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SYNTHESIS AND CHARACTERIZATION OF LIQUID FUEL FROM POLYPROPYLENE AND POLYSTYRENE WASTE PLASTIC VIA CATALYTIC PYROLYSIS

BY:-TIHITNA ABEBE ABIDE

ADVISOR:-Dr. BETELEY TEKOLA

ADDIS ABABA,ETHIOPIA

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SYNTHEIS AND CHARACTERIZATION OF LIQUID FUEL FROM POLYPROPYLENE AND POLYSYTRENE WASTE PLASTIC VIA CATALYTIC PYROLYSIS

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BY:TIHITNA ABEBE ABIDE

SUPERVISED BY:Dr.BETELEY TEKOLA

ADDIS ABABA,ETHIOPIA

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DECLARATION

I,the under signed,declare that the thesis covers my own work.in agreement with internationally accepted practices,I dually acknowledged and referred all materials used in this work.

Tihitna Abebe Abide

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Submitted By:

TIHITNA ABEBE ABIDE June,2018

Name ***Signature*** ***Date***

Approved by:

Dr. Eng.ABUEKER YIMAM

Chairman,School of Graduate committee ***Signature*** ***Date***

Dr. BETELY TEKOLA

Thesis Advisor ***Signature*** ***Date***

Dr.Ing.BERHANU ASSEFA

Internal Examiner ***Signature*** ***Date***

Dr.SHIMELIS KEBEDE

External Examiner ***Signature*** ***Date***

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ACRONYMS

- α:-Reference Intensity
- θ:-Theta
- λ:-Lamda
- hkl:-Miller Indices
- a:-Lattice constant
- Å:-Angstroms
- BTX:-Benzene,Toulene,Xylene
- EA:-Elemental Analyzer
- EPA:-Environment Protection Agency
- FCC:-Fluid Catalytic Cracking
- FSAs:-Fly Ash Derived Silica-Alumina catalysts
- FTIR:- Fourier Transform Infra-red
- GC:-Gas Chromatography
- GCV:-Gross Calorific Value
- HDPE:-High Density Polyethylene
- JCPDS:-Joint Committee of Powder Diffraction Standards
- MPa:-Mega Pascal
- MS:-Mass Spectroscopy
- MSW:-Municipal Solid Waste
- MT:-Million Tons
- NC-Non-Condenseable Gas
- NCETRE:-
- PE:-Polyethylene
- PET:- Polyethylene Terephthtalete
- PP:-Polypropylene
- ppm:-Parts Per Million
- PS:-Polystyrene
- PVC:-Poly Vinyl Chloride
- RH:-Rice Husk
- RHA:-Rice Husk Ash
- SWP:-Solid Waste Plastic
- XRD:-X-ray diffractor

ABSTRACT

Catalytic Pyrolysis of polypropylene (PP) and Polystyrene (PS) into fuel like products using silica alumina catalyst that extracted from rice husk was investigated over temperature range of 430-470°C.Burning rice husk at 700^{o}C for 2hrs give rice husk ash and washed and dry at 800^{o}C for 1 hour.Finally the dried silica mixed with aluminum oxide using dry-dry mixing and calcined for 1 hour at 800^{o}C.The prepared catalyst was used for catalytic pyrolysis.The output of catalytic pyrolysis was liquid oil, solid residues (char) and gaseous fraction.The product yields as a function of temperature, time and catalyst amount were studied.High conversion of liquid (44.7%), gas (60.14%) and solid residue (43.4%) was achieved at 450°C with the use of 12.5gm catalyst amount for liquid oil and 5gm catalyst for gas and 470^{o}C with the use of 12.5gm of catalyst for solid residues.The pyrolysis time for high yield conversion of liquid oil and gaseous fraction were 30 minutes and 60 minutes pyrolysis time for solid residues in case of PP and liquid; 48.8% at 430^{o}C in the presence of 12.5gm catalyst amount, gas; 78.286%, and residue; 52.4% at 450^{o}C and 470^{o}C for gaseous and residue in the presence of 12.5gm catalyst for solid residue and 5gm catalyst for gaseous fraction at 30 minutes pyrolysis time for liquid product and gaseous fraction and 60 minutes for residue in case of PS.At higher catalyst amount and lower degradation temperature for PS and moderate for PP with lower residence time the yield of the liquid fuel was higher in both plastic type.The high yield of solid residues (char) and gaseous product was mainly due small cross section of heating, inefficiency of the pyrolyzer and insufficient condenser.Raw waste plastics were analyzed by FTIR.The FTIR spectrum indicates there was a presence of Naphtalenes, Olefins, and Amine, Acid group in both plastic type and Aromatics in PS.The catalyst silica alumina that was used for catalytic pyrolysis analyzed by XRD.XRD graph shows both silica and alumina exist.In addition to this the graph show that the catalyst had amorphous structure.The liquid fractions were analyzed by GC/MS.The results showed that the waste plastics of polypropylene liquid oil consisted of a range of hydrocarbon mainly in Gasoline range (C_5-C_{12}) and liquid oil from catalytic pyrolysis of polystyrene waste consisted a wide range of hydrocarbons mainly distributed within the C_5–C_{27} that was in the range of gasoline, diesel and heavy oil.The liquid product obtained in case of Polypropylene was enriched in the naphtalenes hydrocarbons.Similarly,the liquid product obtained in case of polystyrene was enriched in styrene hydrocarbons with prevalence in gasoline,diesel and heavy oil range hydrocarbons.The liquid fraction that had high yield for both plastic type were also analyzed for fuel properties.Conclusion from the study,liquid oil from PP waste had a lower yield (44.7), density (0.827g/cm^3), viscosity (2.06cSt) and a higher value of flash point (29^{o}C) and calorific value (25mJ/Kg) than liquid oil (0.955g/cm^3, 2.2cSt, 29^{o}C, 20mJ/Kg) from PS waste.Generally the whole results indicated that the derived liquid fractions were fuel-like meeting the fuel grade criteria.

Keywords:Catalytic Pyrolysis, Polypropylene, Polystyrene, Rice Husk, Silica-Alumina, FTIR, XRD, GC/MS.

To Liyu, Kidy, Haymi, Loli, Jojo and Jash.I owe you my every bit .

1. INTRODUCTION

1.1. Background

In modern life, the application of polymers is common.Plastic is a polymer and the term which refers to a wide range of synthetic or semi-synthetic organic amorphous solid materials which are typically of high molecular mass (R. Boopathy Pradeep et al.,2016).Today, plastics materials are very frequent in daily life and provide a fundamental contribution to our society.It is unique material because of their toughness, light weight, resistance to water and chemicals, resistant to heat and cold, low electrical and thermal conductivity, ease of fabrication, remarkable color range, more design flexibility, durability and energy efficiency.Due to those properties it is used in packaging materials, agriculture, construction, insulation, automobile sector,electronic devices, textiles and sports equipment and toys (Arun joshi, Rambir and Rakesh punia,2014).

The rise of the world population has caused the demand of commodity plastics to further increase.According to statistic, the global production of plastic has reached about 299 million tons in 2013 and has increased by 4% over 2012.Since most of the plastics were thrown out after single use, the amount of plastic waste accumulated in the environment each year was at alarming level.In Europe, 25 million tons of plastic ended up in waste stream during the year of 2012.Based on the statistic, about 38% of the plastic waste still went to the landfill, 26% were recycled while 36% were utilized for energy recovery (Association of Plastic Manufacturers Europe,2015).This indicate that the percentage of plastic waste dumped in the landfill was high and it occupied a large space and required a large disposal costs.Also, the degradation of plastics may take up billions of years, thus the continuous disposal of plastic in the landfill would definitely facing social resistance because of the negative impact on the environment.

In the other hand with the depletion of fossil fuels, the energy crisis has become one of the most important technological challenges of the near future.Fossil fuels are non-renewable resources since their generation require millions of years.Fuel reserves are being depleted much faster than they are created.The world's liquid fuels supply meets demand at 87 million barrels per day prior to 2012.By 2030, the world's liquid fuels supply will decrease to 43 million barrel per day, while the demand is expected to rise to 105 million barrels per day.More than 50% of world's fuels will have to be supplied by unidentified sources ("Meeting the world's demands for liquid fuels,"2009).Fossil fuels consist of oil, natural gas and coal, which will last approximately for 40 years, 75 years and 200 years, respectively, at current consumption rates [1](J. M. Shuster, *Beyond fossil fools, the road map to energy independence by 2040*).Furthermore, the production and use of fossil fuels raise environmental problems and concerns.The consumption of fossil fuels produces around 21.3 billion tons of CO_2 per year.There is a net increase of 10.65 billion tons of atmospheric CO_2 per year.It is estimated that natural processes can only absorb about half of the

CO_2 released into the atmosphere ("US department of energy on greenhouse gases.",2012).The amount of CO_2 released into the air increases substantially every year.

CO_2 is one of the greenhouse gases that greatly contribute to global warming, causing the average surface temperature of the Earth to rise.This emphasizes the need of finding alternative carbon natural fuel.Sustainable energy sources, such as solar and wind, attract attention as potential solutions to the energy crisis because they are renewable, cost-effective and pollution free.However,these sources only generate electricity and do not meet the demand for hydrocarbon-based transportation fuels.A liquid transportation fuel is needed that can be derived from renewable sources and can be shipped and stored easily.To meet this need, sustainable and environmental friendly energy sources urgently need to be investigated as viable options. Alternative energy sources, such as plastic (mostly made from oil, natural gas or coal), their waste, are good starting materials to potentially reduce our dependence on fossil fuel (Moinuddin Sarker et al.,2012).
Energy crisis and environmental degradation by polymer wastes have been imperative to find and propose technologies for recovery of raw materials and energy from non-conventional sources like organic wastes, plastic wastes, scrap tires, etc.A variety of methods and processes connected with global or national policies have been proposed worldwide (M.Stelmachowski, 2010).Therefore, plastic recycling is one of the most environmentally friendly solutions to the plastic waste problems (U.S. EPA, 2012).The different types of plastic recycling types can be divided into three (or four) general levels: primary, secondary, and tertiary.Primary recycling processes materials into a product with physical and chemical characteristics similar to the original product.Secondary recycling turns waste into products with characteristics that are less demanding than the original.Tertiary recycling (also known as feed stock recycling)-the processing of waste into fuels or basic chemicals.It should be noted that incineration is sometimes considered recycling where the heat recovery is considered a product in the same way a monomer or oil would (Hind,J.,1999).The waste plastics end up in incineration facilities was hazardous to the environment because of the toxic gases such as carbon monoxide (CO), which causes health hazards; sulfur dioxides (SO_2), which contribute to acid rain; nitrogen oxides (NOx),which contribute to ozone depletion and acid rain; and carbon dioxide (CO_2), a greenhouse gas that contributes to global warming & soot particles which are released during the incineration process.There is the Kyoto Protocol which considers of reducing CO_2 emission by 20% (M. R. Jan, et al.,2010).

Pyrolysis is a tertiary recycling method and degradation process occurring in the absence of oxygen.It prevents the formation of CO_X, NO_X, SO_X due to absence of oxygen.It breaks large hydrocarbon chain into smaller ones, but this type of pyrolysis requires higher temperature and high reaction time.Also resulting fluid have low octane value, higher pour point of diesel and high residue content (Arun joshi, Rambir and Rakesh punia,2014).Pyrolysis appears to be promising technique of conversion of SWP to more usable materials such as gas fuel and/or fuel oil or to high value feed stock for the chemical industry.Degradation of the waste plastic

materials, by heating in an inert atmosphere pyrolysis, is usually conducted at moderate temperatures between 400-800°C.Obtained products are volatile condensable hydrocarbon oil and a non-condensable high calorific value gas and solid residue (J. Nishino. et al.,2003).

The dominant components of domestic plastics are rich in carbon and hydrogen so that there is a good possibility for converting waste plastic into liquid fuels (A.Marcilla. et al.,2007).The extent of reaction, oil yield, and its composition depend on the type of plastic and process conditions (G.Manos,2006).Thermal pyrolysis of plastic materials leads to a wide product distribution and requires high degradation temperatures (S.A.Ammar, D.A.Sawsan Shubar, 2008).By using effective catalysts, these temperatures can be significantly reduced, thereby reducing costs.The catalyst used in the pyrolysis of plastics definitely influences the product.

1.2. Statement of the Problem

Production and consumption of plastics material increase due to its diversified application. Plastics have become an indispensable part in today's world.Due to their light-weight, durability, energy efficiency, coupled with a faster rate of production and design flexibility, these plastics are employed in entire range of industrial and domestic areas.Plastic have molded the modern world and transformed the quality of life.There is no human activity where plastics do not play a key role from clothing to shelter, from transportation to communication and from entertainment to health care(ICPE project).Most of the plastics thrown out after a single use.Because of this plastic wastes are largely dispersed everywhere.The waste plastic that goes to a landfill doesn't degrade for thousands of years,due mainly to their chemical inertness, causing land to be less fertile and environmentally unsafe for its inhabitants.Waste plastic disposed in the landfills is also the source of heavy metals and these metals from the wastes precipitate in the soil.The plants absorb the heavy metal which is deposited in the soil by plastic wastes.Then the plants are consumed by the animals and humans.The heavy metals from the plastic wastes cause cancer and death to both humans and animals.So plastic waste management is biggest problem now due to their non-biodegradability nature.

Aside from the challenge of plastic waste disposal,another global issue is the energy crisis. Transportation consumes one third of the world's energy.The main energy sources for transportation are fossil fuels like coal, oil, and natural gas, all of which are non-renewable sources of energy.Fossil fuels are non-renewable resources and required millions of years for generation.Due to increase in demand fuel reserves are being depleted much faster than they are created.The world's liquid fuels supply will never meet the demand in the coming decades. Moreover, the production and use of fossil fuels are a major sources of environmental pollution, green house gases, and ocean acidification.The consumption of fossil fuels produces net increase of 10.65 billion tons of CO_2 per year.

The current problem in the management of plastic waste and usage of non-renewable energy sources are already posing a serious threat to the environment.With the expected increase in the consumption of the plastic items, the problem will certainly grow correspondingly.In addition to

this the depletion of non-renewable energy sources and the emission of pollutant during and after production of fossil fuel will also continue.So liquid fuel from waste plastics is useful to eliminate greater problem of plastics waste management and is a good alternative method for obtaining new energy resource.Efficient conversion of waste plastics into advanced materials is conspicuous environmental, social and economic benefits.

The major concern of this research is finding possibilities to minimize environmental degradation and energy crisis by the conversion of polypropylene and polystyrene waste plastic into useful liquid fuel via catalytic pyrolysis.The conversion of waste plastic into liquid fuel using catalyst that prepared from rice husk,that is one of agricultural waste, and cause disposal problem.So this also make catalytic pyrolysis,where the catalyst produced from agricultural waste, more attractive in terms of waste management and economy.

1.3. Objectives

1.3.1. General objectives

The general objective of this research is to convert polypropylene and polystyrene waste plastic into valuable liquid fuel via catalytic pyrolysis.

1.3.2. Specific objectives

The specific objectives are:-

- To prepare silica-alumina catalyst from rice husk and characterize the catalyst
- To characterize Polypropylene and Polystyrene plastic waste
- To study the catalytic pyrolysis of polypropylene and polystyrene waste plastic in the production of liquid fuel.
- To investigate the effect of catalyst amount, residence time, reaction temperature and plastic type on the yield of liquid product.
- To characterize the physio-chemical properties of produced liquid fuel.

1.4. Significance of the study

This research, by producing silica-alumina catalyst from rice husk. it will minimize disposal problem of rice husk and cost burden of catalyst.Producing of liquid fuel using polypropylene and polystyrene waste plastics, will contribute for alternative energy source and minimize environmental degradation due to waste plastics and minimizing environmental problem that rise due to use of fossil fuel.This study will able to use as a reference for future study on production of fuel via catalytic pyrolysis specially on catalyst that produced from rice husk.

1.5. Scope of the study

The research work generally covers silica-alumina catalyst,Polypropylene, polystyrene waste preparation and characterization, synthesis of liquid fuel from polypropylene and polystyrene waste plastic through catalytic pyrolysis.The characterization of the prepared catalyst,liquid fuel and solid residues is based on standard procedures and test methods.

2. LITERATURE REVIEW

2.1. Solid Waste in Addis Ababa

Addis Ababa, the capital city of Ethiopia, suffers from poor solid waste management.The city generates a solid waste of more than 200,000 ton each year.This means that about 550 ton of waste per day was generated.The municipality increased the collection rate from 60% to 80% (Addis Ababa city government,2010).About 20% to 30% of the waste generated in Addis Ababa remained uncollected and made the city environment aesthetically unpleasant and affected the city's public health (Tilaye M, et al.,2014).The city council distinguishes six major sources of solid waste: households, street, commercial institutes, industries, hotels and hospitals.From the total generated solid waste households' account for 71%, street 10%, commercial institutions, 9%, industries 6%, hotels 3% and hospitals 1% (Cointreau-Levine S.,1994).Local initiatives create sustainable urban solid waste management play a key role for the collection of waste. Waste collected in Addis Ababa either by pre-collectors, who collect waste from households with a push cart and deliver the waste to the garbage tank or korale (second level waste collectors), who buy used things that people do not need.

After collection of waste done by pre-collectors,the containers that hold a waste are then emptied at Repi and placed back by the government trucks.However, with the fast expansion of the city, now the dump site has been surrounded by settlements.The dump site does not have any proper gas or leachate collection system.This is the cause of environmental degradation (B.Camilla, 2014).From the total solid waste collected 2.9% is plastics/rubber and for 80% collection rate 4,640 ton of plastic waste was collected each year (Addis Ababa city government,2010).

2.2. Plastics and Their Classification

Plastics are macro-molecules, formed by Polymerization and having the ability to be shaped by the application of reasonable amount of heat and pressure or some other form of force (Aguado.J. et al.,2006).Plastics are light weight, durable, and versatile, allowing their incorporation into a diverse range of applications.In recent years, the environmental, social and economic impact of plastics has been the topic of the political agenda, with a focus on sustainable production and the decoupling of adverse environmental effects from waste generation, the disposal of waste plastics has become a major worldwide environmental problem (Baeyens, J.et al.,2010).

Plastics can be categorized by various criteria including chemical composition, chemical structure, stiffness, the type of application, and processing method.From these, the most common categories are chemical composition and structure.Chemical composition classifies plastics by the type of monomer and polymerization (e.g. polyolefins, polyesters, poly-carbonates etc). Chemical structure meanwhile is associated with bonding linearity, branching, and cross-linking. Plastics are further divided into other categories are thermoplastics vs. thermosets. Thermoplastics, make up 80% of the plastics which are most commodity plastics like HDPE or PET, soften when heated since there is little bonding within the molecular chains.

Thermosets meanwhile make up of remaining 20% of plastics produced today, which are plastics found in circuit boards and epoxy resins, thermally decompose while heating (Timothy T Sharobem,2010).There are different types of plastic but coded as 7.Table 2.1 shows types of plastics and their recyclliabity.

Table 2.1:Types of waste plastics and their recyclables(http:/en.wikipedia.org/wiki/ Plastic_recycling)

Mark	Type	Recyclable	Abbreviation	Description
	Type 1	Yes	**PET**	Polyeylene Traphtalate beverages
	Type 2	Yes	**HDPE**	Milk, detergent and oil bottles, toys, containers used outside, blister packages/automotive parts.
	Type 3	Yes,but not common	**PVC**	Food wrap, vegetable oil bottles, blister packages or automotive parts.
	Type 4	Yes	**LDPE**	Most plastic bags, shrinks wrap, garment bags or containers.
	Type 5	Yes	**PP**	Refergerated containers, some bags, carptets, food wrap and most bottle tops,
	Type 6	Yes,but not common	**PS**	Through away utensils, meat packing, protective packing
	Type 7	Some	———	**OTHER.** usually layered or mixed plastic

2.2.1. Sources of Plastic Waste

Plastic wastes can be classified as industrial, commercial, agricultural and municipal plastic wastes according to their origins; these groups have different qualities and properties and are subjected to different management strategies (Buekens AG, Huang H.,1998).Depending on the waste collected area the sources of plastic waste categorized (Moinuddin Sarker, Mohammad M.,2011) as follow:-

Industrial waste (or primary waste) can often be obtained from the large plastics processing, manufacturing and packaging industries.Rejected or waste material usually has good characteristics for recycling and will be clean.Although the quantity of material available is some

times small,the quantities tend to be growing as consumption, and therefore production, increases.

Commercial waste is often available from workshops, craftsmen shops, supermarkets and wholesalers.A lot of the plastics available from these sources will be PE, often contaminated. Agricultural waste can be obtained from farms and nursery gardens in the form of packaging (plastic containers or sheets) or construction materials (irrigation or hosepipes).

Municipal plastic wastes normally remain a part of municipal solid wastes as they are discarded and collected as household wastes.Plastics usually account for about 7% of the total MSW by weight and much more by volume (Buekens, A.G. and Huang, H., 1998).The typical distribution of household plastics as a part of the overall solid waste stream is:Polyolefins 66.9%, Polystyrene 13.3%, PVC 10.3%, PET 5.3% and others 4.2%.Polystyrene and Polypropylene are the largest commodity plastic material in the world after HDPE and polyvinyl chloride in terms of volume respectively (W.Kaminsky, I.Nun˜ez Zorriqueta,2007).

2.2.2. Plastic Waste Management

Waste management is a current, complex subject and has become one of the most important concerns in the field of environment conservation by the modern society.Almost all human activities create waste; especially since the Industrial revolution in the mid-18th century, the amount of waste created increased dramatically around the world.Not only has it increased in amount but also in type and toxicity.Waste management is an issue to most countries around the world and directly related to the economic, social and political status of the country (Meaza Cheru,2016).

The suitable treatment of plastic wastes is one of the key questions of the waste management and is important from energetic, environmental, economical and political aspects (Delattre C.et al., 2001).Even though the recycling rate for post consumer plastics has increased in the recent years, this increase has been only meager coming to only around 1.5%.This increase in the recycling is due to the strict legal regulations and growing awareness.Different techniques for the waste plastic management are being followed today (A. K. Panda, et al.,2010).

2.2.2.1. Land filling of plastic wastes

The major portion of the waste plastics has been subjected to landfill.Waste plastics are not biodegradable; they remain for long period into the landfill.The lack of landfill sites and assessments of the environmental consequences of land filing have led many countries to ban land-filling of combustible wastes, including wet organic waste (Sarker M, Rashid MM.,2013 and Maria FD, Pavesi G.,2006).Land-filling of plastic wastes causes pollution by emitting toxic gases like furanes and dioxins to the environment which are carcinogenic.Various types of additives, I.e.fillers, plasticizers, colorants are used with virgin plastics to make them user friendly, hygienic, durable, UV resistant and economic for the consumers.Hence, plastics can pollute the environment due to presence of various additives.Mostly nonyl phenols, poly brominated diphenyl ethers (PBDEs), di-(2-ethylhexyl) phthalate (DEHP), and Bisphenol

A(BPA), are mixed with the monomers of virgin plastics to act as catalyst in producing polymers and thus enhance other desired properties.Some of these used chemicals are found responsible as hormone -disruptres (Halden RU.,2010).Bisphenol A(BPA),which is extensively used with the epoxy resins of food and beverages containers and as monomer in the polycarbonate plastic of many consumer products, is alarmingly related to cardiac diseases, diabetes as well a abnormal increase of cetain liver enzymes (Lang IA, Galloway TS, Scarlett A.,et al.,2008).PBDEs may be responsible for lowering the immune system, thyroid disruptions and troubles in fertility issues of human being.So, when plastics are used or discarded, the emissions based on these additives are undesirable from an environmental point of view (Siddiqui MN., Redhwi HH.,2009).Not only the emissions but the formation of leach ate due to waste soaked in the soil pollute ground water.Therefore,due to the rising cost, scarcity of land, the generation of explosive greenhouse gases (such as methane), a high volume to weight ratio of plastics, and the poor biodegradability of commonly used packaging polymers make land filling of plastic waste an unattractive option.

2.2.2.2. Incineration of plastic wastes

On the other hand,incineration of wastes has been considered as the highly effective method to reduce the volume of wastes by producing energy.In most countries, it is the traditionally adopted technology.So, there is a widespread concern about the methodologies regarding incineration process and the emissions related to it.Air pollutants like CO, CO_2, NO_X, SO_X, particulate matters (PM), volatile organic compounds (VOCs) and polycyclic aromatic hydrocarbons (PAHs) are found from the plastic waste incineration's ([1] Li C-T.et al.,2001).Almost 30% by weight of waste plastics are converted into CO_2 due to this process with a factor of 25gm/MJ fuel to be compared with other fuels (Sund berg J, Olofsson M.,2004).Though the incineration process converts the waste into energy for industrial uses in some extent, the conversion efficiency and the emitted pollutants are endangerment concerns.Plastic wastes are generally burnt for few seconds in high temperature incinerator with an excess air ratio between 1.0 and 1.8 ([1]Lea WR.,1996).The ash by-products of incineration process are generally land filled so risk based concerns due their carcinogenic threat (World WM.,2011).

Waste products previously dumped in landfill sites, a non-sustainable and environmentally questionable option.But this days Recycling of plastics has gained increasing attention as the land filling and incineration become more expensive and less accepted due to the environmental impacts and it already occurs on a wide scale.Extensive recycling and reprocessing of plastics are performed on homogeneous and contaminant free plastic wastes.Most recycling schemes require a feed-stock that is reasonably pure and contains only items made from a single polymer type, such as high density polyethylene (HDPE) commonly used to make milk bottles, or polyethylene terephthalate (PET) soft drink bottles.However, a substantial fraction of the plastics in municipal waste still ends up in landfills.Realistically, most post-consumer wastes contain a mixture of plastic types and are often contaminated with non-plastic items (Hegberg.et al.,1992).

2.2.3. Recycling of plastics

The main Purpose of plastic wastes conversion into fuel is to Promote resource conservation by obtaining fuel from waste plastics, to Upgrade the properties of wastes as fuel for transportation, storage, feeding to a boiler, calorific value, smooth combustion and qualities of flue gas and ash. It also important to reduce greenhouse gas by using waste plastics for the cleaner fuel production and supporting biomass utilization.Recycling of plastics should be carried in such a manner to minimize the pollution during the process and as a result to enhance the efficiency of the process and conserve the energy (NCETRE, 2016).The recycling of waste polymers can be carried out in many ways.Four main approaches have been proposed presented below (Karayannidis and Achilias,2007; Scheirs,1998):

1. *Primary recycling:*- refers to the 'in-plant' recycling of the scrap material of controlled history. This process remains the most popular as it ensures simplicity and low cost, dealing however only with the recycling of clean uncontaminated single-type waste.

2. *Mechanical recycling (or secondary recycling):*-In this approach, the polymer is separated from its associated contaminants and it can be readily reprocessed into granules by conventional melt extrusion.Mechanical recycling includes the sorting and separation of the wastes, size reduction and melt filtration.The basic polymer is not altered during the process.The main disadvantage of this type of recycling is the deterioration of product properties in every cycle. This occurs because the molecular weight of the recycled resin is reduced due to chain scission reactions caused by the presence of water and trace acidic impurities.Strategies for maintaining the polymer average molecular weight during reprocessing include intensive drying, reprocessing with degassing vacuum, the use of chain extender compounds, etc.

