-C_{21}.

Table 6.3 GC-MS composition of LDPE oil obtained at optimum condition of kaolin catalysed pyrolysis

Peak	**Retention Time in minute**	**Area %**	**Name of the components**	**Molecular formula**
1	3.898	20.97	(3E)-3-Decene	$C_{10}H_{20}$
2	3.976	19.42	(3E)-3-Dodecene	$C_{12}H_{24}$
3	5.324	5.82	(4E)-7-Methyl-4-undecene	$C_{12}H_{24}$
4	5.368	2.56	5-Methyl-4-decene	$C_{11}H_{22}$
5	6.815	12.20	2,5-Dimethyl-2-undecene	$C_{13}H_{26}$
6	6.923	7.18	CIS-2-Dodecene	$C_{12}H_{24}$
7	7.007	6.70	2-Methyl-3-undecene	$C_{12}H_{24}$
8	9.081	4.92	TRANS-2,2-Dimethyl-3-	$C_{13}H_{26}$
9	9.136	3.06	1-Pentyl-2-	$C_{13}H_{26}$
10	9.267	1.86	(3E)-3-Tetradecene	$C_{14}H_{28}$
11	11.874	0.89	2-Methyldecan-1-ol	$C_{11}H_{24}O$
12	20.693	1.66	n-Heneicosane	$C_{21}H_{44}$
13	21.496	2.09	n-Heneicosane	$C_{21}H_{44}$
14	21.925	1.97	Hexadecene	$C_{16}H_{32}$
15	22.266	2.90	n-Hexatriacontane	$C_{36}H_{74}$
Total		100		

6.3.3.3 Fuel properties of oil: All the fuel properties of the oil were tested by prescribed IS methods and summarized in Table 6.4. From the distillation report of the oil it is observed that, the boiling range of the oil is 70-384 °C, which infers the presence of mixture of different oil components such as gasoline, kerosene and diesel in the oil. From this result, it is observed that the fuel properties of the catalytic pyrolysis oil matches with the properties of petro fuels. The liquid product obtained can be distilled to different fractions and be used after proper quality assurance.

Table 6.4 Fuel properties of LDPE oil

Properties	**Value**
Specific Gravity @ 15°C/15°C	0.7794
Density @ 15°C in kg/cc	0.7787
Kinematic Viscosity @ 40°C in Cst	1.89
Kinematic Viscosity @ 100°C in Cst	0.96
Pour Point °C	- 4
Cloud Point °C	4
Flash Point by Abel Method °C	-23
Fire Point Abel Method °C	- 20
Gross Calorific Value in Kcals/kg	10,131
Calculated Cetane Index	76
Distillation :	
Initial Boiling Point °C	70
Final Boiling Point °C	384

6.4 Conclusion

Kaolin catalysed and thermal degradation of low-density polyethylene waste was investigated in a temperature range of 400–500 °C in semi-batch reactor. The catalytic pyrolysis enables polyethylene to be converted into liquid, gas and wax with nearly 100% efficiency. The yield of oil increased by 11.96% and reaction time decreased by 63.8% at 450 °C with 1:2 catalyst to polymer ratio. Compositional analysis of the oil obtained in catalytic pyrolysis concludes that the products mainly consisted of paraffinic and olefinic compounds. Distillation data and other physicochemical properties for fuel oil are comparable with the standard results of physical tests for gasoline, kerosene and diesel fuel oil. So the oils are suitable to be used as fuel oil for different energy purposes. Thus, the catalytic pyrolysis of low-density polyethylene with kaolin leads to valuable resource recovery and reduction of waste problem.

Chapter 7

Pyrolysis of waste thermocol (polystyrene) to value added liquid products

PYROLYSIS OF WASTE THERMOCOL (POLYSTYRENE) TO VALUE ADDED LIQUID PRODUCTS

7.1 Introduction

Thermocol is the commercial name for the expanded polystyrene (EPS) and is produced from a mixture of about 90-95% polystyrene and 5-10% gaseous blowing agent, most commonly pentane or carbon dioxide. This is one of the highest consumed polymers produced due to its versatile application in different fields particularly in packaging. Due to its non biodegradability and high volume it constitutes a major fraction in municipality waste stream [287,288].

Recycling of waste plastics to fuel oil has been attractive and also commercially operated. In contrast to polyethylene and polypropylene, polystyrene can be thermally depolymerised to obtain the monomer styrene with a high selectivity. The oil, thus recovered, produces lots of carbon dioxide when burnt as fuel due to the high aromatic contents in it. Thus, several investigations have focused on the recovery of monomer when recycling of polystyrene is a question.

This work focuses on the pyrolysis of waste thermocol in a batch reactor in presence of kaolin and silica alumina catalyst and to optimize the reaction condition for enhanced yield of liquid fraction. This work also reports on the characterization of the liquid fraction using FTIR and detailed hydrocarbon analyzer for composition.

7.2 Experimental programme: The details about the materials used in this experiment such as waste thermocol, kaolin and silica alumina and their characterization are given in experimental section i.e. chapter 3

7.3 Results and Discussion

7.3.1 TGA of thermocol sample: The TG profile of impure polystyrene sample is presented in Figure 7.1. The polystyrene degradation pattern (TGA) show a very deep diminution above 310°C (10% weight loss) with weight loss of 50% and 90% taking place at 356 °C and 388 °C respectively.

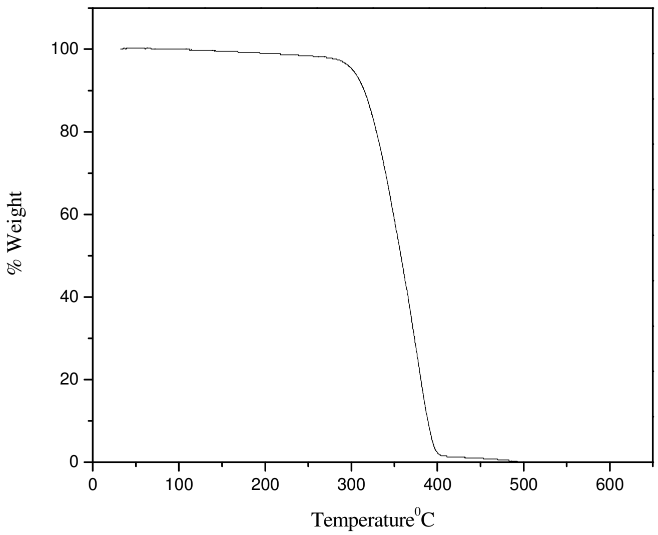


Figure 7.1 TGA of waste polystyrene

7.3.2 Results of pyrolysis

7.3.2.1 Effect of temperature on product distribution

The effect of temperature on the polystyrene degradation was studied in absence of catalyst. Figure 7.2 shows that the reaction time decreased with the increase in temperature and Figure 7.3 represents product distribution for pyrolysis of waste thermocol at different temperatures ranging from 350 °C to 550 °C in absence of the catalyst. The results show that the pyrolysis liquid yield increased from 50 wt.% to 93 wt. % as the temperature increased from 350 °C to 500 °C then decreased to 89 wt. % when the reaction temperature was increased to 550 °C. The gas/volatile fraction and solid residue yield decreased from 39 wt.% to 4 wt.% and 11 wt.% to 2.5 wt.% respectively when the pyrolysis temperature was increased from 350 °C to 500 °C.

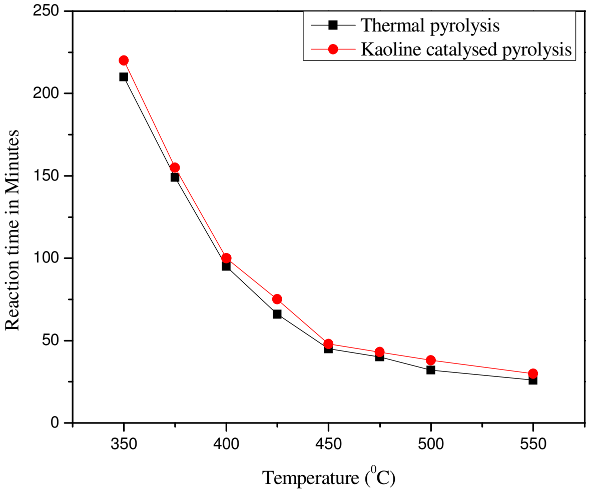


Figure 7.2 Effect of temperature on the reaction time

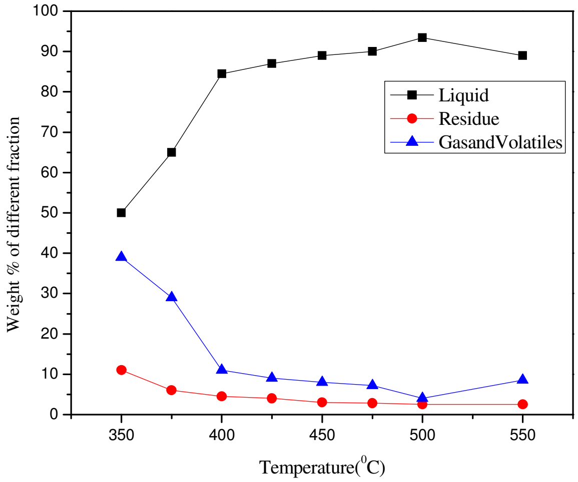


Figure 7.3 Effect of temperature on the product distribution

Comparatively, the residue amount was higher at lower temperature and less at higher temperature indicating that product formed at lower temperature could not get enough energy to come out of the reactor and thus stays for more time inside it. This leads to competitive cross linking reactions resulting in cross linked hard polymer residue and so the cracking of the resulting cross-linked polymer becomes more difficult. The increase of gas yield at higher temperature above 500 °C was due to secondary cracking of the pyrolysis liquid into gaseous product.

7.3.2.2 Effect of kaolin and silica alumina catalyst

To determine the effect of catalyst on the pyrolysis of thermocol, the experiments were conducted using two catalysts, silica alumina and kaolin clay using different plastics to catalyst ratio in solid phase contact mode and at different temperatures. The reaction time increased a little in presence of catalysts. The Figure 7.2 shows the effect of catalyst on product distribution with 1:10 kaolin clay catalyst to thermocol ratio and from the figure 7.4, it is observed that presence of Si-Al has no affect on the oil yield where as kaolin clay marginally increased the oil yield to 94.5wt.% at 500 °C.

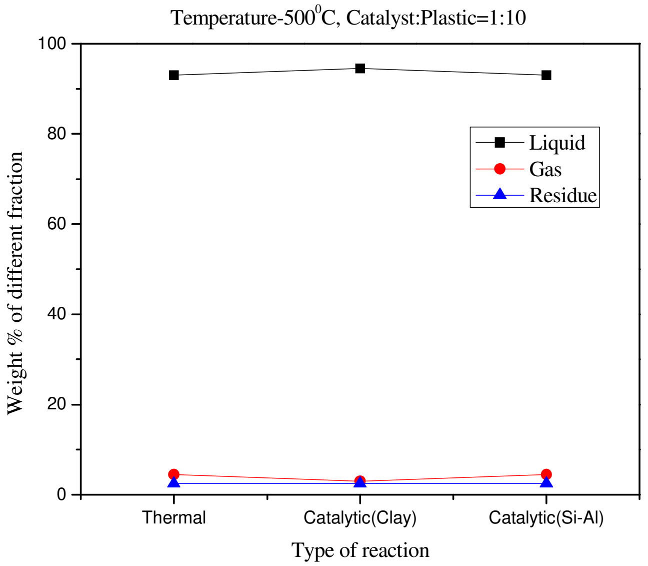


Figure 7.4 Distribution of product in thermal and catalytic reaction

Figure 7.5 indicates that the highest yield of liquid product is obtained in catalyst to thermocol ratio 1:10 at 500 °C. The enhancement of the yield of the liquid product in presence of kaolin clay is for the promoted cracking reactions by its low acid strength distribution and surface area. Whereas the low effectiveness of Si-Al for oil yield is due to promotion of cross linking reaction among adjacent polymeric chains or even inside the same polymer leading to slightly more residue formation owing to higher acidity compared to kaolin [137, 289]. However cross linking reaction is not much significant due to non-availability of sufficiently high acid sites. So the residue amount is not much higher as compared to the other two reactions.

