Synthesis and Characterization of Catalyst for Liquid Fuel Production from Polymer Waste

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Certificate

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Dedication

I dedicate my thesis to all my family members for their continuous support.

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Abstract

Importance of alternate energy has been increasing day by day due to the rapid depletion of crude oil reserves. Besides, in developing countries as in Asia (where the waste management has been a problem), the potential of growth of plastic consumption is very high. Fuel from plastic serves the dual purpose of energy and waste management. Catalytic pyrolysis is so far the most suitable process among other physical and chemical methods that include land filling, mechanical recycling, biological recycling, thermal incineration, partial oxidation, depolymerization, hydro cracking and thermal cracking. One of the most commonly used solid catalysts in polymer degradation studies are zeolites due to their strong acidity, pore size and specific pore structure effects. Amongst the numerous kinds of zeolites investigated in polyolefin pyrolysis, the most commonly used are Beta, USY, ZSM-11, REY, Mordenite, ZSM-5 etc. Some other solid acid catalysts used for plastic pyrolysis include molecular sieves, silica alumina, and MCM-41. Reports on the use of FCC catalysts are also found in literature. Other catalytic materials such as clays (montmorillonite, saponite), reforming catalysts, activated carbon, metal oxides, metal complexes of the type MCln-AlCl3 or M(AlCl4)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.This work was carried out to investigate the effect of temperature and degree of acid treatment of kaolin clay on catalytic cracking of plastic waste material (PP and mixed polymer waste). Untreated kaolin clay and acid treated kaolin clay were characterized by standard BET method and XRD. Product obtained was analyzed by GC-MS and FT-IR. Waste material was cracked thermally and catalytically in a batch reactor in the temperature range 350-500°C for synthesis of liquid fuel. For this purpose, kaolin clay was first treated with different prepared molar solutions of HCl (1M, 3M and 5 M) under reflux condensation at 100°C and atmospheric pressure in a round bottom flask for 4 hours. Cracking activity of untreated kaolin clay was compared with acid treated kaolin clay. It was observed that acid treated kaolin clay performed better than untreated kaolin clay due to high surface area and greater number of acidic sites.

Publications

1. Application of Acid Treated Kaolin Clay for Conversion of Polymeric Waste Material into Pyrolysis Diesel Fuel*
   Muhammad Ali Uzair, Shahid Ansari, Ali Waqas, Ali Afzal, Anees-ur-Rehman
   ICESP 3rd International Conference, Air University, Islamabad
   (Published)
2. Synthesis of Calcium Sulfate Whiskers from Waste Calcium Chloride and Effects of Additives**
   Anees-ur-Rehman, Muhammad Ali Uzair, Shahid Ansari
   APComS Conference, SCME NUST, Islamabad
   (Published)

* Attached as Annex 1

**Attached as Annex 2

List of Abbreviations

HDPE	High density polythylene
LDPE	Low density polythylene
PET	Polythylene terephthalate
PP	Polypropylene
PS	Polystyrene
PE	Polythylene
T	Temperature (°C)
MJ/kg	Mega joule per kilogram
MW	Mega watt
LNG	Liquefied natural gas
MT	Million tons
MSW	Municipal solid waste
MPa	Mega pascal
FCC	Fluid cracking catalysts
M	Molar concentration

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Chapter 1

Introduction

1.1 Overview

Plastic waste generation is on rise as the world is progressing economically and the production and consumption of plastic waste is changing side by side. With the increase in plastic waste, there is a growing concern over the damage of ecosystems, littering and inclusion of solid plastic waste in streams. Plastic waste constitutes the major portion of municipal and industrial waste after food waste and paper waste. The production and consumption of plastic is also on rise in those cities that are less developed or are under development. Main reason being the plastic packaging, plastic bags, bottles (HDPE, PP, and PET etc) and other products that essentially contain plastic as their major component.

Plastic is currently being used as a major component of almost every product including electronic appliances/equipments, storage, automobiles, food containers, stationery items etc. This increase combined with the incapability of cities' managements responsible for solid waste management has led to harmful effects on public health, environment and ecosystems, and littering of sewerage systems.

An opportunity to dispose of the plastic waste and convert it into an energy source can be seized in an environmental friendly way. In this opportunity, there is a way for green house gases emission reduction and energy resource generation which is very high in demand. The goal of energy resource generation has its importance for national and local authorities, where fast growth and development is putting much pressure on natural reservoirs of energy.

Possessing properties such as high heat of combustion and high availability and access, plastic waste is becoming an encouraging source for liquid fuel production. Plastics do not absorb moisture like other wastes, for example paper and wood. Water/moisture content of plastics is negligible compared to biomass, kitchen wastes, paper waste etc. Disposal of plastic waste via different conversion methods into useful sources of energy depends on the kind of plastics, additionally considering the characteristics of other waste that can be used in the processes. Also, for the conversion processes to be efficient and effective, the technologies are chosen on the basis of local environment and other technical properties.

Generally, the conversion of plastic waste into energy source (liquid fuel) needs the feed stocks that are combustible and safe. Composition of plastic waste varies greatly and might contain hazardous materials (sulfur containing compounds) that are harmful to humans and pose threat to the environment.

The methods adapted for the production of liquid fuel from plastic waste rely on the pyrolysis followed by condensation of the hydrocarbons in vapor form. Pyrolysis is the thermal cracking of material that takes place in inert atmosphere under vacuum or in inert conditions e.g. In the presence of nitrogen gas. Plastics that are suitable for production of liquid fuel are fed into the reactor where the decomposition takes place at 400-550° C [1]. Waste plastics inside the reactor are converted into vapor form on achieving reaction temperature from where the vapors travel to the condenser where the vapors condense into liquid fuel (a mixture of various hydrocarbons). Operating conditions, type of reactor and presence of catalyst control the properties of liquid fuel such as boiling point. To meet the end user requirements, fractional distillation is carried out. Importantly kerosene, diesel and gasoline are fractionated. The non condensable gases such as methane, ethane and propane ether be used as such or used as energy source in pyrolysis process.

1.2 Origin of the Problem

1.2.1 Depletion of fossil fuel resources

Current rate of economic progress and development is not in harmony and sustainable if fossil fuels like natural gas, coal or crude oil are not saved. Universal petroleum consumption has been predicted to increase from 86 million barrels per day in 2007 to 92 million barrels of petroleum products per day in 2020 in energy outlook 2010. Consumption of natural gas is likely to increase from 108 trillion cubic feet in 2007 to 157 trillion cubic feet in 2030. If the consumption continues to increase in this way, then the oil and gas reserves will last only 45 and 68 years more. There is a growing need to search and rely on other energy resources such as wind energy, hydel energy, solar energy, biomass etc [2]. The route of energy generation from plastic waste to liquid fuel is also an alternate energy source [3].

1.2.2 Municipal and solid waste management

Sustainable progress and development demands proper waste management strategies and techniques. There has been a large increase in the production of all kinds of goods and products as a result of increase in welfare level in modern society. Due to comparative less cost and resourcefulness plastics are being used in wide range of applications which has led to their fastest growth. Serious environmental crisis is on rise as a huge plastic waste stream reaches each year to final recipients due to less lifetime of plastic usage. Legislation and increase in prices is largely constraining disposal of post consumer plastics; thereby increasing demand for substitutes for waste disposal or land filling. The substitution of current polymers with green polymers/biodegradable with the advancement in green chemistry is too limited at this point [4]. They can and should be substituted once the standards and protocols for degradable polymers are developed to evaluate the specific formulations of materials. There are other alternatives available such as recycling, reuse, source reduction and processed fuel applications. A suitable alternative could be the manufacturing of liquid fuel from polymer waste via pyrolysis under inert conditions in the absence of air, as the calorific value of plastic fuel is comparable to fossil fuel (40 MJ/kg) [5]. From sustainable and ecological point of view, this technique is really attractive.

1.3 Pakistan’s energy crisis

Pakistan is in the middle of worst energy shortage in history. This energy crisis is the greatest drain on shaken economy of Pakistan. The average power requirement of Pakistan is roughly estimated at 18000 MW, but the power sector of the country is able to produce average of only 12000 MW varying during winter and summer seasons [6]. Due to this crisis, the economic development has come to a halt resulting in public unrest and outrages of electricity and gas for a long time. This prolonged problem of energy shortage originated from a fuel mix transformation started twenty years ago, when the country started to rely on imported furnace oil instead of hydropower, resulting in increased power generation costs. Another reason for this energy shortage problem is the huge line losses. These reasons of energy shortage have led to increase in tariffs along with electricity and gas theft. These combined have given rise to phenomenon of circular debt, thereby less payment of bills lead to late payments for import of furnace oil, natural gas or other inputs to the power generation system. Capacity utilization in main industries has reduced to half. Fertilizer industry is the most effected industry due to interruptions in supply of gas resulting in its closure [7]. Energy sector has become a main focus of public policy in recent years.

1.3.1 Natural gas

Original natural gas reserves of Pakistan are on decline. Low cost of natural gas supplied to consumers is a major hindrance in gaining attention of new gas supplies either through increased exploration activities or through import of LNG. Another hurdle is the regional gas pipeline imports [8].

Average daily requirement of Pakistan is about 6.5 billion feet. If these policies continue to persist, Pakistan's natural gas supply can decline from 4 billion cubic feet per day in 2011 to less than 1 billion cubic feet per day resulting in depression of Pakistan's average GDP growth rate during next 15 years.

1.3.2 Oil

Although untouched, with approximation of proven and unproven reserves of oil, Pakistan is still regarded an oil-rich nation. Oil and gas development authority OGDCL combined with other private sector companies had made a number of efforts to discover oil till 80s, however overall extraction has largely remained stagnant at 60,000 barrels per day. Average oil consumption of the country is estimated to be about 410,000 barrels per day. This very high consumption compared to the low production is the main cause of higher energy costs and disturbing the overall trade balance.

1.3.3 Coal

Despite the fact that Pakistan has been gifted with very vast reserves of coal, negligible efforts have been made to utilize them for energy. While total coal reserves of Pakistan are estimated to be 185 billion tones, input of coal in the energy sector stands at 0.1 percent [5]. Most of the reserves have been found in Thar Desert of Sindh, estimating 175 billion tones. Despite the claims of successive governments, very fewer efforts have been made regarding extraction. In order to efficiently solve the current energy crisis, it’s important to tap coal reserves of Pakistan to avoid exhaustion of other limited resources.

1.3.4 Alternative energy

Considering the change in climate and high oil prices, governments have been forced around the globe to promote the use of alternative and renewable energy resources. It’s a matter of surprise that Pakistan’s current share of renewable energy in total mix stands at 32 percent. This high share of renewable energy is primarily composed of hydel power generation. Additionally around 400 to 500 MW of power generation is being carried out through wind farms. There is also a huge potential of solar energy in the country which combined with wind energy roughly estimates to 300,000 MW.

1.4 Objectives of work

The purpose of this research work is to study the thermal and catalytic pyrolysis of polymeric waste material i.e. Polypropylene in a batch reactor with an objective to study the behavior of cracking by changing parameters such as temperature and catalyst.

Summary

In this chapter, the production and consumption of plastic waste has been discussed with a little touch of plastic waste management solution. Furthermore, the current energy crisis in Pakistan has been explained. Pakistan's energy resources are depleting very fast with very little effort being made to explore other resources and utilize them. Pakistan's energy requirements largely depend on crude oil imports which is adversely affecting the country's economy.

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Chapter 2

Literature review

2.1 Definition of plastics

Plastics are universal group of artificial/synthetic or natural materials consisting large molecular chains that have carbon as major portion and other organic or inorganic elements like oxygen, hydrogen, nitrogen etc [1].

Plastics are made of monomers (small molecular unit and building block) through various chemical processes such as

- A catalytic or peroxide initiated polymerization of monomers such as ethylene, propylene, butadiene and styrene copolymers
- A poly condensation of different monomers
- Poly addition of reactive monomer molecules

Plastics are one of the greatest innovations of the century and have proved their reputation to be true. Plastics are being used in various ways and we will depend on them in the upcoming years. Plastics are light weight, do not rot or rust, economical, reusable and conserve natural resources. These are the reasons of our dependency on the plastics. Plastics reduce co_2 emissions during their usage along with conservation of energy. If we want to replace plastics with other conventional materials considering sustainability, then we would have to add 22.4 million tons of crude oil yearly [2, 3]. Plastics have rapidly replaced conventional materials due to continuous advancement in polymer technology, knowledge and economic production.

2.2 Production and consumption of plastic waste

Constant developments tell the story of increased consumption of plastic waste i.e. 10% on yearly basis since 1950. Plastic production all over the world has risen from 1.3 million tons (MT) in 1950 to 245 MT in 2006. Europe is the leading manufacturer of plastics with 25% of total global production of 245 million tons in 2006. A study shows that in USA and Western Europe, consumption of plastics has increased to approximate value of 100 kg/year per capita with possible expected growth up to 130 kg/year per capita. USA is the largest consumer of plastics all over the world utilizing 27.3 MT of total universal consumption (170 MT). Asia currently has consumption of 20 kg/year per capita with greatest potential for growth [4].

In European countries like Poland, Czech Republic and Hungary, plastic consumption is proposed to rise with their economic progress. The average utilization of polymers in India per capita was 1.8 kg in 1998/1999 that increased to 3.2 kg in 2000/2001. Consumption of plastics in china and all over the world is 4 times and 6 times respectively compared to average Indian consumption. Annual production of plastics in Japan is 15 MT and 10 MT of plastic is abandoned. Figure 2.1 compares consumption of plastics over three different periods [4, 5]. Consumption and production rate of plastic waste has increased significantly since the large scale production of plastics that started in 1940s. Nearly 80% of total plastic consumption consists of thermoplastics. Thermoplastics are used for specific applications such as packaging. These are also used in non-plastic applications such as textile fibers and coatings.

Plastic consumption has increased tremendously all over the globe that caused increase in amounts of waste. This increase in waste poses complications and hurdles in its removal. This really is because of the evidence that life time of plastic wastes is very low (approximately 40% have life time less than 30 days) [7]. The life of all polymer consumables varies from country to country and it is 8 years in India; which is much less compared with life service of plastics for Germany which is roughly 14 years [6]. Wastes obtained from production sites and manufacturing industries may contain large portions of plastics along with existence of plastics in municipal waste streams. Plastics are non-biodegradable and are commonly seen in waste streams. Carelessly discarding waste leads to other problems such as drain choking and animal health problems. Problems related to environment rise as plastic waste promotes the throwaway culture combined with inefficiency of systems regarding management of waste.

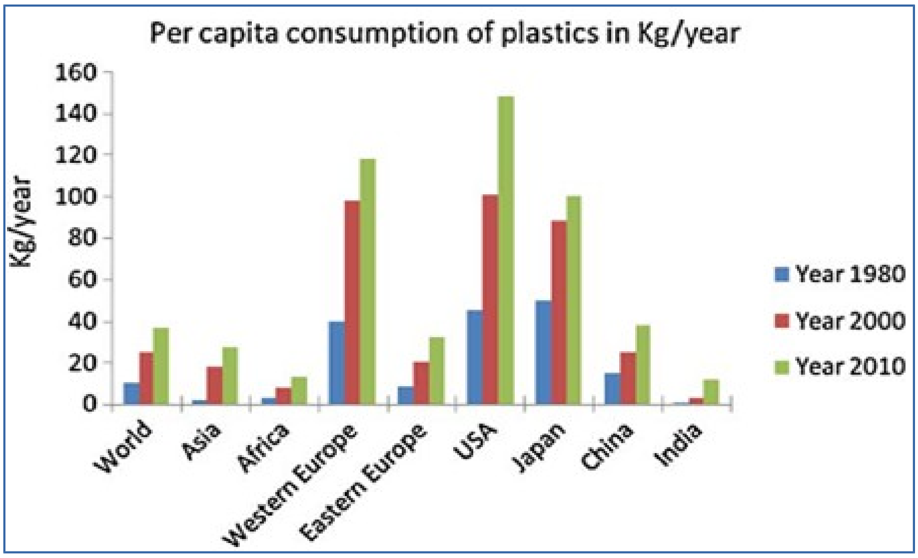

Figure 2.1 Comparison of average consumption per capita per year [5]

Landfills cost has been on increase with the decreasing space. Therefore other options are being considered for plastic waste management. Based on extensive research and testing, there are number of treatment and recycling methods that are economically and environmentally sustainable. Plastic industry has successfully worked on technologies for treating, recovery and management of discarded items. 378,000 tones of polyethylene of the total 388,000 tons of polyethylene that were used for production of different textile industry parts in 2002 were made from polyethylene discarded products [8]. In United Kingdom in 2007, 250,000 tones of plastic waste (almost 95%) from process scrap has been recycled. Plastic waste from market grade adhesives has been recycled from a number of end-products that include automobile parts, textile pasts, films, green houses and appliances.

Separation of waste depending on the type of plastic is the most important step. Removal of paint is one of the main issues among others. Characteristics of plastics can be compromised because of stress concentration caused by these coating materials. Grinding assisted with cryogenic methods can be used to remove coatings. Other ways include abrasion, hydrolysis of coatings in hot water and solvent stripping. In spite of that, there is a strong need to control these processing conditions as none of these techniques are altogether outstanding.

2.3 Sources and properties of plastic waste

Polymer waste is allocated the category of industrial or municipal waste based on the type and origin; these groups experience different management techniques depending on the properties of plastic. Municipal waste consists largely of plastics; additionally large amounts of polymer waste arise as a consequence of faulty product in industry and agriculture [8]. Thermoplastics make 78% of total plastic waste; rest is thermo sets [6].

At present, there are nearly twenty various types of plastics. Out of these, there are five high volume plastic families: PE, LDPE, HDPE, PP, PVC, PS, EPS and PET [11, 12]. Monomers such as high purity ethane, propene and butadiene are used for manufacturing plastics [13]. Polymerization continues with the release of small molecules while the condensation polymers are being formed. Structurally different plastics with different characteristics and results can be formed by changing the reaction conditions during polymerization. Additives which enhance stability and improve processing and mechanical specifications are amalgamated into the monomer resin before conversion [9, 14]. The addition of additives depends on the application of plastics. Examples are plasticizers (40%), enhancers (10%), flame retardants (15%), impact resistance enhancers (10%) or heat and light stabilizers (5%) [13]. Harmful materials are released when these additives undergo thermal cracking. These additives also cause hindrance in mechanical recycling. [15].

2.3.1 Municipal plastic wastes

As plastic waste is dumped and collected as household waste, it essentially constitutes municipal solid waste MSW. The major components of MSW collected plastic waste are polyethylene, polypropylene, polyvinyl chloride, polystyrene, polyethylene terephthalate. There has been a significant increase in percentage of plastics in municipal solid waste [10].