3. *Chemical or Feedstock recycling (tertiary recycling):*-has been defined as the process leading in total depolymerization of PET to the monomers, or partial depolymerization to oligomers and other chemical substances.The monomers could subsequently repolymerized to regenerate the original polymer.

4. *Energy recovery (Quaternary recycling):*-refers to the recovery of plastic's energy content. Incineration aiming at the recovery of energy is currently the most effective way to reduce the volume of organic materials.Although polymers are actually high-yielding energy sources, this method has been widely accused as ecologically unacceptable owing to the health risk from air born toxic substances e.g. dioxins (in the case of chlorine containing polymers).

If the primary and secondary recycling is performed with the plastic products collected from waste stream,they are not reused to produce due to quality concerns (Williams PT,2005).Even if the technique seems to be "a green operation," secondary recycling is not cost effective as it requires high energy for cleaning, sorting, transportation, and processing to make a serviceable product.Practically it is seen that reprocessing of mixed contaminated plastics yields mechanically inferior products lacking in durability compared with the original polymers.Due to low grade utilization of the recycled plastic materials, alternative recycling processes are

evaluated and further improvement is going on.Recycling waste plastics using incineration can taken as an alternative methods but it is not feasible due the release of toxic gases.

In order to decrease the volume of non-degradable plastic waste material and preserving valuable petroleum resources Pyrolysis is one of the best methods.Alternative fuels developed from these waste plastic sources have the potential to overcome many environmental and economical problems by providing a steady, low-cost source of fuel, providing local employment in energy production, and helping organisms live better lives (Buekens AG, Huang H,1998; Scott DS,et al.,1990; Siddhant Pundhir, and Arpit Gagneja, 2016).

The pyrolysis of municipal solid waste is a promising waste to energy or plastic to fuel technology for the sustainable management of plastic waste along with production of liquid oil as a source of energy and char and gases as value added products (Rehan, M.et al., 2016a).The pyrolysis process is an advanced conversion technology that has the ability to produce a clean, high calorific value hydrocarbon from waste plastics.Calorific values of fuel from waste plastics are dependent on the type of waste plastics used for a particular process and operating conditions of the process.

Plastic were derived from petrochemical resources.In fact these plastics are essentially solidified oil.They therefore have inherently high calorific value.The calorific values of some of the plastic materials along with coal and some of the petroleum products are shown in Table 2.2 (Environment and Plastics Industry Council, 2004).

Table 2.2: Calorific values of some plastics materials

Material	**Btu per Second**	**Kilojoules per Kilo**
Coal	11,500	27,000
Diesel Fuel	19,780	46,000
Gas Oil	19,780	46,000
Heavy Fuel Oil	18,490	43,000
Kerosene	20,210	47,000
Light Distillation	20,640	48,000
Light Fuel Oil	18,920	44,000
Medium Fuel Oil	18,490	43,000
Petrol	19,264-20,167	44,800-46,900

PLASTICS		
Polyethylene	20,000	46,500
Polypropylene	19,300	45,000
Polystyrene	17,900	41,600
PET	9,290	21,600
PVC	8,170	19,000

The most common plastics preferred for the feed stock of the production of liquid hydrocarbon are high density polyethylene (HDPE), polypropylene (PP) and polystyrene (PS) which yield a mixture of hydrocarbons.

2.2.3.1. Polypropylene and Polystyrene Plastic Waste

2.2.3.1.1. Polypropylene waste plastic

Polypropylene (PP) is a hydrocarbon polymer made from petrochemicals; having a large amount of volatile matter with high heating value and low ash content (Siddhant Pundhir, and Arpit Gagneja,2016).Polypropylene is prepared by polymerizing propylene which is a gaseous by product of petroleum refining, The polymerizing reaction takes place in the presence of a proper catalyst at a temperature range of 340-360K and pressure range of 30-40atm.Propylene is an unsaturated hydrocarbon which contains only carbon and hydrogen atoms.By polymerization reaction, many propylene molecules are joined together and one large molecule of polypropylene is formed (C. Maier and T. Calafut,1998).

Waste plastics like polypropylene contain 85% of carbon and rest is hydrogen, this makes them extremely suitable for feed-stock recycling with the production of valuable hydrocarbon products. This fact can be explained with the difference in the activation energy of two polymers.PP requires low activation energy to break the C−H bond than polyethylene (PE) because carbon chain of PP polymer contains tertiary carbon atoms which have considerably lower resistance against degradation (A.Marcilla, et al.,2008).

2.2.3.1.2. Polystyrene waste plastic

Polystyrene, also known as *polyvinyl benzene*, is a glass like solid which shows mechanical strength below 100°C.PS is aromatic, non-polar, chemically inert, resistant to water, and easy to process (V. R. Gowariker,et al.,2005).Polystyrene has been a good raw material to convert into fuel (Miandad R, et al.,2016).The reaction temperature needed to degrade this material into vapor and liquid between 350-480°C (Lee K H and Shin D H.,2007).

2.3. Plastics Pyrolysis

In plastics pyrolysis, the macro-molecular structures of polymers are broken down into smaller molecules or oligomers and sometimes monomeric units.Further degradation of these subsequent molecules depends on a number of different conditions including (and not limited to) reaction temperature, residence time, and the presence/absence of catalysts.The production of fuel from plastics is one of the most demanding research topics throughout the world.The most widely used methods for oil production from plastics are Hydro cracking pyrolysis, thermo-chemical pyrolysis and catalytic pyrolysis (Cha, W.S.et al.,2002).

2.3.1. Thermal Pyrolysis

Thermo-chemical treatment breaks large polymers into smaller hydrocarbons of various carbon numbers and boiling point in an inert, air free, or controlled environment at elevated temperature (Sharma BK.,et al.,2014).The thermal decomposition of plastics progress through a radical mechanism which involves 3 different decomposition routes (J. Aguado and D. P. Serrano.,1999) that are listed below:

I. Random scission at any point in the polymer backbone leads to the formation of monomers.These monomers in turn may be subjected to additional random cracking reactions.

II. With end-chain scission, a small molecule and a long-chain polymeric section are formed.

III. The polymer chain may retain its length or the release of the small molecule might be accompanied by the breaking of the polymeric chain.At the end of the reaction, small molecules form.

Thermal pyrolysis of both virgin and waste plastics as well as other hydro-carbonaceous sources has been studied extensively in the past.A good number of these thermal cracking studies are on polyethylene (PE) (Sorum, L.,et al.,2001,[1] Dolezal, Z.,et al., 2001 and Audisio, G., et al., 1984), polystyrene (PS) ([1]Cha, W.S.,et al.,2002,[11] Kim, S.S. and S. Kim,2004, Woo, O.S. and L.J. Broadbelt,1998 and Chan, J.H. and S.T. Balke,1997), and polypropylene (PP) ([1]Faravelli, T., et al.,2001,Syamsiro M.,et al.,2014,Woo, O.S. and L.J. Broadbelt,1998, [1] Kaminsky, W., et al.,2004[1] Onu, P., et al.,1999,Audisio, G., et al.,1984 and Scott, D.S., et al.,1990).On the other hand, only a few have researched the thermal decomposition of other common plastics such as polyvinyl chloride (PVC) ([1]Sakata, Y., et al., 1996 and [1] Miskolczi, N., et al.,2004), polymethyl methacrylate (Onu, P., et al.,1999), polyurethane (Demirbas, A.,2004), and polyethylene terephthalate (Miskolczi, N., et al.,2004).

Cho M-H.,et al.,(2009) studied the thermal pyrolysis of mixed plastic waste, and showed that the production of benzene, toluene and xylene (BTX) increased with reaction temperature.The highest yield of BTX compounds was recorded at 719^{o}C, which was 18%.It was also found that the use of suitable catalyst greatly enhanced the production of BTX compounds at lower temperature compared to thermal pyrolysis.Aromatic compounds are formed as a result of

secondary reactions, as well as the shape selectivity of the catalysts used in pyrolysis.Pyrolysis of polypropylene waste material gives petroleum fuel grade liquid product without using catalyst (Obali Z.,et al.,2012,[1] Nishino J., et al.,2003).

Ali Karaduman (2002) studied the thermal degradation of Polystyrene with various organic compounds, such as phenol, quinone, naphthalene, and diphenylamine at varied temperature range from 350°C to 450°C.The main products of Polystyrene waste pyrolysis were mainly styrene monomer, ethyl benzene, toluene, and methyl styrene.The product spectrum can be described as a function of pyrolysis temperature and used organic compounds.The yield of styrene in liquid products at various temperatures with different organic compounds varies from 60 to 74%.The optimum pyrolysis temperature to maximize styrene monomer yield (about 60%) was 400°C.The amount of styrene was found to increase in the order: diphenylamine < phenol < quinone < naphthalene.

Pyrolyzed PS in the temperature range of 360-520^{o}C and found the product to be comprised mainly of styrene with minor amounts of dimers and trimers (H. Bockhorn, A.,et al.,1998 and [1] W. Kaminsky, M.,et al., 2004).Polystyrene wastes were degraded in a free-fall reactor under vacuum to regain the monomer at varied temperature between 700°C and 875°C and determined its effects on the phase yields, benzene, styrene, toluene, and naphthalene distribution of the liquid output and C_1–C_4 content of the gaseous output.The liquid yield maximized at around 750°C and the styrene yield, at 825°C.In general, operating at higher temperatures lessened the solid residue and increased the gaseous yield and total conversion (Ali Karaduman,2001).

2.3.2. Hydro pyrolysis (Hydro-cracking)

Hydro-cracking is the cracking of larger hydrocarbons, such as polymers, into fuel-range hydrocarbons in the presence of hydrogen at elevated temperatures (Sharma BK.,et al.,2014 and Arthur A.,et al.,2004).Hydro-cracking of polymer waste typically involves reaction with hydrogen over a catalyst in a stirred batch autoclave at moderate temperatures and pressures (typically 423–673K and 3–10MPa hydrogen).The work reported, mainly focuses on obtaining a high quality gasoline starting from a wide range of feeds.Typical feeds include polyolefins, PET, polystyrene (PS), polyvinyl chloride (PVC) and mixed polymers, polymer waste from municipal solid waste and other sources, co-mixing of polymers with coal co-mixing of polymers with different refinery oils such as vacuum gas–oil and scrap tyres alone or co-processed with coal (Buekens, A.G. and Huang, H.,1998).

In hydro-cracking no char was formed in the process and the major products were gases that had a hydrocarbon range of C_{5+}; this process produced double the gas fractions of C_{5+} that were produced from thermal cracking in an inert atmosphere (Siddhant Pundhir, and Arpit Gagneja,2016).Hydro cracking is also more effective when performed with a catalyst.The most widely used hydro cracking catalysts are acidic supporting materials (alumina, silica-alumina, zeolites) loaded with transition metals (Pt, Fe, Ni, and Mo) (Sharma BK.,et al.,2014).For example, Ding et.al.,1997 used a hybrid catalyst containing a 4:1 weight ratio of SiO_2-

Al_2O_3:HZSM-5 loaded with Ni or NiMo.The hydro cracking reaction was carried out at 375^0C and 1000 psig for 1hr.The optimal conditions resulted in conversions up to 99%.The product contained mostly hydrocarbons with a range of $\leq C_{13}$ (Arthur A.,et al.,2004).In general, catalytic hydro-cracking improves the conversion of polymers into hydrocarbons, compared to non-catalytic hydro cracking.

2.3.3. Catalytic cracking:

The non-catalytic or thermal pyrolysis of polyolefins is a high energy, endothermic process requiring temperatures of at least 350-500°C (Murata, K.,et al.,2004,[1] Sorum, L.,et al.,2001 and Faravelli, T.,et al.,2001).In some studies, temperatures as high as 700-900°C are essential in achieving decent product yields (Demirbas, A.,2004, Mastral, F.J., et al.,2002 and Garforth, A.A., et al.,1998).By using effective catalysts, these temperatures can be significantly reduced, thereby reducing costs and obtaining commercially valuable products.

In catalytic conversion, catalysts are added to pyrolysis reactions to improve conversion, improve fuel quality, increase selectivity, and lower the pyrolysis temperature and residence time (Hegberg.,et al.,1992).The acidic nature of most of the catalysts used enhances conversion by protonating the defective sites of polymers forming on-chain carbonium ions (S.A.Ammar, D.A.Sawsan Shubar ,2008).Selectivity and fuel quality vary with the strength of the catalyst's acidity.Acid catalysts with meso and micro pores give higher conversion.Primary cracking takes place in the macro porous surface and once the polymer is cracked, further cracking is enhanced by micro pores (A.Ramesh Babu,2007).The use of a strong catalyst results in the production of lower hydrocarbons ranging between C_3 and C_5.

There are two types of catalysts for cracking of waste plastics.They are natural catalyst and synthetic catalyst.Natural catalysts are such as natural silica-alumina composition, treated bentonite clay, aluminum hydro-silicates and so on.Synthetic catalysts are synthetic silica-alumina, silica-magnesia, alumina-boria, zeolite, activated carbon and Alkaline compounds. Natural catalysts are cheaper than synthetic catalysts.The useful catalysts are available in the pellets form or powder form (M. T. Htet,2010).The other classification of catalysts used for plastic upgrading are Fluid cracking catalysts (FCC), Reforming catalysts, and activated carbon (S.A.Ammar, D.A.Sawsan Shubar,2008).FCC catalysts include zeolite (A.Ramesh.Babu,2007, Buekens AG, Huang H, 1998 and Ding W.,et al., 1997), silica-alumina (Hegberg.,et al.,1992), and clay(Hegberg.,et al.,1992 and Baeyens, J.,et al.,2010).Reforming catalysts include transition metals loaded in silica-alumina (S.A.Ammar, D.A.Sawsan Shubar,2008).Activated carbon is also widely used and can be loaded with or without transition metals.The life of a catalyst can be increased by using a two-step process that involves thermal cracking followed by catalytic cracking (Kiang, et al.,1980).

A number of experimental studies have been carried out by various researchers with the objective of improving liquid hydrocarbons yield from plastics pyrolysis by introducing suitable

catalysts, Common plastics such as PE and PP have already been tested extensively;Common catalysts used in this process are Zeolite, alumina, silica, FCC Catalyst, reforming catalyst.This catalysts tested are mainly those used in the petrochemical refinery industry (Siddhant Pundhir, and Arpit Gagneja,2016).

Venkatesh et al.,(1996) and Shabtai et al.,(1997) have obtained high yields of liquids that consist predominantly of iso-alkanes in the gasoline boiling range from HDPE, PP, and PS at relatively low temperature (300-375ºC) using catalysts such as silica-alumina or zeolite (HY, HZSM-5, mordenite) containing alkaline compounds such as ZnO, CaO and K_2O for the Conversion of Plastic to Hydrocarbon.Tymoshevskyy et al. in 2009 have used pyrolysis method to convert PP, PE, and polystyrene (PS) waste to fuel with trial of several catalysts.They have separated the product of catalytic cracking used in a distillation column into gas, gasoline, light oil, and heavy oil fractions.The catalytic pyrolysis of LDPE was investigated using various fly ash-derived silica–alumina catalysts (FSAs) by Na et al., 2006.

A.Marcilla et al.,2008 conducted catalytic pyrolysis of LDPE and HDPE plastic waste with HZSM-5 catalyst in a batch reactor and observed that the yield and composition of the products depends on the type of polyethylene used.HDPE gave higher N-paraffin's and iso-paraffin's whereas LDPE gave higher olefins at lower temperatures.Guohua et al., 2000 conducted catalytic cracking of HDPE and PP with Silica/Alumina catalysts in a powder particle fluidized bed.Over 86 wt.% conversion of liquid fuel was obtained.Kyong-Hwan et al.,2003 conducted catalytic cracking of HDPE, LDPE and PP using spent Fluidic catalytic cracking (FCC).It was observed that a yield of 89% yield was obtained and LDPE and PP degraded faster than HDPE.Achyut K.Panda et al., 2013 conducted catalytic pyrolysis using kaoline and silica alumina as catalysts. Yield up to 91% was obtained and silica alumina was found better as compared to kaolin in liquid yield.

Akpanudoh,N.S., et al.,2005 conducted catalytic conversion of plastic waste using Y zeolite.The effect of plastic polymer to catalyst ratio-mentioned as the acidity content of the polymer/catalyst system was studied on the creation of liquid hydrocarbons. J.Shahet al., 2005 used Lead sulphide as a catalyst for pyrolysis and observed more than 70% yield of gas and liquid fraction with boiling point up to 350°C.Onwudili et al.,2009 investigated the pyrolysis of polyethylene and polystyrene in a closed batch reactor to study the effect of the temperature and the residence time.The closed batch system can be effectively used to produce high grade fuel-like oils for energy production as well as chemicals.

2.3.3.1. Catalytic Pyrolysis of polypropylene and polystyrene waste plastics

2.3.3.1.1. Catalytic Pyrolysis of polypropylene waste plastics

Polypropylene was cracked thermally and catalytic-ally in the presence of kaoline and silica alumina in a semi batch reactor in the temperature range 400–550^{o}C in order to obtain suitable

liquid fuels.It was observed that up to 450^{o}C thermal cracking temperature, the major product of pyrolysis was liquid oil and the major product at other higher temperatures (475–550^{o}C) are viscous liquid or wax and the highest yield of pyrolysis product is 82.85 % by weight at 500^{o}C (Panda, A.K., Singh, R.K.:,2011).Kaolin catalyst found effective for thermo-degradation of polypropylene waste for conversion into fuel (Panda A.K. and Singh R.K.,2013).Catalytic cracking of polypropylene (PP) waste by using zeolite beta (BEA) catalyst enhances percent of oil as compared to that of without catalyst (Wanchai K. and Chaisuwan A.,2013).Catalytic pyrolysis of polypropylene (PP) has been studied by X.Ji et al.,2001 using a fluidized bed reactor. The gasoline obtained in this study has Research Octane Number (RON) in the range of 84-88 while the cetane index for diesel fuel lies in the range of 40.5-45.3.Some authors studied pyrolysis process for converting mixture of waste tyre and polypropylene into petroleum fuel by using ZnO as a catalyst (Sarker M. and Rashid M.M., 2013).There are several products obtained from the catalytic pyrolysis of PP which are carbon nano-materials (CNMs) of different morphologies (Y. Ando, et al., 2004 and [1] S. Iijima, 1991), wax (P. S. Umare, et al., 2005 and [1] D. S. Achilias, et al., 2007), oil (W.Kaminsky, et al., 2004,[1] M.Sarker, et al., 2012[1] ,D. C. Tiwari, et al., 2009 and Y. H. Lin and H. Y. Yen, (2005) and gases (A.Marcilla, et al., 2008 and [1] L.Sojak, et al., 2007).Most of the works concerned with production of oils from waste PP plastics, conversion efficiency was found to be < 50%.

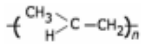
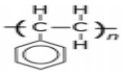
2.3.3.1.2. Catalytic Pyrolysis of polystyrene waste plastics

The use of natural zeolites for catalytic degradation of polystyrene (PS) has been investigated by Lee et al(2001).The performance of natural zeolites after ion-exchanged with NH_4Cl solution on the degradation of PS was as effective as HZSM-5 for the production of liquid oils with carbon numbers of C_5-C_{12} without severe deactivation.Natural zeolite catalyst produced aromatic liquid oils with over 99% of selectivity.This catalyst also showed a decrease of styrene and an increased selectivity towards ethyl-benzene and propyl-benzene compared to that of thermal degradation.Audisio et al.(1990) reported very low selectivity of the styrene in polystyrene degradation with solid acids such as silica–alumina and HY or REY zeolites at 350°C.The main products in their study were benzene, ethyl benzene and cumene.Polystyrene catalytic cracking over amorphous silica alumina (SA) and HZSM-5 zeolite results in a lower conversion than the thermal degradation under the same reaction conditions.Decreasing the plastic to catalyst mass ratio over HZSM-5 leads to a reduced cracking activity.In contrast to HZSM-5 and amorphous silica alumina, HMCM-41 has shown enhanced polystyrene conversion compared to the thermal degradation.The main products resulting from the catalytic cracking over HMCM-41 and SiO_2–Al_2O_3 are benzene, ethyl benzene and cumene.Siddiqui and Redhwi (2009) showed that PS has higher degree of degradation among different types of plastics.It has been shown to degrade almost completely under pyrolysis conditions used (430–440^{o}C, 5.5–6MPa, reaction time 60min, 1wt% catalyst), while PP and PET produced medium to high conversion.In comparison, LDPE and HDPE produced low conversion.

2.3.4. Polypropylene and Polystyrene plastics and their pyrolytic oil composition

Pyrolysis of different types of plastic wastes were produce different composition of pyrolytic oil. Polypropylene and polystyrene waste plastics pyrolystic oil composition were shown in Table 2.3 below.

Table 2.3:Plastic type and their pyroysis oil composition (Miandad et al., 2016; Chen et al.,2014; Sharuddin et al.,2016.).

Plastic type	Pyrolysis oil composition
 Polypropylene	Benzene, Toulene, Xylene, Ethylbenzene, Indene, Biphenyl, 1-heptane,1-octane
 Polystyrene	Styrene, Toulene, Ethyl benzene, Benzene, Xylene, Cumene, Naphthalene, Anthracene,

A lot of research work has been done in thermal, hydro-cracking and catalytic pyrolysis of waste plastics all proves that waste plastics can be converted to useful chemical feed-stock/fuel.

2.3.5. Slow and Fast pyrolysis

Pyrolysis methods differ in their residence time, temperature, and heating rate, which in turn greatly affect the percentages of gas, char, and liquid products in a semi-predictable manner, while the resulting, individual chemical species remain hard to predict and quantify (Balat, M.;et al., 2009 and [1] Mohan, D.; et al.,2006).Pyrolysis methods can be grouped into two large categories, slow and fast (flash) pyrolysis.Slow pyrolysis consists of slow heating rates of 0.1-1°C/s, a residence time anywhere from hours to minutes, and a temperature range of 400–600°C. It has been used for centuries to produce methanol and yields approximately equal quantities of char, gas, and liquid (Balat, M.; et al.,2009,[1] Mohan, D.; et al.,2006 and Bulushev, D.A.; Ross, J.R.H., 2011).Fast pyrolysis is a relatively new, promising technology involving a high liquid yield achieved through rapid heating rates of 10 to >1000°C/s, short residence times of <2s, temperatures of 400–650°C, and rapid quenching of the vapors (Balat, M.;et al.,2009 and [1] Bridgwater, A.; Peacocke, G.,2000).Production of bio-char and bio-oil are common in both conventional and fast pyrolysis.Fast pyrolysis, however, involves control and optimization of operating parameters to lead to high bio-oil yields making it more advanced than slow process.

2.3.6. Effects of process parameters

The research works show that the product distribution (liquid, gaseous and solid residue) can be affected by different parameters which include the polymer (plastic) type, polymer size, polymer to catalyst ratio, catalyst contact mode, reactor type, nitrogen flow rate, reaction temperature, and reaction time.The effect of various process variables is discussed below.

2.3.6.1. Effect of Polymer to Catalyst Ratio.

The increase or decrease of polymer to catalyst ratio affect the conversion rate.Effect of polymer to catalyst ratio has been studied by Akpanudoh et al.,2005.It has been concluded that with the increase in the amount of catalyst, a direct proportionality in terms of the effectiveness was not obtained.The increase in catalyst amount increases the conversion up to particular limit, but a further increase in the catalyst percentage does not give any appreciable increase in the conversion rate.The optimum polymer to catalyst ratio as obtained from studies was 4:1.However, it was also found in the literature that a lesser catalyst ratio would also provide similar degradation, but only at higher reaction temperatures (H. Gulab, et al.,2010).A polymer to catalyst ratio of 10:1 yields 100% conversion within an hour of contact time (Kiang,et al.,1980).Some kind of optimization has to be done with the catalyst ratio and temperature, so that the operation remains economical too.

2.3.6.2. Effect of polymer/ waste plastic type

For different types of plastics their pyrolysis product also different.PE, PS, PP with other plastics gives flue gas pollution and contaminated to reactor by making other unexpected compound.In contamination to reactor resulting liquid may contain alcohol, waxy hydrocarbons and inorganic substance.Type of plastics,their content and product was shown in Table 2.4 below:

Table 2.4: Effect of plastics in production (UNEP,2009).

No.	Types of plastics	Content	Product
1.	PET- Polyethylene terephthalate	Hydro carbons with O_2	Terephthalic acid and benzoic acid
2.	HDPE-High density polyethylene	Hydro carbons	Liquid fuels
3.	LDPE- Low density polyethylene	Hydro carbons	Liquid fuels
4.	PS-Ppolystyrene	Hydro carbons	Liquid fuels
5.	PVC- Polyvinyl chloride	Hydrocarbons with Cl_2	HCL gas & carbonous compound
6.	PP- Polypropylene	Hydro carbons	Liquid fuels
7.	PF- Phenol formaldehyde	Hydro carbons O_2	Carbonous product
8.	PU- Poly urethane	Hydrocarbons with N_2	Carbonous product
9.	PVA- Poly vinyl alcohol	Hydro carbons with O_2	Water and alcohol
10.	PVDC- Polyvinylidene chloride	Hydro carbons with Cl_2	HCL gas & carbonous compound
11.	Nylon(Polyamide)	Hydrocarbons with N_2	Carbonous product

2.3.6.3. Effect of polymer size as a feed stock for pyrolysis

Polymer size was an important parameter in pyrolysis process because that affect the heating rate. The smaller the size of the feed stock, the greater mass and heat transfer.Small feed stock particle sizes (≤2 mm) is agreed to achieve high heating rates (Bridgwater, A.V. & Peacocke, G.V.C.,2000 and Bridgwater, A.V.,2003).A small feed stock particle size is required in order to get rapid heating and complete devolatilization in the pyrolysis process (Bridgwater, A.V.,2007 and Huber, G.W., Iborra, S. & Corma, A.,2006).Therefore,Small Feed stock size in the pyrolysis was preferable.

2.3.6.4. Effect of Catalyst Contact Mode.

Polymer degradation in pyrolysis process affected by catalyst contact mode.There exist two methods of catalyst contact mode:direct catalytic cracking and catalyst reformation cracking.In the direct cracking (liquid phase contact), the catalyst and polymer are mixed together, and then they are placed in the reactor and heated to the reaction temperature.However, in the reformer (vapor phase contact), the polymer is first subjected to thermolysis to produce the volatile fraction.The catalyst is inserted in the path of the moving vapor, and as the vapor moves through the catalyst, the hydrocarbon vapor is degraded to get the required product distribution.The direct catalytic cracking has been used widely due to several advantages, mostly in terms of the energy efficiency, with regards to the use of the reactor, the reaction temperature and the residence time.

