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# **Experimental study of catalysis in plastic pyrolysis**

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**Summary:**

In this study, thermal and catalytic pyrolysis of high-density polyethylene (HDPE), low-density polyethylene (LDPE), polypropylene (PP) and mixtures of LDPE/PP plastics were carried out in a batch autoclave reactor at 460 °C in a nitrogen atmosphere. The aim of this thesis is to study plastic waste pyrolysis using a catalyst to produce an environmentally friendly fuel (diesel). Before pyrolysis, thermogravimetric analysis (TGA) was used to study the thermal and catalytic degradation of the plastics at different heating rates (5, 10, 20, and 30 °C/min). The amount of PP was varied in the mixture to explore its role in the reaction. PP catalysed the mixtures of LDPE/PP as the ratio increases. In the presence of catalysts, CAT-2 reduced the degradation temperature of PP and LDPE and the mixtures while CAT-3 was suitable for all. The TGA results were validated in a batch scale reactor. GC-FID was used to analyse the resulting liquid oil/wax. Thermal cracking results showed that the liquid oil/wax fractions consist of a wide range of hydrocarbon distribution (C<sub>7</sub>-C<sub>40</sub>). High yields of gasoline (C<sub>7</sub>-C<sub>12</sub>) and diesel (C<sub>13</sub>-C<sub>20</sub>) fraction in the liquid products confirm that it is a desirable way for plastics recycling. Catalyst (CAT-2) enhanced cracking at lower temperatures and narrowed the hydrocarbon distribution in the liquid oil/wax to gasoline range fraction (C<sub>7</sub>-C<sub>40</sub>). Thermal cracking gave a wide distribution of diesel, gasoline and heavy hydrocarbon fractions while CAT-2 exhibited high selectivity for gasoline fractions. Unfortunately, the result from analysis of the catalytic liquid oil was not the expected result.

*The University College of Southeast Norway takes no responsibility for the results and conclusions in this student report.*

# Preface

This thesis is the “Experimental Study of Catalysis in Plastic Pyrolysis”. It has been written in fulfilment of the requirements for the award of Master degree (MSc.) in Process Technology, at the University College of Southeast Norway. The thesis was carried out under the supervision of Prof. Lars-Andre Tokheim and an external supervisor, Dr Siw Fredriksen.

The thesis focuses on recycling of plastic wastes to produce environmentally friendly fuel (diesel) and reduce the waste landfilled. Thermogravimetric analysis of the plastic wastes (HDPE, PP and LDPE); mixed and unmixed, was carried out to understand the degradation behaviour of the plastics. Thermal and catalytic pyrolysis of the wastes was conducted in an autoclave reactor to produce liquid fuel. Analysis of the liquid fuel shows the presence of diesel and gasoline fuel range hydrocarbons.

I must say I am satisfied with what I have done so far. I started the pyrolysis experiment on the 18<sup>th</sup> April 2017, approximately three weeks to the deadline for submission because of lateness in the provision of the equipment. It was indeed a great hard work to achieve this result and write the report before the deadline.

I would like to say thank you to my supervisors Prof. Lars-Andre Tokheim and Dr Siw Fredriksen (external supervisor). Your guidance, support and suggestions during this study are immeasurable.

This thesis would not have been a success without the staffs and management of Norner AS. I extend my gratitude to Kjørsti Lindvig (TGA expert), Kjetil Helgesen (GC expert), Charlotte Waag, Kristian-Manuel Villasis Duong, Knut Fosse, Tore Dreng and Kai Arne Sætre (Pyrolysis reactor expert). Thank you all for guidance and training on the use of all the equipment provided by Norner AS for this thesis.

I also want to thank my friends who were there to encourage me when it looked like nothing was going as planned. You all are awesome.

I extend my profound gratitude to every member of the Anene family, for their support and love. A big thank you to my grandmother Mrs Bridget Anene, Gabriel Emefienem Anene, Emeka Charles Anene, Sunday Ignatius Anene, Justin Nkwa Anene, my lovely mother; Philomena Ifezue, my mama in Norway; Nkem Anene; this list is an unending list. Without you all, I would not have made it this far. Words are not enough to express how happy I am to be born into this family. I love you all.

Last but not the least, I thank you God for you are the one that made all come to pass.

Porsgrunn, 15.5.2017

Azubuike Francis Anene

# Nomenclature

## Abbreviation

CSBR	Conical spouted bed reactor
C/F	Catalyst feed ratio
DTG	Derivative thermogravimetric curve
EU	European Union
EOP	End of pipe
FCC	Fluid catalytic cracking
GC	Gas chromatography
GC-FID	Gas chromatography- Flame ionization detector
GC-MS	Gas chromatography-mass spectrometry
HDPE	High density polyethylene
HHV	High heating value
IPW	Industrial plastic waste
LDPE	Low density polyethylene
LPG	Liquefied petroleum gas
MPW	Municipal plastic waste
MSW	Municipal solid waste
N <sub>2</sub>	Nitrogen
PE	Polyethylene
PET	Polyethylene terephthalate
PP	Polypropylene
PS	Polystyrene
PSW	Plastic solid waste
PTF	Plastic-to-fuel
PUF	Polyurethane foam
PVC	Polyvinyl chloride
RDF	Refuse derived fuel
SJA	Safe job analysis
SPI	Society of plastic industry
T <sub>F</sub>	Final degradation temperature
TGA	Thermogravimetric analysis

TG	Thermogravimetry
T <sub>onset</sub>	Onset temperature
T <sub>M</sub>	Maximum degradation temperature
USA	United States of America
WPO	Waste plastic oil
WTE	Waste-to-energy

## **Units**

%	Percentage
°C/min	Degree Celsius per minute
g	Gram
mg	Milligram
MPa	Megapascal
wt %	Weight percentage
vol%	Volume percentage
MJ/kg	Megajoule per kilogram
KJ/mol	Kilojoule per mole
Kmin <sup>-1</sup>	Kelvin per minute
Min	Minimum
Max	Maximum
mg/Kg	Milligram per kilogram
psi	Pounds per square inch
cSt	Centistokes
g/cm <sup>3</sup>	Gram per cubic centimetre
min	Minute
mm	Millimetre
μL	Microlitre

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# 1 Introduction

Plastics are non-biodegradable synthetic organic materials produced by polymerization [1-3]. They contain mainly carbon and hydrogen, same as hydrocarbon fuels such as diesel and petrol [2, 3]. They also contain compounds such as chlorine and nitrogen [4]. About 90% of plastic is produced from fossil fuel, meaning that about 6% of the world's global oil consumption is mainly by plastic [3].

Plastics are an essential part of the human lives and the global economy. The use of plastics has increased immensely over time as it serves as a key component for different sectors such as packaging, construction, transportation, electronics, healthcare, and automobile. Plastics are used in this sectors due to their durability, versatility [3], resistance to corrosion, light weight, excellent thermal and electrical insulation, and low production cost [5, 6]. However, these properties that describe its usefulness also makes it problematic when considering its end of life phase [7]. It was reported that the production of plastics from virgin petroleum feedstock has increased from 15 million tonnes; a value recorded in 1964 to 311 million tonnes in 2014 as shown in Figure 1.1. This value is expected to increase to 318 million tonnes by the year 2050 as plastics are gaining more interest for different purposes [3].

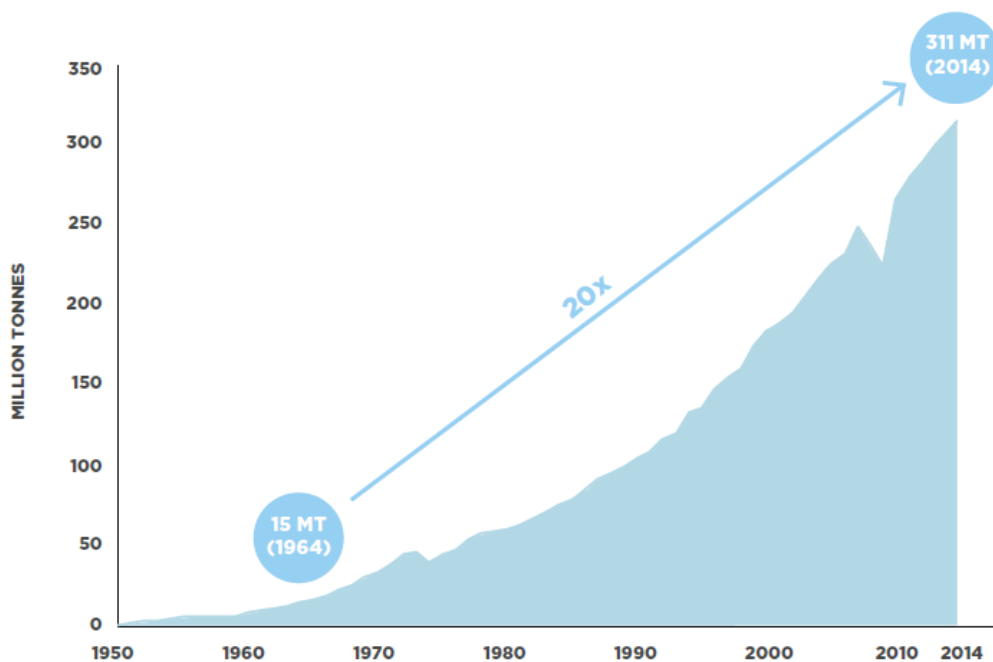


Figure 1.1: Global plastic production [3].

The usage of plastics as a packaging material; to keep food fresh, longer and reduce food waste, due to their barrier properties has increased the global volume of plastic for packaging from 17% to 25% resulting from a good plastic packaging market [3] and the growth in world population [6]. Researchers have speculated that with the current problem of plastic waste dumping into the ocean, the amount of plastic in the sea will be more than the fishes in the sea by the year 2050 [3]. Plastics waste disposed of in the sea is a significant threat to the health of

## 1 Introduction

aquatic lives, because they form a garbage patch and soup [8]. This plastics soup causes the entanglement of turtles, death of sea mammals and birds when they eat the plastic waste [7].

Research in Europe in 2012 showed that 25 million tonnes of plastic ended up in the waste stream. Another study in the United States (US), in the year 2013, showed that 33 million tonnes of plastic waste were generated [6]. On the analysis of municipal solid waste (MSW), which is made up of containers, plastics, aluminium cans, sewage and food wastes. Plastic was discovered to be the third largest generated waste compared to paper and food waste [9, 10].

About 50-70% of municipal plastic waste (MPW) is made up of packaging materials. These materials are produced from polyethylene (PE), polyvinyl chloride (PVC), polystyrene (PS) and polypropylene (PP) [8, 11]. PP, PE and, PS are the most commonly used of these plastics polymers as they are the most found in MPWs [8, 12-14]. PE makes up about 63% of total packaging waste and 69% of total plastic waste [8].

Plastic waste production was estimated to increase at a rate of 4% by 2016 due to their durability, light weight and low cost, which is a major contributor to increasing plastic production [15]. Plastic disposal is a major concern for the world. European statistic in 2015 showed that 38% of plastic waste was landfilled, 26% recycled, and 36% utilised for energy recovery [6]. Today, about 60% of plastic solid waste (PSW) produced around the world is discarded in landfills [8]. In another report by the European Commission in 2016, nearly 50% of plastic waste in the European Union (EU) was landfilled leading to increasing loss of raw materials and energy [7].

Plastics are non-biodegradable and remain in the environment for a long time, prompting the research of different management techniques including, disposal to landfill sites, reusing, recycling, and waste to energy (WTE) [12, 15]. Customary recycling techniques such as washing, grinding and sorting can only recycle 15-20% of all plastic waste [12, 15].