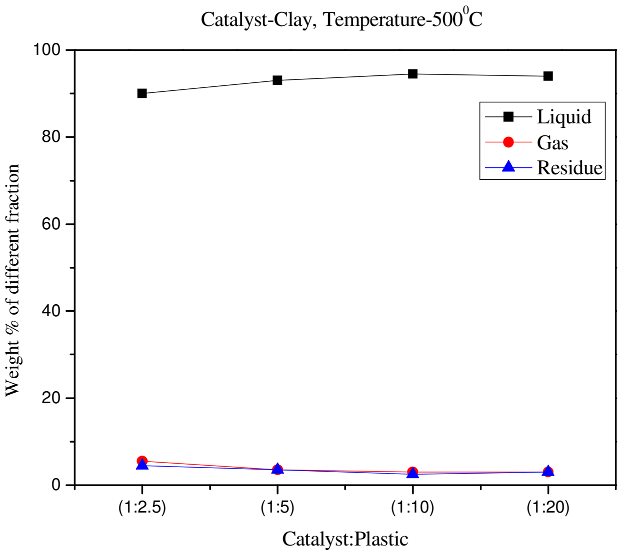


Figure 7.5 Effect of feed composition on the product distribution

7.3.3 Compositional analysis of pyrolysis oil

7.3.3.1 FTIR of oil

Figure 7.6 is the FTIR spectrum of the pyrolysis oil at 500 °C with some significant assignments. The presences of functional groups corresponding to different peaks in the spectra are summarized in Table 7.1. The table indicates that most of the components of the oil are aromatic in nature.

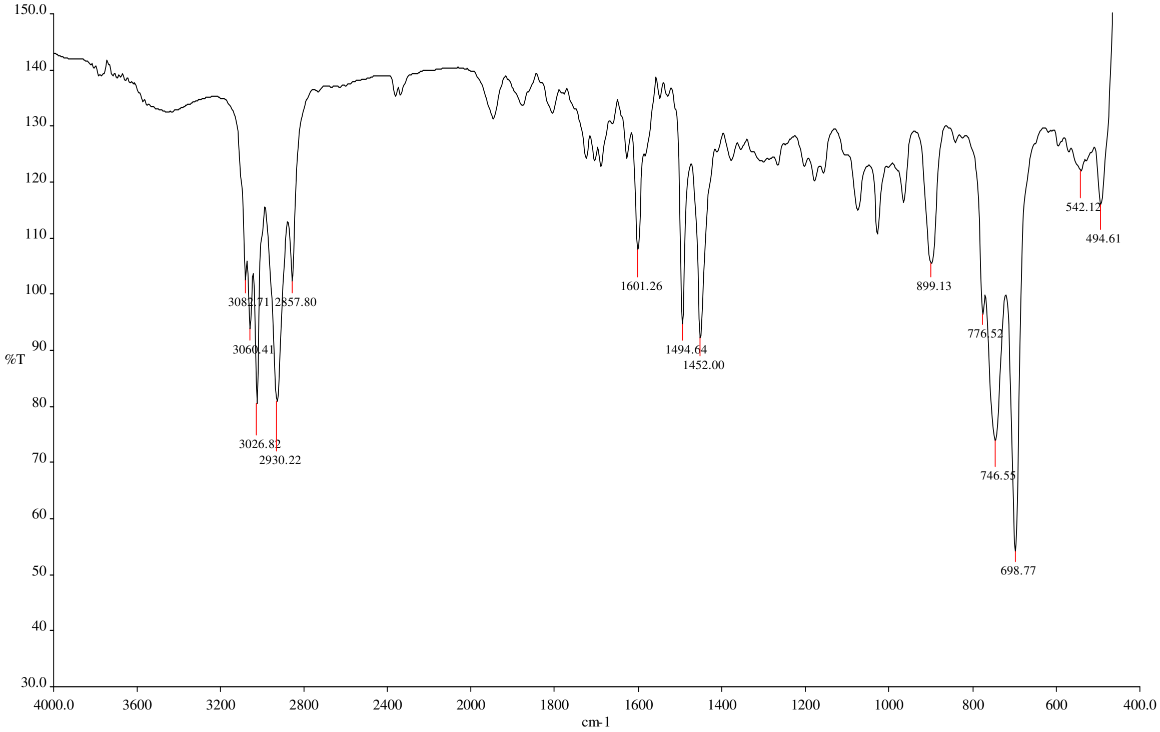


Figure 7.6 FTIR spectra of kaolin catalysed PS oil

Table 7.1 FTIR assignments of thermal pyrolysis PS oil.

Wave number (cm^{-}	Band	Assignments
2857, 2930	$\text{C-H}_{\text{stretching}}$	Alkane
3026, 3060,3082	$\text{C-H}_{\text{stretching}}$	Aromatic ring
1452, 1494	$\text{C=C}_{\text{stretching}}$	Alkene
899, 965	$\text{C-H}_{\text{bending}}$	Aromatic ring
689,746, 776	$\text{C-H}_{\text{bending}}$	Aromatic ring

7.3.3.2 DHA of oil

Table 7.2 shows the PIONA (paraffins, isoparaffins, olefins, naphthenes, aromatics) distribution of liquid products obtained in DHA. This shows that the major components in the liquid are aromatics. Slight increase in the aliphatic components are observed in silica alumina catalysed reaction due to severe cracking.

Table 7.2 PIONA Distribution in liquid products obtained at 500 °C

Type of Reaction	Distribution of different component in liquid (wt.%)				
	n-Paraffins	Iso paraffins	Olefins	Naphthenes	Aromatics
Thermal	0.01	0.29	0.27	0.18	99.25
Catalytic (Clay)	0.06	0.98	0.12	0.20	98.64
Catalytic (Si-Al)	0.16	2.56	0.81	0.82	95.65

Table 7.3 Composition of pyrolysis oil at 500 °C

Composition (wt. %)	Thermal	Catalytic Kaolin	Catalytic Silica Alumina
Benzene	1.48	3.64	7.06
Toluene	2.9	8.1	7.21
Ethyl Benzene	5.1	11.71	24.73
Styrene	77.58	64.65	48.85
Methyl styrene	8.62	9.13	9.1
Xylene	0	0	0.4
C9- aromatics	1.12	0.2	1.3
C10+-aromatics	3.2	2.52	1.35

Table 7.3 Composition of the PS oil.

Both thermal and catalytic degradation are shown mostly aromatic compounds, as they are stable enough and difficult to be further cracked or hydrogenated to paraffins or olefins. Thermal degradation shows the highest selectivity of styrene (77.58 wt.%) which has been reduced to 63.65 wt.% in presence of kaolin clay and 48.85 wt.% in presence of Si-Al. Silica-alumina show a considerable increase in the amount of isoparaffins compared to thermal and kaolin clay catalysed pyrolysis. The amount of ethyl benzene is the lowest in thermal degradation (5.1wt. %) and increased to 12.71 wt.% and 24.73 wt.% using kaolin clay and silica alumina respectively . Thermal degradation of polystyrene starts with a random initiation to form polymer macro-radicals followed by different secondary reactions such as β-session, intermolecular transfer, intramolecular transfer (competing backbiting) and disproportionation reactions, which depends on the temperature [290-292]. The main products are styrene and its corresponding dimers and trimers. Whereas, the acid catalyzed cracking of polystyrene is of carbenium nature [290]. The most likely reaction pathway involves the attack of proton associated with different acid sites to the aromatic rings of polystyrene, due to the reactivity of its side phenyl groups towards electrophilic reagents. The resulting carbenium may undergo β-scission followed by a hydrogen transfer. The possible production pathways of benzene, styrene, methyl styrene, toluene, ethyl benzene etc. are reported by Audisio et al.[135]. The lower yields of styrene obtained on solid acids than those obtained by simple thermal degradation are partially due to its oligomerization reactions and the resulting oligomeric cations, in turn, would be cracked; thus, depending on the relative importance of the various alternatives of the catalytic cracking pathways, some of the main reaction products (benzene, toluene, styrene, indane and derivatives) obtained [293]. Secondly, high acidity also accelerates the hydrogenation styrene to ethyl benzene [294, 295]. As Si-Al has high acidity and surface area compared to kaolin, the cracking and hydrogenation of styrene over its surface is more, which is less achievable on kaolin clay surface. This leads to the increased production of ethyl benzene and low selectivity of styrene. The high selectivity of toluene in kaolin clay catalysed reaction compared to thermal and silica alumina catalysed reaction is due to its low acidity which favors oligomerization of styrene and subsequent cracking to toluene.

8 Conclusion

Study shows that a simple batch pyrolysis method could convert the waste thermocol in the temperature range 350-550 °C using kaolin clay and silica alumina catalyst to value added liquid products. The reaction was affected by temperature, type of catalyst and amount of catalyst. The optimum temperature for obtaining highest yield of liquid fraction (93 wt.%) in thermal pyrolysis is 500 °C. The liquid fraction further increase to 94.5 wt. % by the addition of kaolin clay as catalyst in the 1:10 catalyst to polymer ratio at 500 °C. The yield of liquid fraction is unaffected by the presence of silica alumina. FTIR and DHA analysis of the liquid showed that the liquid products consist of mostly aromatic hydrocarbons. The product distribution of the liquid fraction is significantly affected by the presence of both the catalysts. While styrene is the major product in both thermal and catalytic degradation over the solid catalysts, significant differences are observed in the different aromatic products distribution in presence of catalysts. Both the catalysts show a decrease of styrene and an increased selectivity towards ethyl benzene compared to thermal degradation. Silica alumina shows the lowest amount of styrene and a high increase of ethyl benzene. The liquid product obtained in the thermal pyrolysis thus may preferably be used for styrene monomer recovery, where as the oil obtained in catalytic pyrolysis which contain less amount of styrene and comparatively higher amount of other components (such as ethyl benzene etc.) may be used to obtain these components along with the styrene monomer. The oil obtained from both the thermal and catalytic process may also be used as a blended fuel or feedstock for petroleum refining industry.

Chapter 8

Performance and emission characteristics of DI diesel engine using waste plastic oil

PERFORMANCE AND EMISSION CHARACTERISTICS OF A DI DIESEL ENGINE USING WASTE PLASTIC OIL

8.1 Introduction

Diesel engines are the most preferred power plants due to their excellent drivability and higher thermal efficiency. Despite their advantages, they emit high levels of oxides of nitrogen (NO_x) and smoke which will have an adverse effect on human health. Hence stringent emission norms and the depletion of petroleum fuels have necessitated the search for alternate fuels for diesel engines [296]. On the other hand, the disposal of waste plastic are becoming more and more difficult and need urgent a sustainable approach to recycle or reuse them. Chemical recycling of waste plastics to oil is one of the suitable methods of waste treatment and reuse. Attention is also focused on using oil derived from waste plastics in diesel engines.

Fuels like alcohol, biodiesel, plastic oil and tyre oil, bio oil etc. are some of the potential alternative fuels for the internal combustion engines [297,298,299]. These fuels have been studied as an alternate fuel directly or in blends in diesel engine and the results of performance of some such fuels studied by different researches are summarized below.

Performance, emission and combustion characteristics of a light duty DI diesel engine run on wood pyrolysis oil (WPO) was reported by [300]. In this, a several long run tests were performed on a single cylinder with blends of WPO with different percentage of oxygenated compounds, micro emulsions of WPO in diesel fuel and the results were compared with diesel fuel. It was reported that reliable operation was achieved with 44% of WPO in diethylene glycol dimethyl ether (diglyme). Similar results were obtained with two different emulsions with 30% of WPO in diesel fuel. Residuals were occasionally found to stick on the nozzle stem and sac volume. No trace of corrosion was detected. From the emissions point of view WPO diglyme blends produced lower hydrocarbon (HC) and oxides of nitrogen (NO_x) than diesel fuel with comparable carbon monoxide (CO). It was also reported that no major trouble on the critical components of the engine was noticed.