However, the direct catalytic cracking of plastic wastes have a number of drawbacks which has prevented its commercial success.The first relates to difficulty to recover the catalyst after use, which increases the operational cost.Furthermore, direct contact with plastic wastes was made catalyst deactivate rapidly due to the deposition of carbonaceous matter and the poisoning effect of extraneous elements and impurities such as chlorine, sulfur and nitrogen containing species that may be present in the plastic wastes (Aguado J,et al.,2007).Therefore,separation of catalytic reforming reaction from pyrolysis stage can be applied to overcome these problems.This method has been studied by some researchers (Bagri R, Williams PT.,2002 and Williams PT, Bagri R., 2004) for PE and polystyrene (PS) using zeolite-Y and ZSM-5 catalysts.The results showed an increase in the gas yield and reduction in the oil yield.The use of other catalysts such as silica alumina and Al-MCM-41 have also been investigated by others (Wang JL, Wang LL.,2011and Miguel GS, et al.,2009).Liquid phase contact mode was selected in this research.

2.3.6.5. Effect of Flow Rate of Nitrogen Gas.

The inert gas flowing through the reaction doesn't affect the reaction directly,but it can produce as light change in the liquid yield.Usually the nitrogen flow rate was chosen to be relatively high, in order to move the volatile primary products from the reactor and keep secondary reactions at a minimum.This actually favors the liquid yield.But studies of H.Gulab et al.,2010 indicate that high carrier gas flow rate can enhance the evaporation of liquid products which are collected in the condenser.This falsifies the results of liquid yield.By course of experiments, it has been found that the optimum flow rate is 10mL/min.

2.3.6..6. Effect of reactor type

The low thermal conductivity and high viscosity of plastics are the major problems for the cracking reactor design.Therefore, the reactor design becomes important parameter in feed stock recycling of plastics.Several reactor systems have been developed and used such as batch/semi batch(Miskolczi, N., Nagy, R., 2012), fixed bed, fluidized bed, spouted bed, microwave (Hussain, et al.,2012) and screw kiln.Batch or semi-batch reactors have been used by many researchers because of its simple design and easy operation.

Other factors that affect the liquid yield was shown in Table 2.5 below.

Table 2.5:Other factor that affect the liquid yield

Process parameter	**Results**
Temperature (Demirbas, A., 2004, Bayraktar, O. and E.L. Kugler, 2003, [1] Delattre, C.,et al.,2001, Mastellone, M.L., et al.,2002, Zeng, G.M., et al., 2003)	● Conversion increase with temperature resulting in decrease of aliphatic content ● Dermibas et. al. Observed that gaseous products (C_2-C_4) and liquid products (C_5-C_9) increased and decreased with temperature respectively (Bridgwater, A.; Peacocke, G.,2000). ● Effect of catalyst on the yields and structure of products becomes less significant with increasing temperature (Murata, K.,et al., 2004 and Mastral, F.J., et al.,2002).
Pressure	● Murata et.al.(2004) Demonstrates the inverse relation of pressure to temperature in the pyrolysis of polyethylene.
Residence time (Mastral, F.J., et al.,2002, [1] Luo, G.H., et al.,2000, Mastellone, M.L., et al.,2002, Zeng, G.M., et al., , 2003[1], Liu, Y.,et.al., 2000)	● Key parameter in fludized bed reactors.Generally conversion increases with residence time. ● Miskolczi et.al. Obsrved that the catalyst activity of HZSM-5 and an FCC catalyst decreased with increasing cracking time in the pyrolysis of HDPE waste. ● Effect of residence time on product yield is more prounced at lower than higher temperatures.
Catalyst loading (Aguado, J., et al.,2001, Zeng, G.M., et al., 2003)	● Conversion increases with catalyst loading.

2.4. Catalyst

However, the use of catalyst is the main cost burden for recycling of plastic wastes by pyrolysis. Reducing the catalyst cost is very interesting challenges.Ali *et al*.,2002 concluded that the catalyst cost (type and amount) is a key factor when the economy of both technologies (catalytic cracking and thermal cracking) is compared.Additionally, Cardona and Corma,2000 concluded that a plastic waste catalytic pyrolysis process could only be supported if the catalyst cost was practically zero.For this reason, the search for, cheap catalyst, for plastic wastes catalytic pyrolysis is the key factor of the process.Synthesis of catalysts from renewable materials is an attractive area of active research due to the cost of mining and synthesizing catalysts.Lin et al.(2003) studied the successful synthesis of ZSM-5 and ZSM-48 from the ashes of gasified biomass containing 70–87% amorphous silica.The resulting zeolites showed high silica contents and high crystallinity (>99%).Muradov et al.(2012) studied the catalytic effects of duckweed derived bio-char in the reforming of CH_4-CO_2 at 800°C.Untreated bio-char showed low activity and rapidly deactivated.CO_2 treated bio-char showed higher activity but also deactivated due to carbon deposits from the decomposition of CH_4.

2.4.1. Silica from rice husk

Many plants during their growth take up SiO_2 from the earth.When plants residues are burned, organic materials are broken down as carbon dioxide, water vapors etc.The remaining ash contains inorganic residues, notably the SiO_2.Examples are rice husk ash (RHA), rice straw ash, bagasse ash etc.Of all plant residues, the ash of rice husks contains the highest percentage of SiO_2.Rice husks are the hard protecting covering of grains of rice.Rice hulls are the coating for the seeds, or grains, of the rice plant.To protect the seed during the growing season, the hull forms from hard materials, including opaline silica and lignin (K.Bogeshwaran,et al.,2014).

Rice husk, a form of agricultural biomass, is generated in large quantities as a major by-product in the rice milling industry.The estimated world-wide rice husk production is about 100 million tons, of which about 90% is generated in developing countries.Disposal of these vast amounts of rice husk has been one of the major problems facing the rice milling industry.By burning rice husk, 20% ash is obtained from it (Conradt R.,et al.,1992 and Real C.,et al.,2004).The composition of RHA and its zeolitization behavior are dependent mainly on RH calcination temperature.The complete RH burning at high temperatures (850–1,200^{o}C) produces white, carbon-free, low-reactive crystalline SiO_2, while the incomplete roasting at lower temperatures yields so-called carbonized RHA, containing carbonaceous material and highly reactive amorphous SiO_2 (K.Pimraksa, et al.,2010).

The SiO_2 present in ash has a purity of 94–96% with major impurities like K_2O, Na_2O and Fe_2O_3. It has been shown that purity of SiO_2 obtained by incineration of rice husk can be further extended to 98–99%, if rice husk is subjected to pre treatments like washing with distilled water and boiling with acid such as HCl which helps in removing above mentioned impurities.The SiO_2 obtained by burning rice husk is amorphous and can be transformed to quartz, tridymite and cristobalite by heating it at high temperature over 900^{o}C.The crystal phase, to which form the

amorphous SiO_2 transform depends on the purity of the SiO_2 (Shinohara Y, and Kohyama N, 2004 and Venezia A M,et al., 2001).

The ‘‘SiO_2’’ powder is widely used as raw material for cement, glass, porcelain, refractory, the filler for plastic, rubber and tire and so on.Comparison of natural ‘‘SiO_2’’ and rice husk SiO_2 exhibits two main differences.The first one is that use of natural ‘‘SiO_2’’, destroys nature more or less.On the other hand, rice husk SiO_2 is one of the biological resources.Secondly, the crystal phase of ‘‘SiO_2’’ is quartz while that of rice husk SiO_2 is amorphous.Transforming quartz to tridymite and cristobalite needs high temperature of about 1,400^oC.On the other hand rice husk SiO_2 can transform to cristobalite at low temperature of 1,000^oC.Rice husk SiO_2 can be crushed to very fine powder easily and it is a kind of natural resource, which can be applied as the filler for cosmetics and foods (Mosungnoen W.,et al.,2005).Physical properties of rice husk is shown in the Table 2.6 below:

Table 2.6:- Properties of rice husk (Bajirao S.,et al.,2016)

Molecular weight	60.6
Nature	Amorphous powder
Appearance	White fluffy powder
Odor	Odor less
Melting point	1740^oC
Boiling point	2230^oC
Specific gravity	2.650 at 20^oC
Particle size	1-10µm

Rice husk, that is the source of silica, which is found in Ethiopia and the rice husk ash after treatment(washing and drying) mixed with Aluminum oxide might be used as a candidate catalyst instead of the commercial catalysts.So it was used in this research.Using rice husk ash as a source of catalyst has dual benefit that is zero catalyst cost and reduce disposal problem.

A number of research works have been done to find out the effect of silica alumina as catalyst for the pyrolysis of plastics.It can be seen that with silica alumina, high liquid yield can be obtained. The effects of silica alumina with two different SiO_2/Al_2O_3 proportions; that is, SA-1 (SiO_2/Al_2O_3 ratio of 83.3/16.7) and silica alumina SA-2 (SiO_2/Al_2O_3 = 21.1/78.9) were studied by Uddin et al.(1992).The liquid yield was found to be 68wt% for SA-1 as compared to 77wt% for SA-2.

Therefore, the SA-$_1$ catalyst degraded the polyethylene sample into much lighter hydrocarbon fuel oil than the SA-$_2$ catalyst.Thus it can be concluded that the yield and composition of the liquid products can be controlled by altering the SiO_2/Al_2O_3 ratio.The liquid products are distributed in C_5–C_{20} range.Sakata et al.(1997) was observed that silica-alumina maximized the liquid oil production other than other catalyst so is worth nothing to use zeolite catalyst in plastic pyrolysis that only maximized production of volatile hydrocarbon.

Present research work focuses on use of silica alumina catalyst in catalytic pyrolysis of polypropylene and polystyrene waste plastic into liquid fuel.In this research work silica-alumina was selected as a catalyst.Silica Alumina is white powdery catalyst.It consists of 21.1% SiO_2,78.9% Al_2O_3.This ratio was selected based on literature and the matching composition of some identified elements be showed by XRD.

2.5. Potential Applications of Liquid oil

Liquid oils from pyrolysis of different plastic waste types contained a large number of carbon chains with different fractions that showed their potential utilization as an energy source.Liquid oil utilization as transport fuel requires further upgrading and blending with conventional diesel to improve its quality, cause it contains a high percentage of aromatic hydrocarbons specially for oil that produced from pyrolysis of polystyrene waste.The use of pyrolysis liquid oil as transport fuel has been successfully tested after blending with conventional diesel at different ratios (Demirbas, A.,2004 and Gardy, J.,et al.,2014).Lee et al.(2015) blended 20 and 40% of pyrolysis liquid oil with conventional diesel and concluded that at 20%, a successful engine running was achieved, but there was a decrease of output of 13% and 17% at 2450 rpm and 3500 rpm respectively.Moreover mixing of pyrolysis liquid oil with conventional diesel decreased the physical properties of fuel that resulted in an increase in ignition time and hence reduced the produced torque (Islam, M.R.,2010).

Nileshkumar et al.,(2015) blended pyrolysis liquid oils with conventional diesel with the ratio of 10, 20, 30, 40 and 50% and concluded that at 20% fuel consumption was same as conventional diesel.Moreover, the mechanical efficiency was increased with the increase of pyrolysis oil (Miandad,R.,et al.,2016a).However, increase in pyrolysis liquid oil ratio also increased the exhaust emissions of HC's, CO, and NOx with low CO_2 (Frigo, S., et al.,2014 and Mukherjee, M.K., Thamotharan, P.C.,2014).

Purification and upgrading of liquid oil minimize those pollutant and impurities that exist in the oil and impurities,purification methods and upgrading liquid oil product were listed below in Table 2.7.

Table 2.7:Purification and upgrading of pyrolysis liquid oils (Rehan et al.,2016a; Miandad et al.,2016a; Demirbas, 2004)

Problems	Process	Methods	Products

Acid contamination	Amine treating	Absorption treatment	Liquid HCs and gases free from acid
Contaminants	Desalting	Dehydration via absorption	Crude oil(desalted)
Sulfur and water	Sweetening and drying	Treatment via absorption/ thermal	Dry and sweet HCs
Lubes and middle distillate	Furfural extraction	Absorption via solvent extraction	Lube oil and diesel of high quality
Sulfur contaminants	Hydroxide-sulfurization	Catalytic treatment	Olefins (desulfurized)
Saturated HCs impurities	Hydro treating	Catalytic hydrogenation	Lube,distillate,cracker feed
Color,viscosity index	Phenol extraction	Absorption/thermal solvent extraction	Lube oil of high quality
Asphalt	Solvent deasphalting	Absorption treatment	Asphalt,heavy lube oil
Wax(lube stock)s	Solvent dewaxing	Cool/filter treatment	Dewaxed lube base stock
Oil (unsaturated)	Solvent extraction	Absorption/precipitation via solvent extraction	Gasoline with high octane

The use of pyrolysis liquid oil in a diesel engine is also a promising way to generate electricity (Islam, M.R.,2010 and Rehan, M., et al.,2016a).In addition, the produced liquid oil showed the presence of high aromatic compounds such as styrene, ethylbenzene, and toluene along with others styrene monomers.The recovery of these aromatic compounds from produced liquid oils can be a potential source of precursor chemicals in industries for polymerization of plastic monomers (Miandad, R.,et al.,2016a,Miandad, R., et al.,2016b, Shah, J., Jan, M.R.,2014 and[1] Sarker, M., Rashid, M.M., 2013).According to Nikodinovic-Runic et al.(2011), a biocompatible and biodegradable plastic can be produced from pyrolysis oil of PS plastic waste.

3. METHODOLOGY

3.1. Materials and Equipment

Materials used for feed-stock in the catalytic pyrolysis experiments of this study were polypropylene and polystyrene waste plastics.

All chemicals used in this study were liquid soap and nitrogen gas.The major equipment's used were Fourier transform infrared spectrum (PerkinElmer 65), X-ray difracotgram (Mini-flex 600, Advance with Cu Kα radiation at 40kV and 30mA In angle (2θ) range of 10–70°), Gas-Chromatography coupled with high resolution mass spectrometer (GC-HRMS) (Agilent 7890 chromatograph), Furnace (Carbolite, England (MF03-V3.11)), Condenser (N/A), Chiller (N/A), Oven (Memmert, Germany (100-800)), Digital moisture content measurement device (Ohaus, Switzerland (MB45)), Pycnometer (N/A), Falling (Glass) ball viscometer (Gilmont Instruments, USA(GB-104234), Digital balance (Ohaus, Switzerland (EP214C)), Bomb calorimeter (Cussons technology, England).Tong,Glove and Face mask were used for safety.

3.2. Methods

3.2.1. Waste plastic collection and pre- treatment

The feed stock used for these experiments consist mainly Polypropylene (PP), Polystyrene (PS) products in the form of used plastic, disposable cups, covers etc.Those plastic wastes were collected from home, neighborhoods and waste collection cans.Polypropylene and polystyrene waste plastics were came with dirty and foreign materials.All foreign materials was separated by manually and then waste plastic collected were cleaned and washed with liquid soap.Washed waste plastics were then placed on open trays and kept in the sun for few hours until dry enough to undergo size reduction.After drying waste plastic was cut into small pieces by scissor into 1-2 mm size.

3.2.2. Catalyst preparation

An average of 50gm of rice husk was taken as a feed to a muffle furnace.It was burnt off, at a temperature of 700ºC, with the help of digital temp probe.Heating was continued, till white ash was formed.Total time required for burning the husk was about 2 hrs.Once, the white ash was formed, it was weighed, which was found to be ¼ of the mass of rice husk i.e. 12.5 g.This process repeated until 210 gm of silica was produced.The total experiment run was 17.To do so 4-5 experiment per day on average was done and a total of 4 days were used.

Subsequently,in every batch the ash was repeatedly rinsed with hot distilled water to expel the excess of acid and alkali impurities, and later on oven dried at 800ºC for 1 hour to produce dry silica.The dry silica was mixed with alumina by dry-dry mixing with the ratio of (1:3.74). Afterwards the mixture calcined at 800^{o}C for an hour.After calcination of the mixture of the two the white powder was taken as silica-alumina catalyst.

3.2.3. Characterization of the waste plastic and prepared catalyst

3.2.3.1. Waste plastic characterization

PP and PS waste plastic contains carbon, nitrogen, hydrogen and metals that is added for additives.Those metals were added to the plastics in their production process for the purpose of coloring, hardness, softness and making a good shape.The functional group of plastic material identified by FTIR.FTIR spectrometer simultaneously collects high-spectral-resolution data over a wide spectral range.This confers a significant advantage over a dispersive spectrometer,which measures intensity over a narrow range of wavelengths at a time (Griffiths, P.; de Hasseth, J. A.,2007).The functional group of plastics (PP and PS) samples measured on Spectrum 65 FTIR (PerkinElmer) in the range 4000-400 cm^{-1}, number of scan 4 and resolution 0.5cm^{-1} .

3.2.3.2. Prepared catalyst characterization

Phase identification and crystalline structure of the catalyst was done by X-Ray diffractor (XRD).X-ray powder diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions.XRD investigates crystalline material structure, including atomic arrangement, crystallite size, and imperfections.The analyzed material was finely ground, homogenized, and average bulk composition was determined.XRD instrument, Mini-flex 600, Advance with Cu Kα radiation at 40kV and 30mA used for characterization.The difractogram was recorded by scanning the sample in the angle (2θ) range of 10–70°.

3.2.3. Pyrolysis process

3.2.3.1. Experimental Setup

The detailed experimental procedure of catalytic pyrolysis was given as follow:The pyrolysis reaction was carried out at different temperature, time and catalyst loading for different waste plastic type.Catalytic degradation experiments of waste plastic were carried out in a stainless-steel (length~1 m, internal diameter~50 mm and external diameter~55 mm) batch reactor which was equipped with temperature measurement system.The reactor was fix horizontally.The furnace employed could reach a maximum temperature of 1200^{o}C and it was possible to reach a maximum heating rate of 100^{o}C.min^{-1}.

50 g of the feed-stock (PP and PS waste plastic) sizes of 1-2mm prepared and mixed with the catalyst,before it is being supplied to the heater.After mixing,the mixture was put into the reactor and the reaction system was closed at atmospheric pressure Before starting the heating, nitrogen gases, as a carrier gas, was Purging inside the reactor batch wise to provide uniform heating across the cross-section of the reactor chamber and to create inert environment in the pyrolysis chamber.and then the heater was switch on.The temperature controller was set to the required operational temperature.This temperature were noted.The vapor fraction formed during the pyrolysis of the plastic inside the reactor flows out along with N_2 out of the reactor.After the reaction time was over, the heater was switched off, but the reaction was allowed to take place till the pyrolyzer was cool down.

A glass condenser was connected to the reactor to cool the condensing vapors from the reactor. Water was used as the cooling medium which circulated through the condenser tube.A chiller was used to cool it down to 4^{o}C, and pump it to the condense.The condensed volatile fraction was finally collected from the collecting tanks.Dynamic of pyrolysis process monitored by time measuring the volume of collected oil.The collected Liquid products weighed for the mass balance calculation.The remaining solids deposited in the pyrolyzer was defined as the solid residue.The weight of the solid residue left inside the reactor after the process was noted.Now the process was repeated for different temperatures, time and amount of catalysts.The products of such processes are liquid hydrocarbon mixtures in different temperature range for PP, PS waste plastic, gaseous hydrocarbons and solid residue.Experiments using similar time and temperature (that obtained a higher liquid oil yield) but in the absence of catalyst were also conducted for comparison.fig(3.1) shows experimental setup used for this research.

Figure 3.1:-Lab Setup for Experiments

3.2.4. Characterization of liquid fuel

Different properties of liquid fuel at operating conditions that had a higher yield was tasted and compared with standard results.

Yield of liquid fuel products from each experiment run will calculate using the following formula:

$$\%\text{Yield of liquid fuel} = \frac{(M\text{liquid(condensate)})}{M\text{pyrolysis feed-stock}} \times 100\%$$

The reactor was empty after every run to collect char product inside, and solidified oil (wax) that remain on its walls.Respective masses measured after weighing the samples were then used to estimate the amount of non-condensable (NC) gas product from the experiment.

NC=Mpyrolysis feed stock-(Mchar +Mliquid)

Liquid fuel property like Density, Kinematic viscosity,Flash point, Heating value, and GC/MS was determined for liquid fuel that had higher yield.

3.2.4.1. Determination of the basic physio-chemical properties of liquid fuel

3.2.4.1.1. Density

A small volume of liquid sample was introduced into the density meter's oscillating sample tube. The change in the oscillating frequency of the tube, caused by the increased mass of the tube, was used in conjunction with calibration data to determine the density of the sample.Density could be determined by using the relation below:

$$\rho liquid\ (Kg/m^3) = \frac{Mliquid\ sample}{Vliquid\ sample\ (cylinder)}$$

3.2.4.1.2. Viscosity

Falling ball method was used to determine viscosity of samples.In this method, a sample was transfer to a graduated cylinder containing the ball.Time taken by the ball to fall the height through the medium was record.The following relation was used to calculate the viscosity using the time data.

$$\mu = K(\rho_f - \rho)t$$

Where; μ=viscosity (cp); ρf=density of ball; ρ=density of liquid; t=time of descent (minutes); K=viscometer constant;

3.2.4.1.3. Flash point

Flash point is the lowest temperature at which it can vaporize to form an ignitable mixture in air. Flash point is used to characterize the fire hazards of fuels.The flash point of liquid product was measured according to ASTM D 93-62 method.The liquid fuel was in open cup put in a Bunsen burner and its temperature was gradually increased and monitored using a thermometer.

At specified intervals a test flame is passed across the cup until the vapor of the liquid fuel catch a fire.The temperature recorded on the thermometer at which the fuel show ignition was used as the flash point of the fuel.

3.2.4.1.4. GC/MS of liquid oil

Gas-Chromatography coupled with high resolution mass spectrometer (GC-HRMS) was done by using an Agilent 7890 chromatograph.The oven temperature was programmed at the start 60°C.The ion mass spectra derived were automatically compared to spectral libraries.Standard

solutions were analyzed to verify the identity of the peaks by retention time and provide quantitative analysis.

3.2.4.2. Determination of the basic physical properties of char

Properties of solid residues was analyzed by proximate analysis (moisture, volatile matter, ash content and fixed carbon) for experimental run similar with the higher yield of liquid fuel.

3.2.4.2.1. Moisture Content

A weighed sample of solid residue was placed in a ventilated oven where a temperature of 105.3^{o}C was maintained in accordance with ASTM standard D 2395-02.Dried sample from the oven was withdrawn and weighed every 3 hours until readings confirmed no significant loss of mass.The moisture content (in percent) was calculated according the equation below.

$$\%\text{Moisture} = \frac{(\text{Mintial} - \text{Moven dried})}{\text{Minitial}} \times 100\%$$

3.2.4.2.2. Ash Content

Similarly,ASTM standard D 1102-84 was referred to determine ash content.Oven-dried solid residue sample will weigh, placed in a ceramic crucible to be put in a furnace.It was kept for 4 hours in the furnace at 600^{o}C.Mass of the remaining ash was measured and the initial mass of solid residue sample will divided by the result to calculate percentage content of ash as follows:

$$\%\text{Ash} = \frac{\text{Mash}}{\text{Minitial}} \times 100\%$$

3.2.4.2.3. Volatile matter

Volatile matter refers to the components of a matter, except for moisture, which are liberated at high temperature in the absence of air.This is usually a mixture of short and long chain hydrocarbons, aromatic hydrocarbons and some sulfur.

2g of the sample was heated under a temperature of 850^{o}C for 10 minutes in a partially closed porcelain crucible placed in a muffle furnace.The crucible and its content were retrieved and cooled in adessicator.The difference in weight was recorded and the volatile content determined.

$$\text{Vc}\ (\%) = \frac{\text{Wo} - \text{Wa}}{\text{Wo}} \times 100\%$$

Where, Vc is volatile content in percentage, Wo is the original weight of dry solid residue (g) and Wa is the weight of matter from furnace after cooling (g).

3.2.4.2.4. Fixed carbon (FC)

The fixed carbon content of a matter is the carbon found in the material which is left after volatile materials are driven off.This differs from the ultimate carbon content of the matter

because some carbon is lost in hydrocarbons with the volatile.Fixed carbon is used as an estimate of the amount of coke that was yielded from a sample of a solid residue.Fixed carbon was determined by removing the mass of volatile determined by the volatility test, ash test, and moisture test above, from the original mass of the solid residue.FC was determined using the formula:-

$$Fc\ (\%) = 100 - (Vc + Ac + Mc)$$

Where, Fc is fixed carbon, Vc is volatile content, Ac is ash content and Mc is moisture content.

3.3. Experimental research design

3.3.1. Studied factors

Experimental factors used for the study were selected primarily on basis of the objective set to identify the influence(s) of major process conditions in pyrolysis.Temperature, time and catalyst amount were included in the factors list.The first factor was varied between three level and the second and the third factor had two levels.Factors and their levels was shown on the Table 3.3.

Table 3.1:Factors and their levels

Factors	**Levels**		
Temperature (^{o}C)	430	450	470
Time (min)	30	60	
Catalyst loading (wt.)	5	12.5	

A total of 24 runs (12 catalytic pyrolysis for polypropylene and 12 for polystyrene) was required to complete the experiment.50 gm mass of the plastic waste was used as a feed stock.

3.3.2. Selected Type of Experimental Design and Analysis

Experimental design methods play a major role in engineering design activities, where new products are developed and existing ones improved.Some applications of experimental design in engineering design include Evaluation and comparison of basic design configurations, Evaluation of material alternatives, Selection of design parameters so that the product will work well under a wide variety of field conditions, that is, So that the product is robust, Determination of key product design parameters that impact product performance.There are different techniques to use experimental design methods.They are factorial design and one factor at a time.

Factorial design offered the most effective and efficient technique for obtaining reliable results and valuable information, especially in engineering research including interaction effects. Therefore, a factorial design approach that enabled the inclusion and analysis of multiple factors

at multiple levels was preferred.The desirability to identify the effect(s) of various operating parameters when studying a process is emphasized.Techniques that are commonly used to know such influences on the response involved varying one factor at a time while the others remain constant – the OFAT method; or using factorial designs approaches.While the former had the evident pitfall of overlooking effects due to multiple factors' interactions, for mixed levels factorial design (D-Optimal factorial) was hence used to design the experiment and analyze generated response data.A D-optimal design is generated by an iterative search algorithm and seeks to minimize the co-variance of the parameter estimates for a specified model.D-optimal designs are straight optimization based on a chosen optimality and the model that was fitted (Montgomery 7th Ed).

The laboratory experiment was based on factorial design where the different treatment factors was analyzed for the different combinations of their test levels.The experimental design and analysis of data, as well as the regression computations to statistically fit the response and factors' into a model made use of the software package Design-Expert® 7.Accordingly, 12 (for each plastic type) for the experiment runs were sufficient to provide information about the effect of each factor on the yield of pyrolysis liquids which was considered as the response.The effects of pyrolysis temperature, pyrolysis time and catalyst amount on the percentage yield from the experiment runs were thus studied.The output from the software showing a summary of the design is given in the Table 3.4 below.