Plastics are separated from household wastes for recycling municipal plastic waste. Mechanical separation is required to separate mixed plastic waste [14, 15]. Plastics with higher density compared to water e.g. Polystyrene and polyvinyl chloride and plastics with lower density than water such as polyethylene, polypropylene are separated into two groups using wet separation process. Plastics with lower density are much larger than plastics with higher density. The drawback is that it is impossible yet to mechanically sort out municipal solid waste and get commercial product despite carrying out extensive research on municipal solid waste MSW. Therefore it's a better choice to separately dispose of household waste [10].

2.3.2 Composition of plastic waste:

Waste composition is governed by factors such as economic progress, industrial development, and culture and energy resource utilization. Less developed/developing countries generate more organic waste. Developed countries have the highest portion of municipal solid waste that includes paper, plastic etc. For developed countries, organic waste and inerts decrease, with the increase in paper and plastic waste.

Generally the plastic waste composition includes

- Polyethylene terephthalate

  Soft drink bottles, mineral water bottles and others

- High density polyethylene

  Plastic bags, shampoo bottles, detergent bottles, toys etc

- Polypropylene

  Caps for bottles and containers

- Low density polyethylene

  Shopping bags, dairy product bags, food bags, garment and clothing bags etc

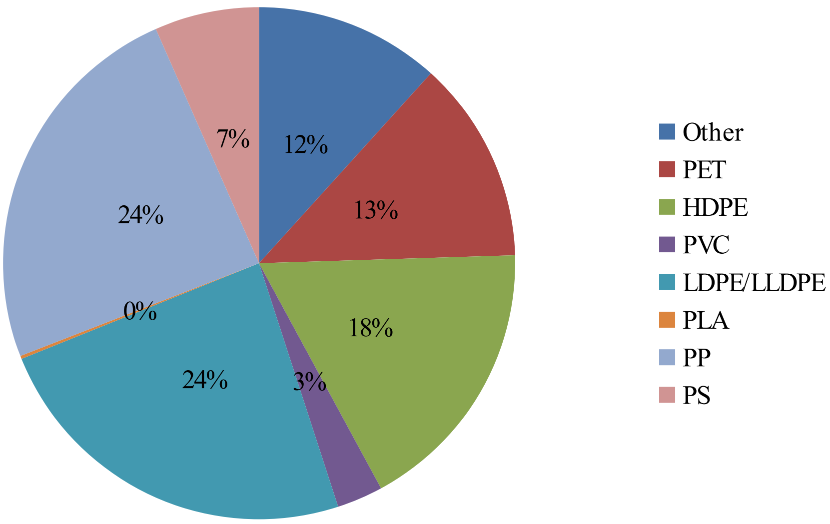

Figure 2.2 Average plastic waste composition based on the type of plastic [8]

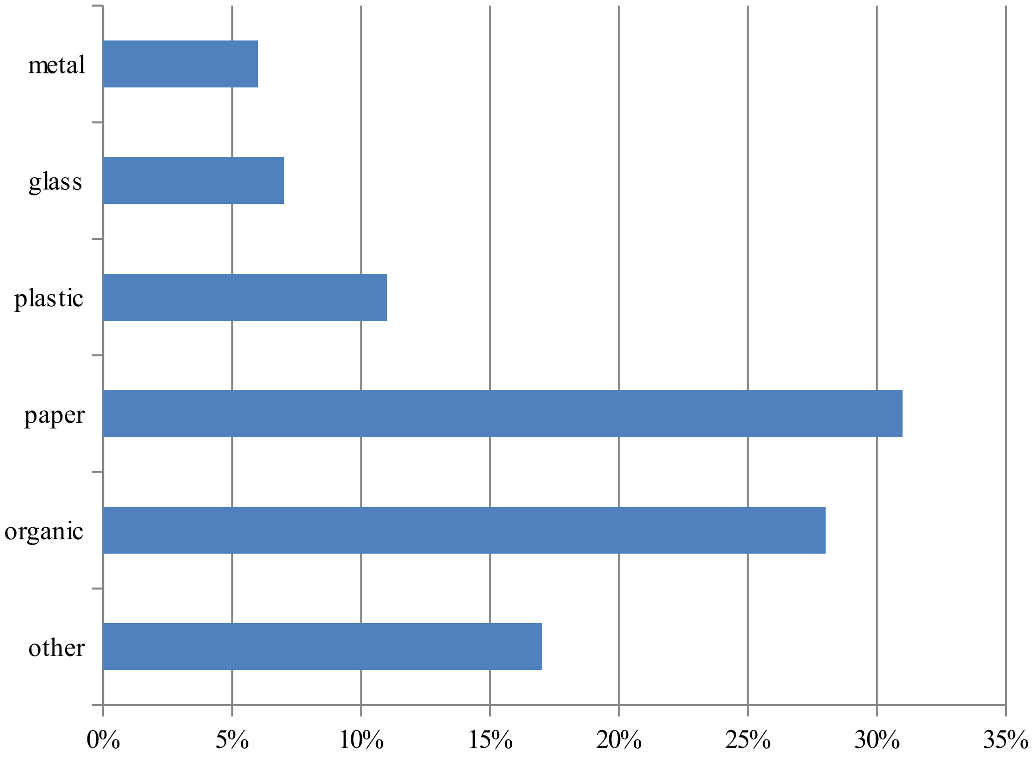

Figure 2.3 Waste compositions in less developed countries [6]

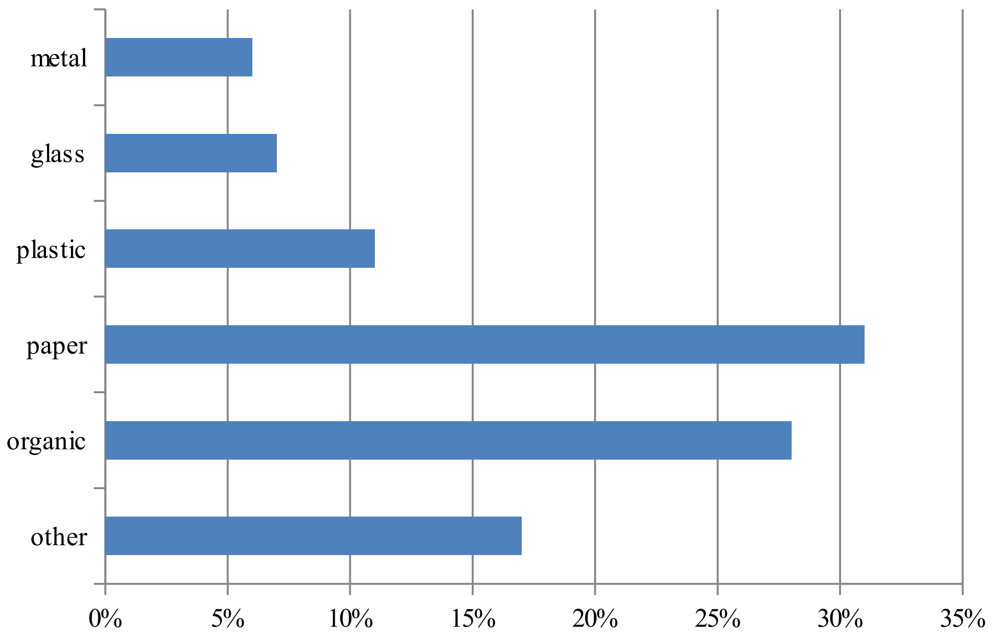

Figure 2.4 Waste compositions in developing countries [6]

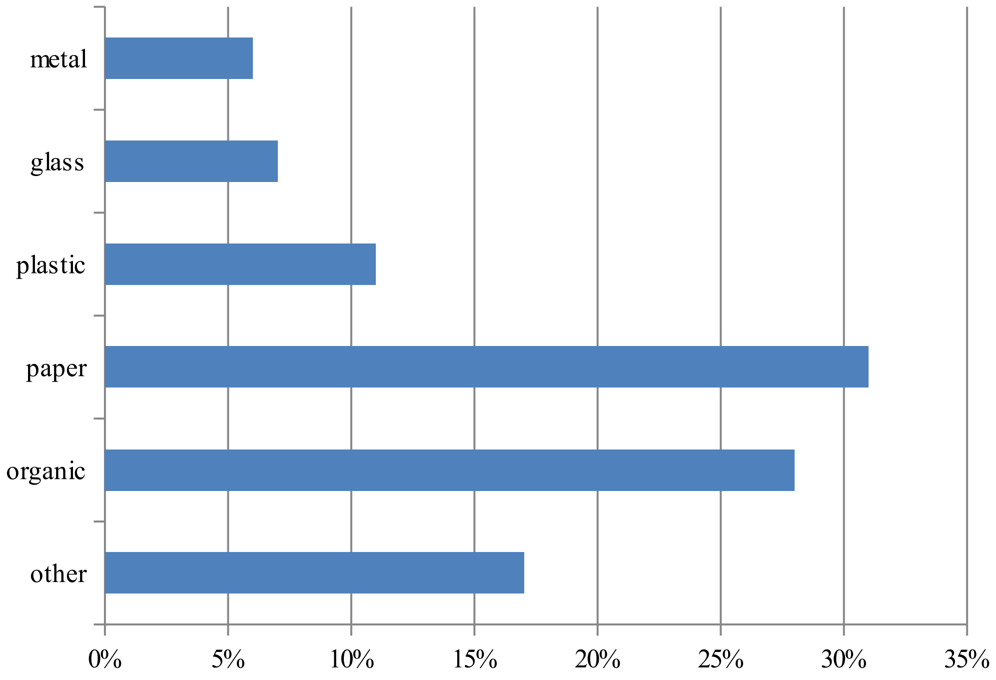

Figure 2.5 Waste compositions in developed countries [6]

2.3.3 Comparison between thermo sets and thermoplastics

Thermo sets and thermoplastics look same but they have different characteristics and applications.

2.3.3.1 Thermo sets

Thermo sets are those polymers that cure irreversibly, retaining their shape and strength when subjected to heat. Thermo sets are made of polymers that when undergo curing process, cross-link together and make an irreversible bond that is chemical in nature. The risk of product re-melting is eliminated in this cross-linking process. This makes thermo sets suitable for high heat applications such as electronics [16]. Thermo sets plastics used in different materials improve the physical and chemical resistance including heat resistance and structural integrity along with increasing mechanical endurance. Thermo sets are generally used for sealing products due to their resistance to deformation.

Pros

- Flexibility in design
- Thick to thin wall effectiveness
- Good aesthetic appearance
- Price effective
- Higher heat resistance than thermoplastics
- Dimensional stability

Cons

- Hindrance to recycling
- Difficult to achieve surface finish
- Cannot be remolded or reshaped

2.3.3.2 Thermoplastics

When heat is applied to thermoplastics, they soften and transform into a fluid. Curing of thermoplastics is completely reversible as the bonds are not chemical in nature. Materials physical properties are not affected when thermoplastics are remolded and recycled.

Mostly the benefits that come from thermoplastics are that they offer high shrink resistance, easy to bend property and high strength.

Pros

- Sustainable manufacturing
- Good recyclability
- Aesthetically better finishes
- Greater impact resistance
- Chemical resistance

- Hard crystalline options
- Remolding ability

Cons

- Higher cost compared to thermo sets.
- Can melt on heating.

2.4 Different ways to manage plastic waste

Need for plastic commodities have increased with increase in world population during previous 40 years. Polymers are biologically non-degradable; therefore it is not easy to return them to natural carbon cycle. There are four main ways available to for plastic waste treatment and recycling, re-extrusion (primary), mechanical (secondary), chemical (tertiary) and energy recovery (quaternary). Each technique has its own plus points that make it useful for specific applications and locations. Proper treatment is the key to plastic waste management and is significant from energy, environmental, financial and legislative point of view [11, 15]. In advanced countries, organic waste and plastics are disposed of by incineration. Majority of the plastic waste in early 2000 is done by land filling (65-70%) and incineration (20-25%). Recycling is only about 10%. In Japan, during decade of 1980, 45 % of plastic waste was subjected to land fill, 50 % incineration and other 5 % underwent separation and recycling. Highest percentage of recycling was estimated for India in 1998 that represented 60 % of plastic waste generated.

2.4.1 Land filling

Mostly, the solid waste including polymers is thrown into landfills. However due to increasing cost, decreasing space, legislative pressures, greenhouse gases generation and poor bio-degradability, landfill is becoming unwanted and unwelcome.

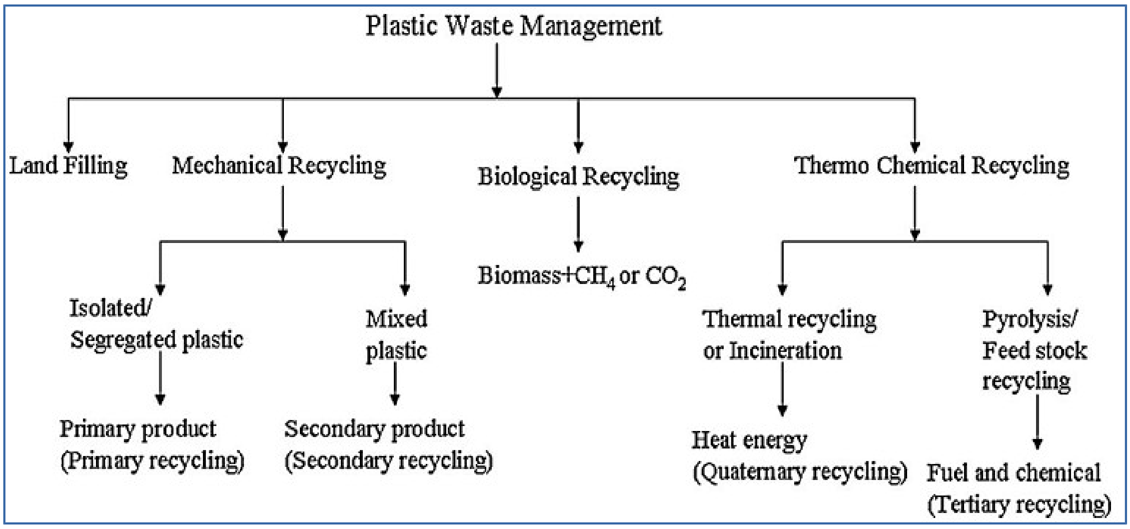

Figure 2.6 Ways to manage plastic waste [16]

2.4.2 Mechanical recycling

In mechanical recycling, used plastics are processed or reprocessed to form new alike products. Mechanical recycling comes under primary and secondary recycling of plastic waste in which homogeneous plastic waste is concerted into products that are of same value and performance or less. It has been learnt from experience that treatment of mixed plastics that are contaminated gives polymer blends that are mechanically of less quality. Additionally they are not durable. Although mechanical recycling seems to be a “green” process, the process is not economic as it requires high energy for cleaning, separating, transportation and processing. Recycling the material from household waste is notably difficult as they are polluted with organic residues. Different technologies like IR spectroscopy, electrostatics and flotation are used to separate plastics automatically according to type. Apparently, plastic recycling via mechanical means is not a suitable option considering the quality of recycled product.

2.4.3 Biological recycling

Industrial products e.g. Tyres made from isoprene are highly resistant to bio-degradation due to the presence of highly efficient antioxidants that are added during their manufacture. This led to extensive research on industrial as well as universities level to develop polymeric materials that come to the expectation of user as well as are biologically degradable [15]. As a result, polymers that are bio-degradable were developed that convert to biomass after some time. These plastics are being successfully used in many countries.

The drawback associated with these degradable plastics is that these will not decompose if disposed of under inappropriate circumstances. For instance, a photodegradable plastic will not decompose in the absence of light. Also, these may become a factor in increasing greenhouse gases emissions such as methane, as methane is released under anaerobic conditions. It may be difficult to sort out degradable and non-degradable plastics or complicate the sorting system. Furthermore, the use of bio-degradable may cause an increase in the plastic waste if people think that these materials will simply decompose [12].

2.4.4 Thermal recycling

Burning of plastic waste for is a feasible option for energy recovery as polymers are hydrocarbons. These hydrocarbon polymers substitute fossil fuels thereby reducing co_2 load on environment. It can be seen from the table that calorific value of polyethylene is same as fuel oil. Incineration is better option for energy recovery as waste plastic can be sold as fuel [18, 19]. Combined incineration of plastic waste and other municipal waste can also be practiced as plastics have high calorific value and therefore can increase the heating value of MSW and can be helpful in an efficient incineration.

Energy recovery by incineration is the most developed and widely used process of thermal treatment of waste but it is only advised as a feasible way to manage waste when the material recovery processes don’t give good results or fail or when the cost is too high.

However the incineration of plastic waste in some developed countries has led to public distrust as burning produces harmful greenhouse gases and other highly lethal toxins. The possible connection that relates plastics fed and production of dioxins and furans is still unknown, though there is a possibility that the presence of chlorine in PVC and other plastics is responsible for formation of these toxic compounds.

Table 2. 3 Calorific values of polymers in comparison with conventional fuels [17]

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

2.4.5 Chemical recycling

In chemical (tertiary) recycling, waste polymers are converted into original monomers or other useful chemicals. The products of chemical recycling are utilized as input for various chemical and industrial processes or as transportation fuels [20]. Chemical recycling is currently the highest form of general development for managing plastic waste. Pyrolysis (catalytic, thermal and hydro cracking), depolymerization and partial oxidation are the ways for chemical recycling of plastics.

2.4.6 Depolymerization

Reversible synthesis reactions can be employed to depolymerize condensation polymers (polyamides, polyesters, nylons and polyethylene terephthalate) to initial diacids and diols or diamides. High conversion to raw monomers can be achieved by depolymerization reactions such as alcoholysis, glycolysis and hydrolysis. However, reverse synthesis reactions are not much efficient in depolymerizing addition polymers that include polyolefin (making 60-70% of municipal plastic waste) [24].

2.4.7 Partial oxidation

Light hydrocarbons, NOx, sulfur oxides and dioxins are released when polymer waste is directly burnt. Although the calorific value of polymer waste is good, but direct burning is harmful for the environment as above mentioned noxious substances are released into the atmosphere. This can be overcome by partial oxidation in which mixture of hydrocarbons along with synthesis gas (CO and

H_2O) [21, 23]. An increase in production of hydrogen and reduction in carbon monoxide content has been observed in co-gasification of polymer waste and biomass. Oxidation through the use of no and o_2 for the manufacturing of chemicals in bulk e.g. acetic acid from polyolefin is also viable.