Studies have been carried out on the feasibility of using wood pyrolysis oil (WPO) as an alternate fuel in internal combustion engines [301]. It was observed that the plain wood oil did not produce self ignition in conventional engine and also resulted in poor spray characteristics. The major drawbacks of the use of wood oil in diesel engine were excessive carbon deposits, injection system clamping, incompatibility with engine lubricants and high acid aggressiveness. It was suggested that fuel improvement would be necessary if WPO is used as an alternate fuel for diesel engine.

S. Murugan et al. evaluated the performance and emission characteristics of a single cylinder direct injection diesel engine fuelled by 10, 30 and 50 percent blends of Tyre pyrolysis oil (TPO) with diesel fuel (DF). The combustion parameters such as heat release rate, cylinder peak pressure and maximum rate of pressure rise were also analyzed. Results showed that the brake thermal efficiency of the engine fuelled by TPO-DF blends increased with increase in blend concentration and higher than DF. NO_x, HC, CO and Smoke emissions were found to be higher at higher loads due to high aromatic content and longer ignition delay. The cylinder peak pressure increased from 71.4 bar to 73.8 bar. The ignition delays were longer than DF [302].

The crude tyre pyrolysis oil was desulphurised and distilled to improve the properties and studied the performance, emission and combustion characteristics of it on a single cylinder four-stroke air cooled engine fuelled with two different blends, 30% tyre pyrolysis oil and 70% diesel fuel (TPO 30) and 30% distilled tyre pyrolysis oil and 70% diesel fuel (DTPO 30). The results of the studies indicated that NO_x is reduced by about 8% compared to tire pyrolysis oil and by about 10% compared to diesel fuel. Hydrocarbon emission is reduced by about 2% compared to TPO 30 operation. Smoke increased for DTPO 30 compared to TPO 30 and diesel fuel [303].

The performance, emission and combustion characteristics of a single cylinder four stroke air cooled DI diesel engine was studied using the distilled tyre pyrolysis oil (DTPO). Engine was able to run up to 90% DTPO and 10% DF (DTPO90). Engine failed to run satisfactorily with 100% DTPO. Brake thermal efficiency increased with increase in percentage of DTPO blends but lesser than DF. About 3% drop in the thermal efficiency was noticed. NO_x was lower by about 21% for DTPO80 and 18% lower in DTPO90 operation than that of DF operation. HC and CO were higher than DF. This may be due to the presence of unsaturated hydrocarbon in the DTPO. Smoke was higher for DTPO-DF blends compared to DF. Longer ignition delay was noticed for DTPO-DF blends compared to DF. It was 2–2.5 °CA longer for DTPO-DF blends compared to DF at full load. Cylinder peak pressures were higher by about 1.6 bar and 2 bar for DTPO80 and DTPO90 respectively than that of DF operation [304].

Waste plastic oil was tested as a fuel in a D.I. diesel engine and its performance characteristics were analyzed and compared with diesel fuel (DF) operation. It was observed that the engine could operate with 100% waste plastic oil and can be used as fuel in diesel engines. Oxides of nitrogen (NO_x) were higher by about 25% and carbon monoxide (CO) increased by 5% for waste plastic oil operation compared to diesel fuel (DF) operation. Hydrocarbon was higher by about 15%. Smoke increased by 40% at full load with waste plastic oil compared to DF. Engine fueled with waste plastic oil showed higher thermal efficiency up to 80% of the full load and the exhaust gas temperature was higher at all loads compared to DF operation [305].

waste plastic oil was used as an alternate fuel in a DI diesel engine without any modification to investigate the performance, emission and combustion characteristics of a single cylinder, four-stroke, air cooled DI diesel engine. The experimental results have showed a stable performance with brake thermal efficiency similar to that of diesel and Engine was able to run with 100% waste plastic oil. Ignition delay was longer by about 2.5 °CA in the case of waste plastic oil compared to diesel. Engine fueled with waste plastic oil showed higher thermal efficiency up to 75% of the rated power. Carbon dioxide and unburned hydrocarbon were marginally higher than that of the diesel baseline. The toxic gas carbon monoxide emission of waste plastic oil was higher than diesel. Smoke reduced by about 40% to 50% in waste plastic oil at all loads [306].

The influence of injection timing on the performance, emission and combustion characteristics of a single cylinder, four stroke, and direct injection diesel engine has been experimentally investigated using waste plastic oil as a fuel. Engine was able to run with

100% waste plastic oil when the injection timing was retarded. Tests were performed at four injection timings (23, 20, 17 and 14 BTDC). When compared to the standard injection timing of 23 BTDC the retarded injection timing of 14 BTDC resulted in decreased oxides of nitrogen, carbon monoxide and unburned hydrocarbon while the brake thermal efficiency, carbon dioxide and smoke increased under all the test conditions. Cylinder peak pressure was found to be marginally lower. Brake thermal efficiency of the engine fueled with waste plastic oil with retarded injection timing was found to be higher. Intensity smoke increased by 35% at full load with retarded injection timing in waste plastic oil operation compared to standard injection timing [296].

The effect of cooled exhaust gas recirculation (EGR) on four stroke, single cylinder, and direct injection (DI) diesel engine using 100% waste plastic oil was studied. Experimental results showed higher oxides of nitrogen emissions when fueled with waste plastic oil without EGR. NO_x emissions were reduced when the engine was operated with cooled EGR. The EGR level was optimized as 20% based on significant reduction in NO_x emissions, minimum possible smoke, CO, HC emissions and comparable brake thermal efficiency. Smoke emissions of waste plastic oil were higher at all loads. Combustion parameters were found to be comparable with and without EGR. Compression ignition engines run on waste plastic oil are found to emit higher oxides of nitrogen. The brake thermal efficiency in waste plastic oil varies from 14% to 30% without EGR compared to 13–29% with 20% EGR. At full load the brake thermal efficiency decreased with increase in EGR flow rate due to high EGR percentages that result in larger replacement of air [307].

This work includes the study of performance and emission of plastic oil obtained by kaolin catalysed pyrolysis of waste polypropylene in a laboratory batch reactor in a DI diesel engine.

8.2 Preparation of waste plastic oil and its characterization

The detail of the procedure of preparation and characterization of plastic oil from waste polypropylene (used plastic disposable glasses) using kaolin at 500 °C with plastics to catalyst ratio 3:1 in a batch reactor has been mentioned in the sections 3.2.4, 5.3.3.2 and

5.3.3.3. The fuel properties of the oil summarized in the table infers that, it can be used as engine oil.

8.3 Experimental set up and test detail

The schematic representation of the experimental set up is shown in Figure 8.1. The research engine specifications are given in Table 8.1. The engine was coupled to an electrical dynamometer to provide the engine load. An air box with U-tube manometer connected to the intake of the engine. The air consumption of the engine was measured with the help of U-tube manometer. Fuel consumption was measured with the help of a burette fitted with a three way cock. One side of the three way cock is connected with fuel line from fuel tank and the second end is connected to the burette and the third way is connected to the fuel supply system. The fuel flow rate was measured on volumetric basis using a stopwatch. Chromel alumel thermocouple in conjunction with a digital temperature indicator was used to measure the exhaust gas temperature. Exhaust emissions from the engine were measured with the help of AVL digas analyzer and smoke density was measured by AVL 437 C diesel smoke meter. A probe was used to receive sample of exhaust gas from the engine. All the experiments were conducted at the rated engine speed of 1500 rpm. Waste plastic oil (WPO) - Diesel Blends of 10%, 20% 30%, 40% and 50% were used to test in the engine. These blends are denoted as 10% B WPO, 20% B WPO, 30% B WPO, 40% B WPO, and 50% B WPO, where the numbers indicate the percentage of WPO in the blend. Higher blends were not used due to detonation in the engine. All the tests were conducted by starting the engine with diesel only and then switched over to run with waste plastic oil blend. At the end of the test, the engine was run for some time with diesel to flush out the waste plastic oil from the fuel line and the injection system.

8.4 Results and discussion

8.4.1 Engine performance: The engine was run up to maximum 50% blend and it started giving noise and vibration at and above this blend. So the different engine performance parameters such brake thermal efficiency, exhaust gas temperature, brake specific fuel consumption etc. were calculated up to 50% blended oil and compared with that of diesel.

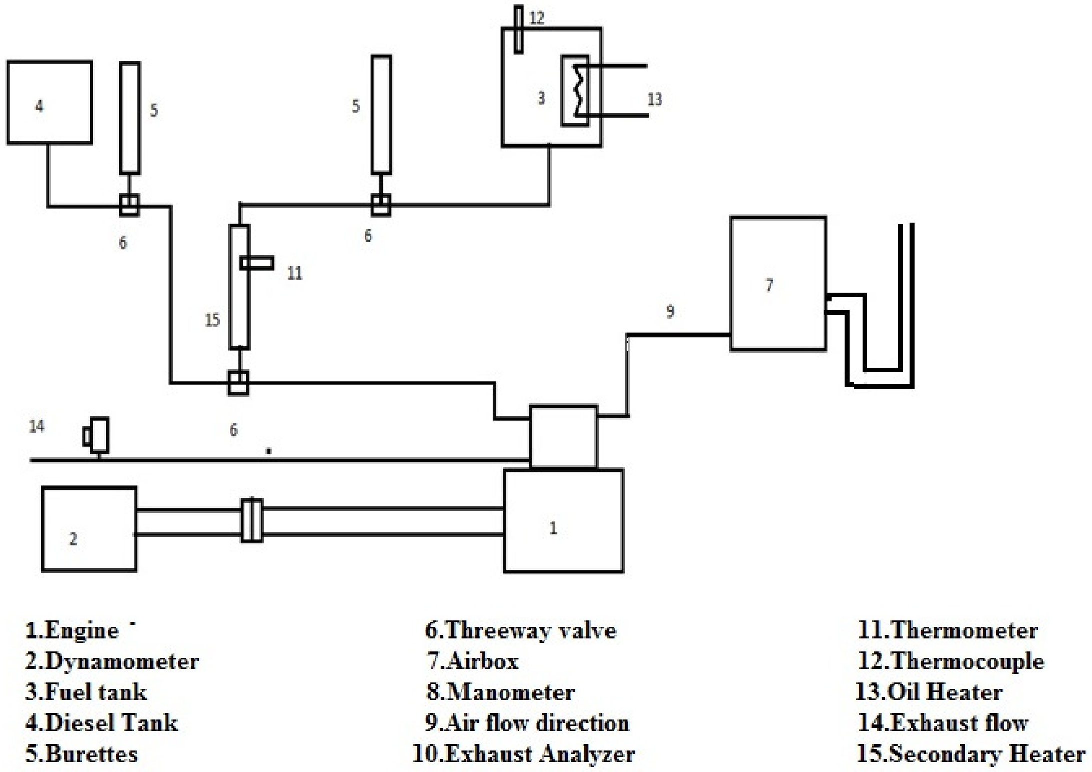


Figure 8.1 Schematic representation of the diesel engine

Table 8.1 Engine specification

Make of model	**cometVCT-10**
Engine type	Four-stroke, CI, direct injection, water cooled twin cylinder,
Bore (mm)	80
Stroke (mm)	110
Compression ratio	17.5:1
Rated power@1500rpm	7.4
Nozzle opening pressure	200
Injection timing (CA)	23 °BTDC

8.4.1.1 Brake thermal efficiency

The variation of brake thermal efficiency with load is shown in Figure 8.2. It can be observed from the figure that the thermal efficiency is 20.83% at full load for diesel. However when the engine is fueled with WPO-diesel blends such as 10% B WPO, 20% B WPO, 30% B WPO, 40% B WPO, and 50% B WPO, it gives the thermal efficiency of 19.96%, 19.91%, 19.14%, 19.18% and 18.91% respectively at full load. Again, it is apparent that the brake thermal efficiency of the waste plastic oil blend is closer or slightly higher to diesel up to 80% load. This may be due to higher calorific value of WPO-diesel blend than diesel as the calorific value of WPO is higher than diesel although the exhaust gas temperature is almost same or marginally higher in case of blend than diesel. Again at full load, the exhaust gas temperature and the heat release rate are marginally higher for waste plastic oil compared to diesel [308]. This may result in higher heat losses and lower brake thermal efficiency in the case of waste plastic oil blend.