Landfilling and incineration of plastic waste is a non-sustainable end of pipe treatment (EOP) of plastic wastes. Moreover, they are the most common methods of waste management [16]. Landfilling was the most favourable method of waste treatment because of its simplicity and lack of awareness of the environmental impact. Landfilling causes water pollution, greenhouse gas emission and local inconvenience [17]. The use of incineration method reduces the amount of space occupied by landfilled waste and improved energy recovery. However, it emits greenhouse gases and toxic air pollutants [16, 17]. These processes are not acceptable anymore under the current internal law [18]. Directive 1999/31/EC on the landfill of waste amended in 2015 restricted the landfilling of waste. The amendment stated that member states should ensure that by the year 2030, the amount of landfilled waste should be reduced to 10% of the total MSW [19]. The commission made another Directive (DIRECTIVE 2008/98/EC) on waste and repealing certain Directives. Directive 2008/98/EC encourages member states to stop the use of incineration or disposal to landfill, and support recycling of wastes whenever possible [20].

Due to disadvantages of conventional recovery method, energy recovery technique became the alternative technique of plastic waste recycling [15]. This WTE or plastic-to-fuel (PTF) technology comprises of pyrolysis (thermal and catalytic), refuse derived fuel (RDF), gasification and plasma arc gasification [12, 15]. However, recycling of plastic waste is costly and challenging because of water contaminations and small separation which is labour intensive. Separation is necessary as plastic wastes are made up of different resin compound,

colour and transparency [6]. Therefore, recycling method should be chosen based on operating cost [21]. However, Pyrolysis of plastic wastes can be carried out without pre-sorting and complex pre-treatment [16].

Pyrolysis is a well-known method of plastics recycling [18]. Fossil fuels, coal, natural gas, and oil are the main sources of energy for transportation, which consumes about one-third of the world's energy. These energy sources are non-renewable, and they are major sources of environmental pollution, ocean acidification and greenhouse gases. The rate of consumption of these fuels is high. Researchers have investigated other alternative ways of producing energy to meet the world's energy demand. Some of the explored sources of energy are; wind, biomass, nuclear, hydroelectric energy [8], solar and geothermal energy [6]. Pyrolysis of plastic waste into valuable energy fuel can reduce the dependence on fossil fuels [6]. Research is ongoing in the production of fuel from plastic waste, which can address the challenges of increasing energy demand and plastic waste management. Conversion of plastics to fuel is a possible process, as they are a petrochemical product with high calorific value [6]. Fuels produced from plastics have fuel properties like fossil fuels and could be clean [8].

Pyrolysis of plastic waste has gained so much interest from researchers, as it is a way of minimising MPW [6], by converting to fuel, which can also help mitigate energy crisis [8]. The products of pyrolysis are liquid oil, solid residue, and gases [15]. Reactor type, plastic type and applied process parameters (temperature and residence time) determine the yield and quality of pyrolysis product [6, 9, 13]. Pyrolysis liquid oil can be used in boilers, turbines, furnaces, and in diesel engines without upgrading. Although, thermal pyrolysis has some limitations such as temperature dependency, the presence of impurities in the oil and residues, and difficulty in pyrolysis of PE and PP due to their crossed chain hydrocarbon. Catalytic pyrolysis was developed to overcome the limitations of thermal pyrolysis [15].

Pyrolysis is a green technology, as the gaseous by-product which possesses a substantial amount of calorific value is reused in the pyrolysis plant to compensate the energy requirement [6]. According to Kunwar *et al.*, “*techno-economic evaluation plays an important role in the commercial success of the plastics-to-fuel conversion*” [8]. Pyrolysis of wastes is an efficient waste management process, and it is cost effective, less pollution and lower capacity of landfill [6].

### 1.1 Aim of Study

The aim of this thesis is to experimentally study plastic waste pyrolysis (thermal and catalytic) to improve pyrolysis process using catalyst, to produce environmentally friendly fuel (Diesel).

This study reviews the progress of thermal and catalytic pyrolysis of plastic waste. Factors affecting pyrolysis processes such as temperature, retention time, feedstock composition and the use of catalysts were reviewed to have a good idea of pyrolysis. This investigation was carried out in two different steps. Firstly, the thermogravimetric analysis (TGA) of HDPE, LDPE, PP and mixtures of LDPE/PP was conducted. The non-isothermal method was used to determine the degradation temperature and ash content of various plastic wastes. Influence of catalysts on the thermogravimetric behaviour of the samples (single and mixed) was also studied.

Lastly, the results predicted by the TGA analysis was validated on a small-scale laboratory reactor. Pyrolysis of virgin HDPE, LDPE, PP and LDPE/PP mixtures were carried out in the

batch reactor in a nitrogen environment (carrier gas), which was characterised by short residence time and atmospheric pressure. Effect of catalyst on the quality and quantity of pyrolysis products was examined. Liquid oil/wax and gases were produced from single and mixed plastic wastes and were analysed using gas chromatography coupled with flame ionisation detector (GC-FID) to determine the hydrocarbon range distributions of the products.

### **1.2 Organisation of this thesis**

This thesis has been organised in 5 chapters. Chapter 1 is the introductory chapter; Chapter 2 contains an in-depth literature review of plastic pyrolysis and factors that influence the process. Chapter 3 is the experimental chapter. It includes the raw materials used in this research paper, the pyrolysis equipment, analytical equipment and their methods. In chapter 4, the results obtained from the TGA analysis; catalytic and thermal were presented and discussed. It presents the results and discussion of the thermal and catalytic pyrolysis. The hydrocarbon composition of the liquid oil/wax pyrolysis products is also in this chapter. Chapter 5 presents the conclusion and suggestion for further studies on the pyrolysis of plastic waste.

## 2 Literature review

Plastic waste conversion into liquid fuel requires feedstocks which are combustible and non-hazardous. Plastics wastes may have a different composition as some plastics contains additives, sulphur and other hazardous substances which are disastrous to humans and the environment [15, 22]. Plastics have very low moisture content compared to the water content of biomass [23].

The conversion temperature, the quality of the fuel produced, pretreatment requirement, the energy consumption by the recycling process chosen, the flue gas composition, and the potential corrosion of the equipment depends on the types of plastics [24].

There are different methods of plastics wastes management as stated briefly in chapter 1. However, this study focuses on the recycling of plastics (Virgin polymers) by pyrolysis (WTE). Researchers have studied the pyrolysis of plastic waste extensively in the absence of oxygen. The following subchapters give an in-depth review of the recycling of plastic waste to fuel (diesel) by pyrolysis process.

### 2.1 Types of plastics and uses

Plastics are divided into two main types [1, 24, 25];

1. Thermoplastics and
2. Thermosets polymers

#### 2.1.1 Thermoplastics

These are the types of plastic that can melt or soften by the application of heat, and remoulded into one plastic products. Examples of these are polyethylene, polypropylene, and polystyrene [1, 24-26]. Some examples of thermoplastics are shown in Figure 2.1.

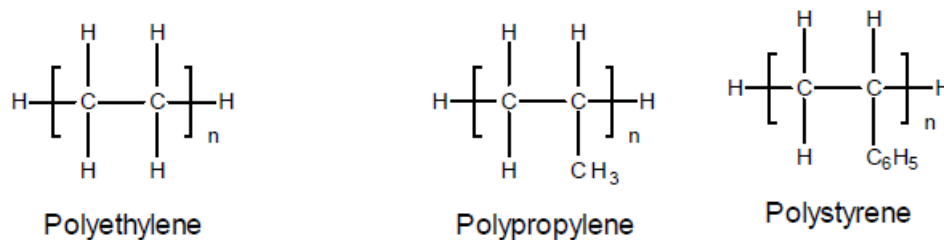


Figure 2.1: Types of thermoplastics [27]

#### 2.1.2 Thermosets

These are plastics that can only be shaped into a different product just once. Heat treatment of these plastics after solidification is not right as they char on the application of excess heat. Examples of thermosets are melamine formaldehyde, phenol formaldehyde and urea formaldehyde [1, 24, 25].

These plastic types, their uses and identification symbols are shown in Figure 2.2



Figure 2.2: Plastic types, identification symbols and packaging applications [3].

It can be deduced from Figure 2.2 that plastic cut across almost all our daily life activities. The identification symbols were made by the Society of Plastic Industry (SPI) [2] for easy sorting of plastic wastes.

## 2.2 Sources of plastic waste

Plastic wastes are divided into two main types: industrial plastic waste (IPW) and municipal plastic wastes (MPW)[4, 8, 10]. These wastes have different properties, qualities, and different management approach [10, 26].

### 2.2.1 Industrial plastic waste

IPW's are the waste product of plastic packaging, manufacturing and processing industries. Industrial plastic wastes are made up of wastes from spare parts of cars in the automotive industries (front grill, seat coverings, battery, and fan blades), electrical and electronic companies (Television screens, and cable sheaths), construction and demolition companies [25, 26]. Industrial plastic wastes are homogeneous and free of contaminants, making them useful for downscaling into lower-grade products [8, 12, 28, 29]. Industrial waste can be recycled easily by remoulding and pelletization because of their homogeneity [26, 30].

### 2.2.2 Municipal plastic waste

Municipal plastic wastes are collected as household wastes as they are a major component of MSW [12, 25]. Municipal plastic wastes are heterogeneous as they contain different materials, such as low-density polyethylene (LDPE), high-density polyethylene (HDPE) [13], polystyrene (PS), polyethylene terephthalate (PET), polypropylene (PP), and polyvinyl chloride (PVC) [8, 12, 28, 29]. MPW obtained from MSW are food containers, feed bags, carbonated drink bottles, electronic equipment, plumbing pipes, thermal insulation foams, wire, cable, vending cups and disposable cups [25].

Recycling of MPW involves separation of the plastics from other household wastes [26]. Mechanical separation is one of the main processes of separation of these wastes. This method is not so efficient as a low marketable fraction is obtained. Moreover, the sorting of waste at home is the most encouraged and efficient method for separation of plastic waste from MSW before disposal. Thermal cracking of plastics to hydrocarbons is the best method of recycling of MPW since it is made up of mixed resins [25, 26].

## 2.3 Pyrolysis

Pyrolysis is the degradation of long-chain polymer molecules into smaller molecules by intense heating and in the absence of oxygen [6, 30]. It is the thermal decomposition of polymers or substances in the presence of an inert gas (e.g. Nitrogen) [4]. Pyrolysis process can be described as low, medium and high-temperature pyrolysis depending on the temperature used for the decomposition of the plastic [18]. Pyrolysis process produces a broad range of product (gas and liquid hydrocarbon fuel) which can be used as fuel and sources of chemicals. Pyrolysis can be thermal or catalytic [4, 30]. The wide range of product distribution is a drawback of pyrolysis as it requires upgrading of the liquid hydrocarbon fuel before use [16]. Gases obtained with high heating value (HHV) during pyrolysis can be utilised in the process to reduce the energy input, thereby making it a self-sustained process [9]. The liquid production is enhanced by low-temperature pyrolysis, while high-temperature processes favour gas production [18]. Another product of pyrolysis is char, and the liquid product consists of naphthene's, aromatics, olefins and paraffin [4].

Pyrolysis of plastic waste produces raw materials (petrochemical compounds) for the manufacture of new plastics. Mixed and contaminated plastics can be used for this process. Pyrolysis process is an endothermic process, and it involves the breaking of bonds. The decomposition of polymers in pyrolysis occurs through the elimination of small molecules, depolymerization, or random cleavage [30].