Table 3.2:Analysis of variance (ANOVA) for yield of oil from PP

Design summery										
Study Type Factorial **Runs** 12 **Initial design** D-optimal Co-ordinate exchange **Blocks** No blocks **Design model** Reduced cubic										
Factor	**Name**		**Unit**	**Type**	**Low actual**		**High actual**	**Low coded**	**High coded**	**Mean**	**St.Dev**
A	Temperature		^{o}C	Numeric	430.00		470.00	-1.00	1.00	450.00	16.330
B	Time		min	Numeric	30.00		60.00	-1.00	1.00	45.00	15.000
C	catalyst		gm	Numeric	5.00		12.50	-1.00	1.00	8.75	3.750
Response	**Name**	**Unit**	**Obs**	**Analysis**	**Mini-mum**	**Maxi mum**	**Mean**	**St.Dev.**	**Ratio**	**Trans**	**Model**
Y_1	Yield pp	%	12	Polynomial	23.5	44.7	31.147	7.517	1.902	None	R2FI

Table 3.3:Analysis of variance (ANOVA) for yield of oil from PS

Design summery										
Study Type Factorial **Runs** 12 **Initial design** D-optimal Co-ordinate exchange **Blocks** No blocks **Design model** Reduced cubic										
Factor	**Name**	**Unit**	**Type**	**Low actual**	**High actual**	**Low coded**	**High coded**	**Mean**	**St.Dev**	
A	Temperature	^{o}C	Numeric	430.00	470.00	-1.00	1.00	450.00	16.330	
B	Time	min	Numeric	30.00	60.00	-1.00	1.00	45.00	15.000	
C	catalyst	gm	Numeric	5.00	12.50	-1.00	1.00	8.75	3.750	
Response	**Name**	**Unit**	**Obs**	**Analysis**	**Mini-mum**	**Maxi-mum**	**Mean**	**St.Dev.**	**Ratio**	**Trans**	**Model**
Y_1	Yield PS	%	12	Polynomial	12.285	48.88	28.312	11.446	3.979	None	R2FI

4. RESULTS AND DISCUSSION

4.1. Characterization of rice husk and prepared catalyst

The Moisture content and ash content of the rice husk was 8.89% and 25.22% respectively.The rice husk had low moisture content while its percentage ash content was found to be around one-fourth of the mass of the rice husk that used to prepare the ash.The moisture content indicate the the amount of water present in the matter.The ash content is the measure of the total amount of inorganic components present within a matter.So the lower the moisture content and the average ash content made the ash suitable for the preparation of catalyst.Similar tends were obtained in literature(Bajirao S. Todkar,et al.,2016 and K.Bogeshwaran,et al.,2014).

Characterization of the prepared catalyst was done by X-ray powder diffraction (XRD).The XRD analysis was shown in fig(4.1) below :

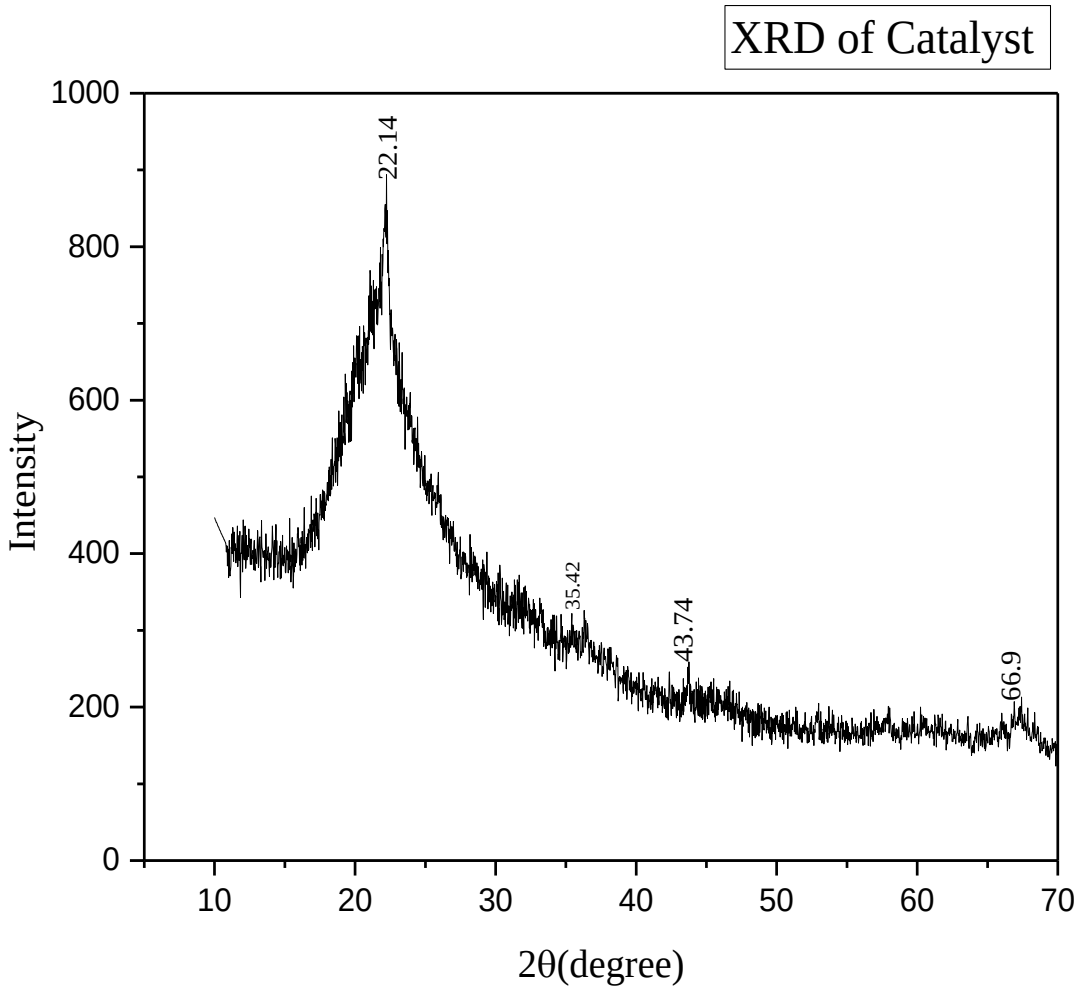


Figure 4.1:- XRD pattern of silica-alumina catalyst

X-ray diffraction (XRD) was applied to identify the type of catalyst mineral contained in the sample and the crystallinity of the catalyst sample.The type of mineral was shown by the position

of diffraction angle (2θ (degree)), while the crystallinity of a sample was shown on its intensity. Fig 4.1 showed that the XRD pattern of silica-alumina samples and shows one main peak in the 2θ region, i.e. 22.14^{o},and the other three were 35.42^{o}, 43.74, 67.42^{o}.The value of 2 theta were around the given value that was given on the standard peak Table 4.1 and shown below:

Table 4.1:Standard X-Ray diffraction pattern of Silicon dioxide and Aluminum oxide

CuKα_1 λ=1.540598Å ; temp.25±1		**Internal standard Si , a=5.43088Å**		
Degree(Å)	Reference intensity α±1	(h k l)	2theta(^{o})	Phase name
4.257	22	1 0 0	22.14	Silicon dioxide(SiO_2) (Marlene C., et al.,1981)
1.3820	67	2 1 2	66.9	
CuKα_1 λ=1.540562Å ; temp.25±1; a=5.43088Å				
1.7400	34	0 2 4	35.42	Aluminum oxide (Huang.T. ,et al., 1990)
3.4797	45	0 1 2	43.74	

Comparing the difractogram of the sample with those of the standards in the JCPDS (*Joint Committee on Powder Diffraction Standards*) data, it was concluded that the sample belongs to silica and alumina.Nezamzadeh-Ejhieh A.,Shams-Ghahfarokhi Z.,(2013) and Tao L.,et al.,(2011) were obtained similar results in a commercial ZSM-5 the presence of aluminum and silica was shown in 2 theta degrees 13°, 23° and 45°.Kong D. L.et al.,(2007),were also found that two significant strong peaks at 2theta ~38.47 and 44.72 where referred as aluminum, detected from the aluminum-based XRD sample holder.Similar graphical representation also found in literature (carlos sergio et al.,2015 and W. Widayat and A N. Annisa,2017).

The color of the ash generally reflects the completeness of the combustion process as well as the structural composition of the ash.The color of the rice husk ash formed in this research were white.The color of the ash formed were white,the degree of crstallinity of synthesized catalyst was quite low (Phung TK.,2015).So this made the ash an amorphous structure.The color of the catalyst was white this because the calcined temperature was below 1000^{o}C.Nair D G,2006; Sharma N K, et al.,1984 and Shinohara Y, KohyamaN.,2004; was observed that the transition from amorphous to crystalline silica of rice husk takes place with the increase in the temperature >1000^{o}C and bright white color ash was seen indicating total transformation of RHA to amorphous silica.The broad refection was obtained at 22.14^{o} and the broad reflection between 10-35^{o} with relatively similar intensities was indicates the matter had amorphous structure (Komnitsas *et al*.,2007).So it would be possible to conclude the structure of the prepared catalyst had an amorphous structure.

Amorphous silica-alumina shows a great activity on cracking polyethylene and polypropylene to lighter hydrocarbons.Since amorphous silica-alumina appears to have a higher fraction of total acidity in the strong acid range, it might tend to favor tight binding of carbonium ions to the surface and to carry out continuous cracking.It generated a pronouncedly high yield of lighter olefins due to strong acidity, but was far inferior to zeolites in the formation of aromatics and branched hydrocarbons because of amorphous structure (Azhar uddin M.,et al.,1997).

4.2. FTIR analysis of Polypropylene and Polystyrene plastic waste

Fourier-transform infrared spectroscopy (FTIR) is a technique used to obtain an infrared spectrum of absorption or emission of a solid, liquid or gas.The functional group of plastics (polypropylene and polystyrene) samples measured on Spectrum 65 FTIR (PerkinElmer) in the range 4000-400 cm^{-1}, shown in fig (4.2) and (4.3) below :

4.2.1. FTIR analysis of polypropylene plastic waste

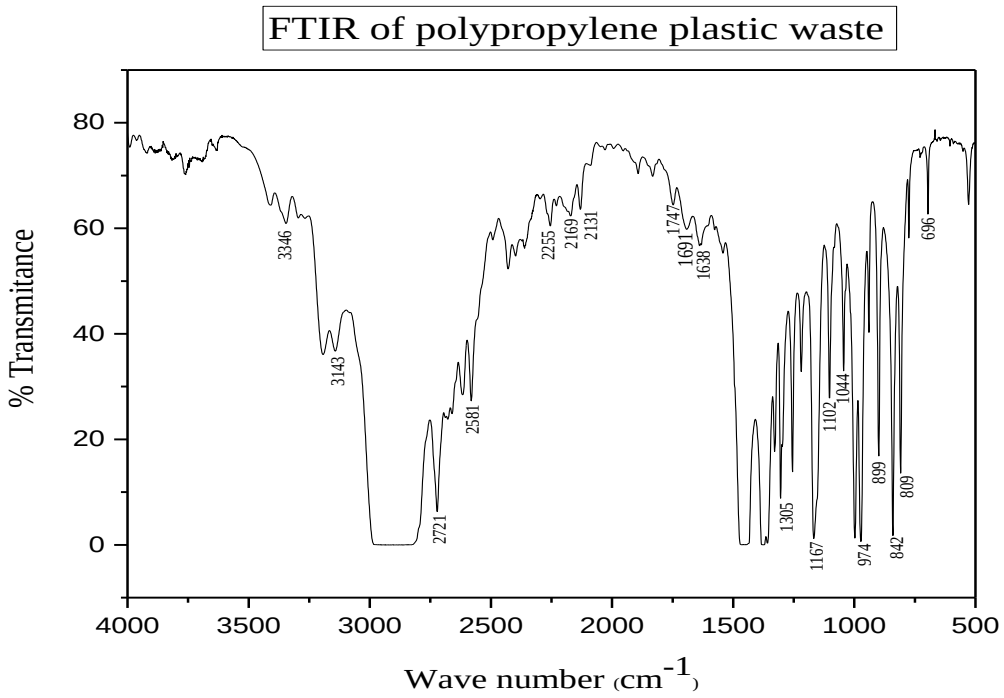


Figure 4.2:- FTIR spectrum of polypropylene plastic waste

FTIR analyses of polypropylene plastic wastes was shown in the above figure.According to the Figure, the following types of functional groups in wave number were significantly appeared in the same analyses.In wave number 3346 cm^{-1} O-H stretch, H-bonded, Alcohol was the functional group.For wave numbers 3143, 2721 and 2581 cm^{-1} the functional group were O-H stretch, Acid. For wave numbers 2255, 2169 and 2131 cm^{-1} the functional group were C≡C stretch, Alkyne.For wave numbers 1747 and 1691 cm^{-1} the functional group were C=O stretch, Carbonyl.Wave number 1638cm^{-1} had a functional group of C=C stretch, Alkene.1102 cm^{-1} wave number the functional group was C-O stretch, Alcohol.For wave number 1044 the functional group was C-O

stretch, Ether. 974, 899, 842, 809, 696 cm^{-1} wave numbers the functional group were =C-H bending, Alkene.Similar trends in literature was obtained (M.R.Shindikar and M.Y. Khaladkar,2017).IR absorption frequencies of organic functional group was shown on Table 4.2 and 4.3.

Table 4.2:IR Absorption Frequencies of Organic Functional Group (Silverstein,et al.,1981)

Wave number(cm^{-1})	Frequency of wave length(cm^{-1})	Type of vibration	Nature of functional group
3346	3200-3600	O-H stretch,H-bonded ,	Alcohol
3142	2500-3300	O-H stretch,	Acid
2721	2500-3300	O-H stretch,	Acid
2581	2500-3300	O-H stretch,	Acid
2255	2100-2260	C≡C stretch,	Alkyne
2169	2100-2260	C≡C stretch,	Alkyne
2131	2100-2260	C≡C stretch,	Alkyne
1747	1670-1820	C=O,stretch,	Carbonyl
1691	1670-1820	C=O,stretch,	Carbonyl
1638	1620-1680	C=C , stretch,	Alkene
1102	1080-1360	C-N,stretch,	Amine
1044	1000-1300	C-O,stretch,	Ether
974	675-1000	=C-H,bending,	Alkene
899	675-1000	=C-H,bending,	Alkene
842	675-1000	=C-H,bending,	Alkene
809	675-1000	=C-H,bending,	Alkene
696	675-1000	=C-H,bending,	Alkene

4.2.2. FTIR analysis of polystyrene plastic waste

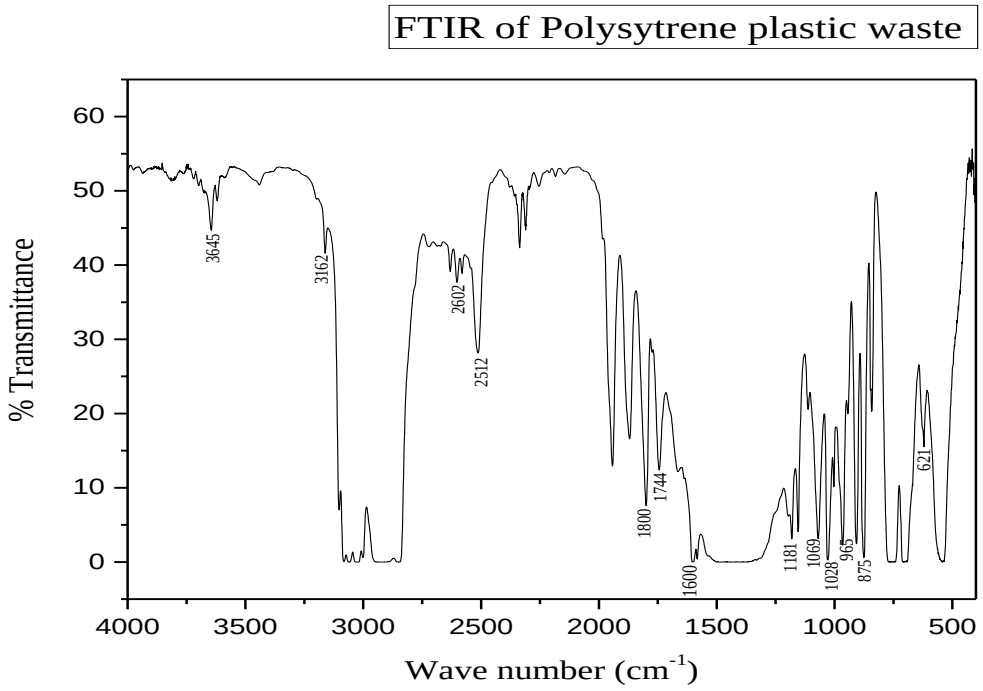


Figure 4.3:-FTIR spectrum of polystyrene plastic waste

FTIR analyses of polystyrene(PS) plastic wastes was shown in the above figure.According to the Figure, the following types of functional groups in wave number were significant appeared in the same analyses.In wave number 3645cm^{-1} O-H stretch, free Alcohol was the functional group.Wave numbers 3162, 2602 and 2512 cm^{-1} the functional group were O-H stretch, Acid.For wave number 1800 and 1744 cm^{-1} the functional group were C=O stretch, Carbonyl.The functional group of C=C,stretch,Aromatic was for the wave length 1600 cm^{-1}.Wave number 1181cm^{-1} functional group was C-N stretch, Amine, For wave number 1069 cm^{-1} functional group was C-O stretch, Alcohol.For wave number 1028 cm^{-1} the functional group was C-O stretch, Ether.For wave number 965 and 875 cm^{-1} the functional group were =C-H bending, Alkene. Similar trends was observed in literature(Tong Li, Chunlln Zhou and Mlng Jiang,1991).

Table 4.3:IR Absorption Frequencies of Organic Functional Group (Silverstein,et al.,1981)

Wave number (cm^{-1})	Frequency of wave length (cm^{-1})	Type of vibration	Nature of functional group
3645	3500-3700	O-H,stretch,free Alcohol	Alcohol
3162	2500-3300	O-H,stretch,	Acid
2602	2500-3300	O-H,stretch,	Acid

2512	2500-3300	O-H,stretch,	Acid
1800	1670-1820	C=O,stretch,	Carbonyl
1744	1670-1820	C=O,stretch,	Carbonyl
1600	1400-1600	C=C,stretch	Aromatic
1181	1080-1360	C-N,stretch,	Amine
1069	1050-1150	C-O,stretch,	Alcohol
1028	1000-1300	C-O,stretch,	Ether
965	675-1000	=C-H,bending,	Alkene
875	675-1000	=C-H,bending,	Alkene

FTIR analysis of PP and PS plastic waste was in the range of 696-3346 cm^{-1} and from 875 to 3645 cm^{-1} respectively.Similar trends were obtained in literature.Miandad R.et.al.,2017 were obtained FT-IR analysis of plastic feed-stock ranging from 674 to 3353 cm^{-1}.

Therefore, Alkene, Amine, Acid, Alcohol, Carbonyl and Ether group were significantly appeared in both plastic type according to the above figures.Functional group presented on the two plastic waste shows that the potential of the plastic waste to produce liquid fuel.

4.3. Pyrolysis result

4.3.1. Catalytic Pyrolysis of Polypropylene plastic waste

50gm polypropylene plastic waste and different amount of catalyst taken with different pyrolysis temperature and time to complete the experiment.Factors that affect the product mass in catalytic pyrolysis of PP waste was shown on Table 4.4 below.

Table 4.4:Factors with product mass from catalytic pyrolysis of PP waste

Run	Factors			Product mass(gm)		
	Temperature (^oC)	Catalyst amount (gm)	Time (min)	Solid	Liquid	Gas
1.	450	5	30	7.6	12.33	30.07
2.	450	5	60	18.1	12.75	19.15
3.	470	5	30	12.8	12.9	24.3
4.	430	12.5	30	15	21.325	13.675

5.	450	12.5	30	10	22.35	17.65
6.	450	12.5	60	11.2	16.6	22.2
7.	470	12.5	30	13	18.4	18.6
8.	470	12.5	60	21.7	13.1	15.2
9.	470	5	60	14.3	13	22.7
10.	430	5	30	12.5	11.75	25.75
11.	430	5	60	17.6	12.45	19.95
12.	430	12.5	60	7.58	19.9	22.52

Mass of non-condensed gas calculated using the mass balance relation:

MNC = Mpyrolysis feed stock(Mwaste plastic +Mcatalyst)− (Mliquid +Mchar+Mcatalyst)

The maximum liquid fuel produced was 22.35 gm at 450^{o}C for 30 minutes using 12.5gm catalyst (run#5).Solid product was maximum at 470^{o}C for 60 minutes and for the same amount of catalyst with liquid fuel (run#8).The highest amount of gas, on the other hand, was produced at 450^{o}C for 30minutes and using 5gm catalyst (run#1).

4.3.2. Catalytic Pyrolysis of Polystyrene plastic waste

The effect of different pyroltic operating conditions such as temperature, time and catalyst amount on product mass with 50gm polystyrene plastic waste shown in Table 4.5 below.

Table 4.5:Factors with product mass from catalytic pyrolysis of PS waste

Run	Factors			Product mass(gm)		
	Temperature (^{o}C)	Catalyst amount (gm)	Time (min)	Solid	Liquid	Gas
1.	430	5	30	17.4	6.1425	24.4575
2.	470	5	30	10.6	8.425	30.975
3.	430	12.5	30	5	24.44	20.56
4.	470	5	60	9	12.945	28.055
5.	450	5	60	10	11.8	28.2
6.	450	12.5	60	15.6	15.079	19.321
7.	430	5	60	22.6	10.45	16.95

8.	430	12.5	60	10.2	19.047	20.753
9.	470	12.5	60	26.2	13.25	10.55
10.	450	5	30	2	6.857	39.143
11.	450	12.5	30	4.6	22.22	23.18
12.	470	12.5	30	5.6	19.215	25.185

The maximum liquid fuel produced was 24.44 gm at 430^{o}C for 30 minutes using 12.5gm catalyst (run#3).Solid product was maximum at 470^{o}C for 60 minutes and for the same amount of catalyst with liquid fuel (run#9).The highest amount of gas, on the other hand, was produced for at 450^{o}C and 30 minutes residence time using 5gm catalyst (run#10).

4.4. Statistical Analysis

Reduced cubic model was selected according to analysis results which showed significance of the mode for both case.

4.4.1. Statistical analysis of the yield of liquid oil from polypropylene waste

Statistical analysis of experimental data showed that the main effect (catalyst amount) and the interaction effect (temperature-catalyst amount and time-catalyst amount) had the strongest effect on liquid yield.On other hand time and temperature (main effect) had less and their interaction had no effect on liquid fuel yield for catalytic pyrolysis of polypropylene plastic waste.Analysis of variance of the yield of liquid oil from PP waste shown in Table 4.6 below.

Table 4.6:ANOVA(Analysis of Variance) of yield from PP

Response 1 **Yield of PP** **ANOVA for response surface Reduced 2FI model**						
Source	Sum of squares	df	Mean square	F-value	P-value Prob>F	
Model	**646.17**	**5**	**129.23**	**24.30**	**0.0006**	**Significant**
A-Temperature	32.20	1	32.20	6.06	0.0491	
B-Time	42.23	1	42.23	7.94	0.0304	
C-Catalyst	443.96	1	443.96	83.49	<0.0001	
AC	65.27	1	65.27	12.27	0.0128	
BC	62.52	1	62.52	11.76	0.0140	

Residual	31.90	6	5.32			
Cor Total	678.07	11				

The ANOVA summary for PP was given in Table 4.6. The model is significant with F-value of 24.30.There is only a 0.06% chance that a "Model F-Value" this large could occur due to noise. The parameters having an F-statistics probability value less than 0.05 are said to be significant.In this study, the probability of model F statistics value was <0.0006 indicating that the model suggested by the software was highly significant.A, B, C, AC and BC are significant terms.

4.4.2. Statistical Analysis of the yield of liquid oil from polystyrene waste

The statistical analysis result showed the yield of liquid fuel from catalytic pyrolysis of polystyrene plastic waste strongly affected by temperature, and catalyst amount (main effects) and the interaction (temperature-catalyst amount and time-catalyst amount) effects were highly significant.Time also significant and the interaction between time and temperature were not significant.Analysis of variance of the yield of liquid oil from PS waste shown in Table 4.7:

Table 4.7:ANOVA(Analysis of Variance) of yield from PS

Response 1 **Yield of PS** **ANOVA for response surface linear model**						
Source	Sum of squares	df	Mean square	F-value	P-value Prob>F	
Model	**1567.91**	**5**	**313.58**	**432.74**	**<0.0001**	**Significant**
A-Temperature	19.50	1	19.50	26.91	0.0020	
B-Time	7.45	1	7.45	10.29	0.0184	
C-Catalyst	1069.04	1	1069.04	1475.25	<0.0001	
AC	124.81	1	124.81	172.24	<0.0001	
BC	347.11	1	347.11	479.01	<0.0001	
Residual	4.35	6	0.72			
Cor Total	1572.26	11				

The ANOVA summary for PP was given in Table 4.7.The model is significant with F-value of 432.74.There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise. The parameters having an F-statistics probability value less than 0.05 are said to be significant.In

this study, the probability of model F statistics value was <0.0001 indicating that the model suggested by the software was highly significant.A, B, C, AC and BC are significant terms.

4.5. Effect of Processing Conditions on Product Distribution

Pyrolysis processes are influenced by the reaction temperature, residence time, and the composition of raw material (Miandad R,et al.,2017).Amount of catalyst in the feed composition, residence time, and pyrolysis temperature significantly influenced the distribution of products separately (main effects) and interacting (interaction) effects.The main effects and the interaction effect of temperature, time and catalyst amount had an influence on the product spectra obtained. Small variations were observed between the amounts of products obtained from respective pyrolysis experiments that ran for different times and temperature while the amount of catalyst remained the same.Effects of reaction temperature, residence time and catalyst amount on product distribution were discussed below.

4.5.1. Effect of Temperature

4.5.1.1. Effect of temperature on product yield from catalytic pyrolysis of Polypropylene plastic waste

The products of catalytic pyrolysis of waste plastic are separated into gas, oil, and solid residue. In Catalytic pyrolysis of polypropylene the higher liquid product mass was obtained at 450^{o}C and it had the value of 22.35 gm.The maximum yield of solid residue (char) was recorded at 470^{o}C and gaseous fraction at 450^{o}C.The mass of liquid product increase slightly with the increase in temperature from 430^{o}C to 470^{o}C when the time and amount of catalyst was fixed at 30 minutes and 5gm respectively.For 60 minutes and 5gm catalyst amount the liquid product mass increase with the increase in temperature.For the condition 30 minutes residence time and 12.5gm catalyst amount the mass of the liquid fuel increased from 430^{o}C to 450^{o}C and decreased when the temperature increased from 450^{o}C to 470^{o}C.The mass of the liquid product was decreased with the increase of temperature from 430^{o}C to 470^{o}C for the condition 60minutes time and 12.5g catalyst amount.Product mass with respect to pyrolytic temperature at given catalyst amount and residence time was shown in fig(4.4).