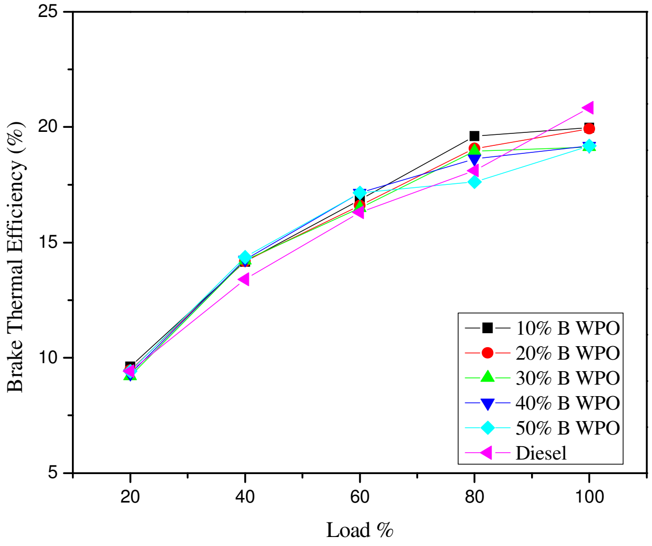


Figure 8.2 Variation of thermal efficiency with load

8.4.1.2 Exhaust gas temperature

The variation of exhaust gas temperature with load is shown in Figure 8.3. The exhaust gas temperature varies from 350 °C at low load to 490 °C at full load for diesel whereas in the case of WPO-diesel blends it varies from 340 °C to 490 °C for 10% B WPO, 350 °C to 500 °C for 20% B WPO, 340 °C to 500 °C for 30% B WPO, 360 °C to 520 °C for 40% B WPO, and 370 °C to 530 °C for 50% B WPO, as the load increased from 20% to 100%. The increase in exhaust gas temperature with engine load is due to the more amount of fuel required by engine to generate the extra power needed to take up the additional loading [309,310]. It is observed that, the exhaust gas temperature in the case of different blends is marginally higher as compared to diesel. The increased exhaust gas temperature may be due to higher heat release owing to ignition delay leading to detonation.

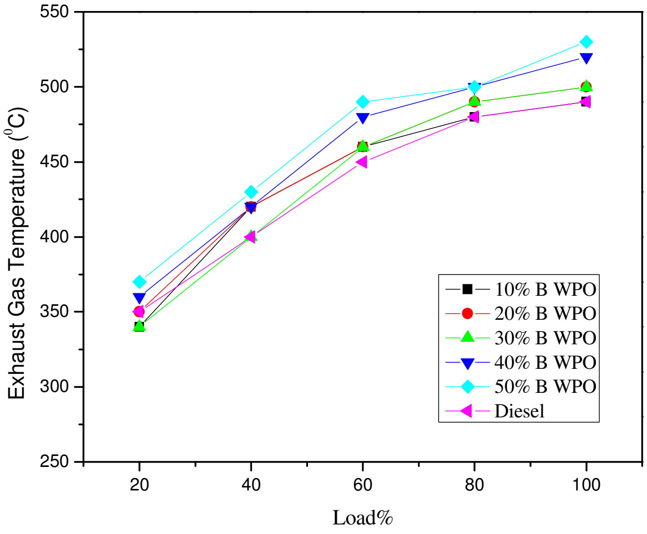


Figure 8.3 Variation of exhaust gas temperature with load

8.4.1.3 Brake specific fuel consumption

Brake specific fuel consumption measures how efficiently an engine is using the fuel supplied to produce work. Figure 8.4 shows the comparisons of the brake specific fuel consumption of WPO-diesel blend with diesel. The brake specific fuel consumption varies from 0.853 kg/kWh at low load to 0.385 kg/kWh at full load for diesel, and it varies from 0.831 kg/kWh to 0.379 kg/kWh for 10% B WPO, 0.842 kg/kWh to 0.380 kg/kWh for 20% B WPO, 0.842 kg/kWh to 0.380 kg/kWh for 30% B WPO, 0.847 kg/kWh to 0.387 kg/kWh for 40% B WPO, and 0.847 kg/kWh to 0.388 kg/kWh for 50% B WPO. It is clear from the graph that as the load increases the BSFC decreases for all fuels as expected. At the same time, it can be seen that BSFC is marginally less with increase in the concentration of WPO in WPO-Diesel blend. This behavior is obvious since the engine will consume less fuel with blends due to high calorific value of WPO [304].

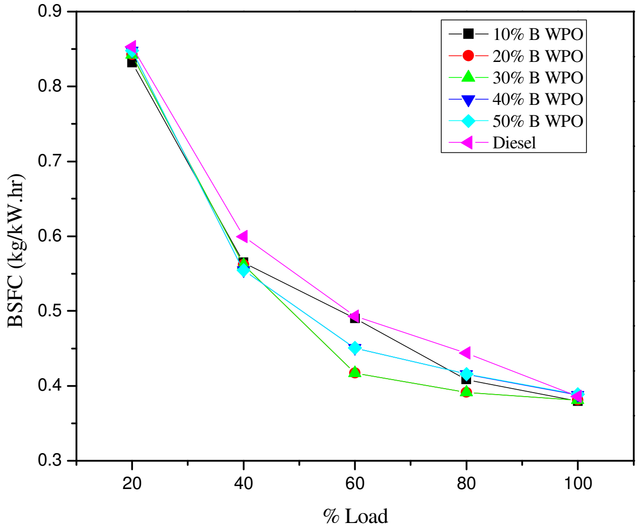


Figure 8.4 Variation of BSFC with load

8.4.2 Emission analysis

Internal combustion engine emissions have been major contributor to air pollution. Vehicle emissions are divided into two groups; regulated and unregulated pollutants. Regulated pollutants are carbon monoxide (CO), oxides of nitrogen (NO_x), and unburned hydrocarbon (HC) fuel or partly oxidized HC. The levels of emissions of these pollutants are specified by legislations. Unregulated pollutants include polycyclic aromatic hydrocarbons (PAHCs), methane, aldehydes, carbon dioxide, other trace organic emissions and carbon deposits. Carbon deposits increase engine wear, while some of the PAH isomers are known to be carcinogenic and mutagenic. The comparison of results of different emissions using different waste plastic oil blend and diesel is summarized below.

8.4.2.1 Oxides of nitrogen: The oxides of nitrogen in the emissions contain nitric oxide (NO) and nitrogen dioxide (NO_2).

The formation of NO_x is highly dependent on in-cylinder temperature, stoichiometry, oxygen concentration and residence time for the reactions to take place [311].

Figure 8.5 shows the comparison of oxides of nitrogen with load. It can be noticed that the NO_x emission increases in the waste plastic oil operation. NO_x varies from 8 ppm at 20% load to 45 ppm at 100% load for diesel and from 13 ppm at 20% load to 130 ppm at 100% load for 50% B WPO. It varies from 9 ppm to 49 ppm for 10% B WPO, 9ppm to 52 ppm for 20% B WPO, 12ppm to 114ppm for 30% B WPO and 12ppm to 118ppm for 40% B WPO with lower and higher load. CI engines are always run lean and emit high amounts of NO_x nonetheless. At high load, with higher peak pressures, and hence temperatures, and larger regions of close to stoichiometric burned gas, NO levels increase [312]. The reason for the increased NO_x in WPO blends compared to diesel may be due to the higher heat release rate and higher combustion temperature (due to higher ignition delay) which is attributed to the presence of some fraction of petrol range fraction. Increased ignition delay of waste plastic oil promotes premixed combustion, by allowing more time for fuel to be injected prior to ignition. Again, plastic oil contains some oxygenated hydrocarbons which promote better combustion and thus the formation of NO_x in exhaust.

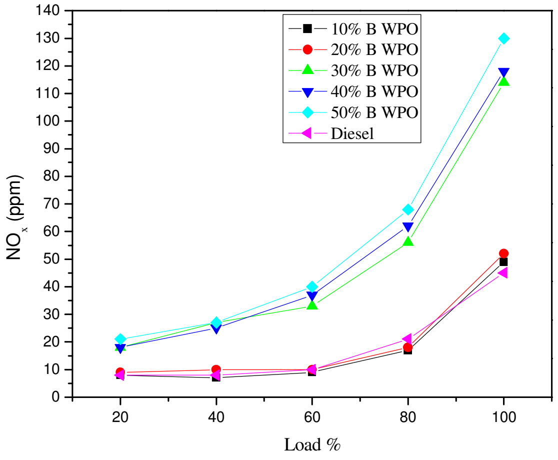


Figure 8.5 Variation of NO_x with load

8.4.2.2 Unburned hydrocarbon

The term hydrocarbon means organic compounds in the gaseous state; solid hydrocarbons are part of the particulate matter. Typically, unburned hydrocarbons are a serious problem at light loads in CI engines [313]. Unburned hydrocarbon is a useful measure of combustion inefficiency. Unburned hydrocarbon consists of fuel that is incompletely burned. At light load, large amounts of excess air and low exhaust temperature and lean fuel air mixture regions may survive to escape into the exhaust. The variation of unburned hydrocarbon with load for tested fuels is shown in Figure 8.6.

The hydrocarbon emission is increasing with the increase in percentage of WPO in the blend. HC varies from 9ppm at no load to 12ppm at full load for DF, and it varies from 38ppm at no load to 47ppm at full load for 50% B WPO. Similarly for 10% B WPO, it varies from 9ppm at low load to14ppm at full load, for 20% B WPO it varies from 10ppm to 16ppm, for 30% B WPO it varies from 19ppm to 33ppm and for 40% B WPO it varies from 30ppm to 47ppm from no load to full load. At no load high fuel supply lead to higher hydrocarbon, at lighter loads due to charge homogeneity and higher oxygen availability, the unburned hydrocarbon level is less, whereas at higher load ranges due to higher quantity of fuel admission, unburned hydrocarbon increases.

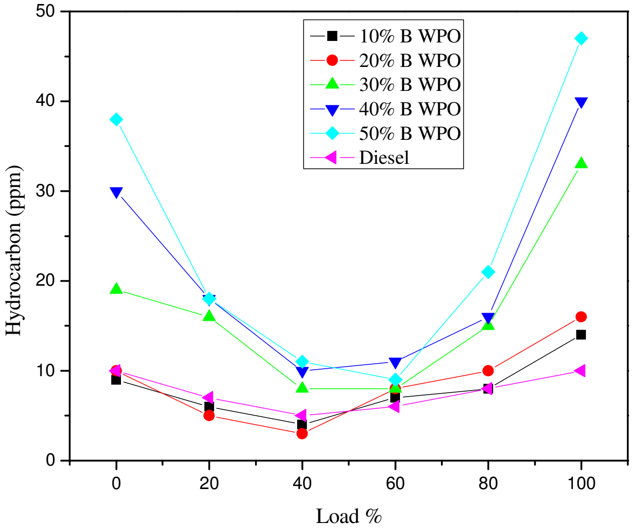


Figure 8.6 Variation of hydrocarbon with load

The higher HC emission in blend compared to diesel may be attributed to two reasons. One is that the fuel spray does not propagate deeper into the combustion chamber and gaseous hydrocarbons remain along the cylinder wall and the crevice volume and left unburned [314]. The other one is unsaturated hydrocarbons present in the WPO which are unbreakable during the combustion process [315, 316].