2.4.8 Cracking/pyrolysis

Pyrolysis, also called thermolysis (Greek: pur = fire, thermos = warm, luo = loosen) involves chemical and thermal degradation that leads to molecules smaller in size [22]. Symbolically, the term thermolysis sounds more relevant than pyrolysis, as fire entails the existence of oxygen, and therefore reactive and oxygen containing intermediates. However, for achieving higher quality and yield and for safety purposes, air is excluded in many pyrolysis processes.

Useful lower molecular weight compounds form as a result of cracking. Cracking is done in three different ways [25]

- Hydro cracking
- Thermal cracking
- Catalytic cracking

2.4.8.1 Hydro cracking

Hydro cracking of polymer waste involves catalytic reaction of polymer with hydrogen in a stirred batch reactor at mild pressures and temperatures (423-673 k and 3-10 MPa hydrogen) [26].

Two main chemical reactions occur in the hydro cracking unit: degradation of heavier hydrocarbons into lighter and unsaturated hydrocarbons, and then the saturation of these fresh unsaturated hydrocarbons using hydrogen. Temperature increase and heat is released when the saturation occurs. Hydrogen also acts as temperature controller as it is inserted at various points of the reactor. Several catalysts that are used in refining hydro cracking reactions have been studied and include transition metals (such as Pt, Ni, Mo, and Fe) supported on acid bases (e.g. Alumina, amorphous silica-alumina, zeolites, sulfated zirconia) [18,27]. These catalysts possess degrading and hydrogenating abilities.

2.4.8.2 Thermal cracking

Sometimes referred to as pyrolysis, thermal cracking involves chemical breakdown of polymeric materials by heating in oxygen-free atmosphere. Thermal cracking is carried out between 350 °C and 900 °C [28, 29]. The products are solid residue (carbonized char) and a volatile component. Process conditions and type of plastic dictate the products of pyrolysis. A drawback of thermal pyrolysis is that the process requires high temperatures. Also the products obtained are of broad range. Catalytic pyrolysis addresses these problems.

2.4.8.3 Catalytic pyrolysis

Catalytic pyrolysis involves cracking of plastic using a suitable catalyst. The drawbacks of thermal pyrolysis are overcome by catalytic pyrolysis as catalyst decreases the parameters of reaction such as reaction temperature and time.

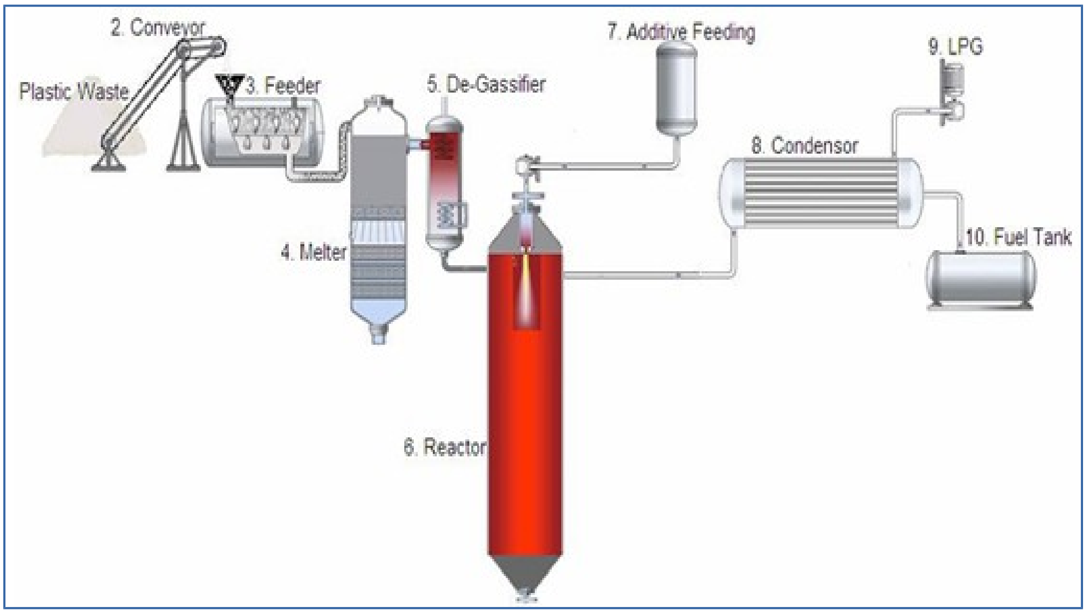

Figure 2.7 Alka Zadgoankar's process for conversion of plastic waste into liquid hydrocarbons/energy [11]

Additionally, catalytic pyrolysis gives narrow product distribution of carbon atom number with peak at lighter hydrocarbons and occurs at significantly less temperatures.

Table 2.4 Comparison of fuels from Alka's process and regular gasoline [11]

Properties	Regular gasoline	Plastic waste fuel
Color	Orange	Pale yellow
Specific gravity at 28° c	0.7426	0.7254
Specific gravity at 15°c	0.7528	0.736
Gross calorific value	11210	11262
Net calorific value	10460	10498
API gravity	56.46	60.65
Sulfur content by weight	0.1	<0.002
Flash point ° C	23	22

Cloud point °C	<-20	<-20
Pour point	<-20	<-20
Reactivity with MS	Nil	Nil
Reactivity with chlorine	Nil	Nil
Reactivity with aluminium	Nil	Nil
Reactivity with copper	Nil	Nil
Reactivity with stainless steel	Nil	Nil

2.5 Catalysts for cracking plastics

Heterogeneous catalysts are the most widely used catalysts for cracking of plastics. They can have impact on the type of upgrading reactions that occur, the rate of reaction, and the distribution of products [16, 17]. Catalyst is in a different phase to the reactions in a heterogeneous catalyst system. This system is widely applied in pyrolysis. The advantage is that they can tolerate severe reaction conditions (up to 1300° c and 35 MPa) and can easily be separated from the gas and/or liquid products and reactants. Heterogeneous catalysts are porous materials and possess high surface areas. Reactions are more efficient when the surface area is high as the reactions take place on the surface of the catalyst. Zeolites are the most applied shape selective catalysts [17, 18]. Catalyst porosity and shape are critical parameters. Hydro processing catalysts are bi functional as they carry hydrogenation and cracking abilities [19].

Zeolites, silica-alumina, alumina, FCC catalysts and reforming catalysts have been studied for pyrolysis of plastics [20]. These are used for cracking and processing heavy hydrocarbons in petroleum sector. Though several catalysts have been investigated, zeolites and mesoporous materials are most important due to their high porosity, acidic properties and high surface area. Zeolites having acidic properties like hzsm-5 and h-ultra stable y-zeolite are more effective in converting polyolefins than those having less acidic properties such as amorphous silica-alumina and mesoporous MCM-41. When commercial aspects are taken into account, cheaper catalysts like silica-alumina give good selectivity [21].

Summary

Plastic consumption all over the world has been increasing on a yearly average of approximately 10%. Developed countries are the largest consumers of plastics, while there is a huge potential of plastics consumption in developing countries especially in the regions of Asia. A number of ways have been developed for plastic waste management and/or energy recovery that include land filling, mechanical recycling, chemical recycling etc; yet catalytic pyrolysis has been found to be the most sustainable of all processes. The catalysts that have been tested in various research activities include silica-alumina, FCC catalysts, shape selective catalysts like zeolites, transition metals etc. of all these catalysts, zeolites and clays have been found to show remarkable results due to their surface area and acidic properties.

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Chapter 3

Methodology

3.1 Materials

3.1.1 Plastics

Waste polypropylene (used plastic disposable glasses) was collected from junkyards of National University of Sciences and Technology (NUST). Waste plastic disposable glasses were washed and reduced to smaller pieces by scissor. Thermo gravimetric analysis of the waste plastic was performed by Perkin Elmer TGA analyzer in a silica crucible at temperature range of 25-550° C at heating rate of 10°C/min. The melting point of waste sample is 172°C [1] which confirms that the sample is polypropylene.

Figure 3.1 Polypropylene disposable glasses

3.1.2 Catalyst

Kaolinite is a clay mineral. Rocks that are abundant in kaolinite are called kaolin or china clay [2, 5]. Kaolinite is soft almost white clay that is an essential component in the production of china and porcelain [3]. Kaolinite is a major ingredient in kaolin which usually consists of quartz and mica along with feldspar, illite, bauxite, and halloysite [4-9].

Use of clays and alumino silicates as catalysts is as old as concept of catalysis. Benonites and kaolinites were among the first acid-activated catalysts. Acid-activated catalysts are still a charm for researchers compared to the dominant zeolites currently used in petrochemical industries due to their low cost. Additionally the structure and dimensions of the pores of clays are more suitable than zeolites for cracking of large molecules [10].

Numerous ways have been suggested in literature to improve the structure and other properties of clays which are intercalation, thermo chemical treatments and chemical activation [11].

The catalyst used in this research, commercial grade kaolin clay was obtained from Sigma Aldrich. Hydrochloric acid (36.5%) was also obtained from Sigma Aldrich. Nickel nitrate 98% (Sigma-Aldrich), hydrochloric acid, kaolin clay, distilled water were used for the preparation of catalysts.

3.2 Methodology

One set of experiment was comprised of two steps as following

1. Acidification of clay
2. Catalytic pyrolysis

3.2.1 Acidification of clay

Acid treatment of clay was carried out by adding 50 g of clay to 500 ml of hydrochloric acid solution of different concentrations (1 M, 3 M and 5 M). Reflux condensation was used for acid treatment at temperature range of 80-100 °C and atmospheric pressure in a round bottom flask. Reflux condensation was done for 6 hours. 500 ml ice cold distilled water was then added to rapidly quench the clay suspension. Resulting content was repeatedly washed with distilled water and filtered to remove any unspent acid. Drying was carried out in an oven at 120 °C overnight. Subsequently, calcination was done at 500° C for 4 hours and grounded in mortar pastel to powder form. The untreated sample is named as CC while treated samples are named as CC1M, CC3M, CC5M (numbers refer to the different concentration of acid used).

CC3M was used as support for other sample named as CC3M5 (5 indicates the weight percent of active metal nickel on support). Nickel on acid treated clay was prepared by incipient wetness impregnation method. The nickel loading was 5 weight percent as metal. The required amount of support was calcined at 500° C for 4 hours. Metal precursor was then dissolved in 50 ml water and subsequently the solution was poured on the support and stirred for 30 minutes approximately.

Then, the sample was dried at 100° C and was ground to fine powder after complete evaporation.

The clay samples were characterized by using XRD technique to understand the consequences of acid treatment.

3.2.2 Catalytic pyrolysis:

For each experiment, 20 g of waste polypropylene samples were used. In each reaction, kaolin clay treated with different molar concentrations of hydrochloric acid (1 M, 3 M and 5 M) was used for pyrolysis in the batch reactor heated at 20° C/min up to desired temperature. The condensable liquid products were collected at the other end and weighed. After reaction, solid residue left in the round bottom flask at the reaction end was weighed. Weight of gases was calculated using the mass balance. Operating temperatures for the reaction were in the range of 400-500° C. Reaction time was calculated from the start of reaction exceeding the room temperature till the completion of reaction (the time when no liquid comes from the tube end).

3.3 Catalyst characterization techniques

Clay samples were characterized by x-ray diffraction (XRD)

3.3.1 X-Ray diffraction

X-ray diffraction analysis of kaolin clay and hydrochloric acid treated kaolin clay was done using Philips Analytical instrument at an angle of two theta.

3.4 Analysis of oil

Composition of oil was determined using GC-MS and functional group by FTIR.

3.4.1 Fourier transformation infrared spectroscopy:

FTIR of the oil obtained by plastic cracking was done at various temperatures in a PerkinElmer spectrum 100 Fourier transformed infrared spectrometer with resolution of 4cm^{-1}, in the range of 400-4000cm^{-1}. Reference used to know the functional group was Nujol Mull.

3.4.2 Gas chromatography and mass spectrometry:

GC-MS of oil was carried out using GC-MS-QP 2010 ultra (Shimadzu) to know the composition of oil. The composition was found by comparing with NIST library.

Figure 3. 2 Experimental setup of pyrolysis 1

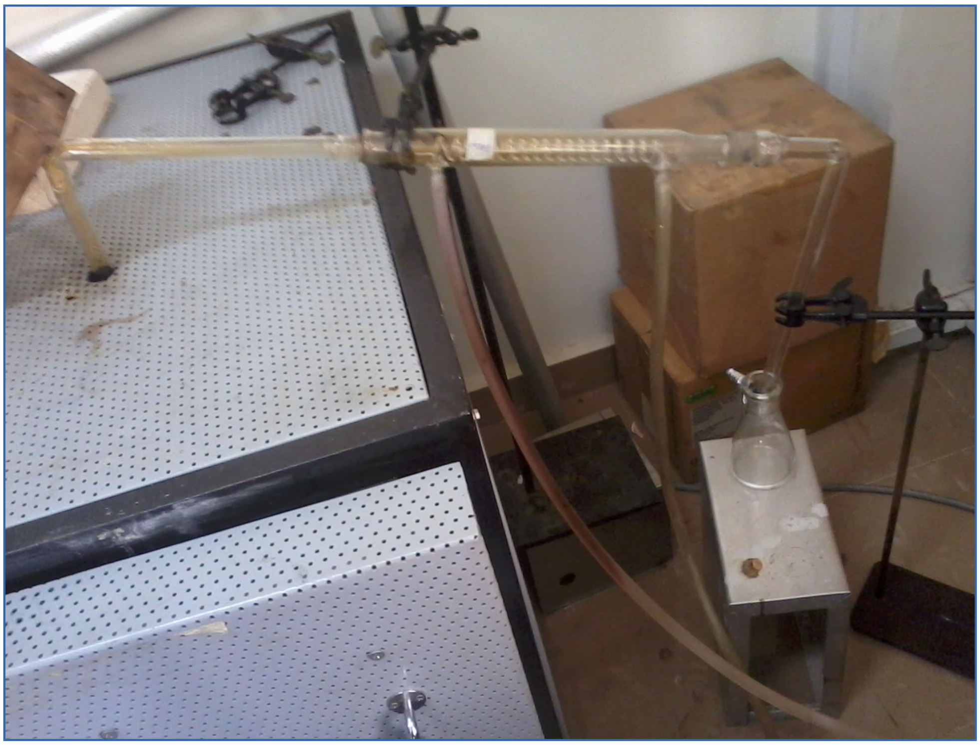

Figure 3.3 Experimental setup of pyrolysis 2

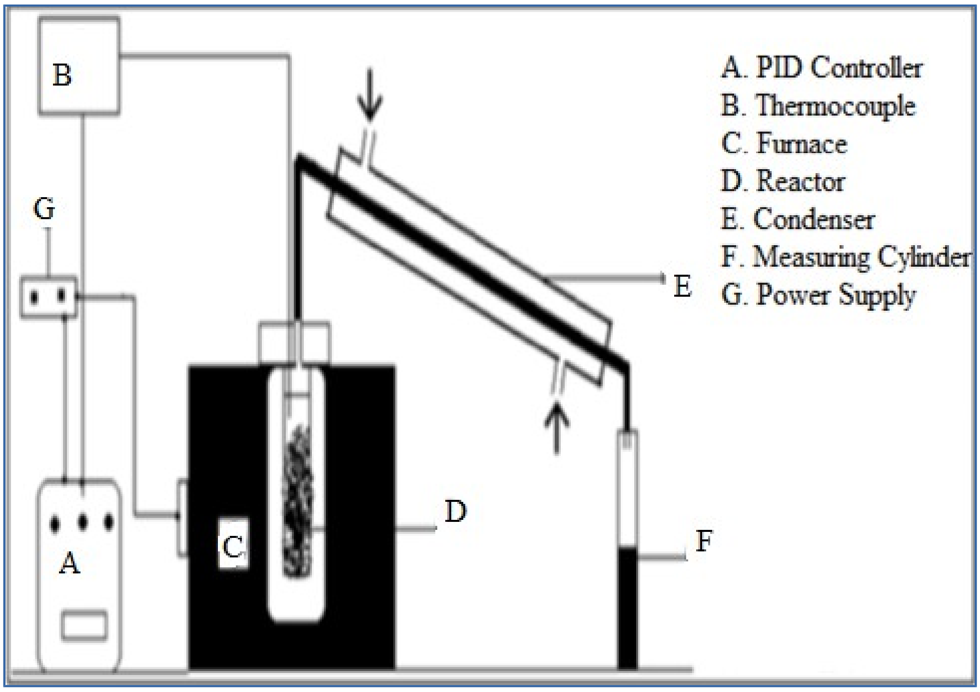

Figure 3.4 Schematic representation of experimental setup

Figure 3.5 Experimental Setup (Condenser)

Summary

Polypropylene was selected as a sample out of all plastics because it constitutes the major part of plastic waste composition. Clays are abundantly available and economic. Besides the availability, little work has been done on clays. Previous research has shown that acidity of clays can be enhanced by treating them with acids. Batch reactor was used for the pyrolysis. Effect of temperature and degree of acid treatment on the product and the reusability of catalyst have been studied.

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Chapter 4

Results and Discussion

4.1 Effect of hydrochloric acid treatment on kaolin clay

4.1.1 XRD analysis

XRD analysis was used to investigate the changes in the structure of clay due to hydrochloric acid treatment of clay. Figure shows the profile of untreated kaolin clay

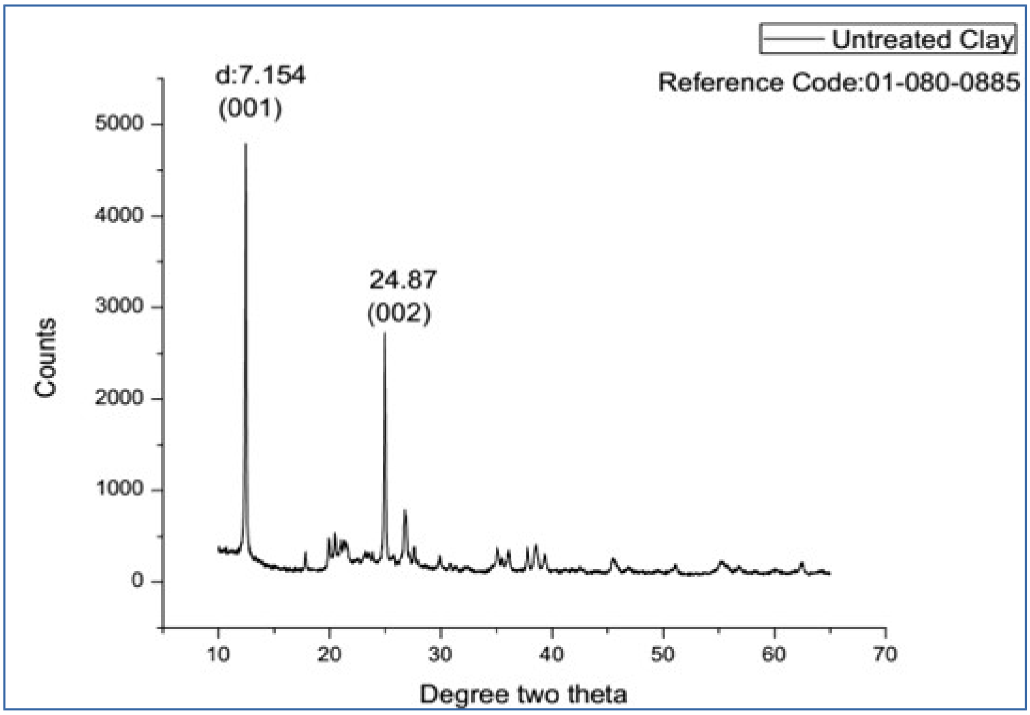

Figure 4.1 XRD analysis of untreated clay

XRD of untreated kaolin clay shows well defined reflections at 2 theta valued of 12° and 25° related to d values of 7.154 and 24.87 respectively. These peaks correspond to reflections from (001) that are characteristic peaks of kaolin clay [1]. The peaks corresponding to 2 theta values of 34-36°, 38-42°, 45-50° and 54-63° vary for different origin kaolinites [2-6].