## 2 Literature review

Polymers degradation depends on their chemical structure. The carbon-carbon bonds of the polymer are broken (degraded) during pyrolysis, due to the low thermal stability of tertiary carbon atom. PP is less stable than PE (LDPE and HDPE) because of the possession of tertiary carbon atom [30, 31]. Contaminants can influence mechanism of degradation of polymers. In thermal pyrolysis, the mechanism of degradation is described as free radicals, while in catalytic pyrolysis, it is ionic mechanism [30]. Onwudili et al. reported that co-pyrolysis of PS and PE influenced the conversion of PE by lowering its temperature. Higher oil yield and char was obtained compared to the single plastic pyrolysis [29].

Factors that affect pyrolysis process are mainly temperature, feed composition, type of reactors, type of fluidising gas, catalyst type, particle size, catalyst loading, and polymer-to-catalyst ratio. They affect plastic conversion to products, and the quality of the fuel obtained [6, 8, 30, 32]. For example, the addition of PS to the pyrolysis of PE and PP catalyses the process [8].

Many studies on the pyrolysis of plastic waste have been carried out. However, pure polymers (Virgin) and unmixed polymers are the most investigated [13, 30] with little emphasis on polymer blends [33].

### 2.3.1 Thermal pyrolysis

Thermal pyrolysis is the thermal degradation of plastics in the absence of oxygen/air [30]. It is an endothermic process that does not use catalyst [15]. This process involves heating of the polymers to high temperatures (350-900 °C), to break their macromolecules to smaller molecules [30]. The thermal cracking process can be of two types: first is pyrolysis at low temperatures to obtain more yield of waxes and reduced yield of oil and gases; secondly, pyrolysis at higher temperatures (e.g. 700 °C) to get a higher yield of gases and reduced yield of waxes and oil [34].

The products of thermal pyrolysis can be of low quality. The products are divided into liquid (oil), solid (ash /residue) and non-condensable gas (gases) fractions. The liquid fraction is made up of hydrocarbons in the range of C<sub>4</sub>-C<sub>12</sub> (gasoline), C<sub>12</sub>-C<sub>23</sub> (diesel), C<sub>10</sub>-C<sub>18</sub> (Kerosene) and C<sub>23</sub>-C<sub>40</sub> (motor oil). Temperature and residence time have an enormous impact on the products obtained [30].

Thermal pyrolysis involves the transfer of hydrogen from the polymer structure and the degradation of the carbon chain. Thermal degradation proceeds through four different mechanisms: initiation, propagation / free radical transfer, termination and β chain scission [35]. Thermal cracking is easier for the less stable polymer. PP degrade easily followed by LDPE and HDPE [30, 36, 37].

Thermal pyrolysis yield a wide range of hydrocarbon (C<sub>5</sub>-C<sub>80</sub>) due to its degradation mechanisms. Thermal pyrolysis product yields are of limited commercial value, which is one of the drawbacks of this method [30]. Thermal pyrolysis utilises huge amount of energy [34, 37]. The low quality of the liquid fractions is due to low octane number, the presence of impurities (Sulphur, nitrogen) and the presence of high solid residue [15]. Catalytic pyrolysis was proposed to improve the product yield and reduce cracking temperature [30, 37].



### 2.3.2 Catalytic pyrolysis

This process involves the use of a catalyst. Catalytic pyrolysis produces liquid oil of higher quality at lower residence time and temperature compared to thermal pyrolysis [15, 16, 38]. Catalytic pyrolysis follows two different decomposition mechanisms; thermal cracking, and catalytic cracking ( $\beta$  scission, desorption and carbenium ions adsorbed on the surface of the catalyst) [30]. Catalytic pyrolysis produces a narrower distribution of hydrocarbons with a high market value [34, 36].

Two types of catalyst; homogeneous and heterogeneous (alumina, zeolites, silica-alumina, FCC, mesostructured catalyst (e.g. MCM-41), and nanocrystalline zeolites (e.g. HZSM-5)) catalyst are used for pyrolysis of plastic wastes. Heterogeneous catalysts are more favourable because of ease of separation and recovery at the end of the reaction than homogeneous catalysts [16, 30]. Heterogeneous catalysts have more than one phase, and they are economically preferable [6].

Catalyst favours the yield of lighter hydrocarbons, gasoline products, and gases [8, 15]. It lowers the activation energy of plastic during pyrolysis, thereby lowering the energy requirement. The distribution of the products obtained depends on the type of polymer, their sources and structures [8, 36].

Several authors had reported different values of activation energy of polymers when they studied their kinetics. Aboulkas et al. reported the activation energy of HDPE as 238-247 kJ/mol, LDPE as 215-221 kJ/mol, and PP as 179 - 188 kJ/mol [39]. Yan et al. reported average apparent activation energy values obtained from analysis of virgin LDPE and PP as 413 kJ/mol and 362.6 kJ/mol respectively, while waste LDPE and PP have values of 253.7 kJ/mol and 241.9 kJ/mol, respectively [13]. However, Silvarrey and Phan reported the activation energy obtained from TGA analysis of MPW for HDPE as 375.59 kJ/mol, LDPE as 67.61 kJ/mol, and PP as 261.22 kJ/mol. They concluded that mechanism of decomposition of the polymers is complex because of the variation in the kinetic model and activation energy with conversion and heating rate [14].

Product distribution is controlled by the selection of appropriate catalyst. The properties of a catalyst such as surface area, pore size distribution, pore volume, pore structure, and the number of acid sites influence the performance of a catalyst. The selection of catalyst for a process depends on the feedstock (PP, LDPE, and HDPE) and the desired product [36]. The cracking efficiency of catalyst depends solely on the chemical and physical characteristics. Catalytic pyrolysis is advantageous over thermal pyrolysis [30].

Advantages of catalytic pyrolysis are degradation at a lower temperature (lower energy consumption), reduced costs, increased selectivity, faster-cracking reactions, smaller residence time, inhibiting the formation of undesirable products, increase product yield with higher value, and production of liquid products with a lower boiling point [30, 40].

Almeida et al. reported that the presence of contaminants and chemical changes that occur in the structure of the polymers could affect the decomposition process, however, most work has been done with pure polymers. Nevertheless, the catalyst can be deactivated in a process due to the formation of coke on the surface. In conclusion, catalyst affects the economy of a process because of replacement cost [30] and the quantity, since a significant amount is required for a continuous process [40].

## 2.4 Factors affecting pyrolysis

In plastic pyrolysis, process parameters determine product yield and composition. These parameters affect the products (liquid oil, gaseous and char) obtained during pyrolysis of plastic. The critical parameters that affect pyrolysis are temperature, type of reactors, residence time, catalyst, particle size, type of fluidising gas and its rate, pressure, and feedstock composition [6, 15, 29]. Some other factors affecting pyrolysis of plastic are catalyst loading and polymer to catalyst ratio which affects plastic conversion and fuel quality [8]. Some of these factors and their effects are described in the following subchapters.

### 2.4.1 Temperature

Temperature determines the quantity and quality of pyrolysis products, as it controls the cracking reaction of the polymers to yield liquid and gases. However, it has little effect on the quantity of char produced. High temperatures result in the cracking of C-C bonds to yield short carbon chain, whereas low temperature leads to the yield of long chain hydrocarbons [15].

The thermal decomposition of plastics is complex. Plastics have different thermal behaviour and reactivity, leading to the differences in the composition of the pyrolysis products of plastics [13]. TGA has been used by researchers to study the thermal degradation and kinetics of organic materials during pyrolysis [35]. It measures the change in mass of samples (e.g. Plastics) in a pyrolysis process as a function of temperature and time [6, 9, 12, 36, 41]. TGA analysis of samples is carried out in an inert atmosphere at a constant heating rate and increasing temperature [30]. The analyser produces two different types of graphs: thermogravimetric analysis (TGA) curve and the derivative thermogravimetric analysis curve (DTG). TG curve gives information on weight loss of a substance as a function of time and temperature, while the DTG curve provides information on the degradation step during the process which as shown by the number of peaks [6]. The results from TGA helps to plan, design, operate and have excellent control of pyrolysis process [41].

Sriraam et al. studied thermal and catalytic pyrolysis of PP, PE, PS and PUF. Thermal pyrolysis showed that all plastic samples degraded between the temperature range of 400 °C and 450 °C. However, PE degraded at a higher temperature compared to the others. In catalytic screening, Zeolite catalysts were more effective in reducing the degradation temperature of PE and PP, while spent FCC was very efficient for the degradation of PS and PUF (polyurethane foam) [36].

Yan et al. studied the thermal decomposition of LDPE and PP using TGA at different heating rates (10,20,30 and 50 °C/min). They found out that the optimum heating rate was 10 °C/min. The increase in heating rate increases the thermal degradation of polymers. At a heating rate of 10 °C/min, they observed that virgin PP degraded at a temperature range of 396-459 °C, with maximum degradation occurring at 441 °C. LDPE degradation took place at a higher temperature (415-474 °C). At 460 °C, maximum decomposition was attained. They pyrolysed PP and LDPE in a semi-batch reactor at 420 and 460 °C. The Higher liquid product was obtained from pyrolysis of PP (84.83 wt%) than LDPE (84.30 wt%). No significant difference was observed in the gas yield as LDPE gave 14.23 wt% while PP yield was 13.67 wt%. This high yield of gases was the effect of higher temperature, the shorter residence time of volatiles and atmospheric pressure [13].

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From the kinetic study of co-pyrolysis of rubber seed shell with HDPE carried out by Chin et al. The TG analysis showed that the thermal degradation of HDPE started at about 378-404 °C and the degradation completed at about 517 - 539 °C, at different heating rates (10 Kmin<sup>-1</sup> - 50 Kmin<sup>-1</sup>) [42]. Jung et al. reported that the decomposition of PE and PP occurred within the same temperature range of 400 - 500 °C from TGA analysis. However, it was stated that the decomposition of PP took place at a lower temperature (< 400 °C) compared to thermal degradation of PE. PP degraded at a faster rate than PE due to their carbon structure [31].

Marcilla et al. studied the catalytic pyrolysis behaviour of PE-PP mixtures using TGA. They discovered that the maximum thermal degradation temperature of single PP was 447 °C, while that of single HDPE was 467 °C. They concluded that the thermal degradation of LDPE occurred at a lower temperature compared to HDPE because of the instabilities in the tertiary carbon of the polymer. However, the mixture of both polymers overlapped during decomposition compared to the single polymers [33]. In another research by Marcilla et al. on thermal and catalytic pyrolysis of PE (HDPE and LDPE) over HZSM5 and HUSY zeolite catalysts. They discovered that the polymer was converted to liquid/wax (LDPE = 93.1 wt% and HDPE = 84.7 wt%), and gas (LDPE = 14.6 wt% and HDPE = 16.3 wt%) products at 550 °C, without any residue in the thermal pyrolysis process. Influence of both polymers was studied; they observed that both (LDPE and HDPE) are very similar. However, a convincing difference was seen in the 1-olefins present in the liquid oil obtained from LDPE and HDPE [43].