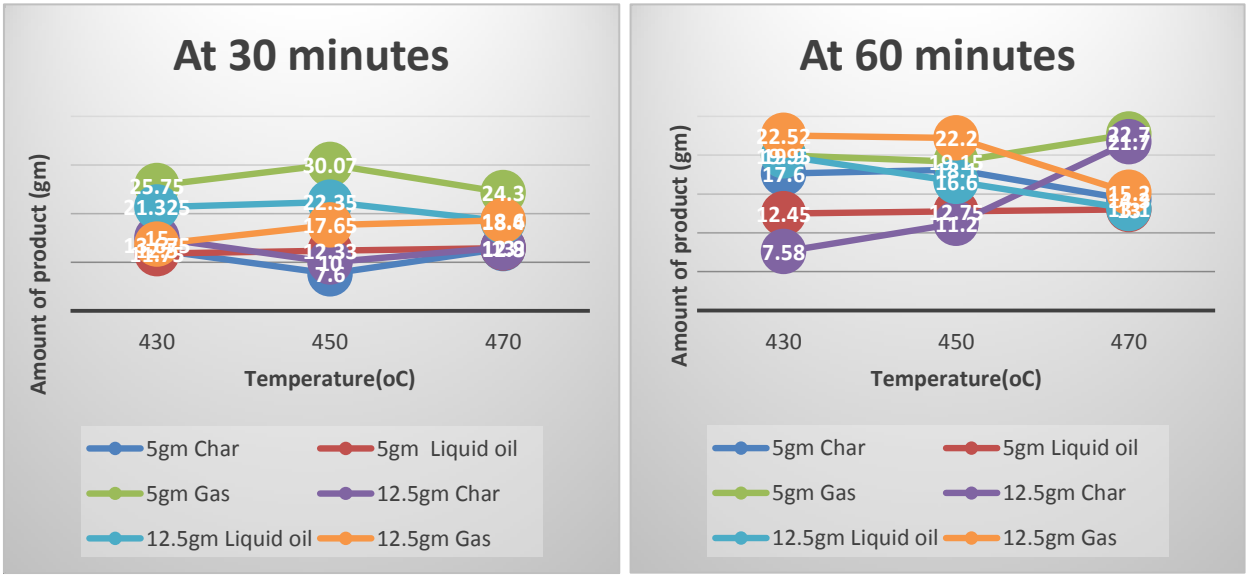


Figure 4.4:Amount of Products from Pyrolysis at different Temperature, time and catalyst amount of liquid oil from catalytic pyrolysis of PP waste

4.5.1.2. Effect of temperature on product yield from catalytic pyrolysis of Polystyrene plastic waste

The higher liquid oil mass was 24.44 gm and this was obtained at 430^{o}C pyrolysis temperature, 30 minutes residence time and 12.5 gm catalyst amount.The maximum mass of solid residues (char) and gaseous fraction was recorded at 470^{o}C.The mass of liquid product increase with the increase in temperature when the temperature raise from 430^{o}C to 470^{o}C and the time and amount of catalyst was fixed at 30 minutes and 5 gm respectively.Same is true for the condition 60 minutes residence time and 5 gm catalyst amount with the increase in temperature their was an increase in liquid product mass.At 30 minutes pyrolysis time and 12.5 gm catalyst amount the mass of liquid product was decreased.Same is true for 60 minutes reaction time and 12.5 gm catalyst usage, their was an increase in mass of liquid product with the increase in temperature. Product mass versus temperature at given catalyst amount and time was shown in fig(4.5).

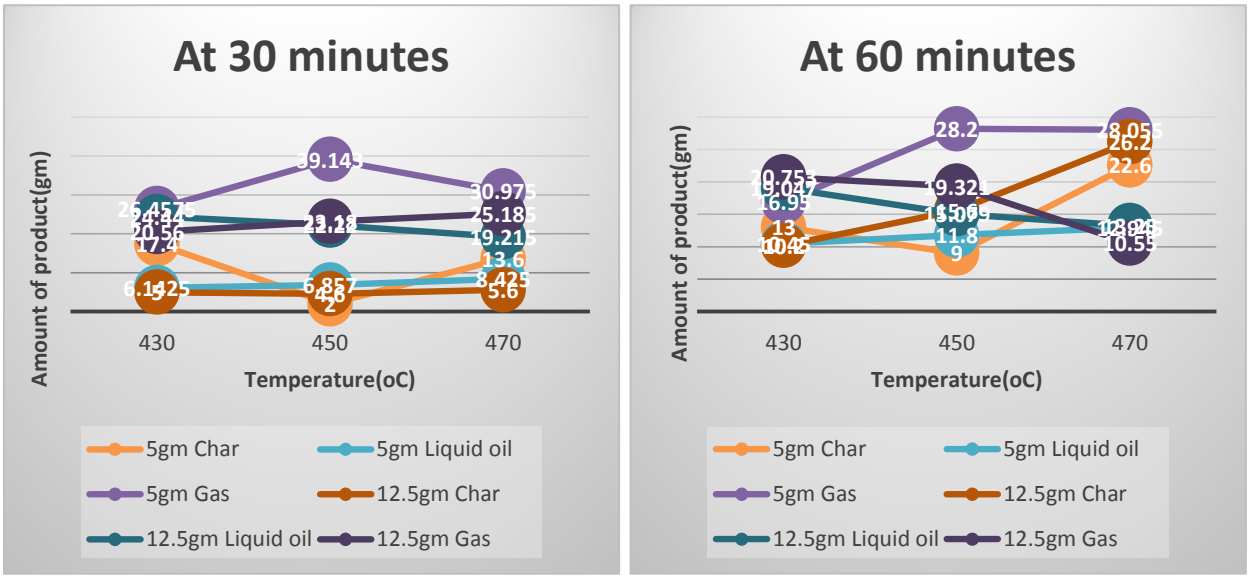


Figure 4.5:Amount of Products from Pyrolysis at Different Temperature, different time and for different catalyst amount for liquid oil from catalytic pyrolysis of PS waste.

Generally the effect of pyrolytic factors (main effects) and their interaction effects shown in the above figures.The effect of temperature with constant time and catalyst amount in the product mass are significant.Statistical analysis of process factors showed similar results.

4.5.2. Effect of reaction time

The lower the time was taken to proceed the process, the higher mass of the liquid product in both polypropylene and polystyrene plastic waste.Fig.4.4 and 4.5 shows that the higher the time was give the lower yield for both plastic type.But this was not true for gaseous fraction of catalytic pyrolysis of polystyrene and solid residues of both waste.Statistical analysis showed that effect of time in product mass was significant for both plastic type.

4.5.3. Effect of catalyst amount

The higher the catalyst amount gave, the higher the yield of liquid product and solid residues mass for catalytic pyrolysis of both polypropylene and polystyrene waste at lower and higher temperature respectively.The lower amount of the catalyst was give lower and higher liquid product at lower and higher temperature respectively this was shown in fig 4.4 and 4.5.Solid product (bio-char) increased with increasing amount of catalyst.The lower amount of catalyst give a higher mass of gaseous fraction.The effect of catalyst amount in the product mass was highly significant and similar trends was shown also in statistical analysis data.

4.6. Liquid fuel yield

4.6.1. Liquid fuel yield from Catalytic Pyrolysis of Polypropylene waste

The yield of liquid fuel from catalytic pyrolysis of polypropylene plastic waste with respect to different operating conditions shown in table 4.8 below.

Table 4.8: Liquid fuel yield from catalytic pyrolysis of polypropylene plastic waste

Run	Factors			Yield (%)
	Temperature (^{o}C)	Catalyst amount (gm)	Time (min)	Liquid
1.	450	5	30	24.66
2.	450	5	60	25.5
3.	470	5	30	25.8
4.	430	12.5	30	42.65
5.	450	12.5	30	44.7
6.	450	12.5	60	33.2
7.	470	12.5	30	36.8
8.	470	12.5	60	26.2
9.	470	5	60	26
10.	430	5	30	23.5
11.	430	5	60	24.9
12.	430	12.5	60	39.8

4.6.2. Liquid fuel yield from Catalytic Pyrolysis of Polystyrene waste

At different operating conditions the yield of liquid fuel from catalytic pyrolysis was shown in Table 4.9 below.

Table 4.9:Liquid fuel yield from catalytic pyrolysis of polystyrene plastic waste

Run	Factors			Yield(%)
	Temperature (^{o}C)	Catalyst amount (gm)	Time (min)	Liquid
1.	430	5	30	12.285
2.	470	5	30	16.85
3.	430	12.5	30	48.88
4.	470	5	60	25.89
5.	450	5	60	23.6
6.	450	12.5	60	30.1577
7.	430	5	60	20.9
8.	430	12.5	60	38.094
9.	470	12.5	60	26.5
10.	450	5	30	13.714
11.	450	12.5	30	44.44
12.	470	12.5	30	38.43

4.7. Effect of Processing Conditions on Liquid Fuel Yield

Percentage yield data obtained was plotted against pyrolysis temperature, pyrolysis time and various amount of catalyst used.

4.7.1. Effect of temperature

4.7.1.1. Effect of temperature on liquid oil from pyrolysis of polypropylene waste plastics

The yield of a liquid fuel from polypropylene plastic waste increased from 23.5% to 25.8% as the temperature increased from 430^{o}C to 470^{o}C when 5 gm catalyst was used at 30minutes residence time.The yield start to increased from 42.65 to 44.7% as the temperature increased from 430^{o}C to 450^{o}C then decreased to 36.8% when the reaction temperature was reached at 470^{o}C at the 30 minutes reaction time and 12.5 gm catalyst usage.At 60 minutes reaction time the liquid yield increased from 24.9% to 26% and decreased from 39.8% to 26.2% for 5 gm and 12.5 gm catalyst amount respectively.Effect pyrolytic temperature on the yield of liquid fuel from PP waste with various catalyst amount and fixed time was shown in fig(4.6).

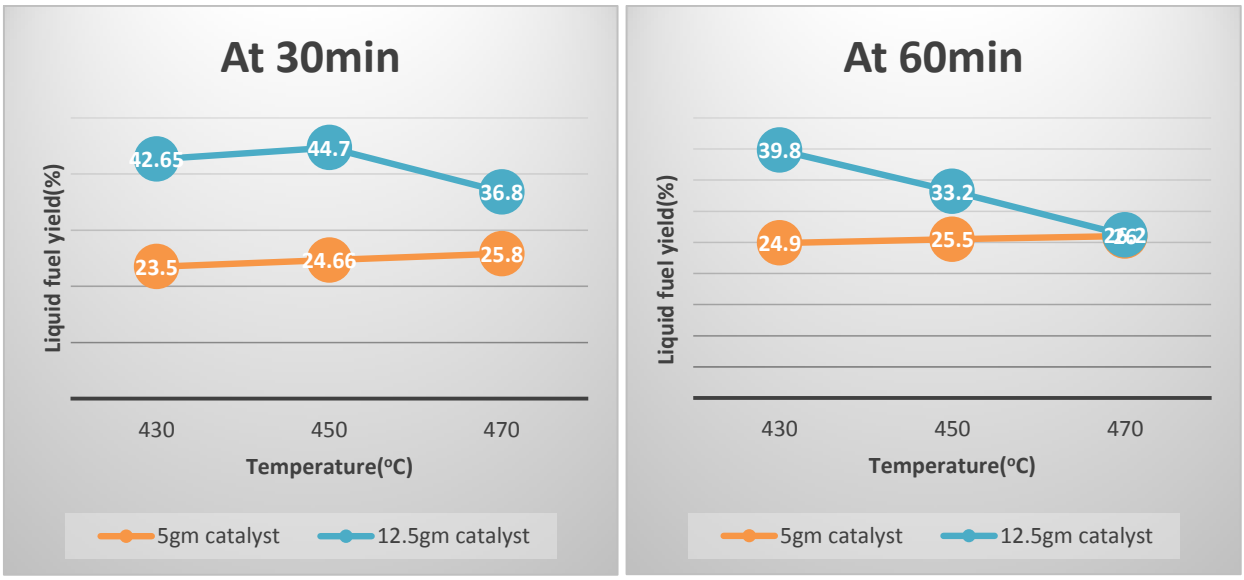


Figure 4.6:Effect of pyrolysis temperature (catalyst amount=5 and12.5gm, time t=30 and 60min) on liquid yield of PP waste

4.7.1.2. Effect of temperature on liquid oil from pyrolysis of polystyrene waste plastics

The yield of a liquid fuel for polystyrene plastic waste increased from 12.285 to 16.85% with increase in temperature from 430^{o}C to 470^{o}C at 30 minutes residence time and 5 gm catalyst amount. The yield start to decrease from 48.88% to 38.43% with the increase in temperature at 30 minutes residence time and 12.5 gm catalyst amount.The yield increased from 20.9% to 26% and decreased from 38.094% to 26.2% as the temperature increased from 430^{o}C to 470^{o}C for 60 minutes reaction time and 5 gm and 12.5 gm catalyst loading respectively.Effect pyrolytic temperature on the yield of liquid fuel from PS waste with various catalyst amount and fixed time was shown in fig(4.7).

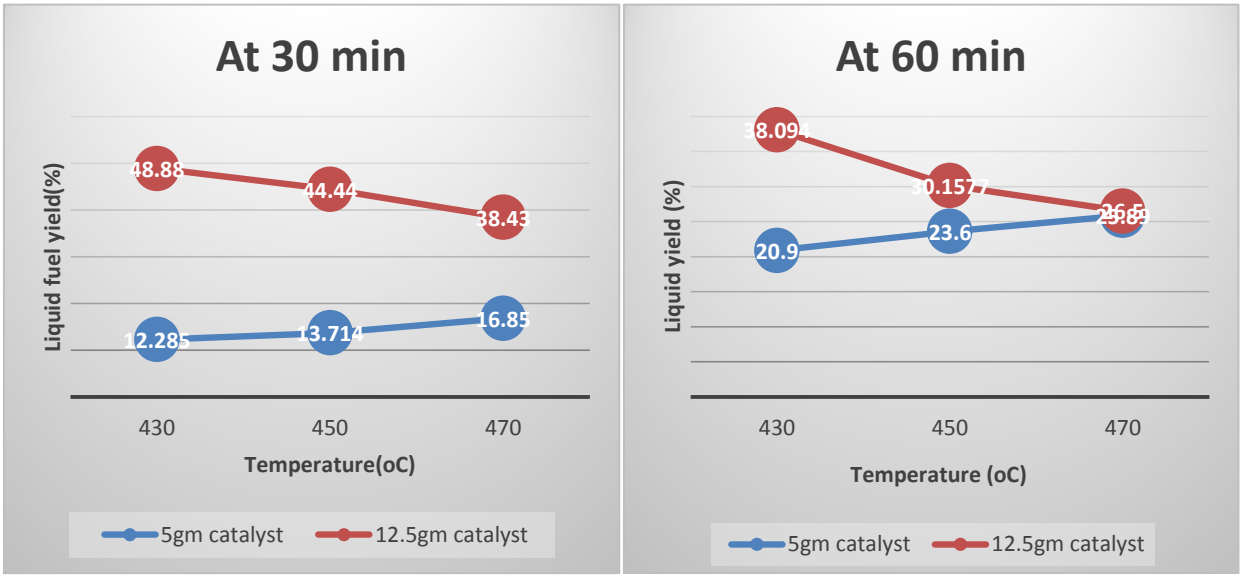


Figure 4.7:–Effect of pyrolysis temperature (catalyst amount=5 and 12.5gm, time t=30 and 60min) on liquid yield from PS waste

Generally,From the above data the increase in temperature increase the yield of liquid fuel when lower amount of catalyst was used and decreased when higher amount of catalyst was used in catalytic pyrolysis of both plastic waste (PP, PS).This was because the effect of catalyst on yield at higher temperature was less significant (Hernandez, M.D.,2005).Similar trends shown in other literature's.The maximum yield was observed at a temperature range of about 400 to 450^{o}C (Sonawane YB.,et al.,2015).Beyond this temperature, the yield of liquid oil was decreased and increased gaseous fraction (Kaminsky W, et al.,2004 ,Onay O, Koca H.,2015 and Serrano D P, et al.,2001).Li,et al.,(1999) and Hernandez,et al.,(2007) had been reported that as reaction temperature increased, gas yield was also increased while liquid yield was decreased.

4.7.2. Effect of time

4.7.2.1. Effect of time on liquid oil from pyrolysis of polypropylene waste plastics

The yield of liquid fuel from catalytic pyrolysis of polypropylene waste increased from 23.5% to 24.9%, 24.66% to 25.5%, and from 25.8% to 26% with increase in pyrolysis time from 30 minutes to 60 minutes at 430^{o}C, 450^{o}C, 470^{o}C pyrolysis temperature respectively and at 5gm catalyst amount. The yield decreased from 42.65% to 39.8%, 44.7% to 33.2% and 36.8% to 26.2% as the pyrolysis time increased from 30 minutes to 60 minutes and 12.5 gm catalyst loading at 430^{o}C, 450^{o}C and 470^{o}C pyrolysis temperature respectively.Effect pyrolytic time on the yield of liquid fuel from PP waste with various temperature and fixed catalyst amount time was shown in fig(4.6).

4.7.2.2. Effect of time on liquid oil from pyrolysis of polystyrene waste plastics

The yield of liquid fuel from polystyrene waste increased from 12.285% to 20.9%, 13.714% to 23.6%, and from 16.85 to 25.89% for 430^{o}C, 450^{o}C, 470^{o}C pyrolysis temperature respectively with 5 gm catalyst amount as the pyrolysis time increased from 30 minutes to 60 minutes.For the same operating temperature and 12.5 gm catalyst, yield decreased from 48.88% to 38.094%, 44.44% to 30.1577%, 38.43% to 26.5% with increase in pyrolysis time from 30 minutes to 60minutes.Effect pyrolytic time on the yield of liquid fuel from PS waste with various temperature and fixed catalyst amount was shown in fig(4.7).

Generally,the yield of liquid fuel increased with increase in time when the temperature increased at lower amount of catalyst was used and decrease when higher amount of catalyst was used.The higher yield liquid was achieved at lower reaction time in the pyrolysis of both plastic type. Similar trends were observed with other literature.With an increase in residence time, the presence of higher catalyst amount reduce the catalytic activity and decrease the liquid yield (Miskolczi, N., et al.,2004 and Luo, G.H., et al.,2000).Bridgwater, A.V.,2012; Bridgwater, T..2006 and Hoekstra, E., et al.,2009 were obtained maximum bio-oil yield in short vapor residence time.

4.7.3. Effect of catalyst amount

4.7.3.1. Effect of catalyst amount for pyrolysis of polypropylene waste plastic

The yield increased from 23.5% to 42.65%, 24.66% to 44.7% and from 25.8% to 36.8% with increase in catalyst amount from 5 gm to 12.5 gm at temperature of 430^{o}C, 450^{o}C, 470^{o}C respectively at 30 minutes pyrolysis time.At 60 minutes residence time the yield of liquid oil increased from 24.9% to 39.8%, 25.5% to 33.2% at 430^{o}C and 450^{o}C and then slight increase from 26% to 26.2% at 470^{o}C when the amount of the catalyst increased from 5 gm to 12.5 gm.The increase in polymer to catalyst ratio in pyrolysis of polypropylene waste plastics decrease reaction time and increase the yield of liquid oil (Lin and Yang,2007).Effect catalyst amount on the yield of liquid fuel from PP waste with various temperature and fixed time was shown in fig(4.6).

4.7.3.2. Effect of catalyst amount for pyrolysis of polystyrene waste plastic

The yield of a Liquid fuel from PS waste increased from 12.285 to 48.8%, 13.714 to 44.44% and from 16.85 to 38.43% with an increase in catalyst amount from 5 gm to 12.5 gm at 430^{o}C, 450^{o}C and 470^{o}C respectively for 30 minutes residence time.As the catalyst amount increase from 5 gm to 12.5 gm the yield of a liquid oil increased from 20.9 to 38.094%, 23.6 to 30.1577%, and from 25.89 to 26.5% at 430^{o}C, 450^{o}C and 470^{o}C respectively for 60 minutes pyrolysis time.Effect pyrolytic catalyst amount on the yield of liquid fuel from PS waste with various temperature and fixed time was shown in fig(4.7).

Generally,Conversion of liquid yield increased with the increase of amount catalyst when temperature was increased and at lower pyrolysis time.Slight increase in the yield of liquid oil was obtained with the increase in catalyst amount when the temperature was increased and at higher pyrolysis time.Therefore, the yield of liquid product increased with increase catalyst loading (Zeng, G.M., et al.,2003 and Akpanudoh, N.S., et al.,2005).Adrados, A.,et al.,2012 and Miskolczi N,et al.,2004 were observed that Effect of the catalysts on the yields and structure of products becomes less significant with increasing temperature.

4.8. Comparison of Liquid Fuel yield from Pyrolysis of Polypropylene and Polystyrene Plastic Waste

From this study the yield of liquid fuel from catalytic pyrolysis of polystyrene plastic waste (48.8%) was higher than liquid fuel from polypropylene plastic waste (44.7%).The higher liquid fuel obtained at lower temperature and time with higher catalyst amount for liquid fuel from pyrolysis of polystyrene waste whereas with the same pyrolysis time and catalyst amount, the higher yield of the liquid fuel was obtained at moderate temperature for pyrolysis of polypropylene waste.

Ciliz et al.,(2004) reported that PS produced maximum fraction of liquid oil in comparison to PE and PP plastic types.According to Siddiqui and Redhwi (2009), this maximum degradation of PS was due to its simple structure in comparison to other plastic types.Lee et al.,2002, have reported the influence of plastic type on liquid, gas and residue yield for pyrolysis of plastic wastes.The

pyrolysis of polystyrene, due to the structure of stable benzene-ring, shows higher liquid yield than that of polyolefinic polymer (PE, PP) with a straight hydrocarbon structure.Polystyrene is less cracked to gas product of 5 carbon numbers or less.Hence, the product distribution is strongly dependent on the plastic type including in municipal plastic wastes.According to Lee et al.,2002, waste PS showed higher liquid yield and higher initial degradation rate in the catalytic degradation than waste PP and PE, because PS is mainly converted into stable aromatic components as liquid phase and also the low degradation temperature.

The other comparison were between the yield of liquid fuel that obtained from thermal and catalytic pyrolysis of the two plastic type with the same operating conditions.The operating condition selected similar with catalytic pyrolysis that had higher liquid yield.From this in thermal pyrolysis of polypropylene waste at the same operating temperature (450^{o}C) and time (30 min) the yield of the liquid fuel decreased from 44.7% to 35% and thermal pyrolysis of polystyrene plastic waste had a liquid oil yield of 40% at 430^{o}C and 30 minutes that had lesser yield than that obtained from catalytic pyrolysis of polystyrene waste that was 48.88% at the same operating condition.

The major draw back of thermal degradation of plastics was the requirement of high temperature and pyrolytic time to achieve higher yield of liquid oil.Catalytic degradation therefore provides a means to address these problems.The used catalyst reduce the reaction temperature, promote decomposition reaction, and reduce pyrolytic residence time.Catalytic pyrolysis were an economical and effective alternative way of recycling plastic wastes (PP and PS) than thermal pyrolysis.

4.9. Model Analysis

The main effect of operating parameters were used for model generation.The output of different model summary statistics, shown in Tables below.The model summery statics focus on the model maximizing Adjusted R-Squared and Predicated R-squared.Model summery for liquid oil from pyrolysis of PP and PS were shown in Table 4.10 and 4.11.

Table 4.10:Model summery for oil from Pyrolysis of PP

Source	Std.Dev	R-Squared	Adjusted R-Squared	Predicted R-Squared	PRESS	
Linear	4.47	0.7645	0.6762	0.4508	372.42	
2FI	**2.09**	**0.9677**	**0.9290**	**0.7750**	**152.60**	**Suggested**
Quadratic	2.08	0.9745	0.9297	0.7323	181.50	Aliased
Cubic	1.97	0.9943	0.9373	-0.2309	834.63	Aliased

The 2FI model is suggested for model generation.This table shows that "Pred R-Squared" of 0.7750 is in reasonable agreement with the "Adj R-Squared" of 0.9290.

Table 4.11:Model summery of oil from pyrolysis of PS

Source	Std.Dev	R-Squared	Adjusted R-Squared	Predicted R-Squared	PRESS	
Linear	7.72	0.6971	0.5835	0.2976	1104.33	
2FI	**0.93**	**0.9973**	**0.9940**	**0.9840**	**25.13**	**Suggested**
Quadratic	0.95	0.9977	0.9937	0.9800	31.38	Aliased
Cubic	1.63	0.9983	0.9815	0.6368	571.06	Aliased

Therefore, 2FI model is suggested for model generation.Moreover, as shown in the Table, "Pred R-Squared" of 0.9840 is in reasonable agreement with the "Adj R-Squared" of 0.9940.For both experiment Adjusted and predicted R-squared values are reasonably agreed.

4.10. Interaction effects using model graphs

4.10.1. Yield of the a Liquid fuel from catalytic pyrolysis of PP waste

4.10.1.1. Interaction of temperature(A) and time (B) at constant catalyst loading

The interaction effect of Temperature and Time is increasing the yield of liquid fuel as both parameters decrease with constant catalyst of 12.5, as shown in Fig.(4.8).The effect of decreasing the time on the liquid yield show a pronounced increase than temperature.The maximum liquid yield of 44.7% was obtained at time of 30 min and 450^{o}C temperature and minimum value was observed at the 60 minutes and 470^{o}C temperature with a value of 26.2%.

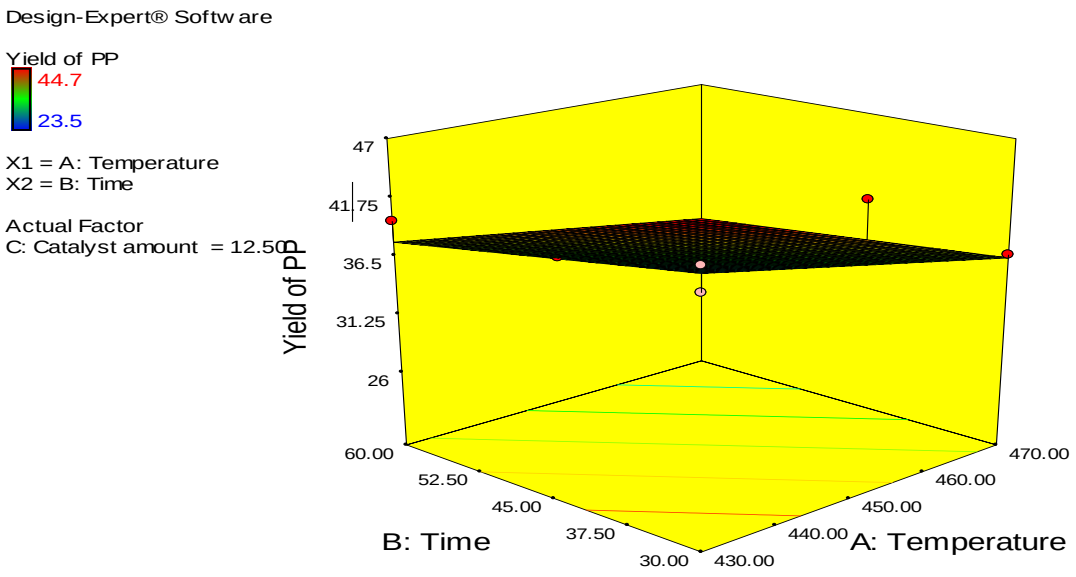


Figure 4.8:3D surface plots for yield of oil from PP waste at constant 12.5gm catalyst, AB interaction

4.10.1.2. Interaction of time (B) and catalyst loading (C) at constant temperature

Interaction effect of time and catalyst loading is increasing the yield of liquid fuel as time increased at lower catalyst amount and decreased at higher time and with increased catalyst loading at constant temperature of 450^{o}C, as shown in Fig(4.9).The effect of increasing catalyst loading on the liquid yield show a pronounced increase than time.The maximum liquid yield of 44.7% was obtained at time of 30 min and 12.5 gm catalyst amount and minimum value was observed at the 30 minutes and 5 gm catalyst amount with a value of 24.66%.