When the clays were treated by different molar solutions of hydrochloric acid, the peak intensities of clays were found to decrease as the concentration of hydrochloric acid increased. The reason is the disorder that occurs in structure due to acid treatment which had an effect on the crystalline order of the clay [7].

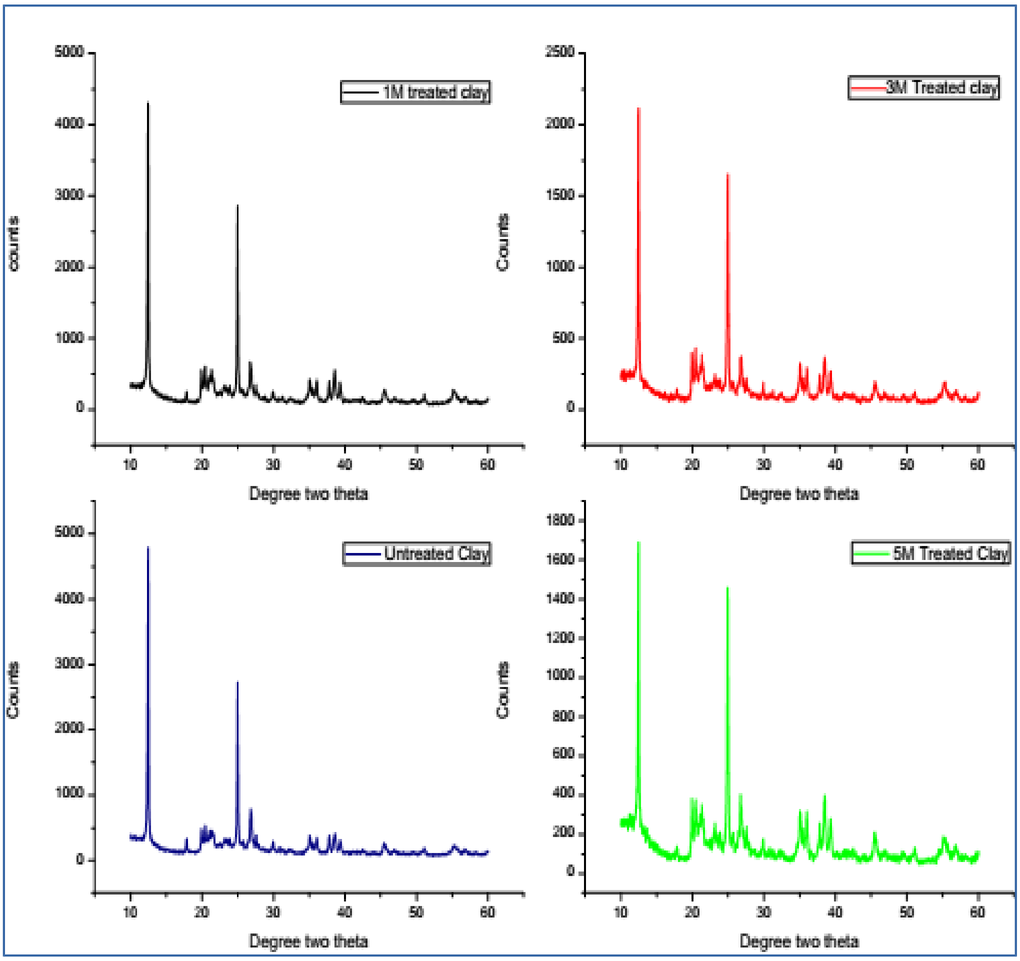

Figure 4.2 Comparison of XRD analysis of Clays untreated and treated with different molar concentrations of HCl

It was observed that as the molar concentrations of hydrochloric acid increased, the result was large degree of characteristic peak reduction. Since leaching was quite sever in case of 3 M and 5 M treated clay, the structure of clay material went near to amorphous phase as compared to crystalline phase.

Additionally, nickel was impregnated as an active metal on 3 M hydrochloric acid treated kaolin clay, as the highest yield was obtained using 3 M HCl treated kaolin clay. Characteristic peaks of nickel were matched using reference code of nickel i.e. 00-004-0850, and the peaks were matched which indicated the presence of nickel in kaolin clay.

4.1.2 TGA of polypropylene samples

Thermo gravimetric analysis of waste polypropylene was carried out in order to know the thermal properties.

Figure 4.4 shows the weight loss as a function of temperature. Degradation of waste polypropylene started at approximately 280 °C. Half of the weight loss had occurred by near 400 °C. Complete weight loss had occurred by 440 °C.

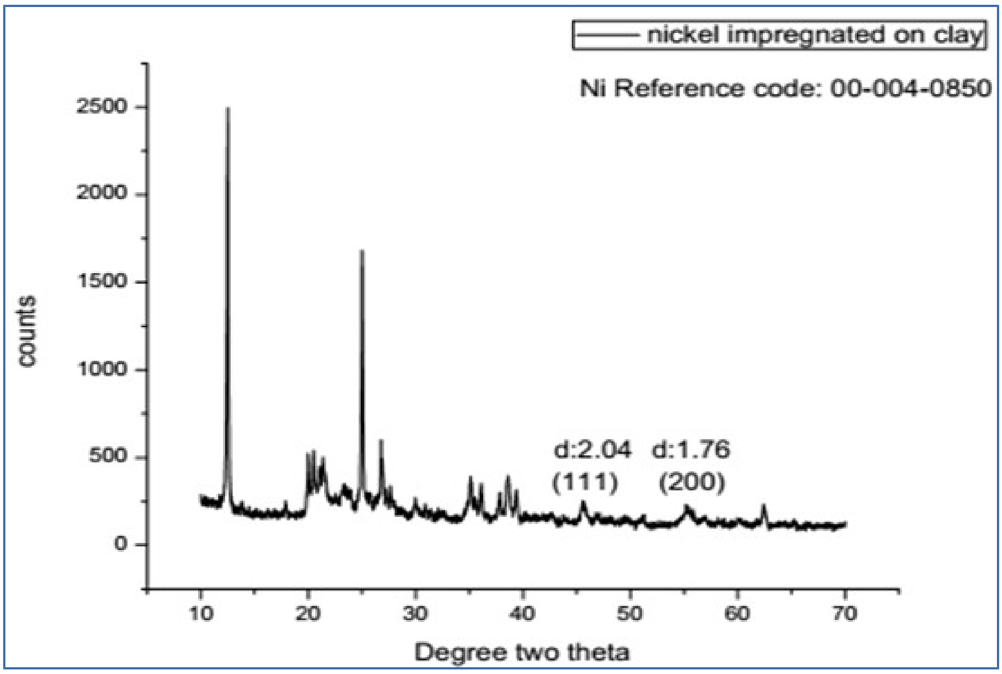

Figure 4.15 XRD analysis of clay with 5% active metal Nickel

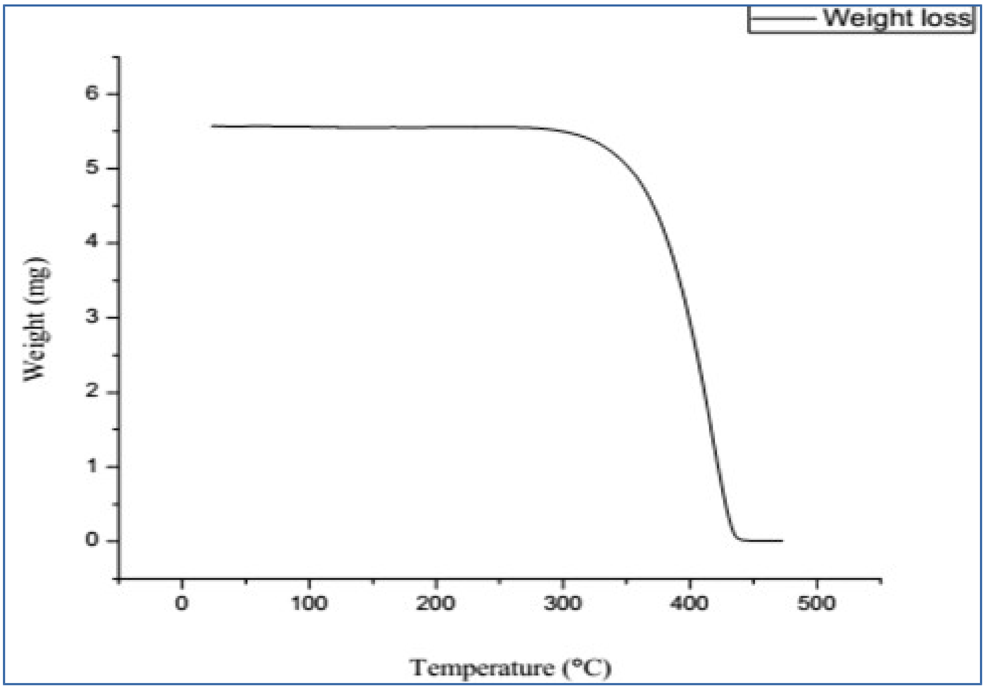

Figure 4.16 TGA analysis of polypropylene.

4.2 Results of pyrolysis

4.2.1 Pyrolysis in the absence of catalyst

Thermal degradation of waste polypropylene was carried out. The condensable products in thermal pyrolysis are high viscous liquids, and some in wax form.

4.2.2 Effect of presence of catalyst

Thermal and catalytic cracking of waste polypropylene was carried out in presence of kaolin clay as catalyst with polypropylene to catalyst ratio 3:1. Polypropylene to catalyst ratio used for all reactions was 3:1. Rate of production of oil increased with use of acid treated kaolin clay compared to pure clay. Reaction time decreased and oil yield increased for pure clay and acid treated kaolin clay compared to thermal pyrolysis. Also, as the degree of acid treatment increased from 1 M to 3 M hydrochloric acid, the liquid yield increased with increased molar concentration of acid. When the reaction was carried out using 5 M hydrochloric acid treated clay, the gas yield increased and liquid yield decreased in comparison to 3 M hydrochloric acid treated clay. The higher yield of gas is due to higher acidity [8]. Condensable products in catalytic pyrolysis, even at higher temperatures were also less viscous liquid and not high viscous liquid or in wax form compared to thermal pyrolysis. All the changes explained above can be described due to its mesoporous surface and acidity, which facilitated the degradation of polypropylene [9, 10].

The percentage liquid obtained from 5% nickel impregnated on 3 M hydrochloric acid treated clay was same as obtained using 3 M hydrochloric acid treated clay, yet the products were different along with FTIR assignments.

4.2.3 Reusability of catalyst:

Reusability of kaolin catalyst was studied by regenerating the catalyst a number of times in the cracking of catalyst and results are shown in the following table. It was observed that liquid yield in grams almost remained the same up to two time repeated use after the first use. After that the liquid yield decreased significantly. It is also noteworthy that reaction time increased with repeated use of catalyst.

Table 4.1 Percentage liquid yield obtained by using different catalysts

	No catalyst	Pure clay	1 M HCl treated clay	3 M HCl treated clay	5 M HCl treated clay
Liquid yield (gram)	11.09	12.13	12.89	14.98	12.27
Gas yield (gram)	5.8	5.45	5.41	4.43	6.94
Residue (gram)	3.11	2.42	1.7	0.59	0.79
% liquid conversion	55.45 %	60.65 %	64.45 %	74.9 %	61.35 %

Increase in reaction time and decrease in liquid yield may be due to the carbon deposits on the catalyst and other impurities on the surface. 3 M hydrochloric acid was regenerated after fourth time by calcining it inside a muffle furnace at 800°C for one hour. When the catalyst was regenerated at higher temperatures, the deposited carbon burnt off and the regenerated catalyst gave almost the same activity as that of first time use.

Table 4.14 Reusability of the catalyst

No. Of times reused	Weight of oil in grams	Weight of gas in grams	Weight of residue in grams	Reaction time in minutes
Fresh	14.98	4.43	0.59	50
First time	14.94	4.36	0.7	58
Second time	14.22	4.26	1.52	63
Third time	12.18	4.20	3.62	72
Regenerated	14.73	4.39	0.88	58

4.3 Characterization of liquid products:

The oil samples were analyzed using characterization techniques FTIR and GC-MS for functional group identification and detailed composition respectively.

4.3.1 FTIR analysis of oil:

The figures and tables below indicate the FTIR of thermal and catalyzed pyrolysis oil at 500° C. From the tables and figures, it is clear that the oil mostly consists of alkanes, alkenes and some oxygenated compounds. The presence of oxygenated compounds is due to the fact that pyrolysis setups were not performed in vacuum conditions.

Table 4.15 FTIR Assignments of Oil Obtained in Thermal Pyrolysis

Wave Number	Vibration type	Nature of functional group
739	C-H bend	Alkenes, phenyl ring substitution
888	C-H out of plane bend	Alkenes
967	C-H bend	Alkenes
1156	C-O stretch	Alcohols, ethers, carboxylic acids, esters
1378	C-H Scissor and bend	Alkane
1458	C=C stretch	Alkenes
1650	C=C stretch	Alkenes
2727	O-H stretch	Carboxylic acids, aldehydes
2872	C-H stretch	Alkanes
2926	C-H stretch	Alkanes
2957	C-H stretch	Alkanes

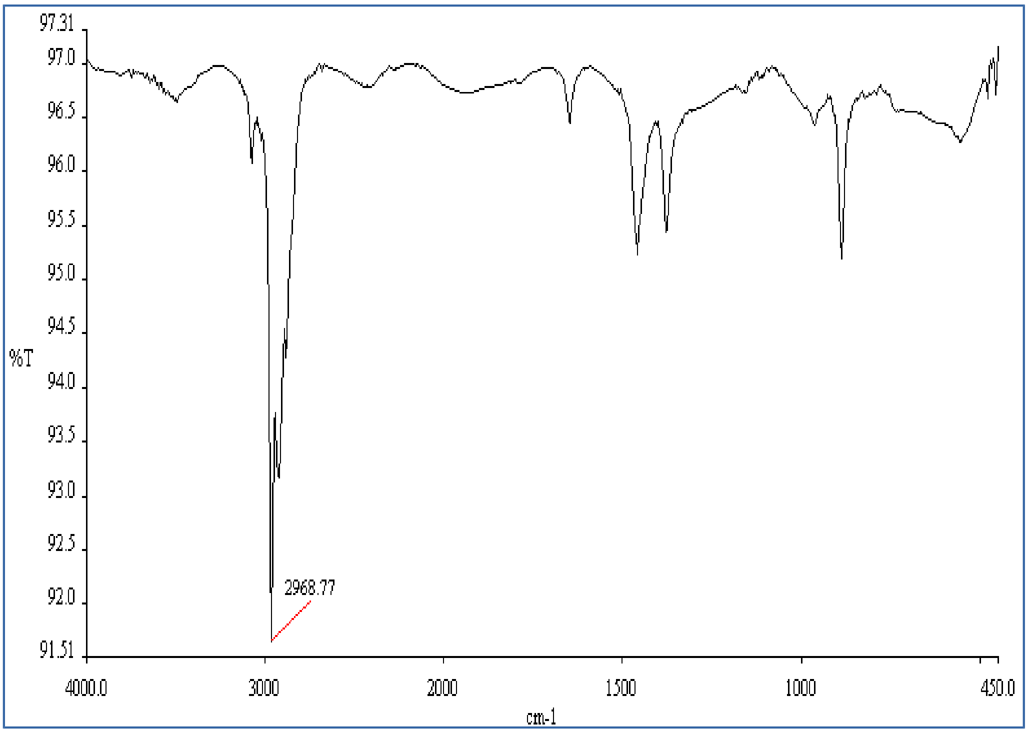

Figure 4.17 FTIR of Oil Obtained in Thermal Pyrolysis

Table 4.16 FTIR Assignments of Oil Obtained 3M Treated Kaolin Clay as Catalyst

Wave Number	Vibration type	Nature of Functional Group
888	C-H out of plane bend	Alkenes
967	C-H bend	Alkenes
1157	C-O stretch	Alcohols, Ethers, Carboxylic acids, Esters
1378	C-H Scissor and Bend	Alkane
1456	C=C stretch	Alkenes
1650	C=C stretch	Alkenes
2872	C-H stretch	Alkanes
2927	C-H stretch	Alkanes
2958	C-H stretch	Alkanes
3075	=C-H stretch	Alkenes