Onwudili et al. studied the effect of temperature on the degradation of virgin LDPE and PS in a closed batch autoclave reactor using N<sub>2</sub> at an initial pressure of 0.3 MPa. Effect of temperature (300-500 °C) and residence time (60 min) was the objective of their research. They observed that at 350 °C and pressure of 0.8 MPa, LDPE only melted to a white substance. Further increase in temperature to 400 °C, yielded 94.7 wt% viscous, whitish brown waxy substance. At 500 °C and a pressure of 4.3 MPa, the liquid yield was reduced to ~70 wt%. The conversion of oil started at about 410 °C, with maximum oil yield (89.5 wt%) and lesser gas yield (10.0 wt%) obtained at a temperature of 425 °C and pressure of 1.60 MPa. At 450 °C, oil production decreased due to increase in temperature causing more cracking of liquid oil (72.4 wt%) to produce more gas (25 wt%) and char (1.75 wt%) at a pressure of 2.45 MPa. At 425 °C, the liquid oil contained more of paraffin (44 wt%, C<sub>12</sub>-C<sub>18</sub>) followed by olefins (11.6 wt%), and a significant quantity of aromatics (9.5 wt%). The properties of oil (hydrocarbon range of C<sub>5</sub>-C<sub>30</sub>) produced at 450 °C are comparable to properties of diesel and gasoline fuels. The effect of temperature on pyrolysis of PS was investigated between 300 °C and 500 °C with experimental pressures between 0.31 MPa and 1.6 MPa. PS started degrading at about 350 °C. At 425 °C and pressure of 1.26 MPa, the oil yield of 97 wt% was obtained but decreased (80 wt%) as temperature increased to 450 °C, and pressure of 1.47 MPa. As the temperature increase to 500 °C and pressure of 1.6 MPa, the liquid yield dropped to 67 wt%, gas yield was about 2.5 wt%, and the rest was char. The oil consists mainly of aromatic compounds which increase as the temperature increases from 400 °C to 500 °C. They concluded that increase in temperature in PS degradation altered the component making up the aromatic products, while in LDPE, it favours the formation of an aromatic compound and decreases the proportion of alkanes. The pressure reported in the system was as a result of gas production which increased the internal pressure of the reactor during each experiment run [29].

Onwudili et al. also investigated the effect of temperature on the co-pyrolysis of LDPE (70%) and PS (30%) from 350 °C to 450 °C. They reported a higher gas production at 350 °C

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compared to the single plastics. At 425 °C, the amount of gas produced increased to 8.6 wt%, a liquid yield of 90.2 wt%, and a slight yield of char (1.2 wt%). At 450 °C, the amount of char and gas from the mixture was 3.5 wt% and 12.8 wt% respectively. However, the oil product from the mixture was higher than the amount produced by each plastic. The analysis of liquid oil yield at 450 °C and 500 °C shows an enormous amount of compounds comparable to those present in gasoline and diesel fuels [29]. Conclusively, the closed batch reactor can effectively degrade HDPE and PS to produce high-grade oil that can be used as an alternative fuel.

Jing et al. studied mild cracking of polyolefins to liquid hydrocarbon in a closed batch reactor. They studied the effect of temperature (370 °C to 420 °C) on the liquid product yield of HDPE, and mixture of HDPE and PP. They observed that at 370 °C, HDPE decomposed to produce liquid oil of about 98.01 wt% and gaseous product of 1.99 wt%. Liquid product yield decreased (88.25 wt%.) as the temperature increased to 420 °C. For the mixture of HDPE and PP, liquid product yield was 94.86 wt% at 370°C. A further temperature increase to 420 °C, decreases liquid product yield to 88.36 wt%. However, they reported that the presence of PP decreased the cracking temperature. The pressure in the system increased with increase in temperature from 0.87 MPa to 4.81 MPa for single HDPE, and 2.50 MPa to 5.31 MPa for the mixture (HDPE/PP) [28]. Shah et al. studied the thermal degradation of LDPE / PP mixture in a closed batch reactor at different temperatures and residence time. At 275 °C and residence time of 80 min, an oil yield of 48.6 % was obtained, and a maximum pressure of 18 psi was observed in the reactor [44].

Mastral et al. investigated the influence of temperature on the pyrolysis of HDPE in a fluidised bed reactor. It was discovered that at 650 °C, the main pyrolysis product was wax + oil (79.7 wt% yield). At 685 °C, gas of yield of 64.2 wt% was obtained. The maximum gas yield was obtained at 780 °C as shown in Figure 2.3. They concluded that influence of temperature on the pyrolysis product distribution is high. As shown in Figure 2.3, an increase in temperature caused an increase in gas composition, while wax + liquid oil yield decreased [45].

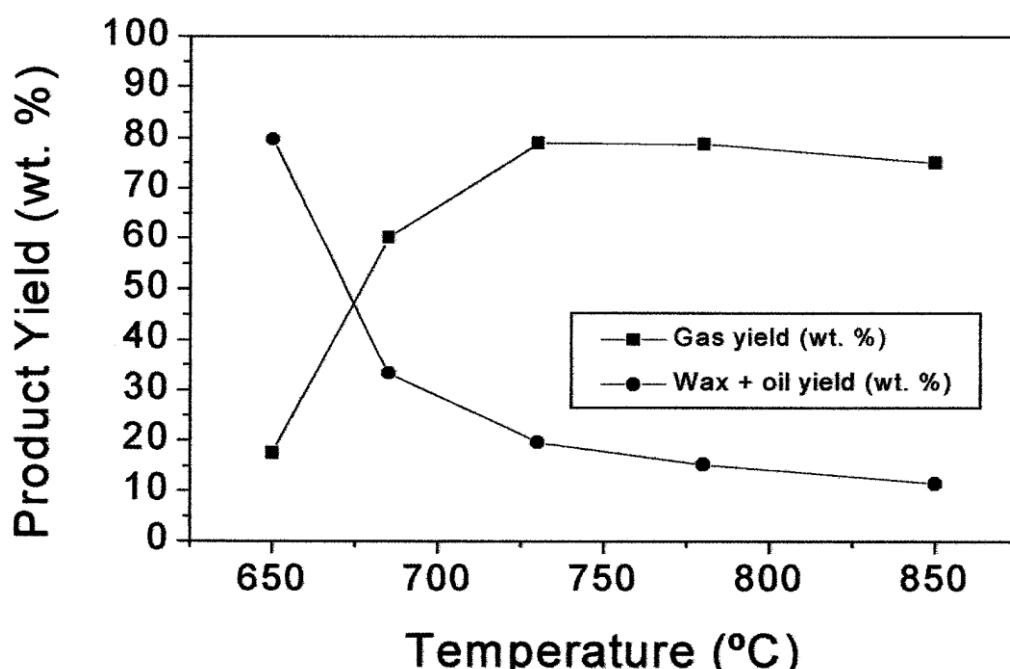


Figure 2.3: Effect of pyrolysis temperature on product distribution [45]

Temperature has been reported to have a greater influence on the product composition (liquid, gas, and char) for all plastics. Anuar et al. suggested from their review on pyrolysis of plastic waste that for liquid production, the process should be operated at a temperature range of 300 -500 °C. When gases and char are the desired product, operating temperature should be greater than 500 °C [6].

Williams et al. studied the analysis of products from the pyrolysis and liquefaction of single plastics and waste mixture, using a batch autoclave reactor at 500 °C, the residence time of 60 min and nitrogen (N<sub>2</sub>) as a carrier gas. The pressure of the N<sub>2</sub> was within the range of 0.2 MPa and a final pressure of 10 MPa. The final reactor pressure recorded by the gauge was 18 MPa. As shown in Table 2.1, thermal pyrolysis of PE and PP (virgin plastic) at 500 °C gave a high yield of liquid fraction (oil) and no char was formed, while PS gave a higher yield of residue (27 wt%). PP gave a higher yield of oil (95 wt%) because of its structure, followed by PE (93 wt%), while PS gave a lower oil yield of 71 wt% [46].

Table 2.1: Product yield from the pyrolysis of PE, PS and PP under nitrogen atmosphere [46]

Plastic	Oil (wt%)	Gas (wt%)	Residue (wt%)
PE	93	7	0
PP	95	5	0
PS	71	2	27

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J. Zeaiter studied the pyrolysis of waste shampoo bottles (HDPE) at 450 - 470 °C, using a Horizontal Carbolite Furnace and a residence time of 45 minutes. N<sub>2</sub> was used to maintain the pressure of the reactor at approximately 0.3 bar. It was observed that the liquid wax obtained was about 78.7 wt%, while the gas and solid yield was 17.8 wt% and 3.5 wt% respectively. The authors analysed the hydrocarbon content of the oil using gas chromatography-mass spectrometer (GC-MS). It was observed that the liquid wax obtained has a higher content of olefins (C<sub>9</sub>-C<sub>19</sub> = 47.2 %) and a lower yield of paraffins (C<sub>13</sub>-C<sub>22</sub> = 30.2%, C<sub>5</sub>-C<sub>12</sub> of 8.1% and C<sub>23+</sub> = 10.9%) [47]. Ciliz et al. studied the pyrolysis of PP and PE mixture using a Gray-kling Assay at a temperature of 600 °C. They reported that the formation of C<sub>3</sub>-C<sub>4</sub> fraction increased with the increase of PP in the mixture [18].

Ahmad et al. studied the effect of temperature on pyrolysis yield of PP and HDPE in a steel microreactor at a temperature range of 250 - 400 °C. They observed that the liquid product from pyrolysis of HDPE was about 98.12%. The liquid yield decreased to 80.88%, the gas yield of 17.24%, and residue of 1.88% at 350 °C. PP had a total conversion of 98.66 % at 300 °C; producing a liquid of about 69.82 %, gas of 28.84 % and residue of 1.34 %. They observed from the GC analysis that the liquid product obtained from HDPE pyrolysis consists of diesel and gasoline range hydrocarbons (C<sub>6</sub> - C<sub>16</sub>), with the diesel range comprising of about 30.8 % (C<sub>13</sub>-C<sub>16</sub>) of the total hydrocarbon yield. PP was also rich in diesel range hydrocarbon; containing about 33.06 % (C<sub>13</sub> - C<sub>16</sub>). They concluded that liquid produce of both polymers could be used as an alternative fuel since they have fuel like properties [5].

### 2.4.2 Feedstock composition

Several papers have been written and published on pyrolysis of plastics. Only a few utilised MPW as their feedstocks. Syamsiro et al. studied fuel from plastic wastes in sequential pyrolysis and the catalytic reforming reactor (batch: two stage reactor). They investigated the effect of feedstock on catalytic (Y-zeolite) pyrolysis of polyethylene bag (PE bag 2) with crushing and washing, (PE bag 1), without crushing and washing, and HDPE (washed and crushed) from MPW at 450 °C [38].

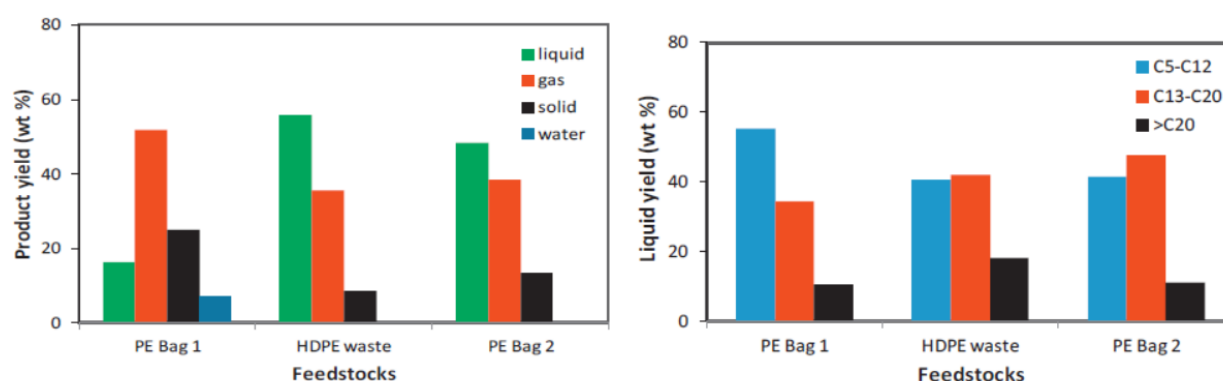


Figure 2.4: Effect of different feedstocks on (a) product yields; and (b) Liquid fraction combination [38]

Figure 2.4 (a) shows that PE bag 1 produced water and solid residue because of the presence of impurities. The impurities catalysed the process, leading to the formation of higher gaseous products. HDPE produced the lowest residue and highest liquid oil fraction. The structure of

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HDPE made it difficult for it to crack to lighter hydrocarbons. The liquid oil produced was classified into three groups; the gasoline ( $C_5 - C_{12}$ ), diesel ( $C_{13}-C_{20}$ ), and heavy oil ( $> C_{20}$ ) fractions, as shown in Figure 2.4 (b). PE bag 2 produced higher diesel fraction than HDPE, and PE bag 1 because of the feedstock composition [38].