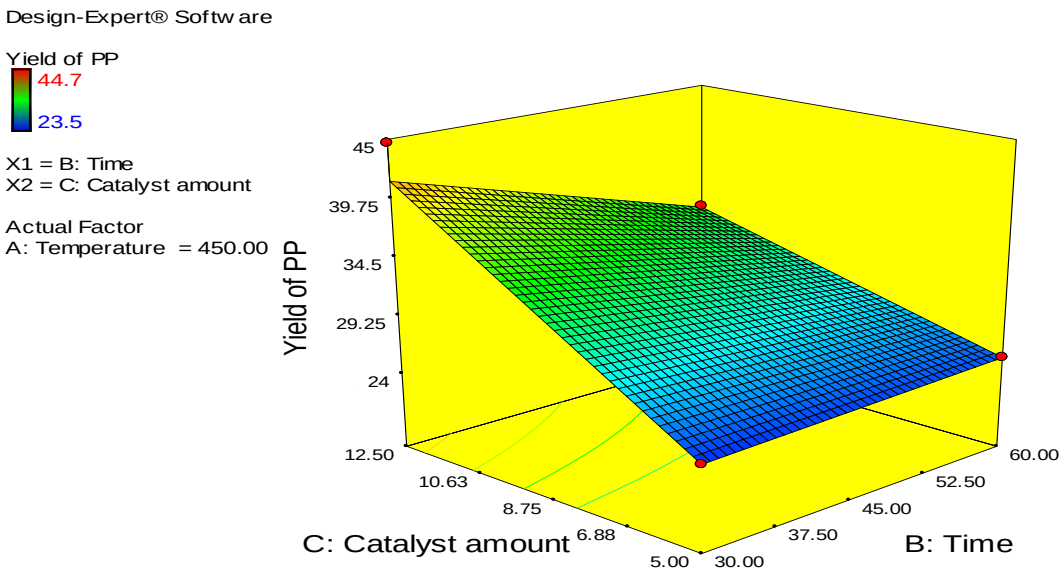


Figure 4.9:3D surface plots for yield of oil from PS waste at constant 450^{o}C, B C interaction

4.10.1.3. Interaction of temperature (B) and catalyst loading(C) at constant time

Interaction effect of Temperature and catalyst is increasing the yield of liquid fuel as the increase in temperature at lower catalyst amount and decrease at higher temperature and with the increase in catalyst loading with constant time of 30min, as shown in Fig(4.10).The effect of increasing the catalyst loading on the liquid yield show a noticeable increase than temperature.The maximum liquid yield of 44.7% was obtained at temperature of 450^{o}C and 12.5 gm catalyst loading and minimum value was observed at the 430^{o}C and 5 gm catalyst amount with a value of 23.5%.

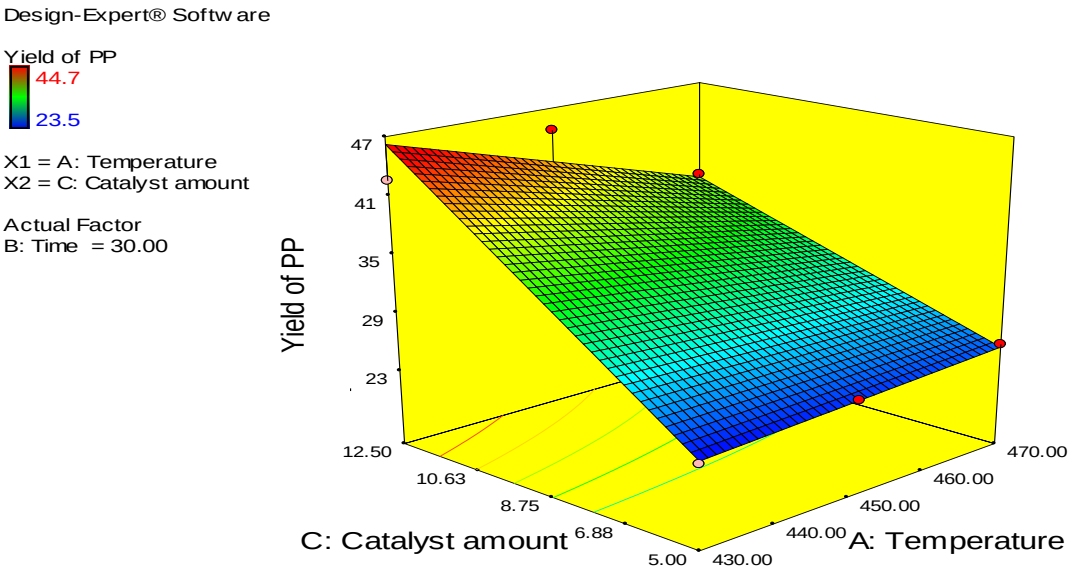


Figure 4.10:3D surface plots for yield of oil from PP waste at constant 30 minute, AC interaction

4.10.2. Yield of a Liquid fuel from catalytic pyrolysis of PS waste

4.10.2.1. Interaction of temperature(A) and time (B) at constant catalyst loading

Interaction effect of Temperature and Time is increasing the yield of liquid fuel as both parameters decrease with constant catalyst of 12.5, as shown in Fig(4.11).The effect of decreasing the time on the liquid yield show a pronounced increase than temperature.The maximum liquid yield of 48.88%was obtained at time of 30 min and 430^{o}C temperature and minimum value was observed at the 60 minutes and 470^{o}C temperature with a value of 26.5%.

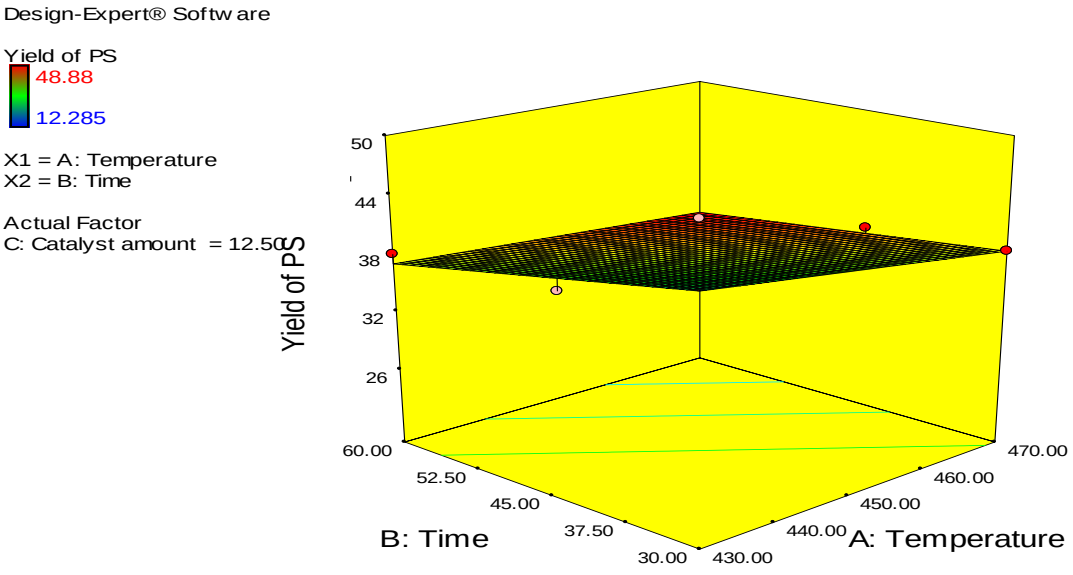


Figure 4.11:-3D surface plots for yield of oil from PS waste at constant 12.5 catalyst amount, AB interaction

4.10.2.2. Interaction of time(B) and catalyst loading(C) at constant temperature

Interaction effect of Time and catalyst amount is increasing the yield of liquid fuel as time increase for lower catalyst amount and decrease at higher time and increase in catalyst loading with constant temperature of 430^{o}C, as shown in Fig(4.12).The effect of increasing the catalyst loading on the liquid yield show a pronounced increase than time.The maximum liquid yield of 48.8% was obtained at 12.5 gm of catalyst and 30 minutes and minimum value was observed at the 30 minutes and 5 gm catalyst loading with a value of 12.285%.

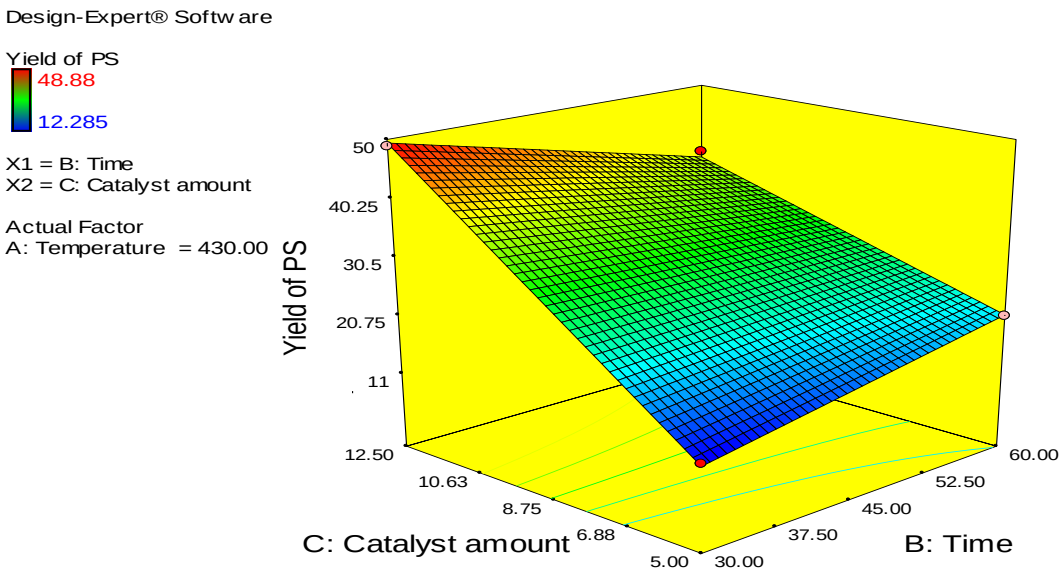


Figure 4.12:-3D surface plots for yield of oil from PS waste at constant 430^{o}C, BC interaction

4.10.2.3. Interaction of temperature(A) and catalyst loading(C) at constant time

Interaction effect of Temperature and Catalyst loading is increasing the yield of liquid fuel as temperature increase for lower catalyst amount and decrease with higher temperature and increase in catalyst loading with constant time 30 minutes, as shown in Fig(4.13).The effect of increasing the catalyst amount on the liquid yield show a pronounced increase than temperature.The maximum liquid yield of 48.88% was obtained at 12.5gm catalyst and 430^{o}C temperature and minimum value was observed at the 5gm catalyst loading and 430^{o}C temperature with a value of 12.285%.

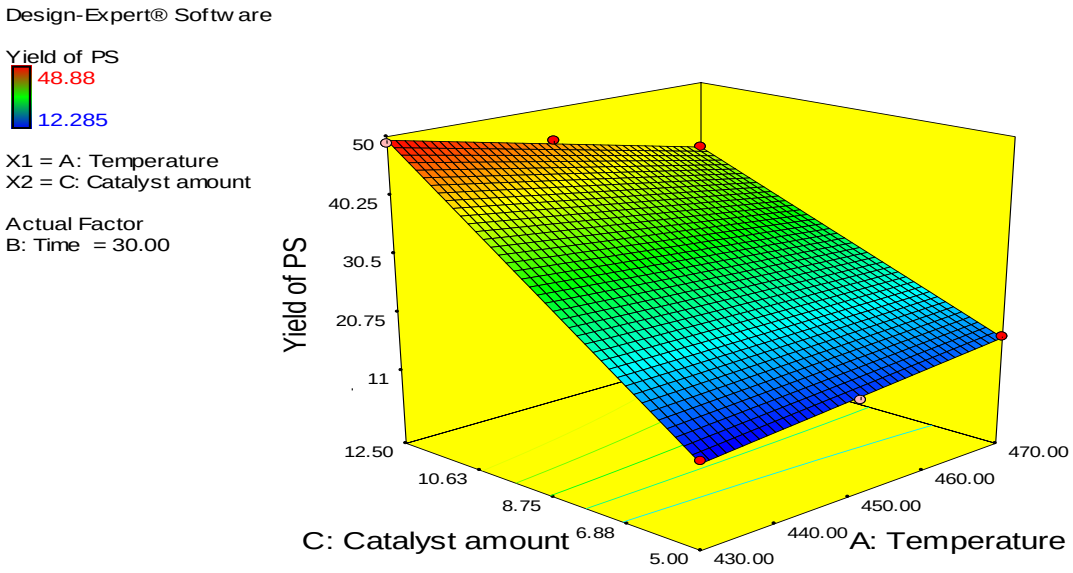


Figure 4.13:-3D surface plots for yield of oil from PS waste at constant of 30 minutes, AC interaction

Additional information about the statistical analysis of the experimental data that used reduced cubic model and diagnostic plots were given in the appendix.

4.11. Liquid Fuel Characterization

The liquid product obtained had a dark-radish color for liquid oil from polypropylene waste and a dark color for oil from polystyrene waste and aromatic smell.The characteristics of pyrolysis liquid oils were characterized using appropriate procedures based on standard ASTM methods. Density, kinematic viscosity, flash point, heating value and GC/MS were used to analyzed the liquid fuel property.

Density is an important property of a fuel oil.If the density of fuel is high; the fuel consumption will be less.On the other hand, the oil with low density will consume more fuel which may cause damage to the engine.Therefore, too low or too high density of fuel oil is not desirable.Viscosity varies with feed stock, pyrolysis conditions, temperature, and other variables.The higher the viscosity, the higher the fuel consumption, engine temperature, and load on the engine.If the viscosity of oil is too high, excessive friction may take place.On the other hand the very low viscosity was attributed to the probable high moisture content of the bio-oil.A low flash point indicates the presence of highly volatile materials in the fuel that is a serious safety concern in handling and transporting.By removing lighter components the flash point of liquid oil from polypropylene and polystyrene waste were increased.

4.11.1. Characterization of Liquid Fuel from Polypropylene Waste

For liquid oil from polypropylene plastic waste, sample from product of run #5 which was carried out at 12.5 gm catalyst, 450^{o}C, and 30 minutes was selected for characterization cause it gave the maximum percentage yield.

The density of fuel from catalytic pyrolysis of polypropylene waste was measured to be 0.827 g/cm^3 and 0.828 specific gravity at 15^{o}C.This density is close to the density of diesel, and gas oil. So the conventional fuel such as diesel oil may be replaced by plastic pyrolysis oil.The viscosity was measured at a temperature of 40^{o}C.It is observed that the viscosity of polypropylene waste plastic pyrolysis oil was 2.06cSt.As per the standard kinematic viscosities of fuel oil (3.5-9.7 mm^2/s),Viscosity of oil, was found to be less viscous (S.Pandian and A. Kamalakannan, 2012 and M.Sarker, et al., 2012).

The flash point of oil from polypropylene waste was 29^{o}C.The flash point of the oil is in the range of gasoline (20.8-38^{o}C) and the standard values of Flash points of fuel oil was found to be ~40ºC (M.Sarker, et al., 2012[1] S.Kumar, and R.K.Singh, 2011).I. Ahmad, et al. Pyrolysis (2014) was obtained density of 0.86 g/cm^3 and flash point of 30^{o}C.The value that obtained from this study was less than the standard values so the liquid fuel was difficult to handle.The calorific value of liquid oil in this study from catalytic pyrolysis of polypropylene waste was 25 mJ/Kg. This value was Hence, it can be said that this liquefied hydrocarbon obtained from pyrolysis of waste plastic can be used for fuel.This was around the half of calorific value of gasoline and diesel range hydrocarbon this might be due to the presence of impurities and there was a need of post treatment before using the fuel directly.Similar trends was obtained by Sonawane YB, Shindikar MR and Khaladkar MY(2015).

4.11.2. Characterization of liquid fuel from polystyrene waste

For liquid oil from polystyrene plastic waste, Sample from product of Run #3 which was carried out at 12.5gm catalyst, 430^{o}C, and 30 minutes was selected for characterization cause it gave the maximum percentage yield.

The density was measured to be 0.955 g/cm^3 and 0.956 specific gravity at 15 ^{o}C which was in the range of the density of heavy fuel oil,diesel and bio-diesel.So the conventional fuel such as heavy oil,diesel oil, kerosene oil, and gas oil may be replaced by plastic pyrolysis oil.The viscosity was measured at a temperature of 40^{o}C and it was observed that the viscosity of waste plastic pyrolysis oil was 2.2 cSt which was in the range of diesel.

The flash point of oil from polystyrene waste was about 24^{o}C which was in the range of gasoline this indicates that these were high volatile matters so difficult to handle.F. Pinto, et al.,(1998) and M. Blazso.,(2006) was obtained a flash point of 26.1^{o}C which was relatively similar result was obtained.The calorific value of oil from polystyrene waste plastic pyrolysis 20mJ/Kg which was half of gasoline, diesel and heavy oil calorific value.The calorific value of PS was commonly lower than the polyolefin plastic due to the existence of the aromatic ring in the chemical

structure which had lesser combustion energy than the aliphatic hydrocarbon (J.A. Onwudili,et al., 2009).

Generally,the calorific value of liquid oil from both plastic type lower than the standard value this was due to the presence of impurities and presence of water particles in the fuel so post treatment were required.Fuel properties of different fuel with pyrolytic liquid oil from PP and PS waste was shown in Table 4.12.

Table 4.12:Fuel properties of different fuel with pyrolytic liquid oil

No.	Fuel properties	Specific gravity $15^oC/15^oC$	Viscousity (cst) at 40^oC	Flash point (^oC)	GCV (MJ/Kg)	Chemical formula
1.	Pyrolysis oil from PP waste	0.828	2.06	29	25	
2.	Pyrolysis oil from PS waste	0.956	2.2	24	20	
3.	Gasoline(NIPER, 1986 and Aguado, J.,et al.,2007)	0.72-0.78	-	20.8-38	42-46	C_4-C_{12}
4.	Diesel(J. Tuttle and T. V. Kuegelgen, 2004)	0.82-0.85	2-5.5	53-80	42-45	C_8-C_{25}
5.	Bio-diesel (J. Tuttle and T. V. Kuegelgen, 2004)	0.88	4-6	100-170	37-40	C_{12}-C_{22}
6.	Heavy fuel oil (Kumar, S., Singh, R.K.:2014)	0.94–0.98	>200	90–180	40	>C_{20}

4.11.3. GC/MS graph

Total experiment runs time 19.414 minutes.MS setup for sample analysis MS scan time 1 to 19.414 minutes.Standard solutions were analyzed to verify the identity of the peaks by retention time and provide quantitative analysis.

4.11.3.1. GC/MS of liquid oil from polypropylene waste plastic

Gas chromatography-mass spectrometry (GC-MS) of the selected oil sample was done to examine its chemical composition.The initial temperature of GC/MS was set at 60^oC and any fuel feed boiling point below this temperature, the MS analyzer, could not analyzed the peaks by

retention time and didn't provide quantitative analysis.This was what happened for liquid oil from catalytic pyrolysis of polypropylene waste.

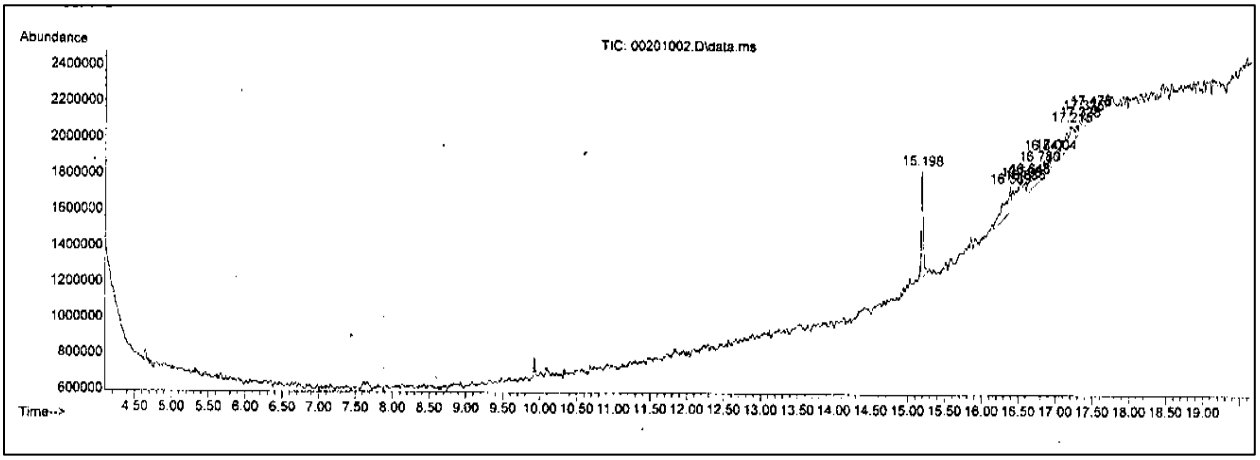


Figure 4.14:-GC/MS graph of liquid oil from polypropylene waste

Because of lower boiling point of liquid oil than the set operating temperature,the MS analyzer didn't analyzed existing compounds.But there are other alternative to know the compound that exist in the liquid oil from catalytic pyrolysis of PP waste.The boiling point ranges of different hydrocarbon shown in the Table 4.13 below.

Table 4.13:Boiling point ranges of different hydrocarbons (H. Andargachew, 2014)

No.	Hydrocarbons	Boiling ranges (^{o}C)
1.	Gasoline	40-190
2.	Kerosene	190-260
3.	Diesel	260-330
4.	Lube oil	330-400

So the boiling point of Fuel from catalytic pyrolysis of polypropylene is below 60^{o}C.Taking the above table as a reference, liquid fuel from PP waste was in the range of gasoline hydrocarbon range.Furthermore, Achilias, et al.,2007 was observed that pyrolysis of the plastic bag made from PE and PP leads to a fraction mainly in the region of C_7-C_{12}, which is in the gasoline region.Gasoline quality fuels consist of hydrocarbons in the C_5-C_8 range.Moreover, most studies observe that the main products obtained in polyolefin (PP and PE) pyrolysis are hydrocarbon gases (C_1-C_4) and liquid gasoline range (C_5-C_{12}) products composed of mainly olefins and paraffins (Murata, K. and Y.Hirano,2002[1];Serrano, D.P. and J. Aguado,2001 and [1]Lin, Y.H. and M.H. Yang,2005).Sakata Y et al.,1997;was also observed that in the application of catalyst of

higher acidity (HY, ZSM-5, silica–alumina based catalysts) results mainly in C_5–C_{12} liquid hydrocarbons.

Based on the evidence that obtained from different literature liquid fuel from thermal and catalytic pyrolysis of polypropylene waste was fall in a gasoline range.Therefore, based on boiling point range and similar trends from different researchers the conclusion was liquid fuel from catalytic pyrolysis of polypropylene waste was in gasoline range.

4.11.3.2. GC/MS graph of liquid fuel from polystyrene plastic waste

GC/MS of liquid oil from polystyrene waste was analyzed and the GC/MS graph shown below:

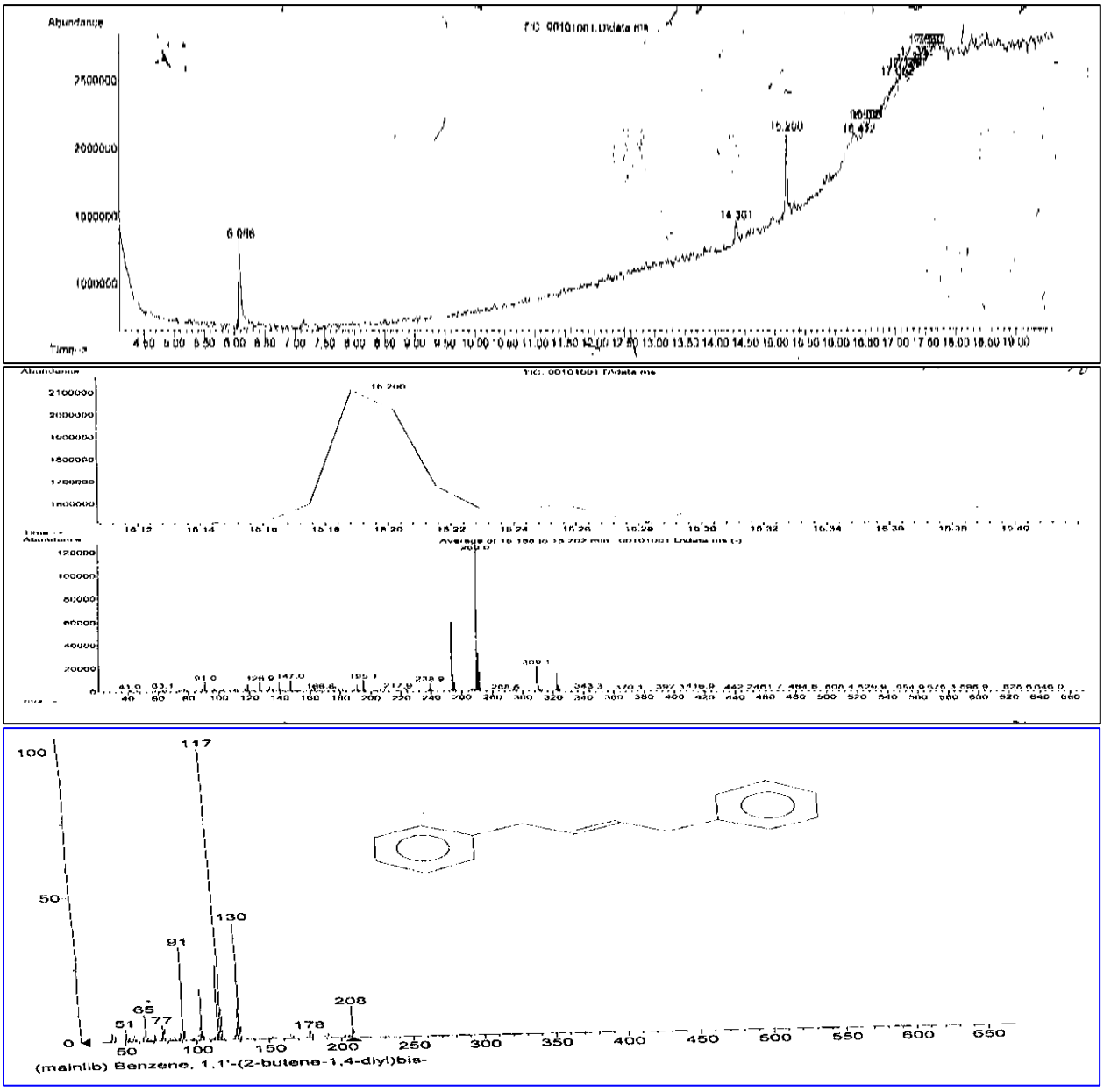


Figure 4.15:-GC/MS graph of liquid oil from polystyrene waste

Table 4.14:GC/MS Chromatogram compounds list of Polystyrene waste plastic to fuel (D:\MassHunter\Library\NIST14.L)

Peak #	Retention time (min)	Compound name	Compound formula	Molecular weight	Area (%)	Reference #
1.	6.086	Styrene	C_8H_8	104.1491	24.88	4955
2.	14.361	Benzenethanamine	$C_9H_{13}N$	135.2062	5.65	15957
3.	15.200	Fluoxetine	$C_{17}H_{18}F_3NO$	309.3261	17.50	167929
4.	16.412	2-Pentanamine	$CH_3(CH_2)_4NH_2$	87.1634	1.02	1930
5.	16.506	2-Pentanamine	$CH_3(CH_2)_4NH_2$	87.1634	2.83	1930
6.	16.551	Benzeneethanamine, 2-fluoro-.beta.,3-dihydroxy-N-Methyl-	$C_9H_{13}N$	135.2062	1.63	52381
7.	17.052	2-Ethoxyamphetamine	$C_{14}H_{11}N$	73.1368	16.42	46994
8.	17.179	Benzenepropanamine,.alpha.-methyl	$C_9H_{13}N$	135.2062	8.58	24042
9.	17.240	2-Pentanamine	$CH_3(CH_2)_4NH_2$	87.1634	1.82	1930
10.	17.317	amphetamine	$C_9H_{13}N$	135.2062	1.55	15918
11.	18.45	2-Pentanamine	$CH_3(CH_2)_4NH_2$	87.1634	1.2	1930
12.	19.01	2-Pentanamine	$CH_3(CH_2)_4NH_2$	87.1634	1.05	1930

Liquid fuel produced from Polystyrene waste plastic was analyzed by gas chromatography and mass spectrometer (GC/MS) seen in fig(4.15) and table 4.14.GC-MS analysis of fuel from PS waste in order to measure retention time and molecular weight of numerous aliphatic, aromatic derivatives and different types of hydrocarbon compounds and hydrocarbon chain ranges from C_5 to C_{27} and showing clear similarities to gasoline, diesel and heavy oil in addition to the oil properties showing closeness to that of gasoline, diesel and heavy oil.