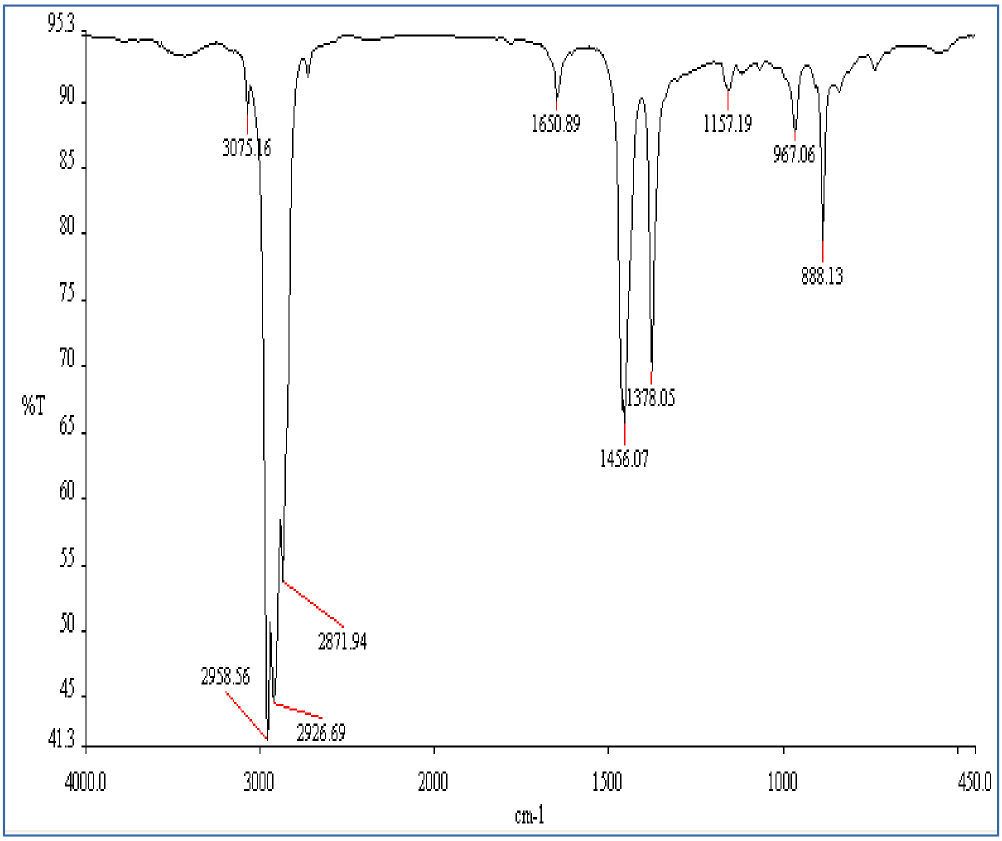

Figure 4.18 FTIR of Oil Obtained 3M Treated Kaolin Clay as Catalyst

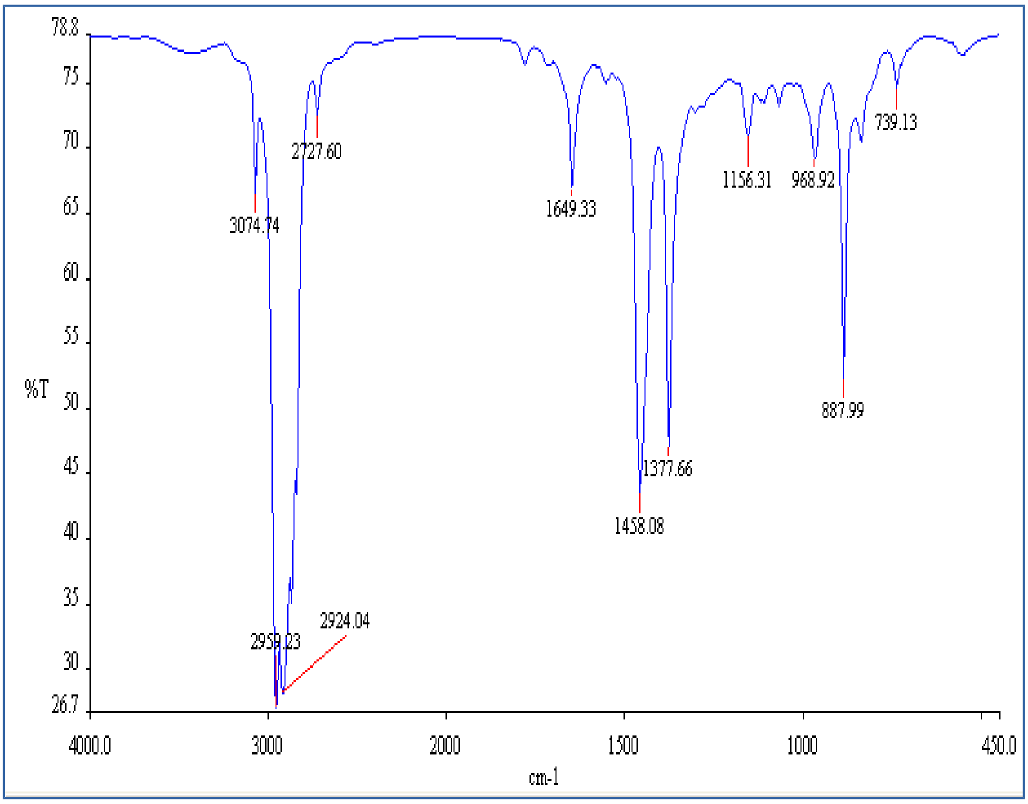

Figure 4.19 FTIR of Oil Obtained using 5% Nickel Impregnated on 3M Treated Kaolin Clay as Catalyst

Table 4.17 FTIR Assignments of Oil Obtained using 5% Nickel impregnated on 3M Treated Kaolin Clay as Catalyst

Wave Number	Vibration type	Nature of Functional Group
739.13	C-H bend	Alkenes, Phenyl ring
887.99	C-H out of plane bend	Alkenes
968.92	C-H bend	Alkenes
1156.31	C-O stretch	Alcohols, Ethers, Carboxylic acids
1377.66	C-H Scissor and Bend	Alkane
1458.08	C=C stretch	Alkenes
1649.33	C=C stretch	Alkenes
2727.6	O-H stretch	Carboxylic acids, Aldehydes
2924.04	C-H stretch	Alkane
2959.23	C-H stretch	Alkane
3074.74	=C-H stretch	Alkenes

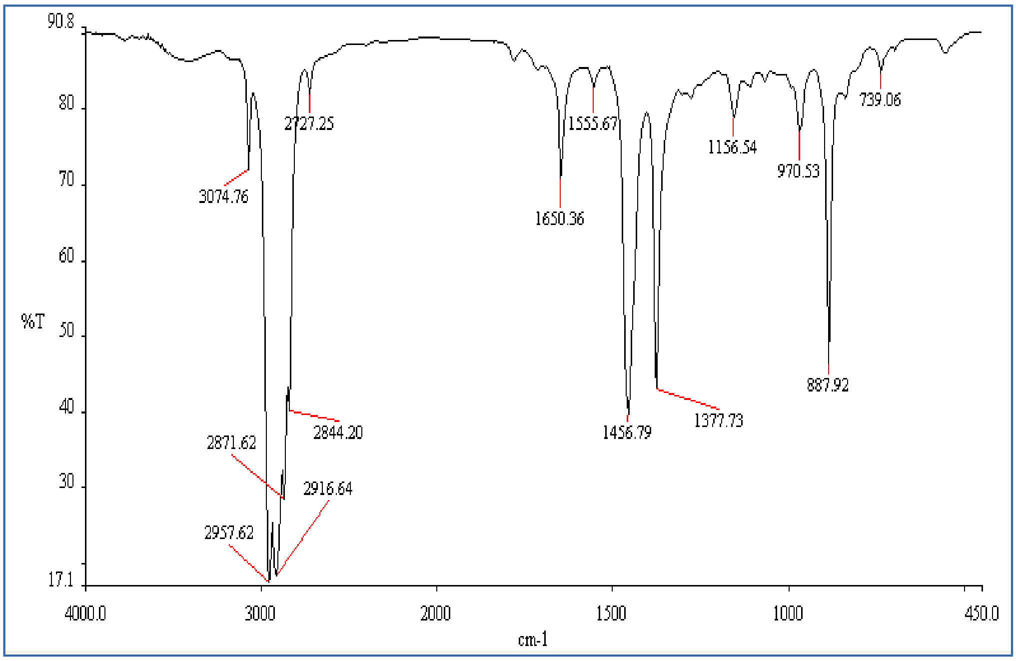

Figure 4.20 FTIR of Oil Obtained 5M Treated Kaolin Clay as Catalyst

Table 4.18 FTIR Assignments of Oil Obtained 5M Treated Kaolin Clay as Catalyst

Wave Number	Vibration type	Nature of Functional Group
739	C-H Bend	Alkenes, Phenyl ring substitution

888	C-H out of plane bend	Alkenes
970	C-H Bend	Alkenes
1156	C-O stretch	Alcohols, Ethers, Carboxylic acids, Esters
1378	C-H scissor and Bend	Alkane
1457	C=C stretch	Alkenes
1650	C=C stretch	Alkenes
2727	O-H stretch	Carboxylic acids, Aldehydes
2844	O-H stretch	Carboxylic acids
2872	C-H stretch	Alkane
2917	C-H stretch	Alkane
2958	C-H stretch	Alkanes
3075	=C-H stretch	Alkenes

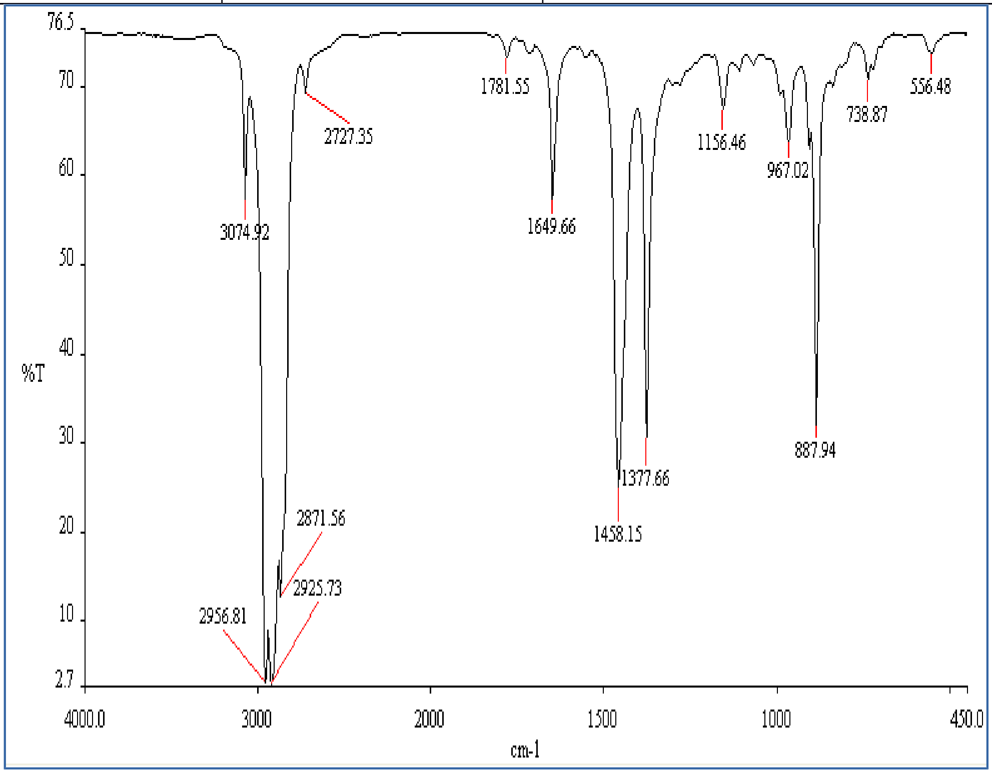

Figure 4.21 FTIR of Oil Obtained Using Kaolin Clay as Catalyst

Table 4.19 FTIR Assignments of Oil Obtained Using Kaolin Clay as Catalyst

Wave Number	Vibration type	Nature of Functional Group
556	C-Cl stretch	Alkyl Halides
739	C-H bend	Alkenes, Phenyl ring
888	C-H out of plane bend	Alkenes

967	C-H bend	Alkenes
1156	C-O stretch	Alcohols, Carboxylic acids,
1378	C-H scissor and Bend	Alkane
1458	C=C stretch	Alkenes
1650	C=C stretch	Alkenes
2727	O-H stretch	Carboxylic acids, Aldehydes
2872	C-H stretch	Alkanes
2926	C-H stretch	Alkanes
2957	C-H stretch	Alkanes
3075	=C-H stretch	Alkenes

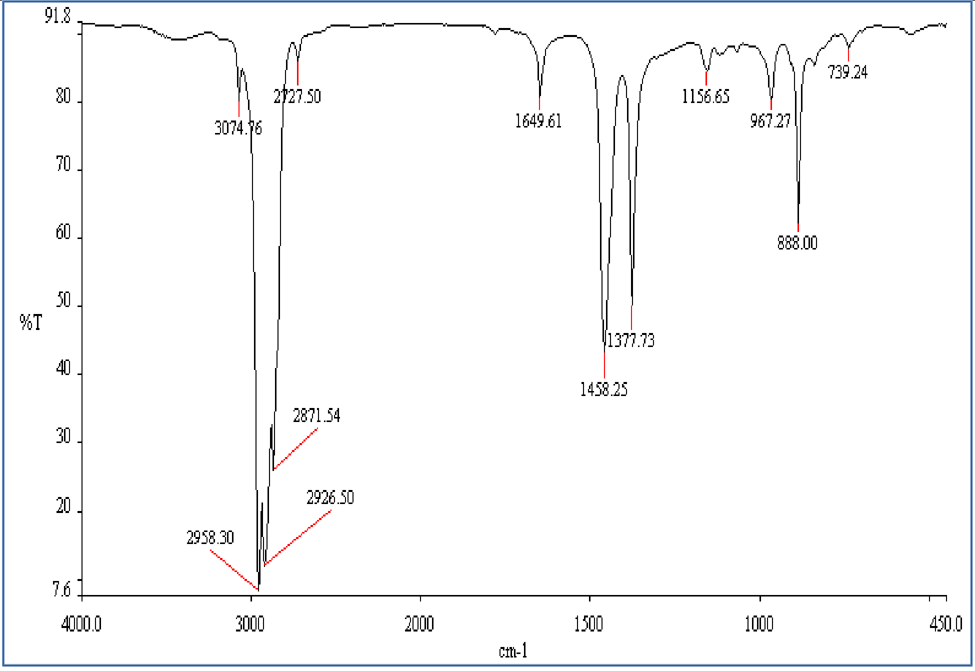

Figure 4.22 FTIR of Oil Obtained using 1M Treated Kaolin Clay as Catalyst

Table 4.20 FTIR Assignments of Oil Obtained using 1M Treated Kaolin Clay as Catalyst

Wave Number	Vibration type	Nature of Functional Group
739	C-H bend	Alkenes, Phenyl ring
-967	C-H bend	Alkenes
1156	C-O stretch	Alcohols, Carboxylic acids
1378	C-H Scissor and Bend	Alkane
1458	C=C stretch	Alkenes
1650	C=C stretch	Alkenes
2727	O-H stretch	Carboxylic acids, Aldehydes
2872	C-H stretch	Alkanes

2926	C-H stretch	Alkanes
2957	C-H stretch	Alkanes
3075	=C-H stretch	Alkenes

4.3.2 GC-MS of Oil

Composition of oil was determined by GC-MS analysis by comparing NIST library. Mostly alkanes and alkenes were found through the analysis. Also, some oxygenated compounds such as aldehydes, ketones and alcohol were also found in oil. The reason being the oxidative degradation of polypropylene, as the reactions was not carried out under vacuum conditions or oxygen free atmosphere. It is reported in some papers that polypropylene is more susceptible to oxidation compared to others as it contains tertiary carbons which form peroxides. Peroxides are further converted to more stable oxygenated compounds such as carbonyl and hydroxyl groups.

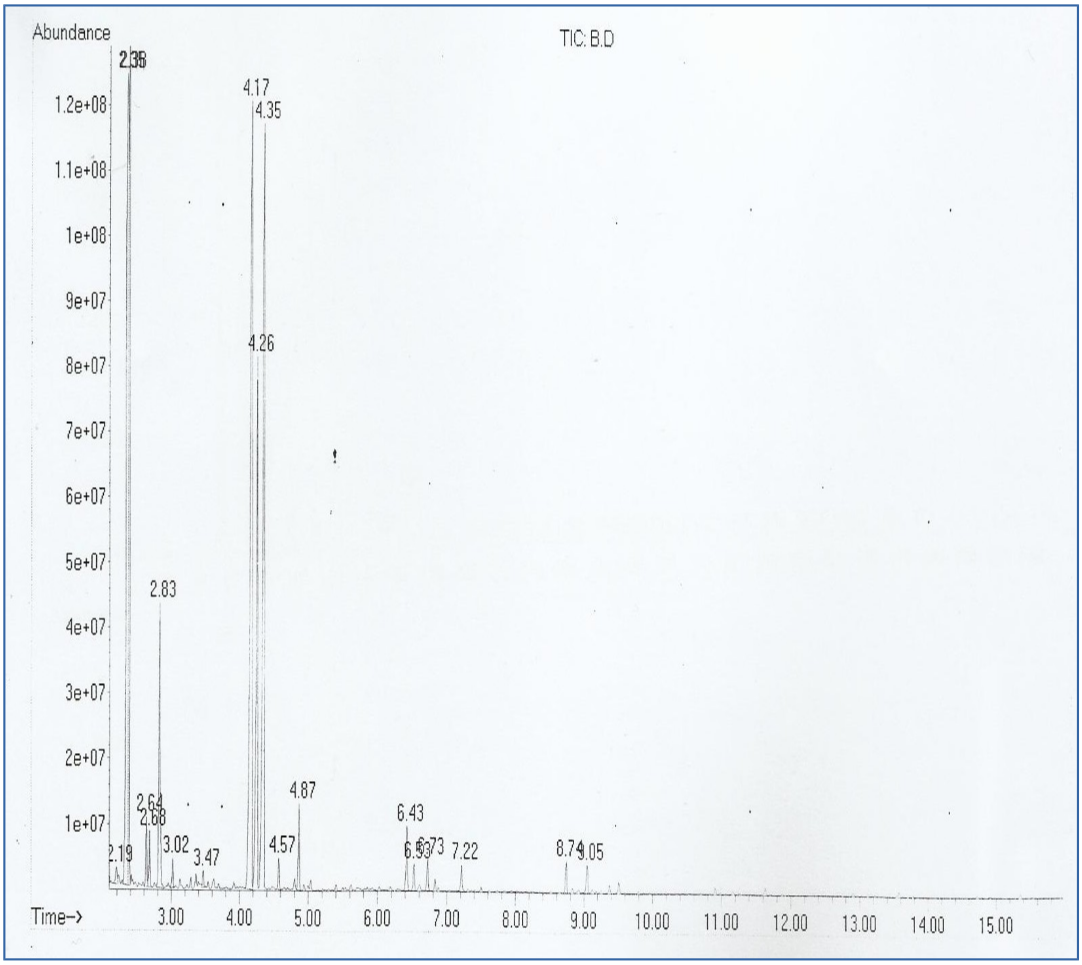

Figure 4.23 GC-MS of oil obtained via thermal pyrolysis (without catalyst)