Table 2.2: Properties of MPW liquid oil produced [38].

Properties	Units	PE bag 1	HDPE waste	PE bag 2	Test method
Density @ 15°C	g/Cm <sup>3</sup>	0.8544	0.7991	0.824	ASTM D1298
Kinematic viscosity	cSt	1.739	2.319	1.838	ASTM D445
Flash point	°C	<10	<10	<10	ASTMD 93
Pour point	°C	24	27	24	ASTMD 97
Water content	% Vol	0.1	0.5	Trace	ASTMD 95
Heating value	MJ/kg	41.45	42.82	46.67	ASTMD 240

They compared the properties of the liquid oil fraction obtained in their study with the properties of commercial diesel fuel (Indonesian government regulation standard) as shown in Table 2.2 and Table 2.3.

Table 2.3: Properties of commercial diesel fuels according to Indonesian Regulation [38].

Properties	Units	Diesel 48 (solar)	Diesel (Pertamina Dex)
Cetane Number		48	51
Density @ 15°C	g/cm <sup>3</sup>	0.815-0.870	0.820-0.860
Kinematic Viscosity @ 40°C	cSt	2.0-5.0	2.0-4.5
Flash Point	°C	min 60	min 55
Pour Point	°C	max 18	max 18
Water Content	mg/kg	max 500	max 500
Sulphur Content	wt%	max 0.35	max 0.05
Ash Content	wt%	max 0.01	max 0.01

From Table 2.2 and Table 2.3, the kinematic viscosity of the MPW was lower than that of commercial diesel fuels for PE bag 2 and PE bag 1. The density of MPW liquid oil is acceptable for its usage as an alternative to commercial diesel. The flash point of commercial diesel was higher than those of MPW liquid oil. A lower flash point from combustion point of view is not good because of storage and transportation of the fuel. The higher water content of MPW liquid oil will affect the performance of the diesel engine when used [38]. Lee Kyong Hwan reported

the effect of mixing two plastics during pyrolysis in a semi stirred tank reactor. HDPE and PS were the plastic polymers studied at 400 °C and in the presence of FCC catalyst. The pressure in the system was not stated [48].

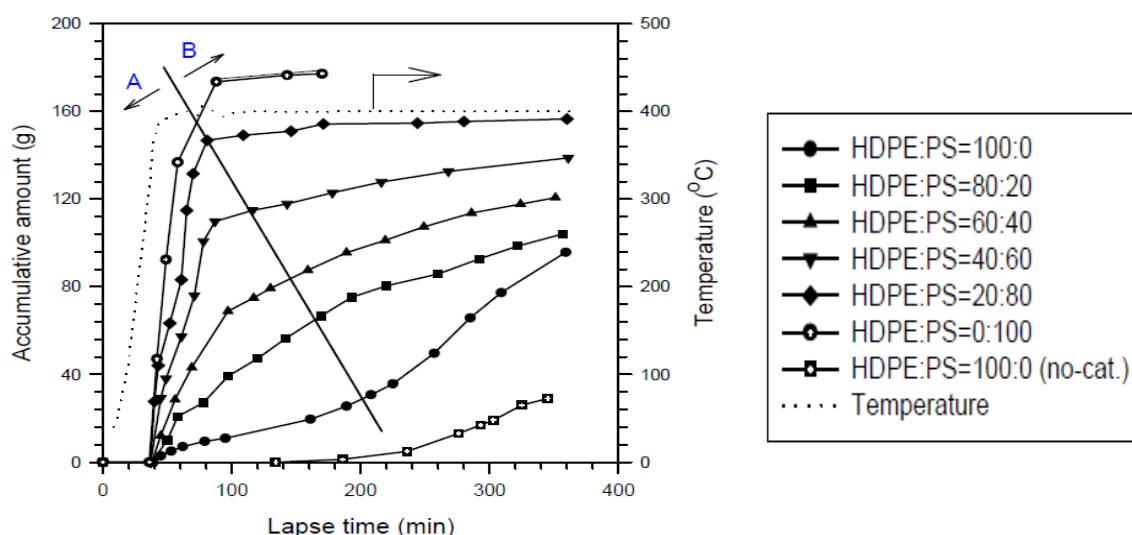


Figure 2.5: Liquid products distribution for catalytic distribution of HDPE and PS mixture [48]

Figure 2.5 shows the cumulative amount of liquid produced by different proportions of HDPE/PS mixture as a function of time. The liquid product increased with an increase in the proportions of HDPE against PS. The pyrolysis of PS gives a higher yield of liquid product. So, when its content in the mixture increases, the liquid products distribution increases. However, the liquid contains more aromatic components because of the benzene-ring structure of PS [48].

### 2.4.3 Type of reactors

The type of reactor used for the pyrolysis of a polymer influences the final pyrolysis product. For every pyrolysis experiment, the type of reactor used is necessary for efficient heat transfer, mixing of catalyst and plastic, and the quality of the final product [6]. Some of the commonly used reactors are discussed below.

#### 2.4.3.1 Batch and semi-batch reactor:

Most researchers used batch and semi-batch reactors for thermal and catalytic pyrolysis of plastic waste, as the process parameters are easily controlled [49]. Batch reactors have no inflow and outflow when the experiment is being carried out. The advantage of the batch reactor is the achievement of high conversion of the reactant to products when left in the reactor for a longer time. However, batch reactor involves high labour costs, the inconsistency of product from batch to batch, and cannot be operated on a large scale [6].



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Semi-batch reactor is like a batch reactor regarding labour cost and small scale operability. However, it is more flexible than batch reactor as it allows the addition of reactant and removal of product simultaneously [6].

Researchers prefer batch and semi-batch reactor for laboratory scale experiment because it is simple to design and easy to control the process parameters [6, 32]. A batch reactor operates at a temperature range of 300 - 800 °C, for both catalytic and thermal pyrolysis [6]. The catalytic process is carried out by mixing plastic and catalyst at a given ratio in the reactor to improve product yield and selectivity [6, 49]. This process has a propensity to form a residue on the surface of the catalyst, which reduces the effectiveness of the catalyst and it is hard to regenerate [6].

The batch reactor was used to study the pyrolysis of PP and HDPE (thermal and with catalyst) at 380 °C and 430 °C. It was reported that the pyrolysis liquid oil yield from thermal pyrolysis was higher than the catalytic pyrolysis liquid oil yield. However, some catalyst (silica-alumina SA-2) could produce more liquid oil than thermal pyrolysis. Batch and semi-batch reactors are the best for thermal pyrolysis when liquid oil is the desired product, but not suitable for catalytic pyrolysis because of the high cost of replacement of catalyst [6].

Seo et al. investigated the catalytic degradation of HDPE in a batch reactor at 450 °C. A liquid yield of 84%, coke yield of 3%, and gas yield of 13% was obtained thermally. They observed a higher percentage of C<sub>6</sub>-C<sub>12</sub> (56.55%) and a lower proportion of C<sub>13</sub>-C<sub>23</sub> (37.79 %) hydrocarbon [50].

Yan et al. studied the thermal cracking of virgin and waste plastics PP and LDPE in a semi-batch reactor, under atmospheric pressure and a temperature range of 420 °C and 460 °C [13].

Table 2.4: Thermal pyrolysis Yields of virgin PP and LDPE at 460 °C [13].

Plastic (virgin)	Pyrolysis yield (wt%)			Carbon distribution (at 460 °C)	
	Oil	Gas	residue	Gasoline	Diesel
PP	84.83	13.67	1.50	C <sub>6</sub> -C <sub>12</sub> (58 wt%)	C <sub>13</sub> -C <sub>22</sub> (36 wt%)
LDPE	84.30	14.23	1.47	C <sub>6</sub> -C <sub>12</sub> (21.30 wt%)	C <sub>13</sub> -C <sub>22</sub> (67.76 wt%)

As shown in Table 2.4, the yield of residue in LDPE was 1.47 wt%, lower than the yield of the residue by PP (1.5 wt%). The oil yield of both plastics (PP and LDPE) was almost the same, no significant difference observed. However, a lesser gas yield was obtained from cracking of PP (13.67 wt%) compared to cracking of LDPE (14.23 wt%). The analysis of the liquid oil yield at 460 °C, showed that the oil fraction from the pyrolysis of PP has a lower diesel carbon range distribution than LDPE as shown in Table 2.4. They reported that the shorter residence time and atmospheric pressure affects products distribution. However, the residence time was not stated [13].

### 2.4.3.2 Conical spouted bed reactor (CSBR)

Researchers proposed CSBR because of de-fluidization caused by molten plastics in fluidised bed reactor. CSBR ensures proper mixing and reduces the risk of agglomeration of particles in

the reactor. CSBR has a lower pressure drop, and it operates with a short residence time. These are the advantages of CSBR over other fluidised bed reactors. The schematic and dimensions of a CSBR are shown in Figure 2.6 [49].

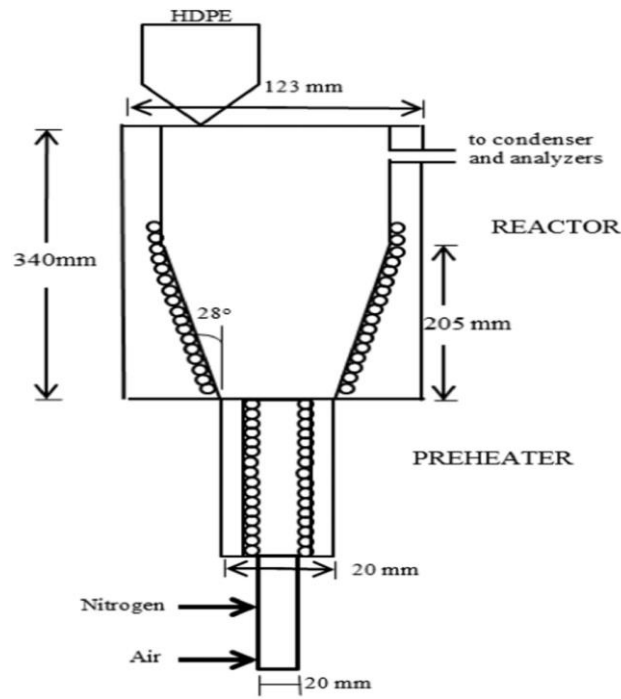


Figure 2.6: Dimension of the conical spouted bed reactor (CSBR) [49]

Some of the challenges of CSBR are catalyst entrainment, catalyst feeding and collection of products. The study on wax production and characterization from LDPE, PP and HDPE pyrolysis at 450 °C - 600 °C using CSBR, showed that HDPE and LDPE yielded 80 wt% wax, while PP produced 92 wt% wax at a lower temperature. It was observed that CSBR handled sticky solid very well compared to fluidised bed reactor. As temperature increases, the amount of wax produced decreases, producing more liquid oil and gases because CSBR was designed specifically for low-temperature pyrolysis to obtain wax [6]. Waxes produced using CSBR at lower temperature were rich in paraffin, while the olefins content increased as temperature increases. Fluid catalytic cracking unit (FCC) can be used to upgrade the wax to commercial hydrocarbon fractions, naphtha, and gasoline [49].