8.4.2.3 Carbon monoxide

Carbon monoxide emission is mainly due to the lack of oxygen, poor air entrainment, mixture preparation and incomplete combustion during the combustion process [317, 318]. Generally, CI engine operates with lean mixtures and hence the CO emission would be low. CO emission is toxic and must be controlled. It is an intermediate product in the combustion of a hydrocarbon fuel, so its emission results from incomplete combustion. Emission of CO is therefore greatly dependent on the air fuel ratio relative to the stoichiometric proportions. Rich combustion invariably produces CO, and emissions increase nearly linearly with the deviation from the stoichiometry [318]. The variation of carbon monoxide with load is shown in figure 8.7. The concentration of CO emission varies from 0.01% at 20% load to 0.13% at 100% load for diesel. For 10% B WPO, it varies from 0.01% at low load to 0.2% for full load and for 20% B WPO it is 0.01% at low load to 0.18% at full load. Again it is noticed that CO emission varied from 0.01% at low load to 0.2 % at full load for 30% B WPO, 0.01 at low load to 0.26% at high load for 40% B WPO and 0.01% at low load to 0.28 at high load for 50% B WPO. The results show that CO emission of waste plastic oil is higher than diesel especially at higher load and higher blend. The drastic increase in CO emission at higher loads is due to higher fuel consumption. The results show that CO emission of WPO-DF blends is higher than DF which may be attributed to poor mixture preparation and local rich regions.

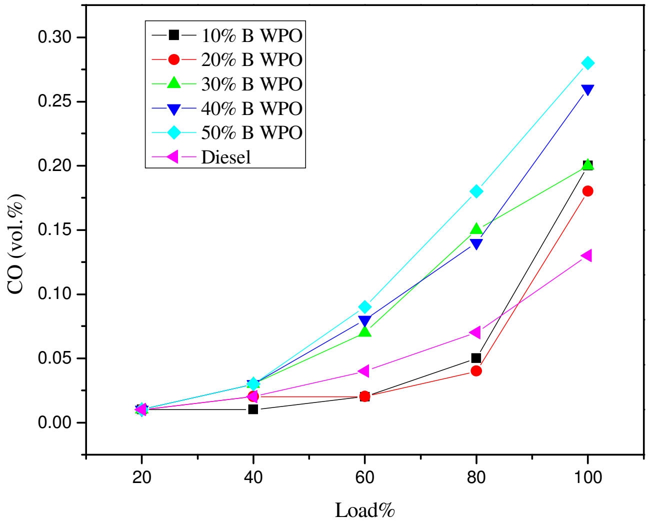


Figure 8.7 Variation of CO with load

8.4.2.4 Smoke

Smoke is nothing but solid soot particles suspended in exhaust gas. Figure 8.8 shows the variation of smoke with load. Smoke varies from 0.2 BSU to 1.45 BSU for diesel whereas in WPO-DF blends it varies from 0.2 BSU to 2.1 BSU for 10% B WPO, 0.3 BSU to 3.4 BSU for 20% B WPO, 0.5 BSU to 4.2 BSU for 30% B WPO, 0.5 BSU to 4.8 BSU for 40% B WPO, and 0.6 BSU to 5.2 BSU for 50% B WPO, as the load increased from no load to full load. It can be noticed that the smoke level for waste plastic oil is higher than diesel. This is due to the non-availability of homogeneous, charge inside the engine cylinder, reduced duration of combustion and rapid flame propagation may also be the reasons for higher smoke intensity [319]. However, at higher load ranges due to insufficient air and abnormal combustion there was a visible white smoke emission.

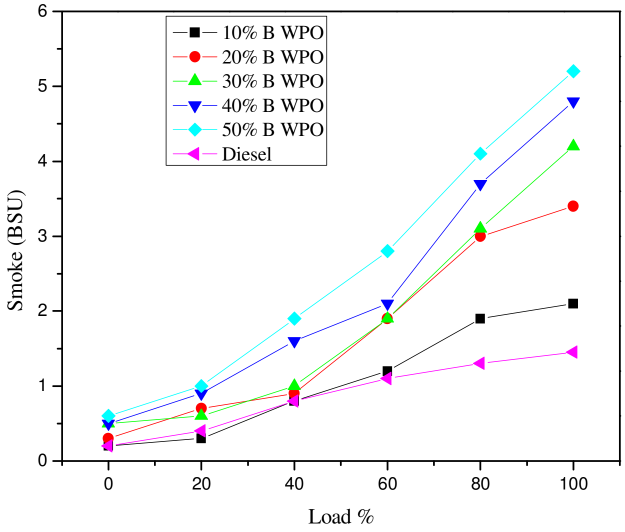


Figure 8.8 Variation of smoke with load

8.5 Conclusion

From the tests conducted with waste plastic oil and diesel blend on a DI diesel engine, the following conclusions are arrived:

- Engine was able to run with maximum 50% waste plastic oil- diesel blends. The engine vibrating at and above this blend.
- Break thermal efficiency of blend was found to be almost same or marginally higher than diesel up to 80% load and somewhat lower at full load.
- Exhaust gas temperature was found marginally higher with blend than diesel operation.
- Break specific fuel consumption was marginally less than diesel.
- NO_x, CO, HC and smoke emissions were found higher than diesel.

Chapter 9

OPTIMIZATION OF PROCESS PARAMETERS BY TAGUCHI METHOD: CATALYTIC DEGRADATION OF POLYPROPYLENE TO LIQUID FUEL

OPTIMIZATION OF PROCESS PARAMETERS BY TAGUCHI METHOD: CATALYTIC DEGRADATION OF POLYPROPYLENE TO LIQUID FUEL

9.1 Introduction

Thermal and catalytic pyrolysis of polypropylene has been reported in the literature. The performances of different catalysts using different reactors in various reaction conditions has been studied by investigators in order to obtain a suitable process for the conversion of polypropylene to liquid fuel (Chapter 2). In the present work different parameters which influence the decomposition of waste polypropylene in a batch process have been identified and summarized in the chapter 5. In this section, with the help of regression modeling an equation has been developed for yield of liquid fuel as a function of temperature, catalyst concentration and catalyst type. Taguchi method is used to optimize the process parameters involved in decomposition of waste polypropylene.

9.2 Materials and methods

9.2.1 Procurement of materials and experimental process: In this experiment waste polypropylene (disposable glass) was degraded using different catalysts such as kaolin (KC), 1M acid treated kaolin (1MKC), 3M acid treated kaolin (3MKC), and 5M acid treated kaolin (5MKC) which are different in terms of their acidity values (Table 4.3 in chapter 4. The detail about the different materials used and experimental methods adopted in this process are mentioned in the experimental section (Chapter 3).

9.2.2 Statistical analysis method: The statistical analysis has been done using MINITAB 14 software with Taguchi method.

9.2.2.1 Design of experiments via Taguchi methods [320]

The Taguchi method involves reducing the variation in a process through robust design of experiments. The overall objective of the method is to produce high quality product at low cost to the manufacturer. The Taguchi method was developed by Dr. Genichi Taguchi of Japan who maintained that variation. Therefore, poor quality in a process affects not only the manufacturer but also society.

He developed a method for designing experiments to investigate how different parameters affect the mean and variance of a process performance characteristic that defines how well the process is functioning. The experimental design proposed by Taguchi involves using orthogonal arrays to organize the parameters affecting the process and the levels at which they should be varied; it allows for the collection of the necessary data to determine which factors most affect product quality with a minimum amount of experimentation, thus saving time and resources. Analysis of variance on the collected data from the Taguchi design of experiments can be used to select new parameter values to optimize the performance characteristic.

9.2.2.2 Steps in Taguchi method [320]

The general steps involved in the Taguchi Method are as follows:

- Define the process objective, or more specifically, a target value for a performance measure of the process. This may be a flow rate, temperature, etc. The target of a process may also be a minimum or maximum; for example, the goal may be to maximize the output flow rate. The deviation in the performance characteristic from the target value is used to define the loss function for the process.
- Determine the design parameters affecting the process. Parameters are variables within the process that affect the performance measure such as temperatures, pressures, etc. that can be easily controlled. The number of levels that the parameters should be varied at must be specified. Increasing the number of levels to vary a parameter at increases the number of experiments to be conducted.
- Create orthogonal arrays for the parameter design indicating the number of and conditions for each experiment. The selection of orthogonal arrays will be discussed in considerably more detail.
- Conduct the experiments indicated in the completed array to collect data on the effect on the performance measure.

- Complete data analysis to determine the effect of the different parameters on the performance measure.

A detailed description of the execution of these steps is discussed next.

9.2.2.3 Determining Parameter Design Orthogonal Array [320]

The effect of many different parameters on the performance characteristic in a condensed set of experiments can be examined by using the orthogonal array experimental design proposed by Taguchi. Once the parameters affecting a process that can be controlled have been determined, the levels at which these parameters should be varied must be determined. Determining what levels of a variable to test requires an in-depth understanding of the process, including the minimum, maximum, and current value of the parameter. If the difference between the minimum and maximum value of a parameter is large, the values being tested can be further apart or more values can be tested. If the range of a parameter is small, then less values can be tested or the values tested can be closer together.

Knowing the number of parameters and the number of levels, the proper orthogonal array can be selected. Using the array selector table shown below, the name of the appropriate array can be found by looking at the column and row corresponding to the number of parameters and number of levels. Once the name has been determined (the subscript represents the number of experiments that must be completed), the predefined array can be looked up. Links are provided to many of the predefined arrays given in the array selector table. These arrays were created using an algorithm Taguchi developed, and allows for each variable and setting to be tested equally. For example, if we have three parameters (voltage, temperature, pressure) and two levels (high, low), it can be seen the proper array is L_4. Clicking on the link L_4 to view the L_4 array, it can be seen four different experiments are given in the array. The levels designated as 1, 2, 3 etc. should be replaced in the array with the actual level values to be varied and P_1, P_2, P_3 should be replaced with the actual parameters (i.e. voltage, temperature, etc.)

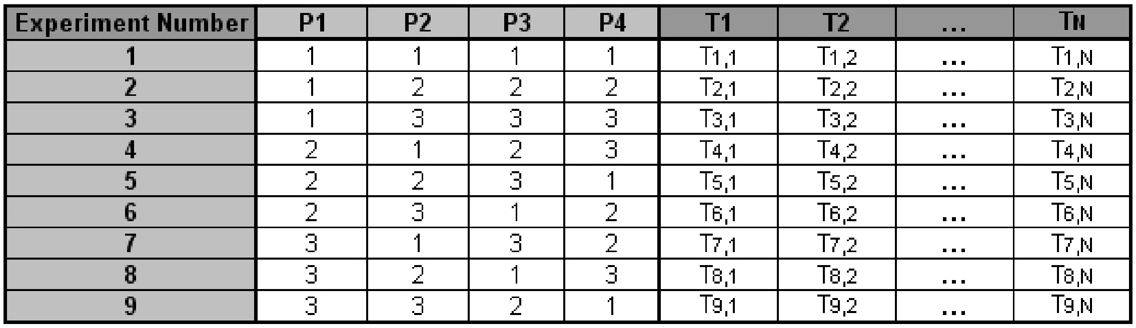
It is important to note that, if the array selected based on the number of parameters and levels includes more parameters than are used in the experimental design, ignore the additional parameter columns. For example, if a process has 8 parameters with 2 levels each, the L_{12} array should be selected according to the array selector.

9.2.2.4 Analysis of experimental data [320]

Once the experimental design has been determined and the trials have been carried out, the measured performance characteristic from each trial can be used to analyze the relative effect of the different parameters. To demonstrate the data analysis procedure, the following L_9 array (Table 9.1) is used, but the principles can be transferred to any type of array.

In this array, it can be seen that any number of repeated observations (trials) may be used. $T_{i,j}$ represents the different trials with i = experiment number and j = trial number. It should be noted that the Taguchi method allows for the use of a noise matrix including external factors affecting the process outcome rather than repeated trials.