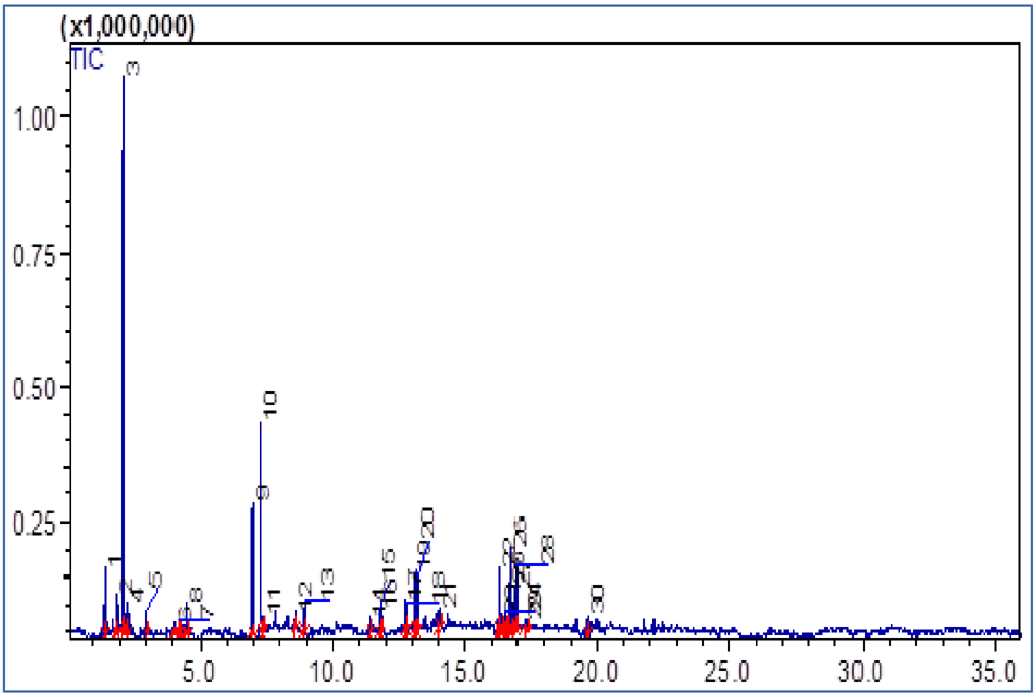

Figure 4.24GC-MS of oil obtained using 3 M treated kaolin clay as catalyst

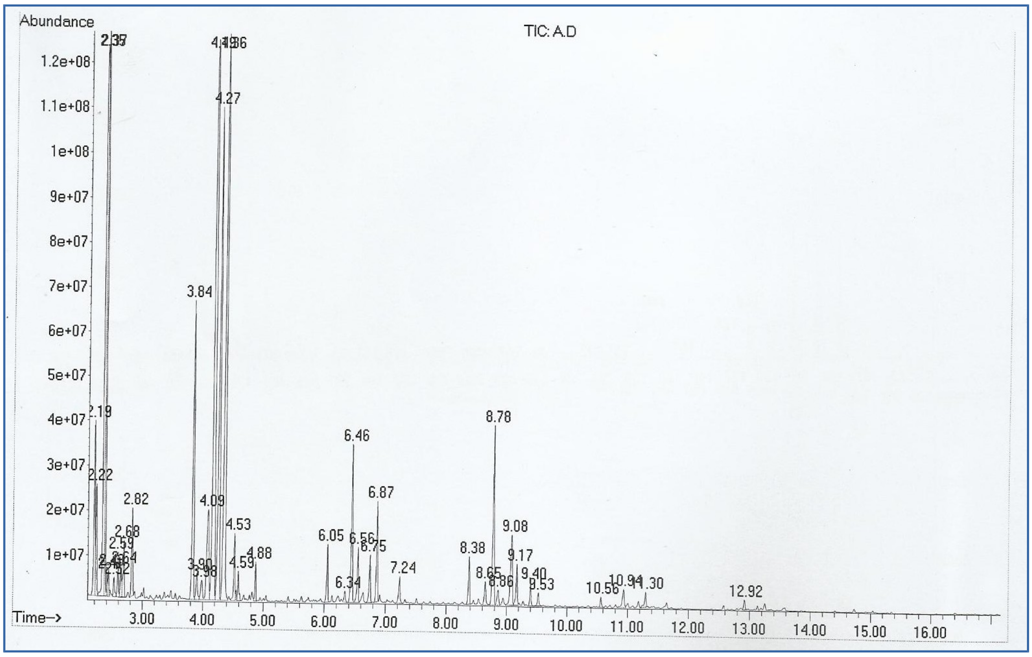

Figure 4.25 GC-MS of oil obtained using 5% nickel impregnated on 3 M treated kaolin clay as catalyst

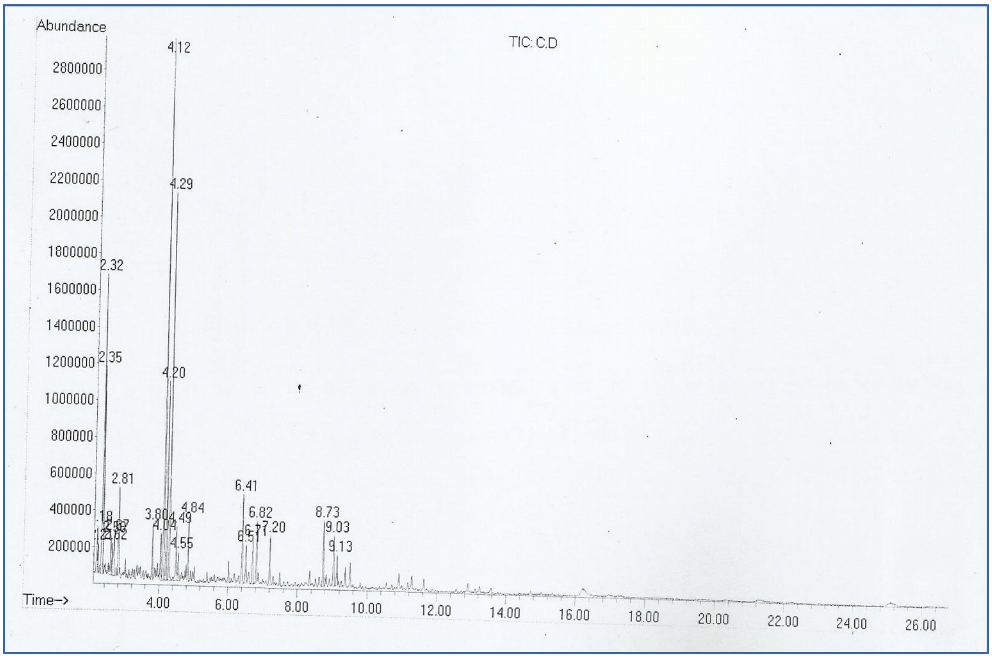

Figure 4.26 GC-MS of oil obtained using 5 M treated kaolin clay as catalyst

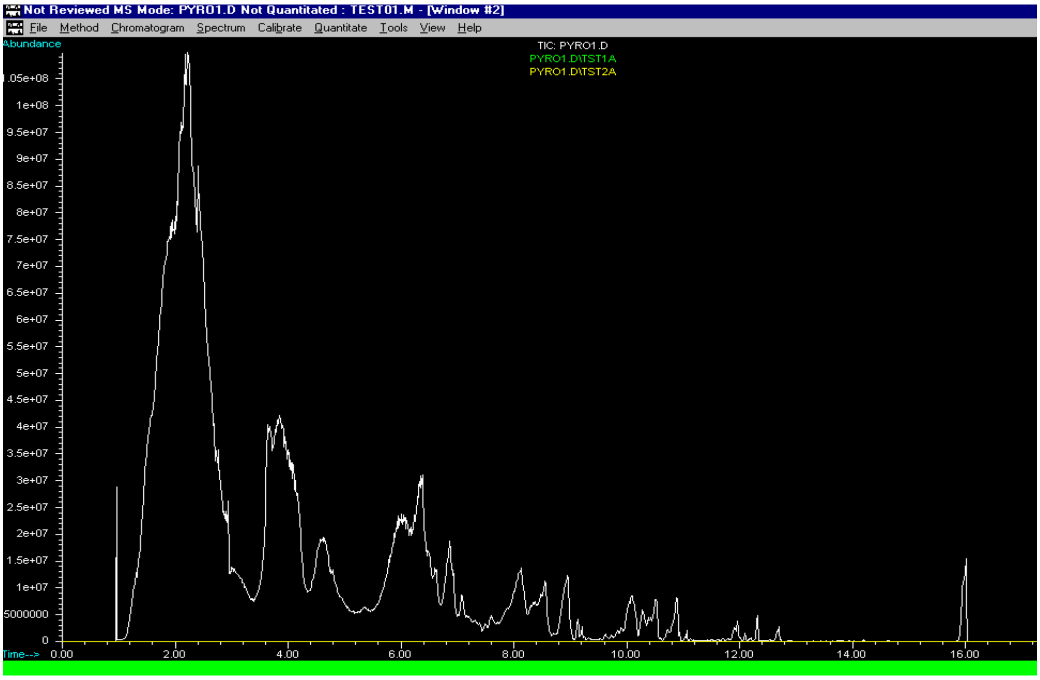

Figure 4.27 GC-MS of oil obtained using kaolin clay as catalyst

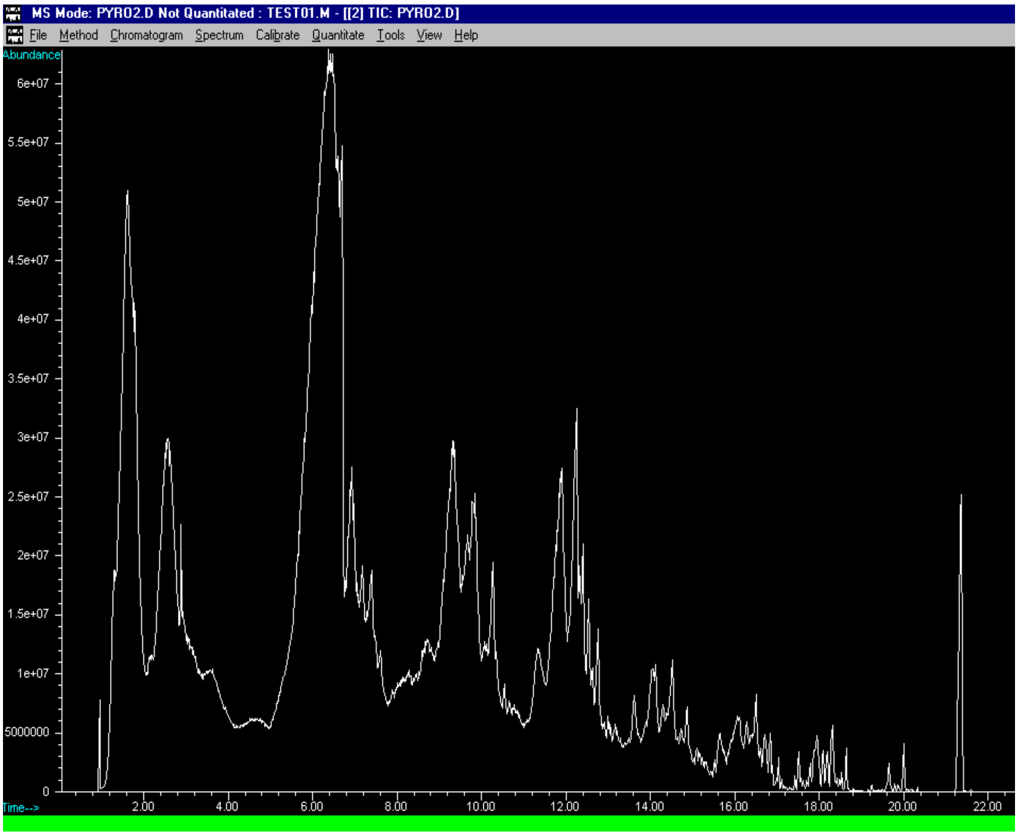

Figure 4.28 GC-MS of oil Obtained using 1M Treated Kaolin Clay as Catalyst

Table 4.21 GC-MS Composition of Oil Obtained in Thermal Pyrolysis

Name of the component	Molecular formula
Cyclooctane	C_8H_{16}
(1α,2α,5α)-2,6,6-trimethylbicyclo[3.1.1]heptan-3-one	$C_{10}H_{16}O$
1,1,3,5-tetramethylcyclohexane	$C_{10}H_{20}$
1,2-dibutyl- cyclopentane	$C_{13}H_{26}$
4-isopropyl-1,3-cyclohexanedione	$C_9H_{14}O_2$
2,3,4-trimethylhexane	C_9H_{20}
5-decene-3,7-diyne, 2,9-dimethyl-	$C_{12}H_{16}$
2,2,5,5-tetramethyl-3-hexene	$C_{10}H_{20}$
Cyclopentane, 1-butyl-2-propyl-	$C_{12}H_{24}$

Table 4.22 GC-MS composition with 3 M treated kaolin clay

Name of the component	Molecular formula
Ethanol	C_2H_6O

2-methyl, 1-pentene	C_6H_{12}
2,4-dimethyl, 1-pentene	C_7H_{14}
2,4-dimethyl, 1,3-pentadiene	C_7H_{12}
2,5-dimethyl, 1-hexene	C_8H_{16}
3,5-dimethyl, 2-hexene	C_8H_{16}
4-methylheptane	C_8H_{18}
1-(1-methylcyclopentyl) ethanone	$C_8H_{14}O$
2,4-dimethyl, 1-heptene	C_9H_{18}
5-ethyl, 2,4-dimethyl, 2-heptene	$C_{11}H_{22}$
2-methyl, 3-methylene nonane	$C_{11}H_{22}$
2,5,5-trimethyl heptane	$C_{10}H_{22}$
2,4-dimethyl,2-decene	$C_{12}H_{24}$
2-isopropyl,5-methyl,1-heptanol	$C_{11}H_{24}O$
2-(dodecycloxy) ethanol	$C_{14}H_{30}O_2$
Pentadecyl ester	$C_{17}H_{31}F_3O_2$
2,4-dimethyl,2-decene	$C_{12}H_{24}$
Cyclohexyl tetradecyl ester	$C_{22}H_{40}O_4$
2,3,7-trimethyl, 2-octene	$C_{11}H_{22}$
2,4-diethyl,1-heptanol	$C_{11}H_{24}O$
2-isopropyl,5-methyl,1-heptanol	$C_{11}H_{24}O$

Table 4.23 GC-MS Composition with 5% nickel Impregnated on 3M Treated Kaolin Clay as Catalyst

Name of the Component	Molecular Formula
Hexylcyclohexane	$C_{12}H_{24}$
1,6-octadiene, 5,7-dimethyl-, (R)-	$C_{10}H_{18}$
Acetic acid, trichloro-, octyl ester	$C_{10}H_{17}Cl_3O_2$
Methyl 7,9-tridecadienyl ether	$C_{14}H_{26}O$
4,8-dimethyl-1,7-nonadiene	$C_{11}H_{20}$
3,7,11-trimethyl-1-dodecanol	$C_{15}H_{32}O$
N-nonylcyclohexane	$C_{15}H_{30}$
Dodecylcyclohexane	$C_{18}H_{36}$
Trans-2,3-epoxydecane	$C_{10}H_{20}O$
2,3,3-trimethyl-1-pentene	C_8H_{16}
2,4,6-trimethyl-3-Heptene	$C_{10}H_{20}$
1-Butanone, 1-cyclohexyl-	$C_{10}H_{18}O$
Bicyclo[3.1.1]Heptan-3-one, 2,6,6-trimethyl-, (1α,2α,5α)-	$C_{10}H_{16}O$
Cyclohexanone, 3,3,5-trimethyl-	$C_9H_{16}O$
Trichloroacetic acid, hexadecyl ester	$C_{18}H_{33}Cl_3O_2$

Table 4.24 GC-MS Composition with 5M Treated Kaolin Clay

Name of the Component	Molecular Formula
Cyclopentane, 1,2,3-trimethyl-, (1α,2α,3β)-	C_8H_{16}
2,4-dimethyl- 2-decene	$C_{12}H_{24}$
Tetradecyl- cyclohexane	$C_{20}H_{40}$
Cyclohexanemethanol	$C_7H_{14}O$
2-decene, 7-methyl-, (z)	$C_{11}H_{22}$
4-methyl-2-undecene	$C_{12}H_{24}$
Cyclohexane, (2-methylpropyl)-	$C_{10}H_{20}$
Cyclohexane, 1,1'-(1,2-dimethyl-1,2-ethanediyl)bis-	$C_{16}H_{30}$
Bicyclo[2.2.1]Heptane-2,5-dione, 1,7,7-trimethyl-	$C_{10}H_{14}O_2$
Cyclopentane, 1-butyl-2-propyl-	$C_{12}H_{24}$
Cyclopropanol, 1-(3,7-dimethyl-1-octenyl)-	$C_{13}H_{24}O$
2,2-dimethyl-3-Heptene	C_9H_{18}

Table 4.25 GC-MS Composition with Kaolin Clay

Name of the Component	Molecular Formula
Cyclooctane	C_8H_{16}
(1α,2α,5α)-2,6,6-trimethylbicyclo[3.1.1]Heptan-3-one	$C_{10}H_{16}O$
1,1,3,5-tetramethylcyclohexane	$C_{10}H_{20}$
1,2-dibutyl- cyclopentane	$C_{13}H_{26}$
Tetradecyl- cyclohexane	$C_{20}H_{40}$
2-(dodecycloxy) ethanol	$C_{14}H_{30}O_2$
Pentadecyl Ester	$C_{17}H_{31}F_3O_2$
2,4-dimethyl,2-decene	$C_{12}H_{24}$
Cyclohexyl tetradecyl Ester	$C_{22}H_{40}O_4$
2,3,7-trimethyl, 2-octene	$C_{11}H_{22}$
Dodecylcyclohexane	$C_{18}H_{36}$
Dodecane	$C_{12}H_{26}$

Table 4.26 GC-MS Composition with 1M Treated Kaolin Clay

Name of the Component	Molecular Formula
Cyclopentane, 1,2,3-trimethyl-, (1α,2α,3β)-	C_8H_{16}
2,4-dimethyl- 2-decene	$C_{12}H_{24}$
Tetradecyl- cyclohexane	$C_{20}H_{40}$
Cyclohexanemethanol	$C_7H_{14}O$
2-decene, 7-methyl-, (z)	$C_{11}H_{22}$
4-methyl-2-undecene	$C_{12}H_{24}$
Dodecylcyclohexane	$C_{18}H_{36}$
Trans-2,3-epoxydecane	$C_{10}H_{20}O$
2,3,3-trimethyl-1-pentene	C_8H_{16}
2,4,6-trimethyl-3-Heptene	$C_{10}H_{20}$
1-Butanone, 1-cyclohexyl-	$C_{10}H_{18}O$
Dodecylcyclohexane	$C_{18}H_{36}$
Dodecane	$C_{12}H_{26}$

Summary

Kaolin clay was treated with different molar concentrations of hydrochloric acid. The best yield of liquid fuel from pyrolysis of polypropylene was obtained when kaolin clay treated with 3M Hydrochloric acid was used. Kaolin clay treated with 5 M hydrochloric acid gave higher content of gas due to higher acidity. FTIR results confirmed the presence of functional groups to be mainly alkanes and alkenes. Various oxygenated compounds were also formed as a result of partial oxidation, as the process was not carried out in an oxygen free atmosphere.