### 2.4.3.3 Fluidised bed reactor

Fluidised bed reactor is a continuous pyrolysis process, that does not require frequent material charging, and it is less labour-intensive compared to a batch reactor. Fluidised bed has excellent mixing properties and improve heat transfer from the reactor to the polymer. The catalyst used can be replaced with regenerated catalyst without stopping the process. However, de-fluidization can occur in the process when melted plastic stick on the fluidised bed [49]. From an economic point of view, fluidised bed reactor is the most acceptable reactor for large-scale operation [6].

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Jung et al. investigated the pyrolysis of a fraction of waste Polypropylene and Polyethylene for the recovery of BTX (benzene, toluene and xylene) aromatics using a fluidising bed. Temperature ramping between 660 °C to 750 °C was chosen to achieve a higher yield of BTX and the pressure in the system was controlled by burning the excess gases in the stack. Maximum oil yield (61 wt%) for PE was obtained at 660 °C and a gas yield of 36.6 wt%. On the other hand, thermal pyrolysis of PP at 668 °C, maximum oil yield of 43.1 wt% and gas yield of 54.4 wt% was obtained. They reported that as temperature increases, the amount of gas produced by PP increases due to easier degradation of PP and their intramolecular radical transfer. They concluded that the gas produced can be used in a pyrolysis plant as a heating source because of its high heating value (50 MJ/kg) [31].

Fluidised bed reactor (Figure 2.7) is used for the pyrolysis of plastics because of its efficient heat and mass transfer, shorter residence time and similar products. Anuar et al. reported a study on the catalytic degradation of HDPE and PP in a fluidised bed using silica-alumina. They stated that PP produced 87 wt% liquid while HDPE produced 85 wt% liquid at 500 °C. They concluded that fluidised bed reactor is the best reactor for catalytic pyrolysis of plastic waste since the catalyst can be reused and regenerated. Fluidised bed reactor is an economically feasible pyrolysis process. However, some of its drawbacks should be considered [6, 49]. It is hard to avoid secondary reactions in a fluidised bed [43].

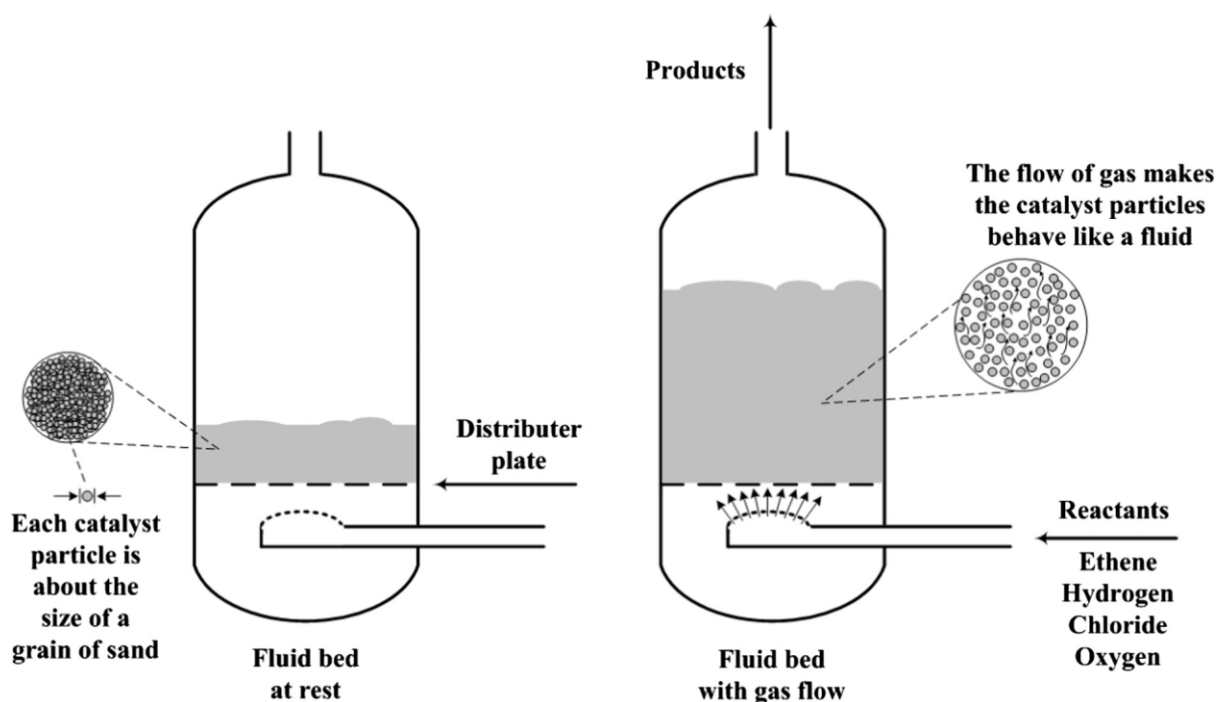


Figure 2.7: Fluidised bed reactor [6]

Other reactors used for pyrolysis of plastic waste are a fixed-bed reactor, rotary kiln reactors and their systems, and tubular reactors [51].

### 2.4.4 Residence time

Residence time is the amount of time the plastic is in contact with the hot surface of the reactor [2]. It is the average amount of time a substance spends in a reactor [6]. In plastic pyrolysis, it is the period taken for the plastic, which was fed into the reactor to start melting until the products are removed [2]. Longer residence time favours the conversion of primary products to the formation of stable thermal products (non-condensable gases and light molecular weight hydrocarbons) in the reactor [8], as a result of secondary cracking reactions of the primary products in the hot zone [29].

Mastral et al. investigated the influence of residence time on the pyrolysis of HDPE in a fluidised bed reactor. They discovered that at a residence time of 1.46 s and temperature of 650 °C, the highest gas yield was obtained (31.5 wt%). The influence of residence time was great as the pyrolysis temperature increases. However, at 685 °C and above, there was no significant influence of the residence time on the gas composition obtained as shown in Figure 2.8. Moreover, fractions of C<sub>1</sub> and C<sub>2</sub> increases while C<sub>3</sub> - C<sub>5</sub> fractions decrease as residence time increases. Conclusively, residence time influences the product distribution and the gas composition [45]. Scott et al. stated in their investigation of Fast pyrolysis of plastic waste that the longer the residence time, the lower the temperature [11]. Residence time is vital as it influences the distribution of the products and becomes more important as temperature increases [45].

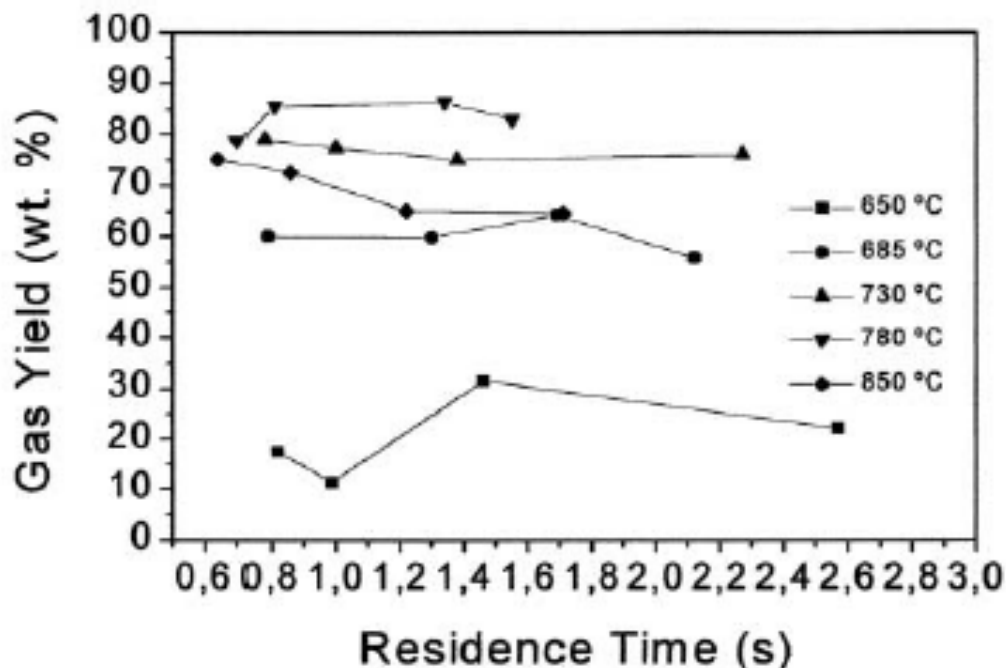


Figure 2.8: Effect of residence time on pyrolysis gas yield [45].

Onwudili et al. studied the effect of residence time and temperature on the composition of products from the pyrolysis of PE and PS. They found that LDPE was totally converted to 91.1 wt% liquid oil, the gas yield of 8.7 wt% at zero residence time, and no char formation at 450

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°C. At 60 min, they observed that the oil yield (72.4 wt%) reduced while the gaseous (26 wt%) and char (1.75 wt%) yield increased. At 120 min, more char and gas was the major product, as a result of secondary reaction (isomerization, aromatization, and hydrogenation/dehydrogenation reactions) which took place because of longer residence time, consuming some oil and favouring the yield of gases and char. The pressure in the reactor at the end of the reaction was in the range of 0.8 - 4.3 MPa. The effect of residence time on pyrolysis of PS was studied at 400 °C from zero to 120 min and experimental pressures from 0.76 to 1.34MPa respectively. The char produced (3.4 wt%) increased as residence time increases to 120 min, 95 wt% liquid was obtained, and gas production was between 0.6 to 1 wt%. The temperature and residence time could be varied or by blending products obtained at different reaction conditions to obtain high-quality fuel fractions [29].

Catalyst has also been used to lower the residence time and temperature of pyrolysis processes, making the overall process economically feasible as it gives the same yield with thermal pyrolysis at lower temperature and residence time [15].

Jing et al. reported the effect of residence time on the degradation of HDPE and HDPE/PP mixture in a batch reactor [28].

Table 2.5: Mild cracking result of HDPE/PP mixture and HDPE [28].

Polymer	Temperature / residence time (°C/min)	Gage pressure (MPa)	Liquid yield (wt%)
HDPE	370/60	0.87	98.11
	390/60	1.58	95.64
	410/20	2.31	94.97
	410/60	3.17	93.40
	420/40	3.87	92.58
	420/60	4.29	90.89
60/40 HDPE / PP	370/60	2.50	94.86
	390/20	3.03	94.34
	390/60	3.61	93.47
	400/20	3.82	92.92
	400/60	4.18	91.62
	420/0	4.13	92.65
	420/60	5.31	88.36

As shown in Table 2.5, HDPE gave a liquid yield of 98.11 wt% at 370 °C and a residence time of 60 min. As temperature increased to 420 °C and residence time of 40 min, the liquid yield decreased to 92.58 wt%. The yield decreased further as the residence time rose to 60 min. The liquid yield of HDPE/PP mixture followed the same trend; as residence time increases liquid

yield decreases. The pressure in the reactor increased with increase in residence time and temperature. They concluded that residence time is an important factor to consider in thermal degradation of plastic wastes and that a longer residence time favours the production of gases. PP catalyses the mixture of HDPE/PP; thereby reducing the cracking temperature and the mixture of HDPE/PP enhances intermolecular hydrogen transfer [28].