Table 9.1 L_9 Array



Experiment Number	P1	P2	P3	P4	T1	T2	...	T_N
1	1	1	1	1	$T_{1,1}$	$T_{1,2}$	...	$T_{1,N}$
2	1	2	2	2	$T_{2,1}$	$T_{2,2}$	...	$T_{2,N}$
3	1	3	3	3	$T_{3,1}$	$T_{3,2}$	...	$T_{3,N}$
4	2	1	2	3	$T_{4,1}$	$T_{4,2}$	...	$T_{4,N}$
5	2	2	3	1	$T_{5,1}$	$T_{5,2}$	...	$T_{5,N}$
6	2	3	1	2	$T_{6,1}$	$T_{6,2}$	...	$T_{6,N}$
7	3	1	3	2	$T_{7,1}$	$T_{7,2}$	...	$T_{7,N}$
8	3	2	1	3	$T_{8,1}$	$T_{8,2}$	...	$T_{8,N}$
9	3	3	2	1	$T_{9,1}$	$T_{9,2}$	...	$T_{9,N}$

To determine the effect each variable has on the output, the signal-to-noise ratio, or the SN number, needs to be calculated for each experiment conducted. The calculation of the SN for the first experiment in the array above is shown below for the case of a specific target value of the performance characteristic. In the equations below, y_i is the mean value and s_i is the variance. y_i is the value of the performance characteristic for a given experiment.

$$SN_i = 10 \log \frac{\bar{y_i}^2}{{s_i}^2}$$

$$Where$$

$$\bar{y}_i = \frac{1}{N_i} \sum_{u=1}^{N_i} y_{i,u}$$

$$s_i^2 = \frac{1}{N_i - 1} \sum_{u=1}^{N_i} (y_{i,u} - \bar{y}_i)$$

$$i = Experiment\ number$$

$$u = Trial\ number$$

$$N_i = Number\ of\ trials\ for\ experiment\ i$$

For the case of minimizing the performance characteristic, the following definition of the SN ratio should be calculated:

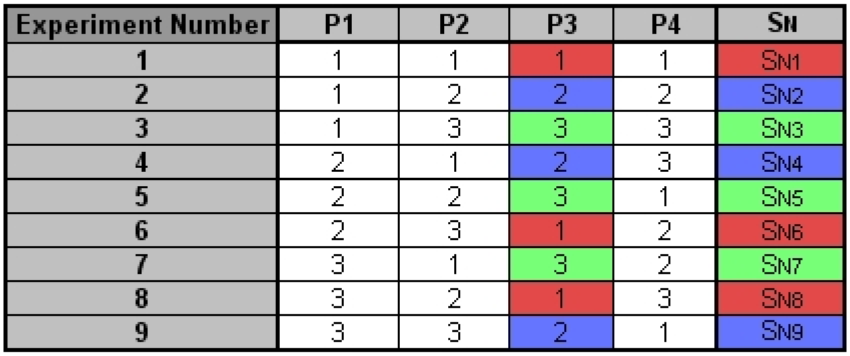
$$SN_i = -10 \log \left(\sum_{u=1}^{N_i} \frac{y_u^2}{N_i} \right)$$

For the case of maximizing the performance characteristic, the following definition of the SN ratio should be calculated:

$$SN_i = -10 \log \left[\frac{1}{N_i} \sum_{u=1}^{N_i} \frac{1}{y_u^2} \right]$$

After calculating the SN ratio for each experiment, the average SN value is calculated for each factor and level. This is done as shown below for Parameter 3 (P3) in the array Table 9.2:

Table 9.2 Experimental parameters and SN ratio



Experiment Number	P1	P2	P3	P4	SN
1	1	1	1	1	SN1
2	1	2	2	2	SN2
3	1	3	3	3	SN3
4	2	1	2	3	SN4
5	2	2	3	1	SN5
6	2	3	1	2	SN6
7	3	1	3	2	SN7
8	3	2	1	3	SN8
9	3	3	2	1	SN9

$$SN_{P3,1} = \frac{(S_{N1} + S_{N6} + S_{N8})}{3}$$

$$SN_{P3,2} = \frac{(S_{N2} + S_{N4} + S_{N9})}{3}$$

$$SN_{P3,3} = \frac{(S_{N3} + S_{N5} + S_{N7})}{3}$$

Once these SN ratio values are calculated for each factor and level, they are tabulated as shown below and the range R (R = high SN - low SN) of the SN for each parameter is calculated and entered into the table. The larger the R value for a parameter, the larger the effect the variable has on the process. This is because the same change in signal causes a larger effect on the output variable being measured.

9.3 Design of experiments in present process

9.3.1 Taguchi approach to parameter design

In the present work, experimental work has been designed in a sequence of steps to insure that data is obtained in a way that its analysis will lead immediately to valid statistical inferences. This research methodology is termed as DESIGN OF EXPERIMENT (DOE) methodology. DOE using Taguchi approach attempts to extract maximum important information with minimum number of experiments [321]. Taguchi techniques are experimental design optimization techniques which use standard Orthogonal Arrays (OA) for forming a matrix of experiments. Using an OA to design the experiment helps the designer to study the influence of multiple controllable factors on the average of quality characteristics and the variations in a fast and economic way. OA's allow screening out few important main effects from the many less important ones. Also it allows us to estimate interaction effects if any and determine their significance [320]

In the present reaction system three operating parameters, each at three levels, are selected to evaluate yield of liquid fuel. The factors to be studied are mentioned in Table 9.3. Based on Taguchi method, the L_{27}-OA was constructed. The reason for using L_{27}-OA is to evaluate the significance of interaction terms. Interaction means the influence of an operating variable on the effect of other operating variable [322].

In the present work only second order interaction terms have been considered viz., (T*A), (T*C), (A*C) but not the third order viz., (T*A*C) where [T = temperature, A = acidity of different catalysts, C = plastic to catalyst ratio].

Table 9.3 Factors and their levels in the experimental design

Level	Temperature [T] (ºC)	Catalyst type defined by their acidity [A] (mmol/g)	Plastics to catalyst ratio [C]
1	450	0.049	3
2	500	0.108	6
3	550	0.210	10

The experiments were carried out according to the L_{27}-OA. The yield of liquid fuel (in wt.%) was considered as Taguchi array response. The L_{27}-OA and response values for yield of liquid fuel are shown in Table 9.4.

9.3.2 Analysis of data

After conducting the experiment, the results were converted into S/N ratio values. The final L_{27}-OA displaying response values and their corresponding S/N ratio values for yield of liquid fuel are shown in Table 9.4.

Table 9.4 L_{27}-OA response values and S/N ratio for yield of liquid fuel

Run no.	Temperature (T)	Catalyst type in terms of acidity(A)	Plastics to catalyst ratio (C)	yield of liquid product in wt.% (Y)	S/N Ratio
1	1	1	1	84.5	38.5371
2	1	1	2	83.5	38.4337
3	1	1	3	80.5	38.1159
4	1	2	1	87.8	38.8699
5	1	2	2	86.5	38.7403
6	1	2	3	85.5	38.6393
7	1	3	1	88.1	38.8995
8	1	3	2	87.2	38.8103
9	1	3	3	86.1	38.7001
10	2	1	1	87.5	38.8402
11	2	1	2	84	38.4856
12	2	1	3	83	38.3816
13	2	2	1	88.5	38.9389
14	2	2	2	87.6	38.8501
15	2	2	3	86.8	38.7704
16	2	3	1	92	39.2189
17	2	3	2	90.6	39.1426
18	2	3	3	89.2	39.0073
19	3	1	1	91.4	37.0861
20	3	1	2	73.55	37.3317
21	3	1	3	72.15	37.1647
22	3	2	1	71	37.0252
23	3	2	2	70.3	36.9391
24	3	2	3	70	36.902
25	3	3	1	79.5	38.0073
26	3	3	2	78.3	37.8752
27	3	3	3	76.3	37.6505

9.3.2.1 Main Effect Plot

Main effects plot for the main effect terms viz. factors T, A and C are shown in Figure 9.1. From the main effect plots, it has been observed that yield of liquid fuel increases with increase in temperature from 450ºC to 500ºC and decreases with further increase in temperature from 500ºC to 550ºC due to the formation of more non condensable gaseous/volatile fractions by rigorous cracking at higher temperature. Yield of liquid fuel increases with use of different catalyst of increasing acidity and increase in plastic to catalyst ratio owing to the increase in the acid centers which is mainly responsible for cracking process.

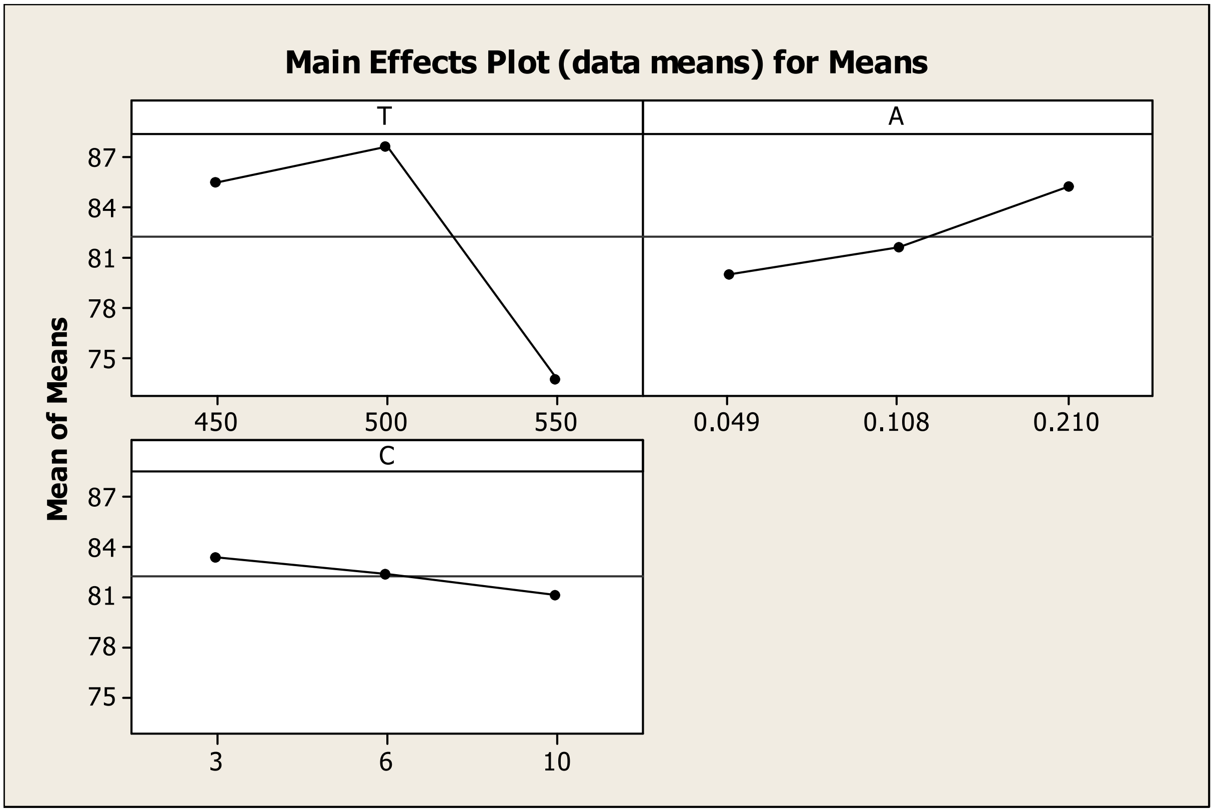


Figure 9.1 Main effect plots

9.3.2.2 Interaction Plot

Whether interactions between factors exist or not can be shown by plotting a matrix of interaction plot. Parallel lines in an interaction plot indicate no interaction. However, the interaction plot doesn't tell if the interaction is statistically significant [323].

Interaction plots are most often used to visualize interactions during DOE. Matrix of interaction plot for yield of liquid fuel is shown in Figure 9.2. It can be seen visually that there are non-parallel lines between temperature and acidity of the catalyst (T and A).The plastic to polymer ratio (C) does not show any significant interaction (parallel lines) for yield of liquid fuel.