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Chapter 5

Conclusions and Recommendations

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 dealt with in the coming days. Current challenges include the need for reduction in costs of waste handling and manufacturing cost along with optimizing the products obtained from plastic waste. One of the ways to reduce the cost of the process is to develop a catalyst for cracking that is novel and efficient, economic and abundantly available on the commercial scale. 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 cracking of polypropylene was studied using kaolin clay as catalyst in a batch reactor. The kaolin has been treated with different concentrations of hydrochloric 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 physio-chemical characteristics. The different oils produced in the processes are analyzed for their composition.

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

Physio-chemical characteristics of acid treated kaolin

- Hydrochloric acid treatment of kaolin under reflux conditions increased the acidity and surface area of kaolin as prescribed in previous researches.

Thermo-catalytic pyrolysis of waste polypropylene using kaolin

- Thermal pyrolysis of waste polypropylene, yield a maximum of 55.45 wt % condensable fraction at 500 °C. Presence of kaolin and acid treated kaolin reduced the reaction time and enhanced the liquid yield. Maximum yield of oil (74.9 wt %) was obtained when 3:1 polymer to catalyst ratio was used at 500 °C. The liquid product obtained in the kaolin catalyzed pyrolysis of polypropylene is low viscous at all temperatures.
- Results obtained show that acid treated kaolin is found better as compared to untreated kaolin in terms of its catalytic activity towards the pyrolysis of polypropylene.
- The GC-MS results of the different oil samples show that different hydrocarbons mostly alkenes and alkanes are present in the oil obtained from pyrolysis of polypropylene. Additionally, alcohols, ketones and other oxygenated compounds were also found in less percentage. The product distribution is narrowed in presence of catalysts.

10.2 Recommendations for future

From the above results it can be concluded that kaolin work very well in the pyrolysis of polypropylene and further studies are required to materialize the process. Recommendations for further work are following:

- Catalytic pyrolysis of mixed polymers using clays and acid treated clays
- 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 (H_2SO_4, HNO_3, H_3PO_4 and CH3COOH) 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
- Development of a continuous process for plastic pyrolysis using suitable catalyst

Annex 1

Application of Acid Treated Kaolin Clay for Conversion of Polymeric Waste Material into Pyrolysis Diesel Fuel

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Abstract**—** *Polymer waste material was subjected to catalytic pyrolysis using acid treated kaolin clay. Waste material was cracked thermally and catalytically in a batch reactor in the temperature range 400-500°C for synthesis of liquid fuel. For this purpose, kaolin clay was first treated with different prepared molar solutions of HCl (1M, 3M and 5 M) under reflux condensation at 100°C and atmospheric pressure in a round bottom flask for 4 hours. The acid treated clay samples were subsequently washed with distilled water and then calcined at 500°C for 4 hours. Cracking activity of untreated kaolin clay was compared with acid treated kaolin clay. It was observed that acid treated kaolin clay performed better than untreated kaolin clay due to high surface area and greater number of acidic sites.*

Keywords—Waste plastic, Pyrolysis, Kaolin, Polypropylene, GC-MS

I. Introduction

Plastics are one of the greatest innovations of the century and have proved their reputation to be true. Plastics are being used in various ways and we will depend on them in the upcoming years. Plastics are light weight, do not rot or rust, economical, reusable and conserve natural resources. These are the reasons of our dependency on the plastics. Plastics reduce CO_2 emissions during their usage along with conservation of energy. If we want to replace plastics with other conventional materials considering sustainability, then we would have to add 22.4 million tons of crude oil yearly [8]. Plastics have rapidly replaced conventional materials due to continuous advancement in polymer technology, knowledge and economic production.

Plastic waste disposal has been identified as worldwide environmental problem. In recent years, attention has been paid more towards the recycling of synthetic polymer waste for solving pollution problems and the reuse of cheap and abundant waste products. Though several methods have been proposed for recycling waste plastics, it is generally accepted that material recovery is not an ideal solution to the present problem, and that energy or chemical recovery is a more attractive one [1].

Catalytic degradation of polyolefins to oil has been preferred over thermal pyrolysis due to narrow product distribution, high reaction rate and lower temperature of degradation. One of the most commonly used solid catalysts in polymer degradation studies are zeolites due to their strong acidity, pore size and specific pore structure effects. Amongst the numerous kinds of zeolites investigated in polyolefin pyrolysis, the most commonly used are Beta, USY, ZSM-11, REY, Mordenite, ZSM-5 etc. Some other solid acid catalysts used for plastic pyrolysis include molecular sieves, silica alumina, and MCM-41. Reports on the use of FCC catalysts are also found in literature. Other catalytic materials such as clays (montmorillonite, saponite), reforming catalysts, activated carbon, metal oxides, metal complexes of the type MCln-AlCl3 or M(AlCl4)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 [2].

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 [3]. The effects of different zeolites as H-Y, Na-Y, H-mordenite and Na-mordenite on the catalytic degradation of polypropylene were studied using thermogravimetry under nitrogen flow [4]. The catalytic cracking of polypropylene was carried out by silica–alumina and H-ZSM-5 at temperatures between 350°C and 420°C and sulfated zirconia at temperatures below 300°C, and also by means of thermogravimetry under helium flow [5]. Meanwhile, Sakata et al. studied the catalytic cracking of polypropylene with silica–alumina catalyst at 380°C in a semi batch reactor without external gas flow [6]. Ishihara et al. 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 [7].

From the study of previous work done, it was found that suitability of all catalysts used previously is due to their acidity and structure. Kaolin is thermally stable and is mildly acidic in nature, which can support cracking temperatures at high temperatures. Cost is also less compared to other acidic materials e.g. zeolites. Acid treatment of clay enhances the acidic properties of clay enabling the cracking of plastic at comparatively low temperature. Therefore in this work, studies have been carried out for thermal and catalytic cracking of polypropylene in batch reactor using acid treated kaolin clay.

II. Experimental

A. Materials:

Waste polypropylene (used plastic disposable glasses) was collected from waste yards of National University of Sciences and Technology NUST. Waste plastic disposable glasses were washed and cut into flakes by scissor. The catalyst employed in this study, commercial grade kaolin clay was obtained from CES, NUST.

Hydrochloric acid (36.5 %) was obtained from Sigma Aldrich. Hydrochloric acid, kaolin clay and distilled water were used for the preparation of catalysts.

B. *Acid treatment of Clay:*

Acid treatment of clay was carried out by adding 50 g of clay to 500 ml of hydrochloric acid solution of different concentrations (1 M, 3M and 5 M). Reflux condensation was used for acid treatment at temperature range of 80-100 °C and atmospheric pressure in a round bottom flask. Reflux condensation was done for 6 hours. 500 ml ice cold distilled water was then added to rapidly quench the clay suspension. Resulting content was repeatedly washed with distilled water and filtered to remove any unspent acid. Drying was carried out in an oven at 120 ° C overnight. Subsequently, calcination was done at 500° C for 4 hours and grounded in mortar pastel to powder form.

C. *Experimental setup and procedure:*

The experimental setup used in this work consists of batch reactor provided with glass tube enclosed in a round bottom flask and open at the other end (Figure 1a and 1b). High temperature furnace is provided by K type thermocouple fixed inside. Vertex PID controller VT9626 with the accuracy of T/C±1℃ was used to control the temperature of furnace.

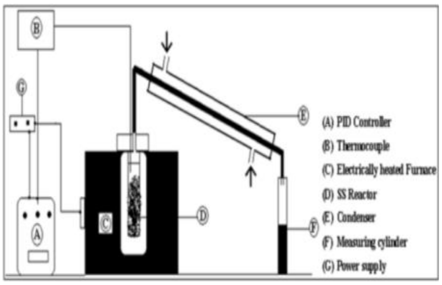

FIGURE 1a. SCHEMATIC REPRESENTATION OF EXPERIMENTAL SETUP

For each experiment, 20 g of waste polypropylene samples were used. In each reaction, kaolin clay treated with different molar concentrations of HCl (1 M, 3M and 5 M) was used for pyrolysis in the batch reactor heated at 20° C/min up to desired temperature. The condensable liquid products were collected at the other end and weighed. After reaction, solid residue left in the round bottom flask at the reaction end was weighed.

FIGURE 1b. EXPERIMENTAL SETUP

Weight of gases was calculated using the mass balance. Operating temperatures for the reaction were in the range of 400-500° C. Reaction time was calculated from the start of reaction exceeding the room temperature till the completion of reaction (the time when no liquid comes from the tube end).

D. *Analysis Methods:*

Analysis of liquid product was done by GC-MS-QP

III. *Results and Discussion*

A. *Effect of Catalyst*

The liquid yield was highest for the reaction when kaolin clay treated with 3M HCl was used as catalyst. Least yield was obtained when the reaction was carried out in the absence of catalyst.

For 3M HCl treated clay, reaction started at 400°C, but reaction completed at 500° C. For 1M HCl treated clay, reaction started at 420°C and completed above 500°C, while reaction started at about 400°C and completed at 470°C for 5M HCl treated clay.

The results of all 4 experiments have been depicted in the table as

	1M HCl treated clay	3M HCl treated clay	5M HCl treated clay	No Catalyst
Liquid Yield (gram)	12.85	14.38	12.21	11.09
Gas Yield (gram)	5.41	4.73	7.07	5.8
Residue (gram)	1.74	0.89	0.72	3.11
% Liquid Conversion	64.25 %	71.9 %	61.05 %	55.45 %

TABLE I YIELD OBTAINED BY CATALYTIC PYROLYSIS OF POLYPROPYLENE AT 500° C

B. *Effect of Temperature on Product Distribution in Thermal Pyrolysis:*

Three fractions namely low and high viscous liquid, non-condensable gases and solid residue were obtained as products of thermal pyrolysis. The liquid fraction obtained at 400°C was less viscous. As temperature increased to maximum 500°C for thermal pyrolysis, liquid yield converted to more viscous form. At high temperature, less liquid yield and more gas yield was due to formation of more non-condensable volatile fractions as a result of severe cracking. Product distribution at different temperatures is summarized in figure 2

C. *Characterization of Liquid Product:*

The oil sample was characterized using GCMS for detailed composition. The GCMS of oil obtained via thermal and acid treated kaolin catalytic pyrolysis is shown in figure. Different components of oil obtained by comparing NIST library are presented in table. Results obtained reveal that oil is composed mostly of alkenes. Additionally, oxygenated compounds such as alcohols and ketones are also found which may be due to oxidative cracking of polypropylene in the presence of limited oxygen as the reaction was not carried out in absence of air and under inert conditions.

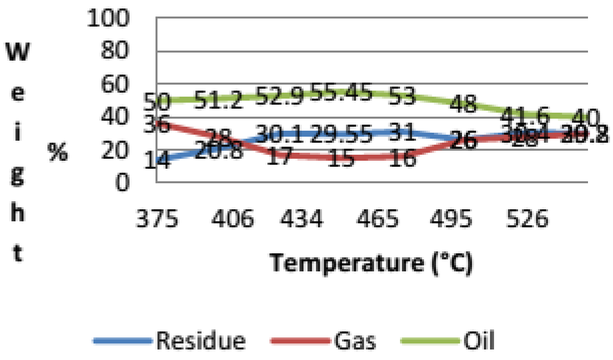

FIGURE 2. EFFECT OF TEMPERATURE ON PRODUCT DISTRIBUTION OF POLYPROPYLENE

TABLE 2 GC-MS COMPOSITION OF OIL OBTAINED VIA CATALYTIC PYROLYSIS WITH 1:3 CATALYST TO POLYPROPYLENE FEED AT 500° C

Peak	Retention Time in Minute	Area %	Molecular Formula
1	1.3	0.2	C_2H_6O
2	1.87	0.1	C_6H_{12}
3	2.16	1.1	$CHCl_3$
4	2.33	0.09	C_7H_{14}
5	3.02	0.07	C_7H_{12}
6	4.05	0.78	C_8H_{16}
7	4.22	0.8	C_8H_{16}
8	4.47	1.1	C_8H_{18}
9	6.97	2.9	$C_8H_{14}O$
10	7.29	4.4	C_9H_{18}
11	7.4	0.8	C_9H_{18}
12	8.61	1.0	$C_{11}H_{22}$
13	8.93	1.2	$C_{10}H_{18}O_3$
14	11.44	0.8	$C_{11}H_{22}$
15	11.78	1.0	$C_{10}H_{22}$

16	11.86	1.1	$C_{10}H_{22}$
17	12.74	1.0	$C_{12}H_{24}$
18	12.82	0.9	$C_{12}H_{24}$
19	13.13	1.5	$C_{11}H_{24}O$
20	13.2	1.42	$C_{14}H_{30}O_2$
21	14.07	0.9	$C_{17}H_{31}F_3O_2$
22	16.275	1.7	$C_{12}H_{24}$
23	16.38	0.82	$C_{22}H_{40}O_4$
24	16.5	0.85	$C_{11}H_{22}$
25	16.64	1.4	$C_{22}H_{40}O_4$
26	16.75	2.08	$C_{11}H_{24}O$
27	16.87	1.3	$C_{17}H_{31}F_3O_2$
28	17	1.70	$C_{11}H_{24}O$
29	17.33	0.8	$C_{11}H_{22}$
30	19.62	0.8	$C_{30}H_{57}F_3O_2$

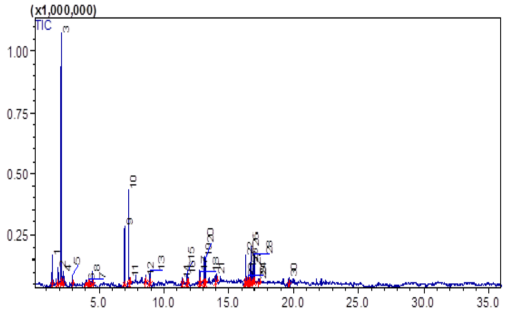

FIG. 3 GC-MS OF OIL OBTAINED VIA CATALYTIC PYROLYSIS WITH 1:3 CATALYST TO POLYPROPYLENE FEED AT 500° C

IV. CONCLUSION

An experimental study on catalytic and thermal pyrolysis of polypropylene was performed to study the effect of catalyst and temperature on the product yield. Acid treated kaolin clay was found to be an efficient and cost effective catalyst for pyrolysis of plastic. Highest yield of liquid hydrocarbons was achieved with kaolin clay treated with 3M HCl. This is due to the fact that acidity of clay increased and thereby increasing the liquid yield. Higher acidity as in the case of kaolin clay treated with 5M increased the gas yield. Furthermore, higher heating rate favors the formation of viscous hydrocarbons. For obtaining low viscous hydrocarbons, less heating is required, thereby compensating the liquid yield.

Acknowledgment

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Formation of Calcium Sulfate Whiskers Using Waste Calcium Chloride by Hydrothermal Method and Effect of Additives

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Abstract:

Calcium sulfate whiskers belong to a class of inorganic minerals that are used as a filler material in paper making, rubber, plastics and polymer composites. In this work calcium sulfate whiskers were prepared by co-precipitation of Na_2SO_4 and $CaCl_2$ discharged from the Solvay process to form calcium sulfate dihydrate (CSD) precursors followed by hydrothermal treatment to convert them into calcium sulfate hemihydrate (CSH) known as calcium sulfate whiskers. The influence of reaction parameters e.g. reaction temperature, molar ratios of raw materials, stirring speed and additives i.e. NaCl and $CaCO_3$ were studied and conditions were optimized. The experimental results revealed that optimum conditions for synthesis of calcium sulfate whiskers by hydrothermal method are: reaction temperature of 25 °C, molar ratio of Na_2SO_4 to $CaCl_2$ being 0.5:1 and stirring speed of 150-250 rpm. The presence of additives, NaCl and $CaCO_3$ lead to formation of precursors with large size and corresponding hydrothermal product with layer shape and having small aspect ratio. These additives changed the solution composition and also changed the equilibrium super saturation that varied the size of precursors. The morphology of whiskers was examined with the field emission scanning electron microscope (SEM). The structures were identified by powder X-ray diffract meter (XRD). SEM results show good morphology of the whiskers. Experimental results revealed that calcium sulfate whiskers were synthesized successfully form Na_2SO_4 and waste $CaCl_2$. The process study provides reasonable solution for the utilization of waste $CaCl_2$ discharged from the Solvay process.

Keywords: Calcium sulfate, whiskers, Solvay process waste, hydrothermal synthesis, additives effect

1. Introduction

Whiskers are short fiber-shaped distinct crystals having high aspect ratio. Aspect ratio is length to diameter ratio (L/D) that is used to characterize the whiskers. High strength, toughness, reduced internal defects such as dislocations due to small diameter; make the whiskers excellent reinforcing [1-5]. Compared to traditional carbon and glass fibers which have short length and are expensive to produce, inorganic whiskers are more effective in strengthening the composite materials. Significant development has been made in the synthesis of inorganic whiskers and their applications in the composite material during the last decade.

Calcium sulfate (CS) come in the category of inorganic chemical compound that has three phases i.e. calcium sulfate dehydrate ($CaSO_4.2H_2O$), calcium sulfate hemihydrates ($CaSO_4.0.5H_2O$) and calcium sulfate anhydrate ($CaSO_4$) which formed in numerous industrial manufacturing and environmental precipitation processes. Calcium sulfate in hemihydrates (HH) form are known as calcium sulfate whiskers [6]. Calcium sulfate whiskers being environment friendly, cost effective and non-hazardous material have wide range of applications in rubber, plastic, pulp and paper-making, ceramics, polymer composites. Calcium sulfate whiskers are thermally stable, resistant to chemicals, reproducible and have good compatibility with plastic and polymers [7, 8].