### 2.4.5 Catalyst

Catalysts are mainly applied in industrial processes and in research, to optimise product distribution and improve selectivity. A catalyst speeds up a chemical reaction in a process but remains unchanged close to the end of the process. It lowers the activation energy of a process and speeds up the reaction thereby increasing the reaction rate. Catalytic degradation of plastics is important as it helps obtain the desired product which is of high commercial value such as fuel (gasoline, diesel) and hydrocarbons of low molecular weight (olefins:  $C_2-C_4$ ) which are highly utilised in the petrochemical industry [6].

The main aim of application of a catalyst to a process in pyrolysis of plastic to fuel is to refine the hydrocarbon distribution, to obtain liquid pyrolysis yield of similar properties to the conventional fuel such as diesel and gasoline [6]. A catalyst increases the rate of cracking reactions that favour the yield of gases and reduces liquid yield. The use of catalyst lowers process residence time and temperature [15].

The use of catalyst improves the quality of liquid oil, as it shortens the chain length of the polymer and reduces the boiling point of the products (PE has a carbon length of  $C_1 - C_{80}$ ) [2, 15]. From an economic viewpoint, catalyst help saves energy as it reduces the cost of heat required to heat up a process, thereby saving the industry some costs spent on energy [6]. The main types of catalysts used for pyrolysis of plastic waste are described below;

#### 2.4.5.1 Zeolite catalysts:

These are crystalline aluminosilicate catalyst with open pores and ion exchange potential. It has a three-dimensional framework, where oxygen atoms link the tetrahedral sides. Different types of zeolite catalysts have different ratios of  $SiO_2/Al_2O_3$  which determines its reactivity and product selectivity [6, 15]. Zeolites have been reported to be efficient in improving the quality of the products obtained during pyrolysis of polymers [30]. The increase in gas and a decrease in liquid oil production is obtained using zeolite catalysts [15].

Pinto et al. selected zeolite catalysts in their study on the effect of a catalyst on pyrolysis of plastic waste (PE, PP and PS) because it favours the transfer of hydrogen from the carbon chains due to its large acid centres. The experiment was carried out in an autoclave reactor at a pressure of 3,3 MPa, temperature of 415 °C and residence time of 20 mins. Zeolite catalysts favour the formation of quality products. They also found out that it has an excellent selectivity for the desired product. However, it enhanced the formation of gaseous products [52]. The use of zeolites catalyst has been found to be efficient in the degradation of PE [40] and PP [53]. Zeolite catalysts produce cleaner fuels (lower Sulphur in diesel and gasoline) and lubricants with enhanced performance [53]. Their textural properties and acid sites favour hydrogen transfer which makes them a good candidate for conversion of plastics waste to gases at relatively low temperature [30].

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Artetxe et al. studied the cracking of HDPE waxes on HZSM-5 catalyst of different acidity in a conical spouted bed reactor (CSBR), using three different zeolite catalysts and a pyrolysis temperature of 500 °C. Table 2.6 shows the properties of the gasoline fractions obtained using zeolites catalyst compared to EU fuel standard. The acidity strength of the catalyst decreases with increase in the ratio of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>. The catalyst with highest acidity ratio (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of 30) gave a higher yield of light olefins and lower yield of C<sub>12</sub>-C<sub>20</sub> fractions compared to the lowest acidic catalyst (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of 280) during the cracking of liquid wax (Table 2.6) [54]. The amount of olefin produced exceeded the standard olefin established by the EU. The catalyst with the highest acidity produced fractions with highest octane number (lower than that of commercial gasoline), aromatics, benzene and lowest olefin. However, the product was sulphur free, which makes it possible to be blended with refinery streams to achieve EU standard [6, 54].

Table 2.6: Properties of gasoline fraction obtained using HZSM-5 zeolites catalyst with different SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> [54]

SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	Octane number	Olefins (vol%)	Aromatics (vol %)	Benzene (vol%)
30	94.1	33.1	43.3	4.2
80	86.7	61.2	13.5	1.3
280	85.9	68.9	6.9	0.46
Required	95	<18	<35	<1

Another zeolite catalyst, HUSY was studied and compared to HZSM5 by Marcilla et al. using HDPE and LDPE in a batch reactor. Table 2.7 shows the result of the quantity of liquid oil and gas obtained from their study at a pyrolysis temperature of 550 °C [43].

Table 2.7: Pyrolysis yield of thermal and catalytic pyrolysis [43]

Yield (mg/100 mg of PE)	LDPE	HDPE	LDPE-HZSM5	HDPE-HZSM5	LDPE-HUSY	HDPE-HUSY
Gases	14.6	16.3	70.7	72.6	34.5	39.5
Liquids/waxes	93.1	84.7	18.3	17.3	61.6	41.0
Coke	-	-	0.5	0.7	1.9	1.9

The gas yield was high when HZSM5 was used on LDPE (70.7 %) and HDPE (72.6 %), while HUSY catalyst gave more liquid yield (LDPE = 61.6 %, HDPE 41.0%). HUSY produced more liquid than HZSM-5 because it possesses weak acid sites, whereas HZSM-5 has strong acid sites and weak acid sites. The liquid yield obtained in the thermal pyrolysis process was higher (LDPE =93.1 % and HDPE = 84.7 %) than the catalytic process. Coke formation was

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significant in HUSY catalyst (HDPE = 0.7 wt%) than HZSM-5 catalyst (HDPE = 1.9 wt%). Their result showed that different zeolite catalysts have different selectivity because of their acidity and pore sizes [43].

Sriraam et al. validated the result obtained from TGA in a batch reactor using a Y-zeolite catalyst. Y-zeolite improved the hydrocarbon distribution and lowered the cracking temperature. They concluded from their finding that the diesel (comparable to ultra low sulphur diesel) and gasoline fuel properties obtained were of better quality compared to that obtained by thermal pyrolysis [36].

Seo et al.[50] investigated the effect of catalyst (ZSM-5) on the degradation of HDPE at 450 °C in a batch reactor. A lower liquid yield of 35 wt% and gas yield of 63.5 wt% was obtained. The liquid yield is higher than the value obtained by Marcilla et al.[43] but lower gas yield. GC-MS analysis gave carbon distribution of 99.92% of C<sub>6</sub> - C<sub>12</sub> and 0.08% of C<sub>13</sub> - C<sub>23</sub>. They also investigated modernite (pellet) and zeolite-Y(pellet) catalyst effect on the degradation of HDPE. The former gave a liquid yield of 78.50 wt%, a gas yield of 18.50 wt%, and coke formation of about 3.00%. The hydrocarbon content of the liquid oil consisted of 71.06 wt% of C<sub>6</sub> - C<sub>12</sub> and 28.67 wt% of C<sub>13</sub>-C<sub>23</sub>. The later (Zeolite-Y), yielded liquid oil of 81.0 wt%, gas (17.50 wt%), and coke (1.50 wt%). The analysis of the liquid oil shows that it consists of mostly C<sub>6</sub>-C<sub>12</sub> (86.07wt%) and C<sub>13</sub>-C<sub>23</sub> (11.59 wt%) hydrocarbons.[50].

Miskolczi et al. studied fuels by waste plastics (a mixture of LDPE and HDPE) using activated carbon, MCM-41, and HZSM-5 catalyst in a horizontal tubular reactor within a temperature range of 530-540 °C. The pyrolysis yield of these catalysts is shown in Table 2.8 [55].

Table 2.8: Comparison of product yield of different catalyst and thermal pyrolysis [55]

Catalyst	Liquid oil yield (%)	Gas yield (%)
Thermal pyrolysis (no catalyst)	42.7	5.1
Activated carbon (C-1)	49.2	7.2
MCM-41 (C-2)	63.9	-
HZSM-5 (C-3)	61.4	21.1

From Table 2.8, MCM-41 gave the highest liquid oil yield (63.9 %), followed by liquid oil yield of 61.4% by HZSM-5 catalyst. HZSM-5 catalyst produced higher gas yield (21.1 %) because of its small pores, while MCM-41 favours liquid oil yield (63.9 %) because of its larger pore sizes. Activated carbon has no significant change in the liquid oil yield (49.2%) and gas yield (7.2%) compared to the thermal pyrolysis yield of liquid oil (42.7%) and gas (5.1%) [55]. From their GC analysis (Figure 2.9), they concluded that the hydrocarbon distribution was from C<sub>5</sub>-C<sub>34</sub>. Thermal pyrolysis contains more of C<sub>14</sub> atoms and has a better distribution in the diesel range carbons. MCM-41 and HZSM-5 have significant influence in the production of shorter chain hydrocarbons (< C<sub>14</sub>), and the concentrations of larger carbon compounds decrease as both favours the production of gaseous products. C-4 to C-7 as depicted in Figure 2.9 represents the different proportion of catalyst mixture used [55].



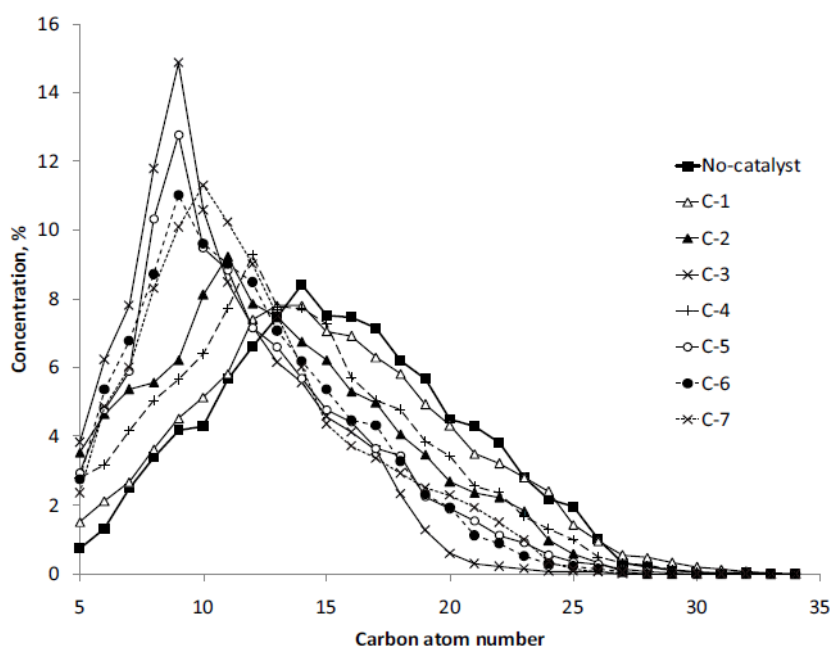


Figure 2.9: Carbon atom distribution in pyrolysis oil [55]

Marcilla et al. found that HZSM-5 catalyst was very effective in reducing the degradation temperature of HDPE and PP. There was more overlapping of the temperature from the uncatalyzed process. HZSM-5 show a narrow temperature range in the degradation of HDPE (374 °C) and PP (361°C). HUSY catalyst was very effective in decreasing the thermal degradation temperature of PP (Thermal = 444 °C, with HUSY = 353 °C) compared to HZSM-5 (361 °C) and FCC (369 °C). On application of the catalysts to HDPE, the influence of HZSM-5 (Thermal = 470 °C, with HZSM-5= 374 °C ) was more pronounced compared to HUSY (382 °C) and FCC (415 °C) [33].

J. Zeaiter studied the yields of products obtained using HUSY and HBeta catalysts on the degradation of HDPE. HBeta catalyst generated the highest gas yield of 95.7% and a liquid wax yield of 2.4%, while HUSY gave a gas yield of 93.2% and liquid wax of 4.9%. Both catalysts gave a high yield of olefins (C<sub>4</sub> - C<sub>8</sub>), because of the strong acid site of both catalysts which favours the cracking of HDPE [47].