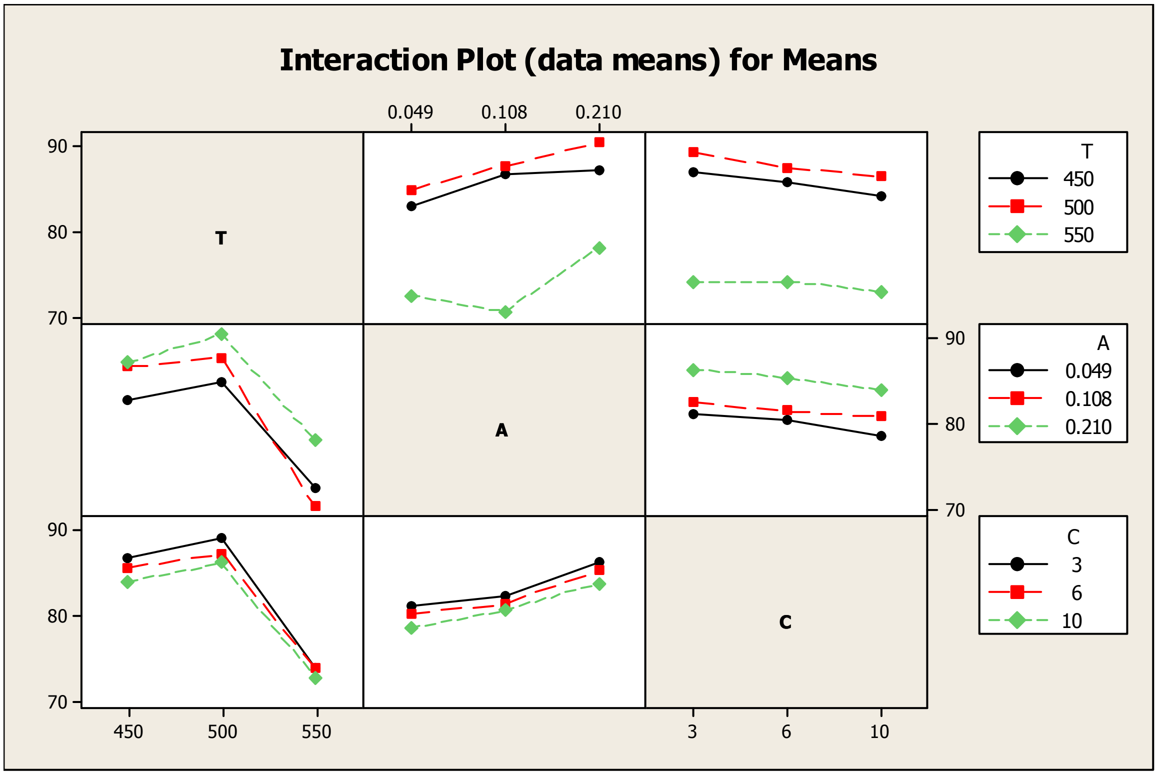


Figure 9.2 Interaction plots

9.4 Result evaluation

There are two different methodologies in carrying out the complete OA analysis. A common approach is to analyze the average result of repetitive runs, or a single run, through ANOVA analysis [321]. Since in the present work there is only one replication, further analysis of OA is done through ANOVA. Once the data for a designed experiment have been collected, the sample information is used to make inferences about the population means associated with the various treatments. The method used to compare the treatment means is known as analysis of variance, or ANOVA [322].

An ANOVA Table breaks down the effect of each factor and the experimental error. In addition, it will also break down all of the possible interactions of the factors. In the present work ANOVA Table for yield of liquid fuel from waste polypropylene has been shown in Table 9.5 using MINITAB 14 software. In this process, it is seen that the significant factors are temperature (T), catalyst type in terms of acidity (A), interaction between temperature and acidity (T*A) and plastic to catalyst ratio (C), written in the decreasing order of significance.

Table 9.5 Analysis of Variance for Means (ANOVA).

Source	DF	SS	MS	P
T	2	1026.06	513.030	0.000
A	2	126.74	63.370	0.000
C	2	23.04	11.521	0.005
T*A	4	46.07	0.887	0.003
T*C	4	3.55	0.296	0.545
A*C	4	1.18	1.075	0.886
Residual error	8	8.60	8.60	1.075
Total	26	1235.24		

It is seen that the (T*A*C) term has completely vanished. The reasoning for this would be that since all three factors and four interactions use up the 26 degree of freedom in this experiment, there was nothing left over with which to measure the error. The solution to this predicament was to pool the effect of non-significant factors and interactions. Interaction (T*A*C) had very small variance. Therefore its degree of freedom and their sum of squares had been pooled together. These pooled figures are removed from their places on the ANOVA Table and an error factor is created [323].

The final ANOVA Table for percentage contribution (exact value in percent) of each of the significant factors in affecting the response value, which is calculated on the basis of ANOVA Table, is shown in Table 9.6. The significant main effect terms and interaction terms in the ANOVA Table 9.6 are computed using the F-ratio as a test statistic [322].

In the process of catalytic decomposition of waste polypropylene in a batch reactor the ranks indicate that temperature has the greatest influence followed by acidity of catalyst and then plastic to catalyst ratio which can be observed in Table 9.7. The optimum condition in this case where in the percentage degradation of pollutant is maximum is at temperature: 500ºC, catalyst type in terms of acidity: 0.21mmol/g and plastic to catalyst ratio: 3.

Table 9.6 Final ANOVA table

Source	DF	SS	MS	F-Ratio	Percentage contribution [SS/SS(Total)*100]
T	2	1026.06	513.030	615.64	83.065
A	2	126.74	63.370	76.03	10.26
C	2	23.04	11.521	13.82	1.865
T*A	4	46.07	0.887	13.82	3.72
Total	26	1235.24			
Pooled error	16	13.33	0.833		1.079

Table 9.7 Response table for mean (Larger is better)

Level	T	A	C
1	85.52	80.02	83.31
2	87.62	81.56	82.39
3	73.62	85.19	81.06
Rank	1	2	3

9.5 Mathematical modeling

A general regression for the complete model was performed using MINITAB 14 software. Regression in MINITAB 14 uses the ordinary least squares method which derives the equation by minimizing the sum of the squared residuals. In the present study, there are three operational factors each at three levels. The complete model for the degradation of pollutants is shown in equation 9.1. The number of terms in the model depends on the degree of freedom of the main effect terms and the corresponding interactions.

$$y = \beta_0+\beta_1x_1 + \beta_2x_1^2 +\beta3x_2 + \beta_4x_2^2 + \beta_5x_3 + \beta_6x_3^2 + \beta_7x_1x_2 + \beta_8x_1x_2^2 + \beta_9x_1^2x_2 + \beta_{10}x_1^2x_2^2 + \beta_{11}x_1x_3 + \beta_{12}x_1x_3^2 + \beta_{13}x_12x_3 + \beta_{14}x_1^2x_3^2 + \beta_{15}x_2x_3 + \beta_{16}x_2x_3^2 + \beta_{17}x_2^2x_3 + \beta_{18}x_2^2x_3^2$$

------------- 9.1

y = yield percentage of liquid fuel

b = model coefficients

x_1, x_2, x_3, = dimensionless coded factors for temperature, catalyst type defined by their acidity, plastic to catalyst ratio respectively.

A simpler reduced model of lower order which provides sufficient information for the prediction of y was found using the F-test statistic [322]. If $F>F_\alpha$, $\alpha=0.05$, then the reduced model does not provide sufficient information and is rejected. A t-test of individual parameters in the regression model was further performed. The t value for each parameter is enlisted in the MINITAB 14 software program [Table 9.8]. To test the null hypothesis H_0: $\beta_i=0$ against the alternative hypothesis $\beta_i\neq0$, a two tailed t-test was performed and H_0 was rejected if $t>t_{\alpha/2}$ or $t< t_{\alpha/2}$ ($\alpha=0.05$). The level of confidence is 95 % i.e. p- value should be less than 0.05. If p-value is less than 0.05 it shows doubt on null hypothesis, which says all sample means equal and effect of that factor on the result is statistically significant [322]. The final prediction equation obtained from MINITAB 14 software for the yield of liquid fuel by the catalytic decomposition of waste polypropylene is as per equation (9.2).

$$y = 82.2556 + 3.2667x_1 + 5.3667x_1^2 - 2.2333x_2 - 0.7x_2^2 + 1.0556x_3 + 1.7778x_1x_2^2 \quad ---9.2$$

The coefficients of model for means are shown in Table 6.

$S = 1.037$ $R^2 = 99.3\%$ $R^2(adj) = 97.7\%$, the parameter R^2 describes the amount of variation observed in yield is explained by the input factors. $R^2 = 99.3$ % indicate that the model is able to predict the response with high accuracy. Adjusted R^2 is a modified R^2 that has been adjusted for the number of terms in the model. If unnecessary terms are included in the model, R^2 can be artificially high, but adjusted R^2 (=97.7 %.) may get smaller. The standard deviation of errors in the modeling, S= 1.037. This indicates that model can explain the variation in yield of liquid fuel to the extent of 99.3% which makes the model adequate to represent the process.

Table 9.8 Estimated Model Coefficients for Means

Term	Coefficient	SE coefficient	T	P
Constant	82.2556	0.1996	412.153	0.000
x_1	3.2667	0.2822	11.574	0.000
x_1^2	5.3667	0.2822	19.014	0.000
X_2	-2.2333	0.2822	-7.913	0.000
x_2^2	-0.7000	0.2822	-2.480	0.038
x_3	1.0556	0.2822	3.740	0.006
$x_1x_2^2$	1.7778	0.3992	4.454	0.002

The residual plot for means of this process is shown in Figure 9.3. This layout is useful to determine whether the model meets the assumptions of the analysis. The residuals are the deviations of the observed data values from the predicted value ŷ and estimate the error terms (e_i) in the model [322]. The e_i are assumed to be random and normally distributed with mean equal to zero and constant standard deviation. If the error terms follow a normal distribution, they will fall on a straight line on the normal probability plot. Because they are estimates of the error terms, the residuals should exhibit similar properties. If the assumptions are valid, plots of the residuals versus run sequence, predicted values, and other independent variables should be random and structure less. If structure remains in the residuals, residual plots may suggest modifications to the model that will remove the structure. Investigation of residuals has been used to evaluate the model adequacy. Residuals are found to be scattered and without any definite pattern which prove the adequacy of the model.

The residual plots in the Figure 9.3 and the interpretation of each residual plot for the present experiment is given below:

a. Normal probability plot indicates the data are normally distributed and the variables are influencing the response. Outliers don’t exist in the data

b. Residuals versus fitted values indicate the variance is constant and a non-linear relationship exists.

c. Histogram proves the data are not skewed and no outliers exist.

d. Residuals versus order of the data indicate that there are systematic effects in the data due to time or data collection order.