All compounds peak intensity was not the same.Some compounds peak intensity is small, some compounds peak intensity is medium and some compounds peak intensity is large.At the initial stage of the analysis phases at retention time 6.086, 24.88% area and molecular weight 104.1491 the compound was Styrene (C_8H_8), retention time 14.361, 5.65% area and molecular weight 135.2062 and 73.1368 compound were benzene-ethanamine ($C_9H_{13}N$) and 2-ethoxy-

amphetamine ($C_{14}H_{11}N$) respectively, retention time 15.2, 17.50% area and molecular weight 309.3261, 87.1634, 225.2842, compound were Fluoxetine ($C_{17}H_{18}F_3NO$), 2-Pentanamine ($CH_3(CH_2)4NH_2$), and 3-Methoxyamphetamine ($C_{12}H_{19}NO_3$) respectively, retention time 16.412, 1.02% area and molecular weight 87.1634 and 558.666, the existing compound were 2-pentanamine ($CH_3(CH_2)_4NH_2$) and Formylhistamine ($C_{27}H_3ON_2O_7S_2$) respectively, retention time 16.506, 2.83% area and 87.1634 molecular weight ,the compound was 2-pentanamine ($CH_3(CH_2)_4NH_2$).For retention time 16.551, 1.63% area and molecular weight 135.2062 compound were benzene-ethanamine, 2-fluoro-.beta., 3-dihydroxy-N-methyl- ($C_9H_{13}N$), For retention time 17.052, 16.42% area and molecular weight 87.1634 and the compound was 2-pentanamine ($CH_3(CH_2)_4NH_2$), retention time 17.179, 8.58% area and 135.2062 molecular weight 135.2062, the compound was Benzene propan-amine,.alpha.-methyl ($C_9H_{13}N$),for retention time 17.240, 1.82% area and molecular weight 87.1634, the compound is 2-Pentanamine ($CH_3(CH_2)4NH_2$), retention time 17.317, 1.55% area and molecular weight 135.2062, compound was Amphetamine ($C_9H_{13}N$).

From this study,The range of hydrocarbon in catalytic pyrolysis of polysyrene waste was C_5-C_{27} this was in the range of gasoline (C_5-C_{12}), diesel (C_{13}-C_{20}) and heavy oil (>C_{20}).Benzene group compounds are present in this fuel because raw materials were used polystyrene waste plastic. Polystyrene waste plastic had benzene group compounds.The same trends was obtained from other literature's.Lee et al. (2002) reported that liquid oil from catalytic pyrolysis of PS consisted of more than 99% of aromatic compounds with small quantities of n-paraffin (0.02%), iso-paraffin (0.1%), olefins (0.03%) and naphthenes (0.1%).Similarly according to Ramli and Abu Bakar (2011), the liquid oil from thermal and catalytic pyrolysis contained 80% and 85-90% aromatic hydrocarbons respectively.The high ratio of aromatic compounds found in the pyrolysis liquid oil from pyrolysis of PS was due to the high stability of these compounds, which inhibited their further cracking or hydrogenation into paraffin and olefins (Kim et al., 002).Styrene was the main component of liquid fuel from thermal and /or catalytic pyrolysis of polystyrene waste plastics.Liu et al. (2000) was obtained styrene monomer and gasoline fraction in pyrolysis of polystyrene plastic waste.Lee et al.,2002 and Ke et al.,2005 studied and both obtained styrene monomer in catalytic pyrolyisis of polystrene waste plastics.Degradation of PS into styrene, including monomer and dimer, was studied by Ukei et al.,2000 using solid acids and bases catalyst.Kim et al.,2003 was obtained styrene monomer at relatively low temperature with a high selectivity in the catalytic degradation of polystyrene plastic waste.

Plastic contained different metals they used as an additive for color, strength and act as a catalyst for polymerization process of monomers.However, the metals, amines and other impurities presented in the waste also exist in the oils formed,thus further treatment for the removal of those impurities was required in order to increase liquid fuel viability to be used as fuel.

Generally, liquid oil from catalytic pyrolysis of polypropylene and polystyrene plastic waste contained some impurities such as sulfur, chlorine, solid residue, moisture, and acids as same as liquid fuel from other plastic wastes.Presence of these impurities not only decreases the quality

of liquid oil but also limits its commercial applications.Hence, liquid oil requires post-treatment including, up-gradation with removal of char particles, and acids removal, and neutralization to improve liquid oil with appropriate condition like stable pH and low corrosivity.

4.12. Solid residue characterization

Proximate analysis of solid residue was shown in Table 4.15 below.

Table 4.15:Proximate analysis of solid residues(char)

No.	Analysis	Value(%)
1.	**Solid residue from pyrolysis of polypropylene waste**	
1.1	Moisture	8.77
1.2	Volatile matter	69
1.3	Ash content	10
1.4	Fixed carbon	12.23
2.	**Solid residue from catalytic pyrolysis of polystyrene waste**	
2.1	Moisture	2.325
2.2	Volatile matter	86
2.3	Ash content	7
2.4	Fixed carbon	4.675

The Lower moisture content indicated presence of higher amount of organic solid product.Effects of the higher value is due to the nature of plastic matter.The lower ash content whereas indicated more positive suitability of the waste in thermo-chemical conversion due to the prevalent organic nature it affirmed.

5. CONCLUSION AND RECOMMENDATIONS

5.1. Conclusion

Both the land-filling and incineration processes of plastic waste management system are identified as sources of pollutant gas emitters.Reprocessing also uneconomical in comparison to the virgin plastic products in terms of commercial values due to polymeric contamination.On the other hand, the world currently consumes large quantities of non-renewable hydrocarbons at an ever-increasing rate.The reserves of fossil fuels are limited, and there are many other problems associated with their consumption.

The study and analysis of this paper showed that polypropylene and polystyrene waste can be used as a fuel.A maximum of 44.7% and 48.88% wt of liquid yield of catalytic pyrolysis of polypropylene and polystyrene waste was achieved respectively.It was seen that pyrolyzing polystyrene at lower temperature and time using maximum amount of catalyst gave had in higher percentage yield.Whereas at moderate temperature, lower time and maximum amount of catalyst gave had in higher percentage yield in case of polypropylene.

Physical properties of rice husk was analyzed rice husk had lower moisture content and average ash content.XRD analysis of catalyst shows that existence of silica and alumina.FTIR of plastic waste used to analysis the existed functional group and the analysis shows that both plastic type contained Alkene, Amine, Acid and Alcohol group in common and aromatics in polystyrene plastic waste.Proximate analysis of solid residues was done and this show that char also can be competitive alternate of energy sources.Fuel properties of liquid oil from both plastic was fulfill gasoline, diesel and heavy oil.The GC/MS result also prove this.Hence made characteristics data available for use as reference in future scientific studies.

Due to similarity of fuel from plastic (polypropylene and polystyrene) waste with conventional gasoline,diesel and heavy oil thus have potential to be used as alternative energy source for transportation.However, presence of high aromatic compounds in liquid oil from polystyrene waste made it unsuitable as a transport fuel until it is upgraded using different post-treatment methods such as distillation, refining or blending with conventional diesel.Overall the study concluded that catalytic pyrolysis can be an effective recycling technique for the polypropylene and polystyrene plastic waste with dual benefits of plastic waste management and energy production.

5.2. Recommendations

The conversion of plastic waste into liquid oil and other valuable products using catalytic pyrolysis process is getting significant attention both as waste management and an alternative energy generation technology.Catalytic pyrolysis of polypropylene and polystyrene plastic waste using synthesized catalyst (Silica-Alumina) from renewable resources rice husk and aluminum oxide give valuable products and further works are still necessary.Future researches that would

be complementary to the present study aiming at investigation of the process are, therefore, strongly recommended to put due focus on the following points:

Detail investigation is required on catalyst production and characterization and its effect on the production and quality of liquid oil specially on polypropylene and polystyrene plastic waste. Because it is a cost effective and environment friendly process.

Future works in the area of this and other similar processes must give due consideration to put adequate budget that will assure comprehensive laboratory facility for complete investigation of the process.

Improving the catalytic pyrolysis liquid oil quality should be studied further by post-treatment methods such as filtration, chemical treatment, by blending it with diesel and other fuels and distillation and refining to remove heavy hydrocarbons and any impurities.This will upgrading a calorific value and other properties of the liquid fuel so future work on this area is required.

Char activation and its evaluation for various environmental application should be given due consideration.Analysis of the bio-char needs to be conducted in order to identify its applicability to meet any other objectives.Accordingly, respective potentials of bio-char from polypropylene and polystyrene plastic waste pyrolysis to be used for alternative energy source; an adsorbent material for heavy metals, odor and toxic gases removal from waste water and exhaust emissions;a source of feed stock for activated carbon;soil amendment if char activation is done.

Thermo-gravimetric analysis (TGA) is the most common technique used to study the kinetics and thermal events involved in pyrolysis of solid raw materials.The measurement of weight loss as a function of temperature and time provided by TGA gives good and reliable information. Catalytic pyrolysis of plastic waste PP and PS using synthesized catalyst widely investigated. Therefore, future works that aim at studying the catalytic pyrolysis of Polypropylene and polystyrene plastic waste would rather employ TGA.This way it would be possible to fully investigate the catalytic cracking behavior of the mixture and determine any activity among the components and analyze the effects.

Due to leakages or lack of proper sealing, condensable and non-condensable gaseous fraction move out from the system.The release of those gaseous product has an effect on the environment. The gaseous fraction had high calorific value So collection of gas product must be available.future work will require for collection and characterization of gaseous product.

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1

APPENDIX

A. Yield of solid residue and gaseous product from catalytic pyroysis of polypropylene and polystyrene waste plastic

A.1. Yield of solid residues and gaseous fraction form catalytic pyrolysis of PP waste

Run	Factors			Yield (%)	
	Temperature (^oC)	Catalyst amount (gm)	Time (min)	Solid	Gas
1.	450	5	30	15.2	60.14
2.	450	5	60	36.2	38.3
3.	470	5	30	25.6	48.6
4.	430	12.5	30	30	27.35
5.	450	12.5	30	20	35.3
6.	450	12.5	60	22.4	44.4
7.	470	12.5	30	26	37.2
8.	470	12.5	60	43.4	30.4
9.	470	5	60	28.6	45.4
10.	430	5	30	25	51.5
11.	430	5	60	35.2	39.9
12.	430	12.5	60	15.16	45.04

A.2. Yield of solid residues and gaseous fraction from catalytic pyrolysis of PS waste

Run	Factors			Yield (%)	
	Temperature (^oC)	Catalyst amount (gm)	Time (min)	Solid	Gas
1.	430	5	30	34.8	48.915
2.	470	5	30	21.2	61.195
3.	430	12.5	30	10	41.12
4.	470	5	60	18	56.11
5.	450	5	60	20	56.4
6.	450	12.5	60	31.6	38.642

7.	430	5	60	45.2	33.9
8.	430	12.5	60	20.4	41.506
9.	470	12.5	60	52.4	21.
10.	450	5	30	4	78.286
11.	450	12.5	30	9.2	46.36
12.	470	12.5	30	11.2	50.37

B. GC/MS

B.1. GC/MS of PP Oil

Integration list

Peak	Start	RT	End	Height	Area	Area %
1	7.558	7.612	7.72	52709.25	293973.97	24.85
2	9.903	9.927	9.967	111785.68	133949.91	11.32
3	15.148	15.188	15.323	602584.94	1183038.57	100

B.2. GC/MS of PS Oil

Integration peak list

Peak	Start	RT	End	Height	Area	Area %
1	6.053	6.079	6.24	624234.42	1622184.54	14.1
2	7.115	7.142	7.209	60681.3	142330.35	1.24
3	14.308	14.354	14.422	147830.56	401322.49	3.49
4	15.141	15.188	15.273	592111.48	1227165.38	10.67
5	17.059	17.584	17.907	340254.77	11501158.54	100
6	18.251	18.297	18.351	94799.79	235321.43	2.05
7	18.526	18.553	18.59	100498.43	186187.66	1.62
8	19.414	19.535	19.562	70857.9	386588.08	3.36

C. Regression Modeling Analysis

C.1. Regression Modeling Analysis on liquid oil from PP

Regression analysis was performed to fit the response functions, i.e. the yield of liquid fuel from PP. An empirical relationship between the response and the input test variables in coded and actual units can be expressed by the following equation:

In Terms of Coded Factors:

Yield of PP =+31.14-2.01*A-1.88*B+6.08*C-2.86*A*C-2.28*B*C

In Terms of Actual Factors:

Yield of PP=-98.21250+0.23292*Temperature+0.2300*Time+20.58550*Catalyst amount-0.038083*Temperature*catalyst amount-0.040578*Time*Catalyst amount

C.2. Regression Modeling Analysis on liquid oil from PS

Similarly, regression analysis was performed to fit the response functions, i.e. liquid fuel yield from PS. An empirical relationship between the response and the input test variables in coded and actual units can be expressed by the following equation:

In Terms of Coded Factors:

Yield of PS =+28.31-1.56*A-0.79*B+9.44*C-3.95*A*C-5.38*B*C

In Terms of Actual Factors:

Yield of PS =-201.23830+0.38276*Temperature+0.78408*Time +30.51882*Catalyst amount-0.052665*Temperature*Catalyst amount-0.095614*Time*Catalyst amount

Therefore,both the equations that derived from the two regression model showed that the experimental and the predicted values were good.This indicates that there is a linearity relationship between the yield of both liquid fuel and the three factors considered in both cases.