Investigators have developed methods for the synthesis of calcium sulfate whiskers which include salt solution method, hydrothermal method, organic water system method, microemmulsion method, electrochemical deposition method, microwave assisted method and ultrasound assisted method [9]. However hydrothermal method is getting more consideration over the last decade due to uniformity of the product and controllable conditions.

Previously calcium sulfate whiskers were manufactured from the gypsum or by reaction of sulfuric acid with lime [10]. Researchers have investigated different materials for production of calcium sulfate whiskers which include flue gas desulfurization (FGD) gypsum, phosphogypsum (PG), calcium dodecyl sulfate, potassium sulfate and calcium nitrate in $CaCl_2$ solution, carbide slag and calcium chloride [11-13]. This work inspects the possibility of making calcium sulfate whiskers by hydrothermal process using sodium sulfate (Na_2SO_4) and the calcium chloride ($CaCl_2$) discharged from the Solvay process. In Solvay process, sodium carbonate (Na_2CO_3) is produced while producing $CaCl_2$ as a byproduct. A huge amount of $CaCl_2$ is discharged each day during the manufacturing of Na_2CO_3, so it is difficult to handle this waste. The $CaCl_2$ produced is either discharged into the lakes, rivers or is dumped on open land sites so it causes environmental issues. By using this waste byproduct natural resources can be saved and environment can be protected.

In current study the synthesis of calcium sulfate whiskers by hydrothermal route were carried out and influence of reaction parameters e.g. reaction temperature, molar ratios of raw materials, stirring speed and additives i.e. NaCl and $CaCO_3$ were studied and conditions were optimized for the preparation of calcium sulfate whiskers with high aspect ratio.

2. Experimental

2.1 Procedure

Sodium sulfate was of analytical grade (AR) and calcium chloride discharge from ICI soda ash plant was collected. Firstly the calcium sulfate dihydrate precursors were prepared by mixing calcium chloride ($CaCl_2$) and sodium sulfate (Na_2SO_4) in solution formed. 20ml of 0.5 - 1.5 mole L-1Na_2SO_4 was mixed into the 0.5 - 1.5 mole L-1$CaCl_2$ at various temperatures. The two solutions were mixed very slowly about 3ml per minute. After mixing the reactants, the stirring was done for 1 h. The slurry so formed was transferred to autoclave having outer shell made-up of stainless steel and inner lining with polytetrafluoroethylene (PTFE) that have 50ml capacity, heated to 120 – 150 °C (3 ° C per minute) and retained in these conditions for about 4.0 – 6.0 h. The hydrothermal product was then cooled down to ambient conditions without any external assistance. The product formed was taken out, washed with distilled water and dried at 105 °C for 2 h. To examine the effect of additives a 0.2-

0.5 mL^{-1} NaCl and $CaCO_3$ were mixed separately in the slurry containing two reactants. Then this slurry was put into the autoclave and repeated the previous procedure.

2.2 Characterization

The morphology of the hemihydrate product formed was examined by Scanning electron microscope (FESEM, JSM-6490LA JEOL, JAPAN). The composition of the product was analyzed by X-ray powder diffractometer (STOE XRD GERMANY).

3. Results and Discussion

The morphology of the precursors is exhibited in figure 1. The XRD pattern of precursors and product formed after hydrothermal treatment is shown in figure 2. Precursors were mainly composed of calcium sulfate dihydrate while hydrothermal product was calcium sulfate hemihydrate by composition.

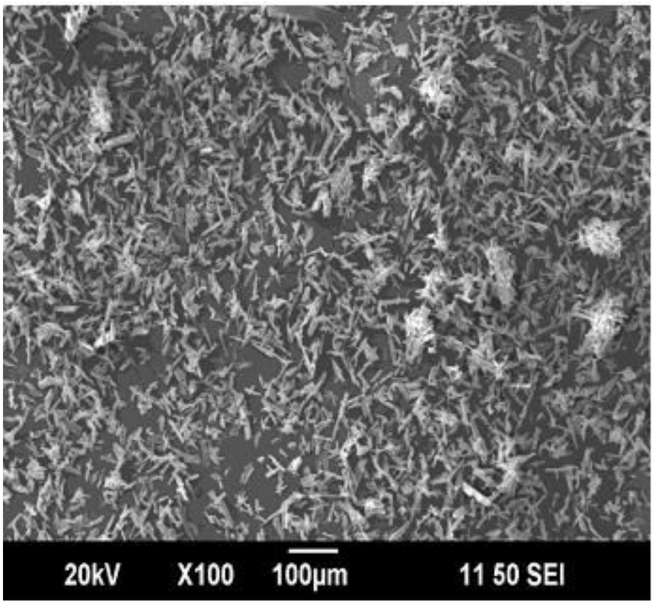

Fig. 1 Morphology of the $CaSO_4.2H_2O$ precursors

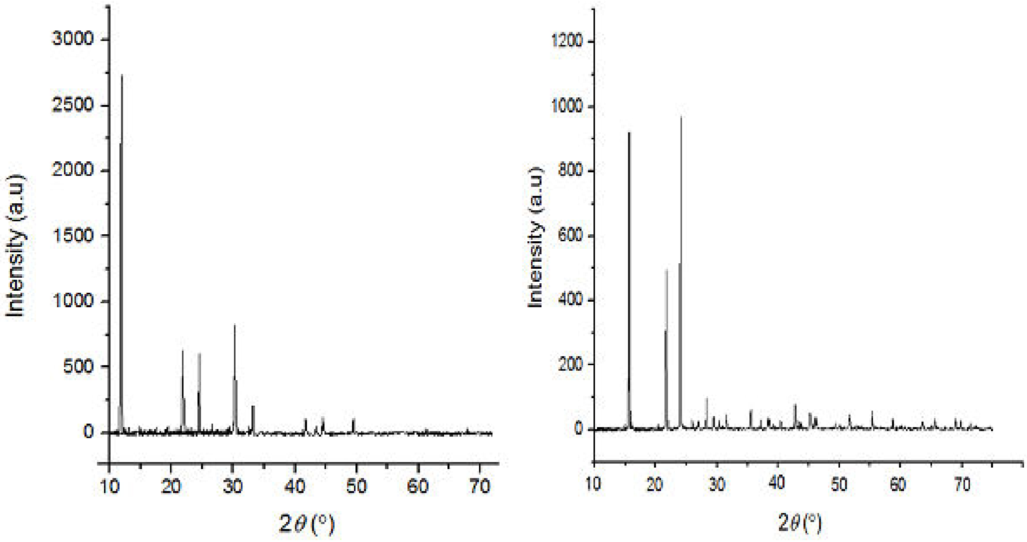

Fig. 2 XRD pattern of (a) $CaSO_40.2H_2O$ precursors and (b) $CaSO_40.5H_2O$ hydrothermal product

3.1 Temperature effect on formation of calcium sulfate whiskers

Figure 3 shows the morphology of calcium sulfate whiskers (CWS) formed at variable temperatures (30 °C, 55 °C and 85 °C) by mixing sodium sulfate into calcium sulfate in solution form. The structural morphology of the final product is directly linked with the temperature at which the CSD were formed. The rise in temperature enhanced the precursor's size and the calcium sulfate whiskers became more non-uniform and heavier as the temperature increased from 30 °C to 85 °C. The variation of structural morphology of precursors and the hydrothermal product with the temperature can be explained on the basis of super saturation at varying temperatures.

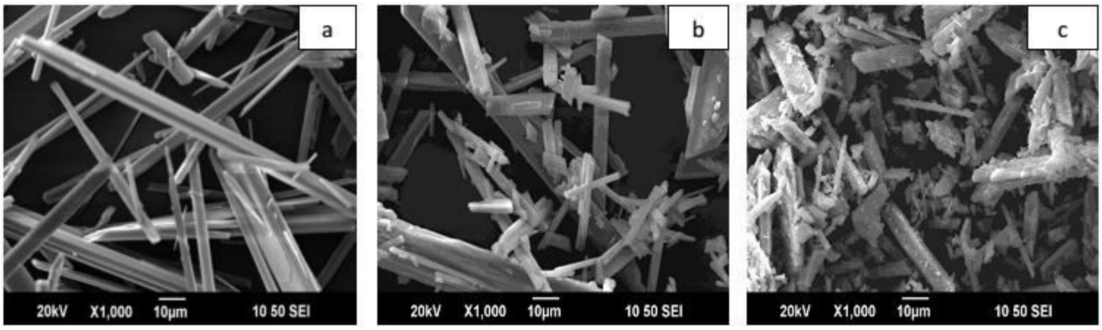

Fig. 3 Effect of temperature on the calcium sulfate whisker formed at (a) 25 °C, (b) 55 °C and (c) 85 °C

Super-saturation (S) in equation form can be written as:

$$S = \frac{[Ca^{2+}][SO_4^{2-}]}{K_{sp}}$$

Where S is the super saturation, Ksp is the equilibrium constant which was calculated out from the HSC software [14] and [Ca2+] and [SO_4^{2-}] are concentration of the soluble Ca^{2+} and SO_4^{2-} respectively. Table 1 exhibits the relationship among temperature, the equilibrium constant (Ksp) and super saturation (S). Data in the table reveals that by increasing the temperature, the Ksp value of $CaSO_4.2H_2O$ decreased which lead to increase in super saturation. Thus, the super saturation at high temperature is greater as compared to low temperature. Super saturation is associated with developing rate of the crystals as in crystallinity theory. The more super saturation, greater will be the growing rate of the crystals. So the formation of CSD precursors is linked with rate of development of the crystals. Low temperature favored the small growth rate so the precursors with smaller size were formed and hydrothermal product with uniform shape and high aspect ratio was formed. Consequently the temperature 30 °C is favorable for the formation of precursors to form uniform hydrothermal product as compared to 55 °C and 85 °C.

Table 1.Influence of temperature on super saturation

Temperature (°C)	Equilibrium constant Ksp	Super saturation S
25	3.1×10^{-5}	201.5
55	2.35×10^{-5}	270.4
85	1.42×10^{-5}	441.6

3.2 Effect of Reactant’s Molar Ratio:

To examine the influence of molar ratio of the starting material on the morphology and aspect ratio of the hydrothermal product the reactants were mixed in solution form by adding sodium sulfate to calcium chloride having molar ratios 1:1, 0.5:1 and 1:0.5 respectively to form precursors. After hydrothermal treatment the product obtained is shown in the figure 4.

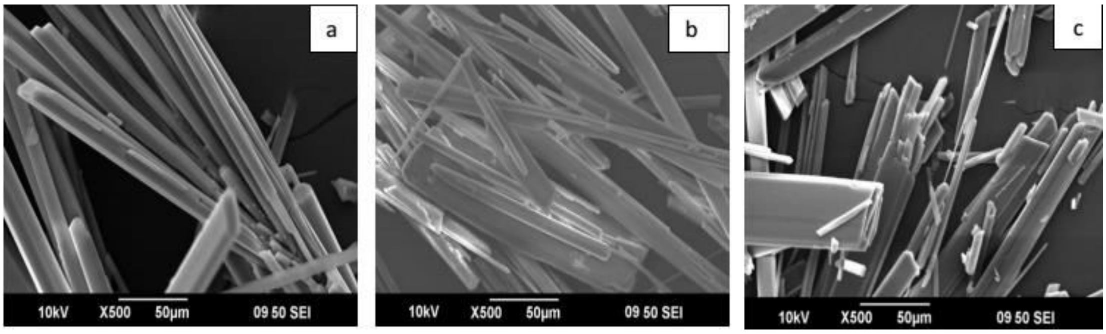

Fig. 4 Effect of molar ratio of reactants (Na_2SO_4 to $CaCl_2$) on morphology of calcium sulfate whiskers (a) 0.5:1, (b) 1:1 and (c) 1:0.5

Fig. 5 shows the trends of super saturation verses time for (a) 0.5:1, (b) 1:1 and (c) 1:0.5. By comparing the data for super saturation with reaction time for above molar ratios, the super saturation was smaller in case of molar ratio of 0.5:1. So the precursors with smaller size were formed which favored the calcium sulfate whiskers having high aspect ratio. Low molar ratio of Na_2SO_4 to $CaCl_2$ was favorable for the development of hydrothermal product with high aspect ratio. Molar ratio being 0.5:1 of Na_2SO_4 to $CaCl_2$ resulted in formation of whiskers having high aspect ratio.

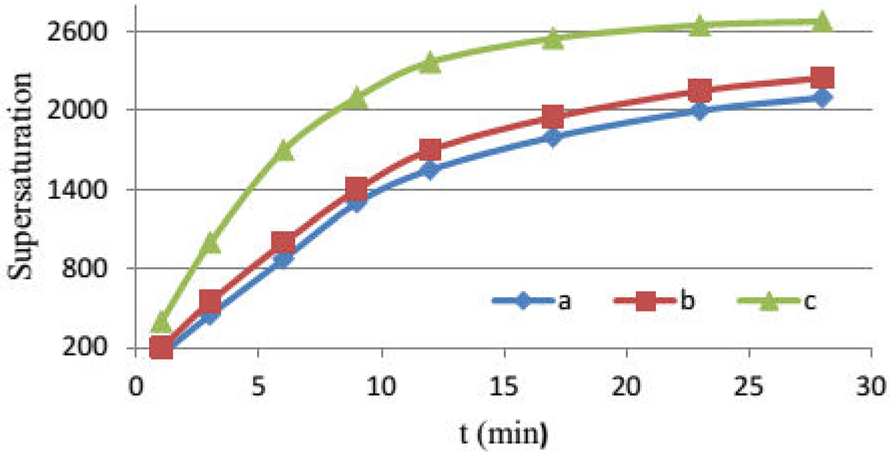

Fig. 5 Effect of molar ratio of reactants on super saturation

3.3 Effect of Additives on the Formation of CSWs

Fig. 6 show the effect of additives i.e. NaCl and $CaCO_3$on the physical appearance and aspect ratio of calcium sulfate whiskers. X-ray diffract meter results confirmed that hydrothermal products are calcium sulfate hemihydrates by composition. In the presence of NaCl the length to diameter ratio of whiskers decreased and as the concentration of the NaCl increased from 0.2-0.5 mol L-1 the aspect ratio decreased further. The effect of $CaCO_3$ was found more prominent on the morphology of the whiskers. The whiskers became thicker and their length decreased further. By the addition of additives, the super saturation increased which led to the formation of precursors with larger size and corresponding hydrothermal product with small aspect ratio.

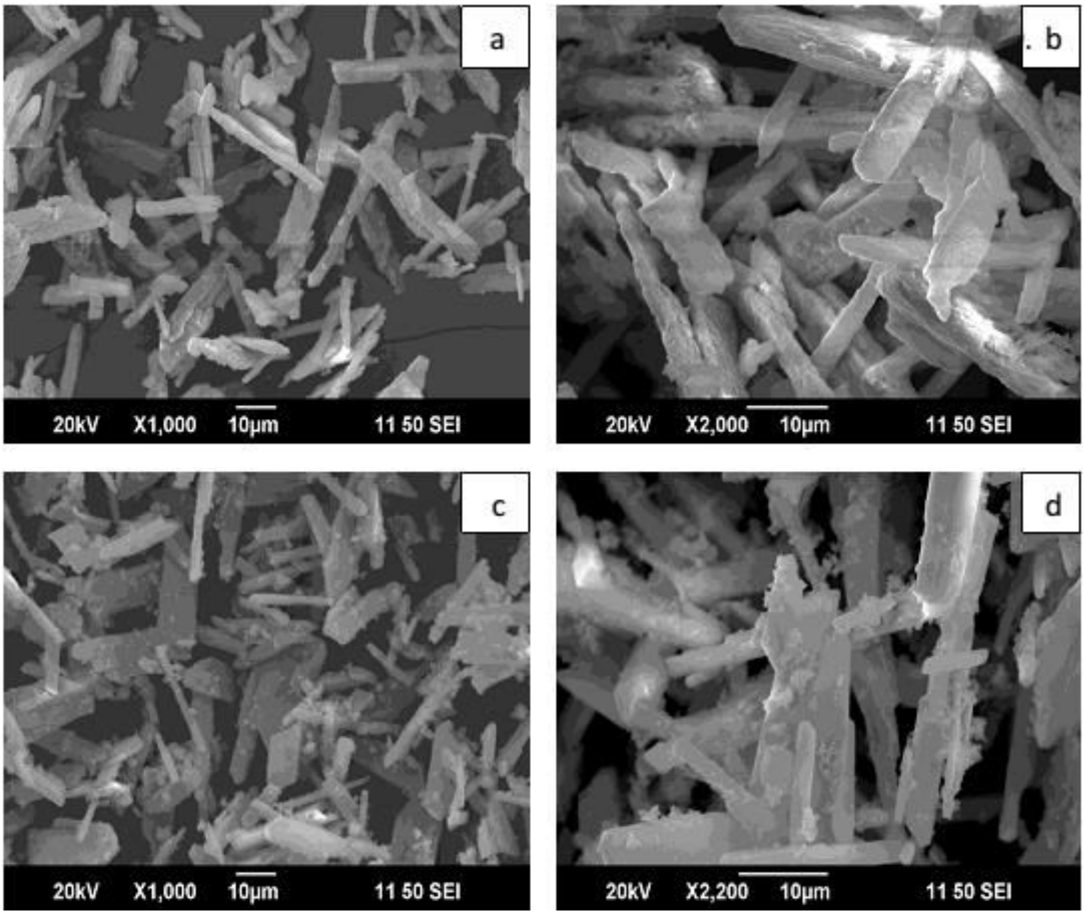

Fig. 6 Effect of additives on CSWs: NaCl (mol L^{-1}) a- 0.2, b- 0.5 and $CaCO_3$ (mol L^{-1}) c-0.2, d-0.5

Conclusion

Calcium sulfate whiskers were synthesized by co-precipitation method followed by hydrothermal treatment by using sodium sulfate and calcium chloride as raw material. Firstly the calcium sulfate dihydrate precursors were formed that were converted to calcium sulfate hemihydrates whiskers. The parameters like reaction temperature, molar ratio of reactants, stirring speed and additives i.e. NaCl and $CaCO_3$ influenced the size of the precursors and aspect ratio of corresponding hydrothermal product. The optimal conditions for the formation of precursors with small size and corresponding hydrothermal product with high aspect are; reaction temperature of 25 °C, by adding sodium sulfate to calcium chloride in molar ratio of 0.5:1 and stirring speed 150-250 rpm. Process study provides reasonable utilization of $CaCl_2$ discharged from the Solvay process.

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