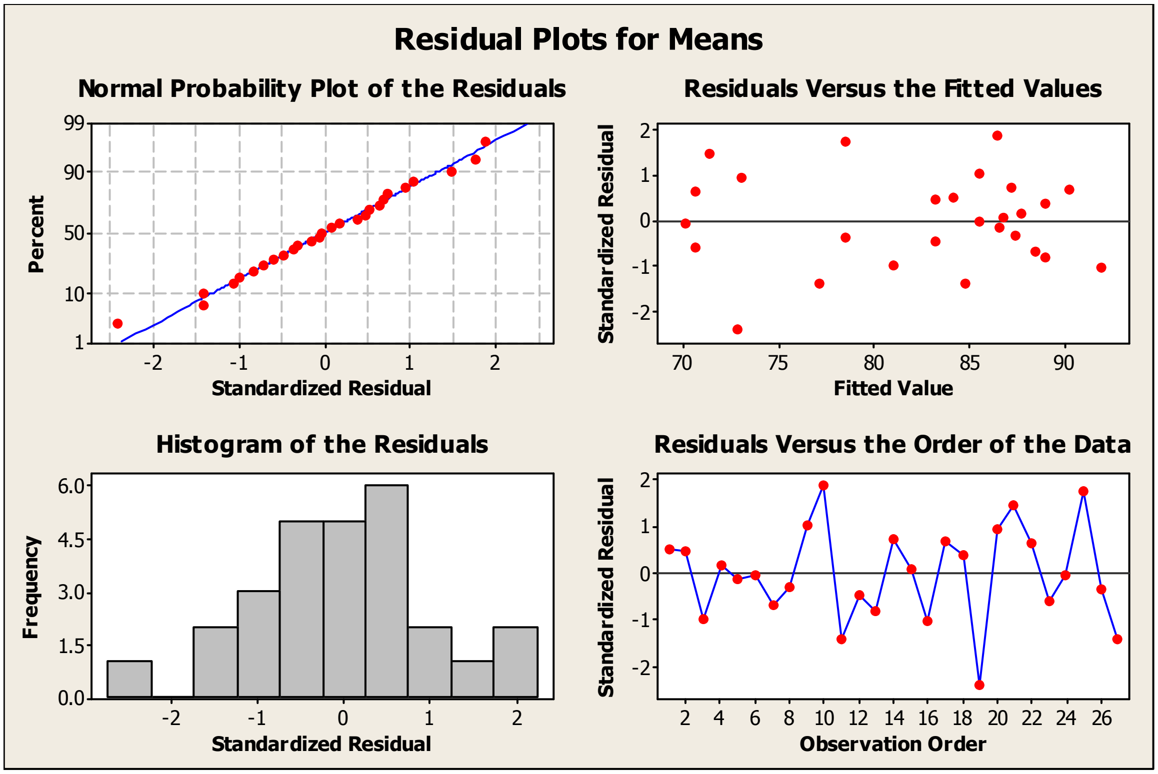


Figure 9.3 Different residual plots for testing the adequacy of the proposed model.

9.6 Conclusion

With these experiments we upgraded our existing knowledge about the influence of the different process parameters on the yield of liquid fuel in a batch process and thus contributed to improving the process's reliability. This study has shown the application of Taguchi method on the performance evaluation of a chemical process for the production of liquid fuel from waste plastics in a batch reactor. The level of importance of the process's parameters is determined by using ANOVA. Moreover, regression modeling has helped us generate an equation to describe the statistical relationship between the process's parameters and the response variable (yield of liquid fuel) and to predict new observations. The simulation experiment was successful in terms of achieving the objective of experiment, which was to quantify the main effects as well as interactions of potentially influential factors on the degradation of pollutants.

Nomenclature

DF Degree of freedom

SS Sum of squares

MS Mean of squares

S/N Signal to noise ratio

R^2 Regression squared

R^2(adj) Adjusted regression

Chapter 10

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE

10.1 Summary and Conclusions

Critical appraisal of the literature reveals that a number of studies have been carried out to study the plastic pyrolysis using different catalysts and reactor set ups at different reaction parameters. A number of process industries have come up based on these research results. However, there are many problems that have come up to be solved in the near future. The present challenges include the need for scale up, minimization of waste handling costs and production cost and optimization of gasoline range products for a wide range of plastic mixtures or waste. One of the ways to reduce the cost of the process is to develop a novel and more efficient catalyst for the process of pyrolysis which would be cheaper, available on commercial scale and should be reusable. So in the present study, the pyrolysis of plastics has been studied using a commonly available material i.e. kaolin clay to know its suitability for this process as a catalyst.

Thermal and catalytic pyrolysis of different plastic wastes such as polypropylene, low density polyethylene and polystyrene using kaolin as catalyst in a batch reactor has been studied. The kaolin has been treated with different concentrations of sulphuric acid with a view to enhance the catalytic property of the resultant clay in the plastic pyrolysis process. The acid treated kaolins are characterized for studying the effect of acid treatment on the different physico-chemical properties. The effect of silica alumina, which has been extensively studied by different investigators for the pyrolysis of different plastics was also studied and compared with that of the catalytic performance of kaolin. The suitable condition for the production of liquid products in different processes has been optimized. The different oils produced in the processes are analyzed for their composition and fuel properties. The oil obtained in the optimum conditions of kaolin catalysed pyrolysis of waste polypropylene has been tested for engine performances and emission in a CI diesel engine.

Following are the brief summary of the conclusions made in the respective chapters.

10.1.1 *Physico-chemical characteristics of acid treated kaolin*

10.1.1.1 Sulphuric acid treatment of kaolin under reflux conditions increased the Si/Al ratio from 0.65 to 8.09, surface area from 23 m^2/g to 143 m^2/g and pore volume from 0.361 to 1.18 cc/g as the acid concentration was increased to 10M.

10.1.1.2 The acidity of kaolin increased from 0.049 mmol/g to 0.210 mmol/g as the acid concentration increased to 5M and decreased to 0.007 mmol/g on treatment with 10M acid.

10.1.2 Thermo-catalytic pyrolysis of virgin and waste polypropylene using kaolin and silica alumina catalyst

10.1.2.1Thermal pyrolysis of waste polypropylene, yield a maximum of 82.85wt.% condensable fraction at 500 °C. Presence of kaolin, acid treated kaolin and silica alumina reduced the reaction time and enhanced the oil yield. Highest yield of oil (87.5wt.%) was obtained at 3:1 polypropylene to kaolin ratio at 500 °C. Thus, the oil yield increased by 7.3% and reaction time decreased by 25.4% at 500 °C with 1:3 catalyst to polymer ratio. The oil obtained in the kaolin catalysed pyrolysis of polypropylene is low viscous at all temperatures.

10.1.2.2 Acid treated kaolin is found better as compared to untreated kaolin in terms of its catalytic activity towards the pyrolysis of polypropylene. The yield of oil fraction increases and reaction time decreases with increase in acid concentration and is optimum for 5MKC.The maximum oil yield obtained using this catalyst is 92%. The yield of oil increased by 11.8% and reaction time decreased by 32.4% at 500 °C with 1:3 catalyst to polymer ratio. Kaolin treated with 10M sulphuric acid i.e. 10MKC doesn’t have any catalytic activity due to severe de-alumination and amorphization leading to negligible acidity value.

10.1.2.3The maximum oil yield using silica alumina as catalyst is 91% with 1:3 catalyst to plastic ratio at 500 °C. The fuel properties of oil obtained using silica alumina is almost similar to the oil obtained in kaolin catalysed reaction.

10.1.2.4The GC/MS results of the different oil samples indicates the presence of different hydrocarbons mostly alkanes and alkenes in the waste polypropylene oil. In addition, some oxygenated compounds such as alcohol, ketone, etc. are also found in the oil in small fractions. The product distribution is narrowed in presence of catalysts. The fuel properties of the oil are comparable with that of petro fuels.

10.1.3 C*atalytic degradation of waste low density polyethylene to liquid fuel*

10.1.3.1 In LDPE thermal pyrolysis, at low temperatures (400 °C to 450 °C) the condensable fraction is less viscous oil, where as with increase of temperature the fraction became highly viscous and waxy (475 °C to 500°C).

10.1.3.2 The recovery of condensable fraction was low 30.8 wt.% at 400 °C, 71.45% at 450 °C, 78.1% at 475 °C and increased to highest yield of 86.65wt.% at 500 °C. Although the rate of reaction increased with increase in the amount of catalyst, but wax like product obtained even in presence of catalyst at temperature at 475°C and above. The yield of liquid fraction at 450 °C was 79.5 wt.% in kaolin catalysed pyrolysis with 1:2 catalyst to plastics ratio. The yield of oil increased by 10.6% at 450 °C with 1:2 catalysts to polymer ratio.

10.1.3.3 Compositional analysis of the oil obtained in catalytic pyrolysis concludes that the products mainly consisted of paraffinic and olefinic compounds. The fuel properties of the oil are similar to the petro fuels.

10.1.4 Pyrolysis of waste thermocol (polystyrene) to value added liquid products

10.1.4.1 The pyrolysis of polystyrene is affected by temperature, type of catalyst and amount of catalyst. The optimum temperature for obtaining highest yield of liquid fraction (93 wt.%) in thermal pyrolysis is 500 °C. The liquid fraction further increase to 94.5 wt. % by the addition of kaolin as catalyst in 1:10 catalyst to polymer ratio at 500 °C. The yield of liquid fraction is unaffected by the presence of silica alumina.

10.1.4.2 FTIR and DHA analysis of the liquid showed that the liquid products consist of mostly aromatic hydrocarbons. The product distribution of the liquid fraction is significantly affected by the presence of both the catalysts.

10.1.5 Performance and emission characteristic of di diesel engine using waste plastic oil

10.1.5.1 The oil obtained in the kaolin catalysed pyrolysis of waste polypropylene is subjected to engine test in a DI diesel engine and the engine was able to run with maximum 50% waste plastic oil- diesel blend. Above 50% blend, detonations occur in the engine and it started vibrating.

10.1.5.2 Brake thermal efficiency of blend is found to be almost same or marginally higher than diesel up to 80% load and somewhat lower at full load.

10.1.5.3 Exhaust gas temperature is found marginally higher with blend than diesel operation. Brake specific fuel consumption is marginally less than diesel.

10.1.5.4 NOx, CO, HC and smoke emissions are found higher than diesel at all blends.

10.1.6 Optimization of process parameters by Taguchi method: catalytic degradation of polypropylene to liquid fuel

10.1.6.1 This study has shown the application of Taguchi method on the performance evaluation of a chemical process for the production of liquid fuel from waste plastics in a batch reactor. In this process, it is seen that the significant factors are temperature, catalyst type in terms of acidity, interaction between temperature and acidity and plastic to catalyst ratio, written in the decreasing order of significance.

10.1.6.2 An equation has been generated to describe the statistical relationship between the process's parameters and the response variable (yield of liquid fuel) and to predict new observations.

10.2 Recommendations for future

From the above results it can be concluded that kaolin work very well in the pyrolysis of three different types of waste plastics and further studies are required to materialize the process. The followings are the recommendations for the future work.

- Pyrolysis of mixed plastics using kaolin and acid treated kaolin.
- Study of pyrolysis of plastics using other clay materials such as bentonite, dickite, nacrite, and halloysite, silica gel and alumina gel, Kieselguhr etc.
- Study of effect of different other acids (HCl, HNO_3, H_3PO_4, CH_3COOH) on the catalytic activity of kaolin and other clays.

- Activation of clay using other methods such as intercalation, mechanical grinding, etc to increase the catalytic activity and its study in pyrolysis process.
- Synthesis of nano clay and its use in pyrolysis studies.
- Develop a continuous process for plastic pyrolysis using suitable catalyst.
- Development of business case for pilot plant and commercial scale production.

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LIST OF FIGURES

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Journal:

1. **Achyut K. Panda,** R.K.Singh, D.K.Mishra, "Thermolysis of waste plastics to liquid fuel A suitable method for plastic waste management and production of value added products- A World prospective" Renewable and sustainable energy Reviews, 14 (1) 2010.
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5. Sachin Kumar, **Achyut K.Panda** and R.K.Singh, A review on Tertiary recycling of high density polyethylene to fuel, Published and available online in Resources, Conservation & Recycling, Elsevier publications.
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2. **Achyut K. Panda**, R.K.Singh, D.K.Mishra, Instrumental Techniques for present Research, National seminar on New Frontiers of Chemical Analysis, Gunupur College, Gunupur, 24-25 March 2009.
3. **Achyut K. Panda,** R. K. Singh, D. K. Mishra, Feed stock recycling of plastics –A Greener Approach to plastic Waste Management, SRK-ISA-RC-24- International Conference on Water, Environment, Energy and Society to be held during 28-30 June 2009, S. R. K. (P.G.) college, Firozabad.
4. Gaurav Kumar, R.K.Singh**, Achyut K. Panda**, Pyrolysis of Eucalyptus wood to bio-oil, SRK-ISA-RC-24- International Conference on Water, Environment, Energy and Society to be held during 28-30 June 2009, S. R. K. (P.G.) college, Firozabad.
5. **Achyut K. Panda** and R. K. Singh, Thermolysis of waste polystyrene to value added products, 2010 International Conference on Environmental Science and Technology April 23-25,2010, Bangkok, Thailand, (ICEST 2010)

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