D. Experimental Design and Analysis Data

D.1. Diagnostic Plots

D.1.1.Diagnostic Plots for liquid oil from PP

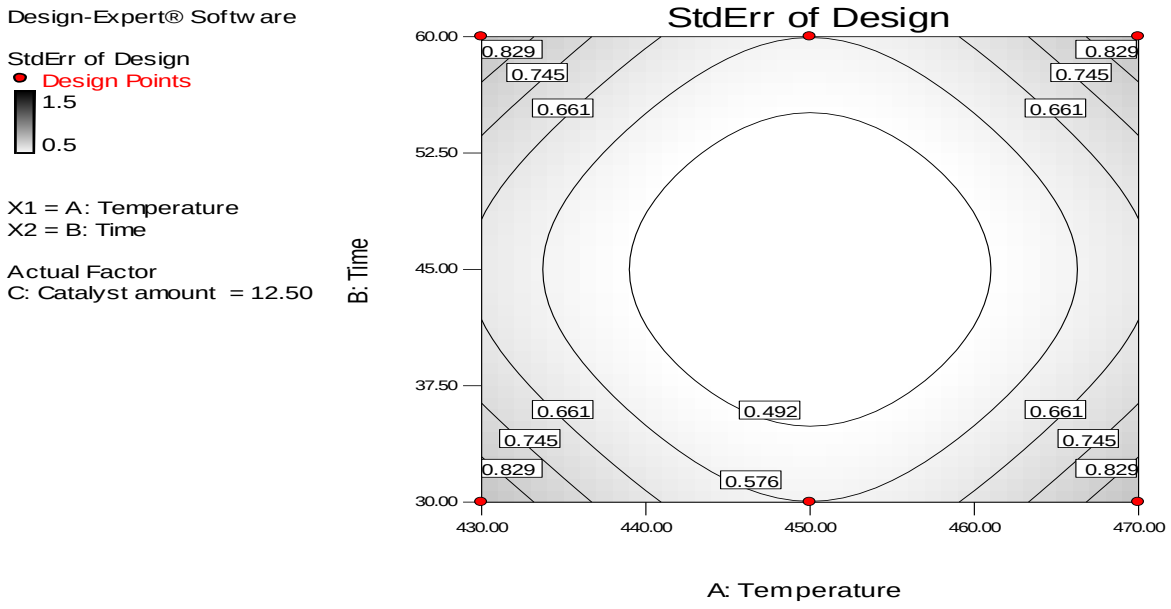

Figure D-1.1 – Standard Error of Design

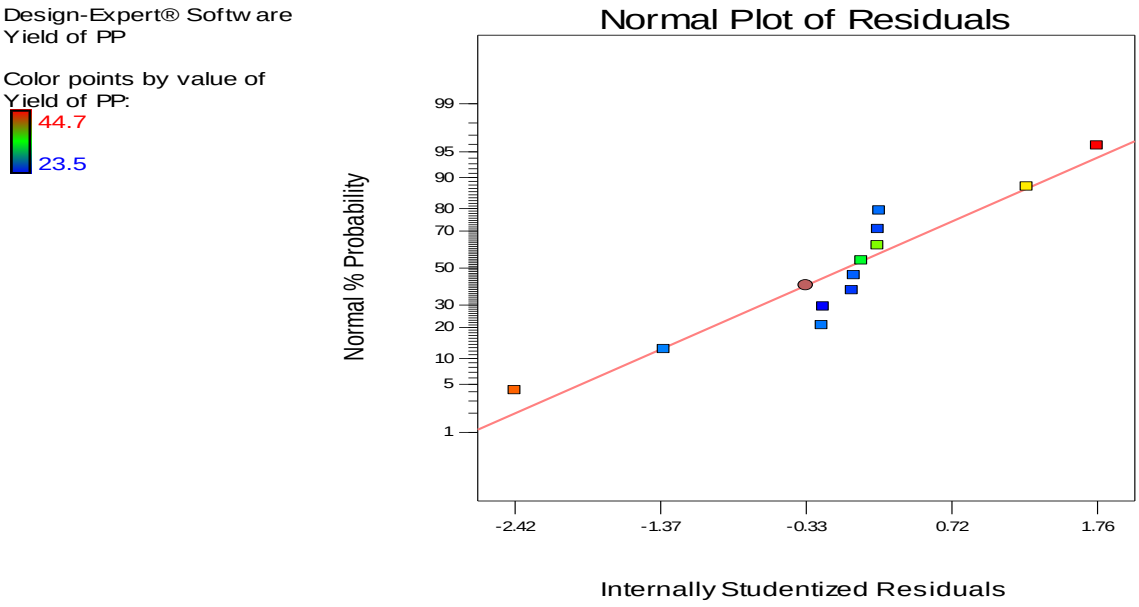

Figure D-1.2– Normal Plot of Residuals

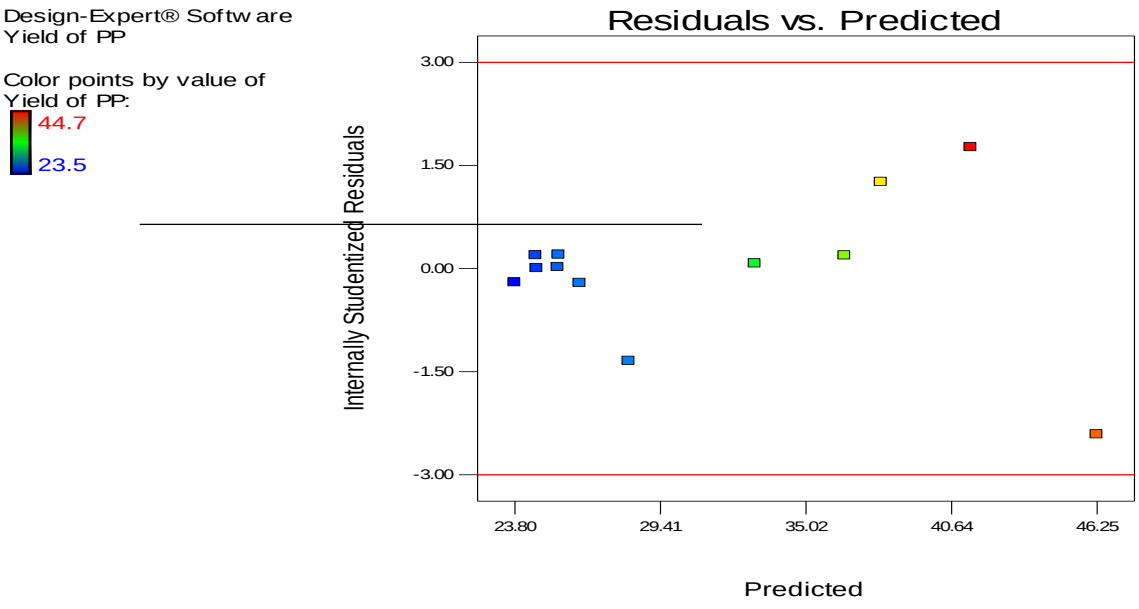

Figure D-1.3 – Plot of Residuals vs. Predicted Values

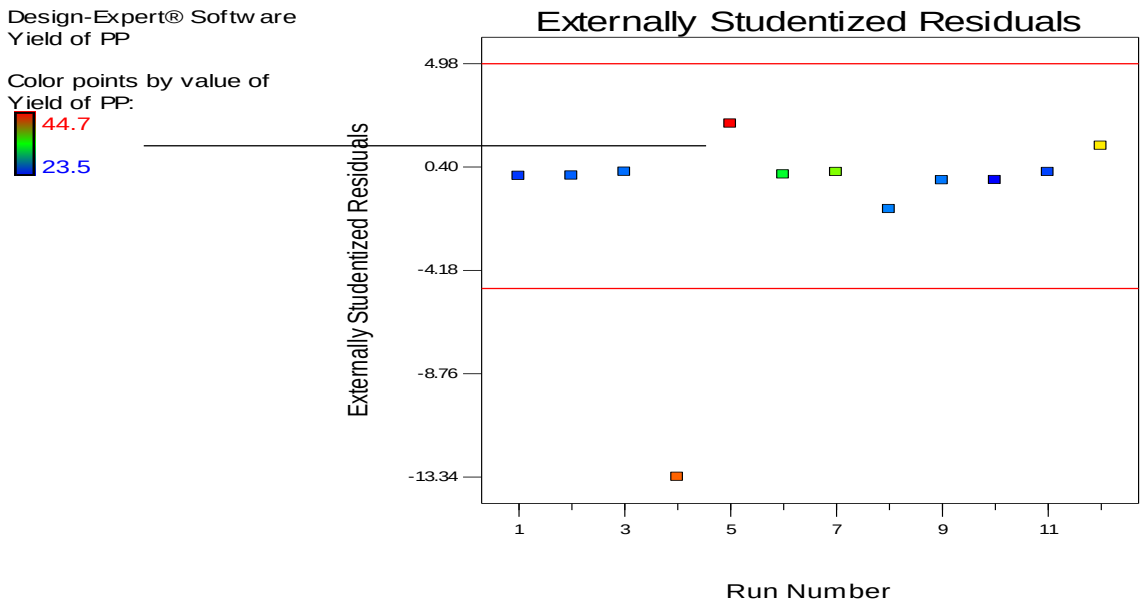

Figure D-1.4 – Plot of Externally Studentized Residuals

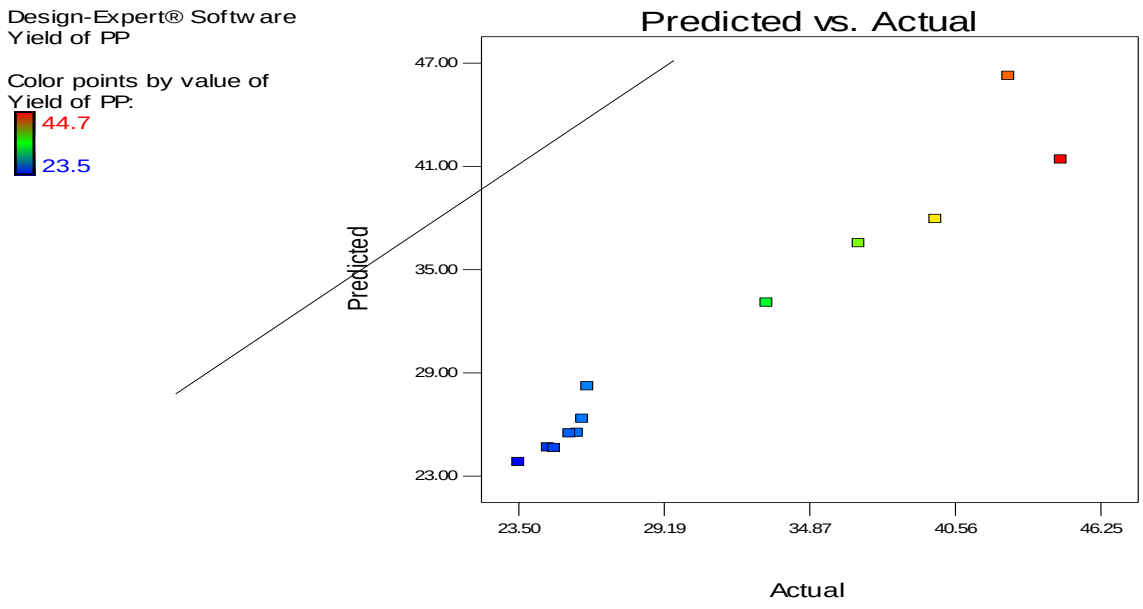

Figure D-1.5 – Plot of Predicted vs. Actual Percentage Yield Values

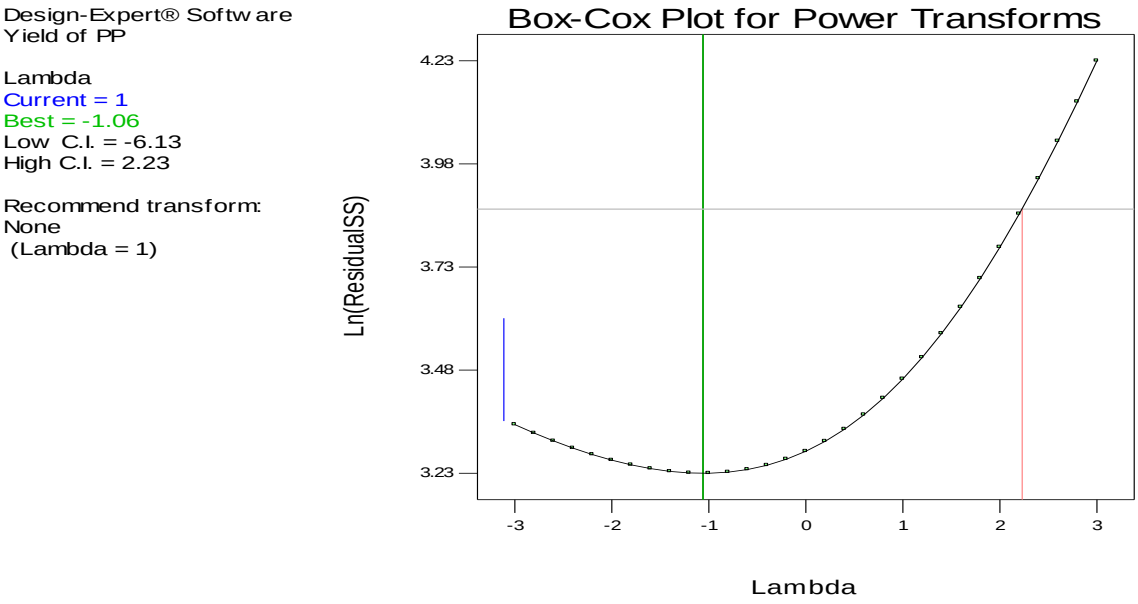

Figure D-1.6 – Box-Cox Plot for Power Transform

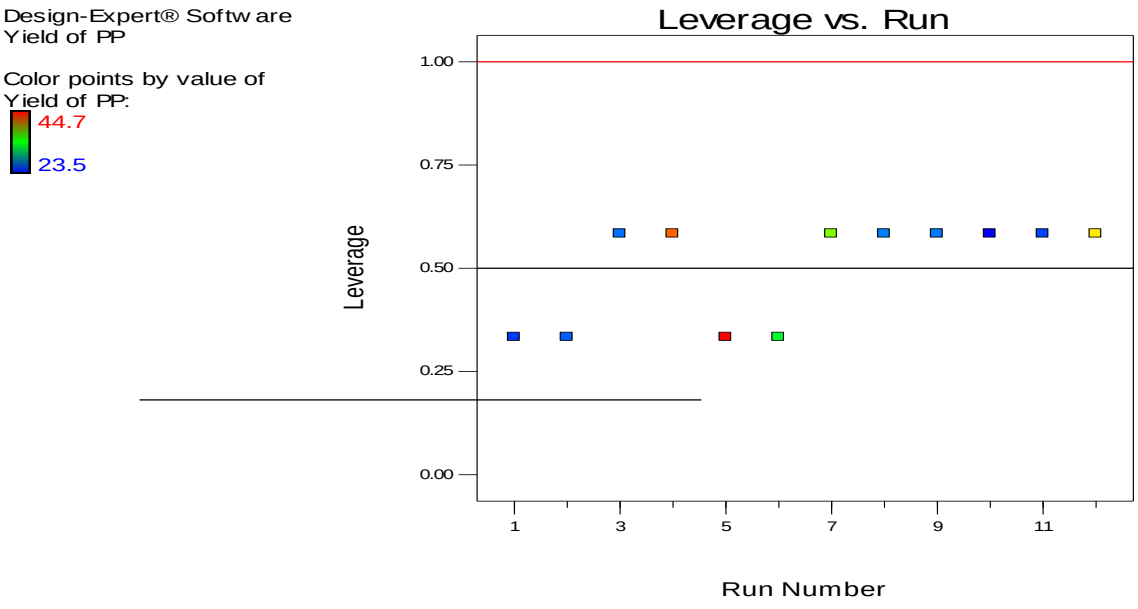

Figure D-1.7 – Plot of Leverage vs. Run

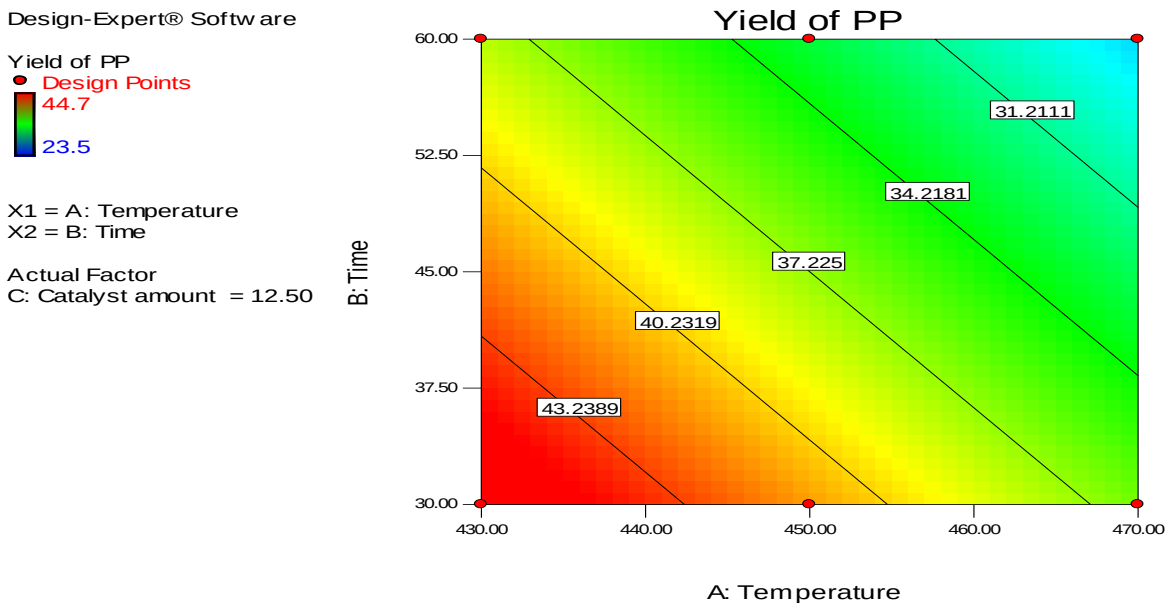

Figure D-1.8 - Model Graph for Percentage Yield

D.1.2.Diagnostic Plots for liquid oil from PS

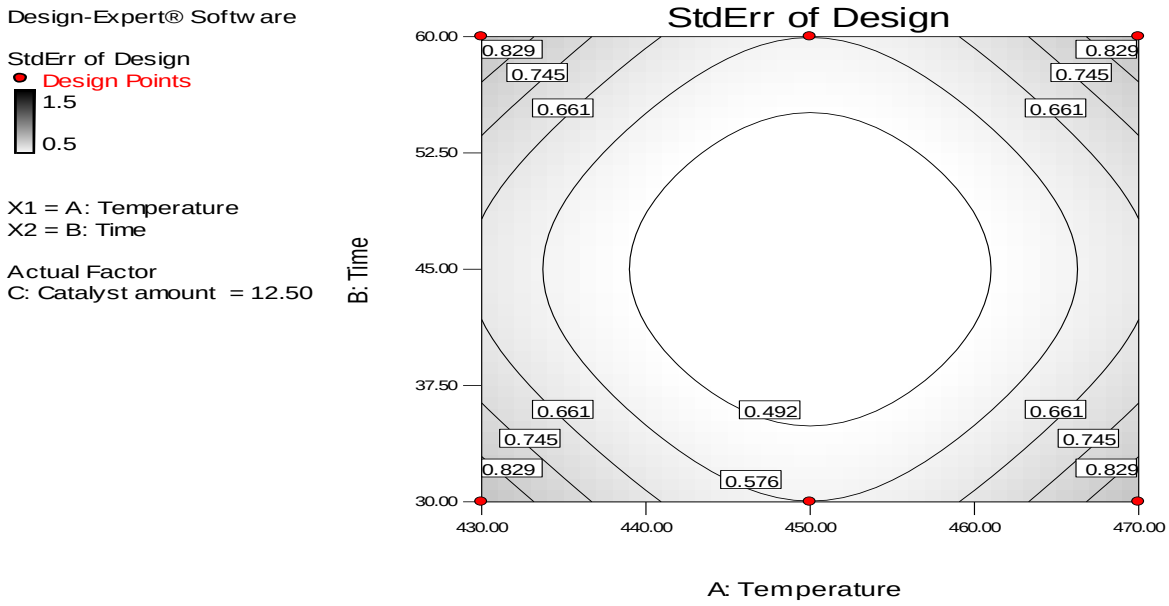

Figure D-2.1 – Standard Error of Design

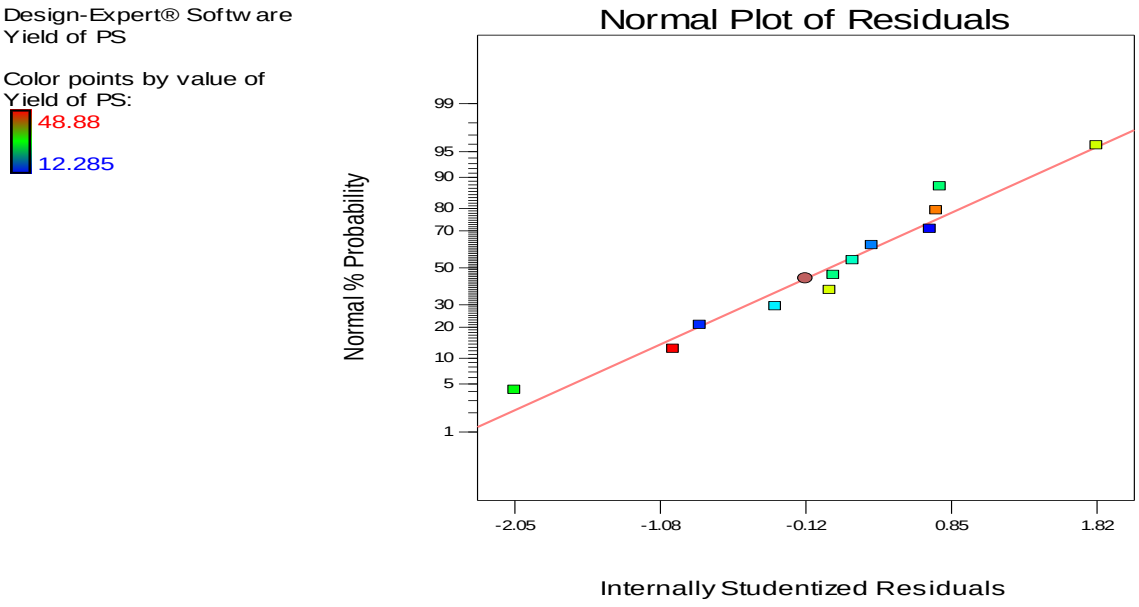

Figure D-2.2 – Normal Plot of Residuals

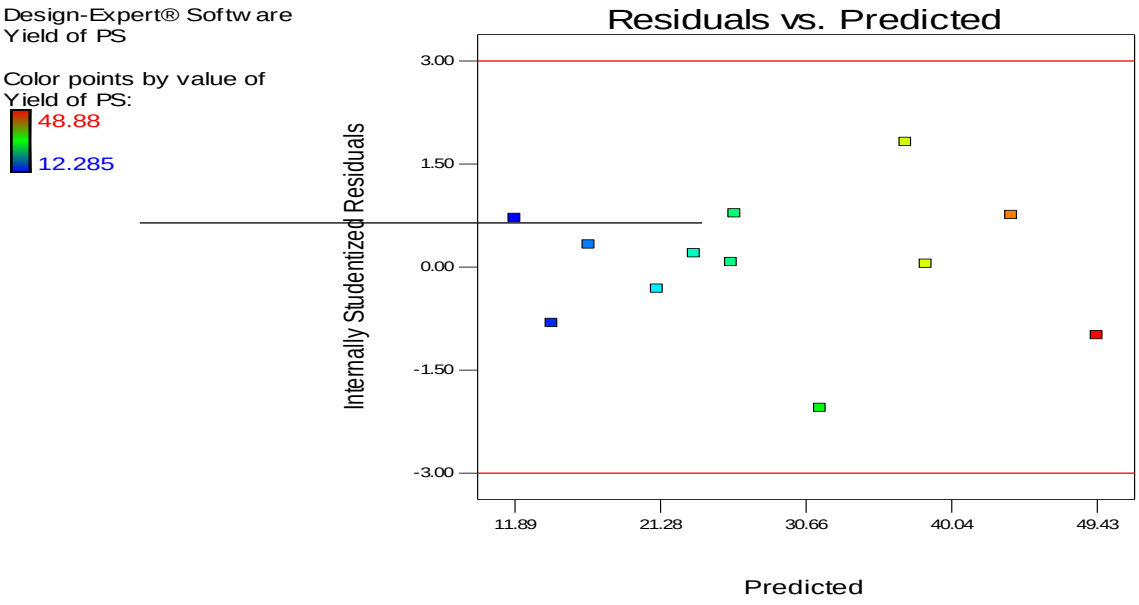

Figure D-2.3 – Plot of Residuals vs. Predicted Values

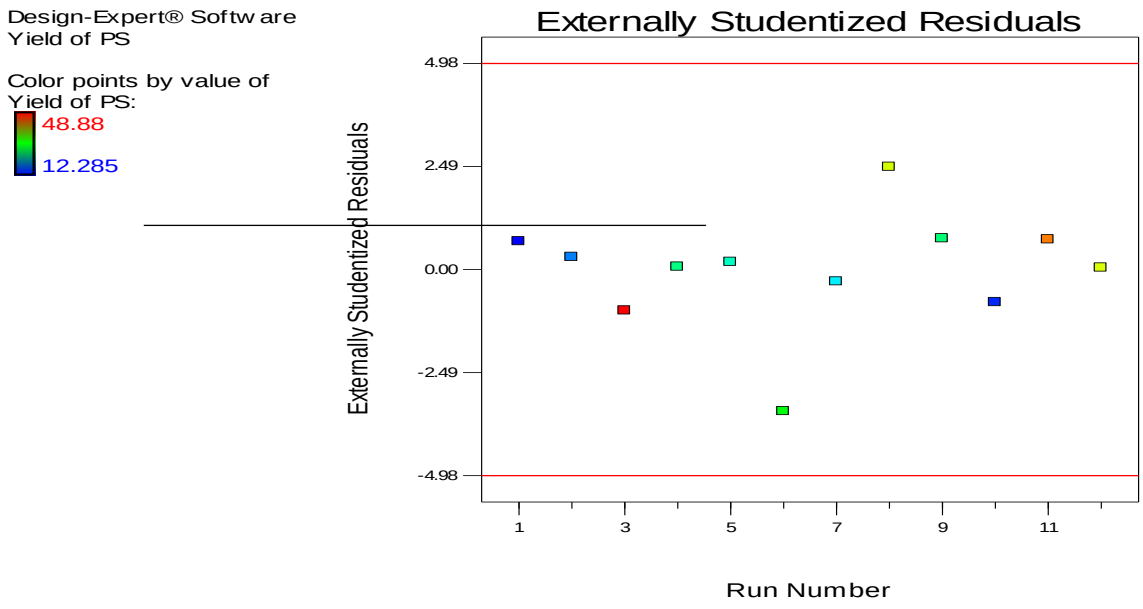

Figure D-2.4 – Plot of Externally Studentized Residuals

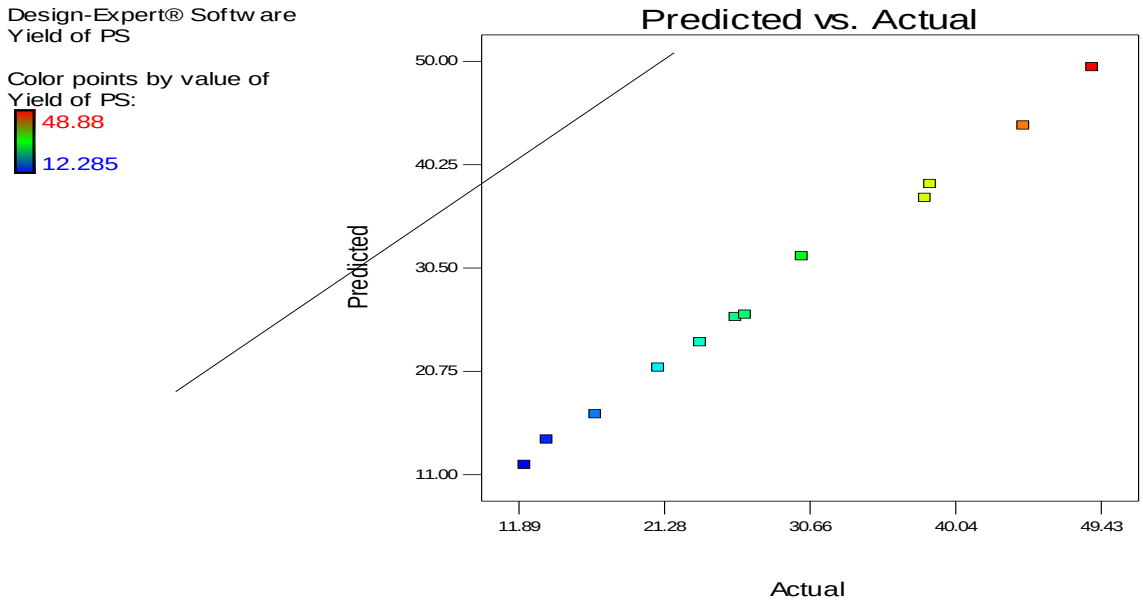

Figure D-2.5 – Plot of Predicted vs. Actual Percentage Yield Values

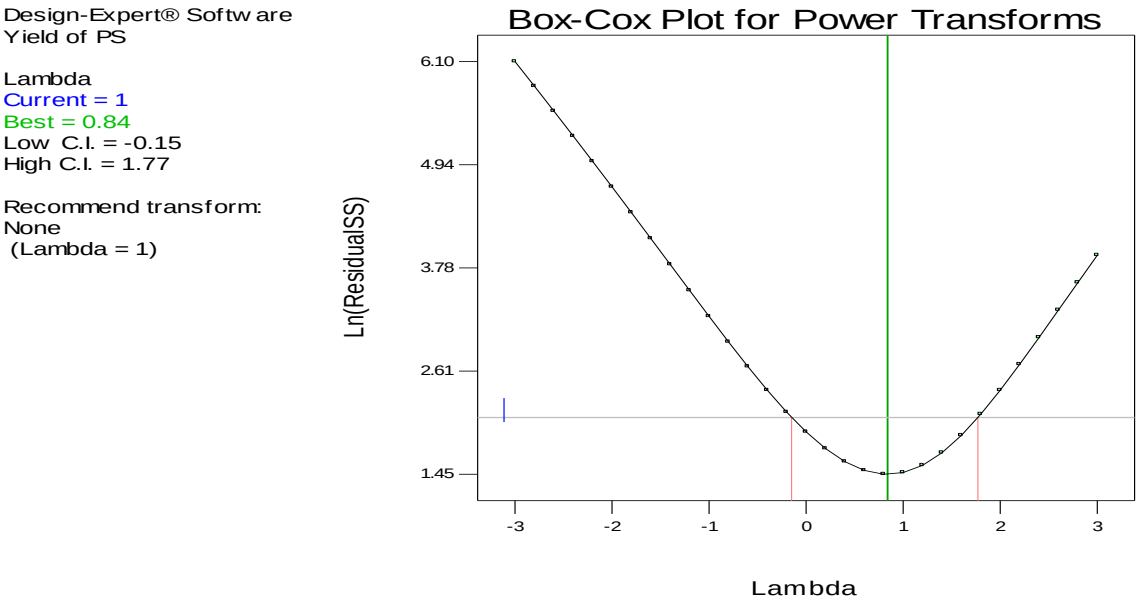

Figure D-2.6 – Box-Cox Plot for Power Transform

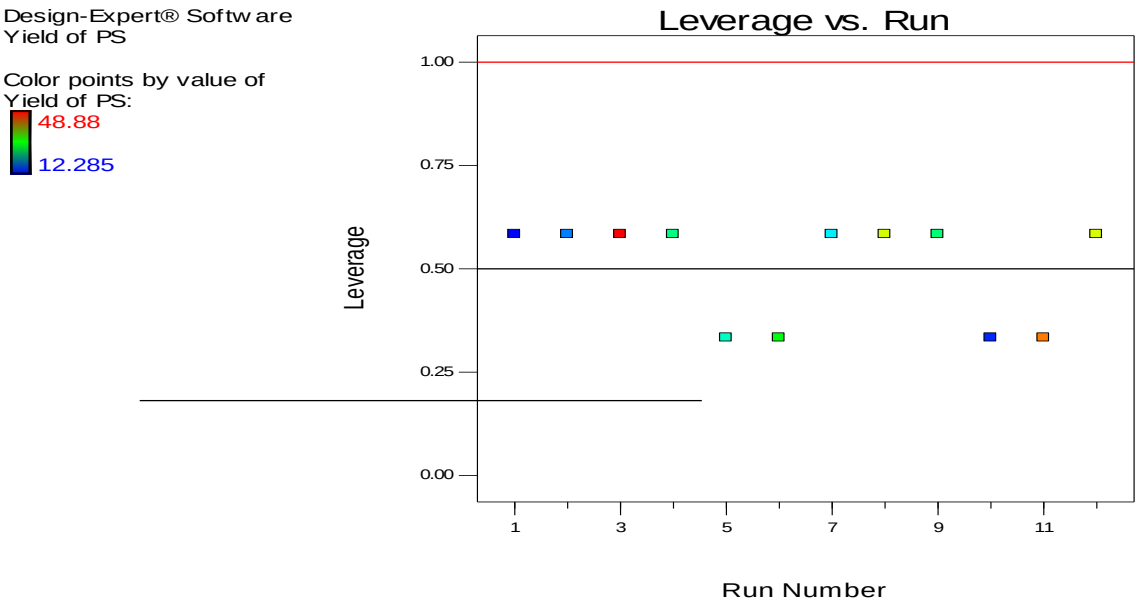

Figure D-2.7 – Plot of Leverage vs. Run

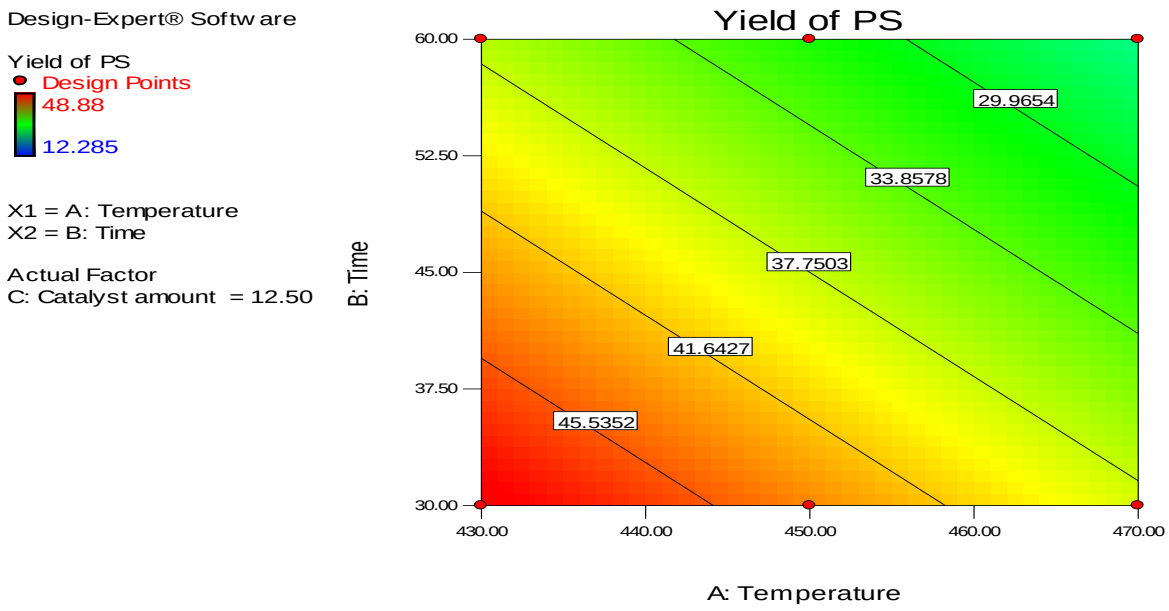

Figure D-2.8 - Model Graph for Percentage Yield

E. IR Absorption's table

Principal IR Absorption's for certain Functional groups

Functional group names	Absorption ranges(cm^{-1})	Type of vibration
Alkanes,	3000-2800	H-C-H Asymmetric and Symmetric stretch
	1500-1440	H-C-H Bend
Alkenes	3100-3000	C=C-H Asymmetric stretch
	1675-1600	C-C=C Symmetric stretch
Alkynes	3300-3200	≡C-H Stretch
	2200-2100	C≡C Stretch
Aromatic rings	3100-3000	C=C-H Asymmetric stretch
	1600-1580	C-C=C Symmetric stretch
	1500-1450	C-C=C Asymmetric stretch
Phenol s and alcohols	3600-3100	Hydrogen bonded O-H stretch
Carboxylic acids	3400-2400	Hydrogen bonded O-H stretch

	1730-1650	C=O Stretch
Ketones	1750-1625	C=O Stretch
Aldehydes	1750-1625	C=O Stretch
	2850-2800	C-H Stretch off C=O
	2750-2700	C-H Stretch off C=O
Esters	1755-1650	C-O Stretch
	1300-1000	(C-O Stretch)
Ethers	1300-1000	(C-O Stretch)
Amines-Primary	3500-3100(two peaks)	N-H Stretch
	1640-1560	N-H Bend
Amines-Secondary	3500-3100(one peak)	N-H Stretch
	1550-1450	N-H Bend
Nitriles	2300-2200	C≡N Stretch
Nitro-groups	1600-1500	N=O Stretch
	1400-1300	N=O Bend
Amides	3500-3100	N-H Stretch
	1670-1600	C=O Stretch
	1640-1550	N-H Bend

F. Catalyst before and after use

Prepared catalyst before use

Prepared catalyst after use