Syamsiro et al. also investigated the effect of a catalyst on the degradation of municipal plastic waste (PE bag 2). Figure 2.10 (a) shows the products yield obtained and Figure 2.10 (b) shows the carbon number atom distribution of waste plastics oil (WPO) over Y-zeolite and natural zeolite catalysts [38].

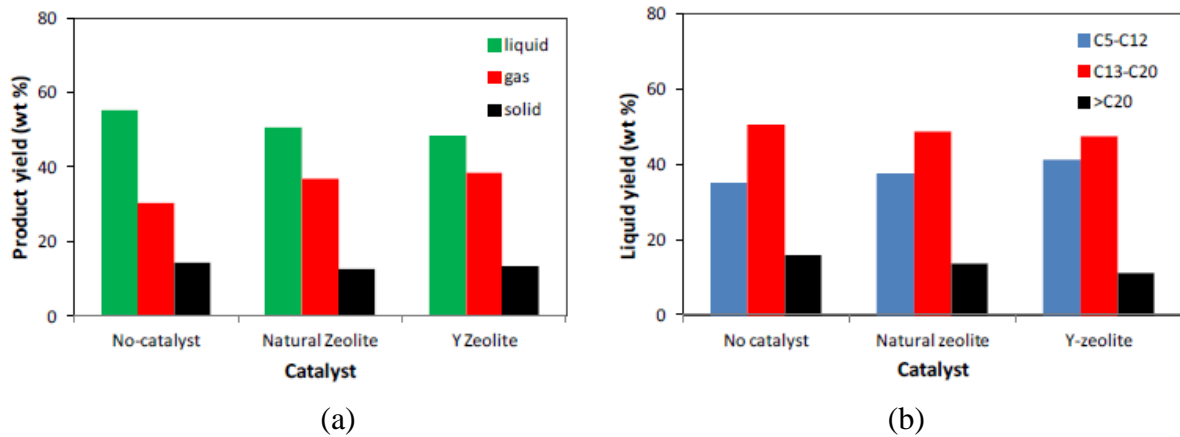


Figure 2.10: Effect of the catalyst of on the product yield and liquid oil composition of PE bag 2 [38].

The catalyst improved the cracking reaction of the pyrolysis gas, as it reduced the liquid fraction yield obtained without a catalyst. The Y-zeolite catalyst produced lower liquid fraction than the natural zeolite catalyst, because of the differences in their activity sites. The effect of the catalysts on the pyrolysis product of PE bag 2 is not significant as shown in Figure 2.10. This insignificant effect might be because of the presence of impurities. The impurity contains some toxic materials that deactivate the catalysts. The diesel fraction ( $C_{13} - C_{20}$ ) was almost the same in all conditions. Gasoline fraction ( $C_5 - C_{12}$ ) increased from the No-catalyst condition, followed by natural zeolite catalyst and finally Y-zeolite catalyst (Figure 2.10) because of the cracking of heavy hydrocarbon chains into lighter chain hydrocarbon fractions. They concluded that the quality of plastic liquid oil was lower than the quality of commercial diesel. Therefore, blending of plastic liquid oil with diesel fuel is required. [38].

Kaixin et al. investigated the catalytic activity of microporous and mesoporous catalysts in the pyrolysis of waste PE and PP mixture in a batch reactor. Pyrolysis of PE/PP mixture was carried out at a temperature of 500 °C. However, they observed that the thermal decomposition of single PE took place within the temperature range of 355 - 477 °C, while PP decomposed at 329 - 467 °C. Three microporous (HUN-ZSM-5, C-ZSM-5, and  $\beta$ -zeolite) and three mesoporous (Al-MCM-41, KFS-16B, Al-SBA-15(w)) catalysts were investigated. The microporous catalysts showed a high yield of gas products. Reduced oil and wax yields were obtained compared to the mesoporous catalysts, which gave a high liquid yield and lower gas products. Al-SBA-15 produced the highest oil and wax yield (89.1%) and lowest gas yield (10.9%) followed by thermal pyrolysis, which has oil and wax yield of 71.9 % and gas yield of 27.6% (Figure 2.11). The microporous catalysts showed good cracking activity, with the highest gas yield of 57.7% produced by the C-ZSM-5 catalyst. The acidity and textural properties of the catalysts determined the yield. They concluded that catalytic pyrolysis products could be a potential alternative to fossil fuel [16].

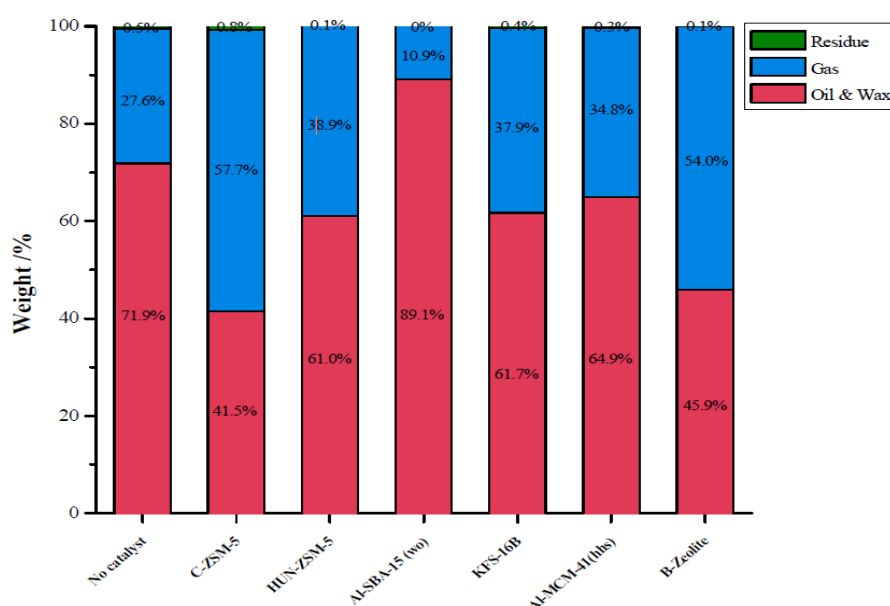


Figure 2.11: Pyrolysis yield of PE/PP mixture over different catalyst [16].

Analysis of oil and wax (Figure 2.12) showed that Al-SBA-15 catalyst has excellent selectivity for  $C_{13}$  -  $C_{20}$  fractions, which is the carbon number range for diesel fraction. They reported that catalyst has a very good potential to produce diesel from plastic wastes. Thermal decomposition also gave a wide range of carbon distribution ( $C_6$  -  $C_{40}$ ), where the diesel range fractions ( $C_{13}$ - $C_{20}$ ) was relatively high (41.4%). However, the  $C_6$ - $C_{12}$  fraction was relatively higher (51.0%). The fuels produced by thermal decomposition requires upgrading before use as engines operate on fuel with narrow carbon range [16].

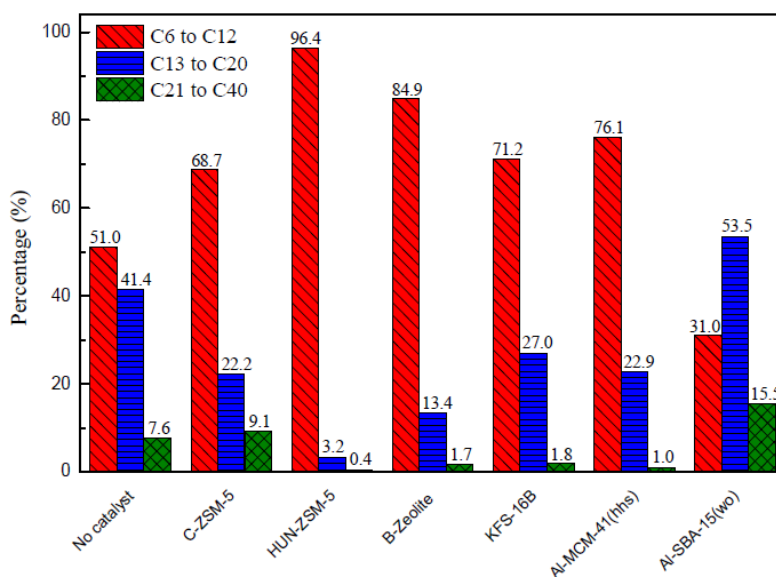


Figure 2.12: Carbon number distribution of the liquid and wax products [16].

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Kyong-Hwan Lee investigated different zeolites catalysts (Zeolite Y; with and without clay, ZSM5, modernite; with clay or alumina as a supporter) for the upgrading of MPW oil in a fixed bed reactor. ZSM5 converted most of the heavy hydrocarbons into the gaseous product, while modernite with clay has a low conversion of heavy hydrocarbons to gas. They concluded that the result was influenced by the catalysts [48]. Shah et al. studied the effect of zeolite catalyst on low-temperature conversion of LDPE/PP mixture using a batch reactor at different temperatures. At 255 °C, 51.19 % of the pyrolytic oil was produced. The maximum pressure measured in the reactor at the end of the pyrolysis process was 8 psi. They concluded that the oil could be used as an alternative fuel [44]. López et al. studied the catalytic effect of ZSM-catalyst on the pyrolysis of plastic waste in a batch reactor at 440 and 500 °C. They reported higher gas yield (39.8 wt%) and liquid oil (58.4 wt%) with a high content of aromatics at 500 °C. At 440 °C, similar yield as that obtained from the thermal analysis (thermal; 65.2wt% and ZSM-5; 56.9 wt%) was obtained. ZSM-5 improves energy saving and reduces the cost of operation [40].

Besides the maximisation of volatile hydrocarbon yield during pyrolysis, zeolite catalysts (HZSM) has been recommended because of its efficiency and longer cycle time. It has an extremely low deactivation rate and can be regenerated effectively [6].

### 2.4.5.2 Fluid catalytic cracking (FCC) catalyst

FCC catalyst is typically used for refining of crude oil into lighter and desirable liquefied petroleum gas (LPG) fractions, as well as gasoline fractions. FCC is made from silica-alumina with the binder; a zeolite crystal and non-zeolite acid matrix [6]. Zeolite-Y is the main component of FCC catalyst that has been used over the years due to its thermal stability and product selectivity [6, 53]. FCC catalyst used in pyrolysis is a by-product (spent FCC catalyst) of FCC process in petroleum refining. This catalyst is usually contaminated, but it is very valuable when applied in pyrolysis [6].

The effectiveness of spent FCC catalyst has been studied and compared with thermal (non-catalyzed) pyrolysis of HDPE. Kyong-Hwan Lee et al. carried out this investigation in a semi-stirred batch reactor operated at 430 °C under atmospheric pressure and a residence time of 4 h. They found that liquid oil yield increased from 75.5 wt% obtained by thermal pyrolysis to 79.7 wt%, and the gaseous product reduced slightly from 20 wt% (thermal) to 19 wt% on application of the catalyst. The residue obtained from catalytic degradation (0.9 wt%) was small compared to that obtained from the thermal process (4.5 wt%). In the non-catalyzed process, first liquid yield was formed at 430 °C after 30 min while in the catalysed pyrolysis, the liquid formation was observed at 350 °C, showing that the use of FCC catalyst improved the conversion of reactant and increased the rate of the reaction [56].

The use of spent FCC catalyst has some limitations that must be taken into account when choosing this catalyst. Some of these constraints are; a polymer to catalyst ratio (less than or equal to 20 wt% for maximum liquid yield) and conditions of the catalyst (severe/mild steaming and fresh FCC) [6].

Table 2.9: Product distribution of FCC under different condition [6].

Type of FCC catalyst	C <sub>1</sub> -C <sub>4</sub> (gaseous) (wt%)	C <sub>5</sub> -C <sub>9</sub> (medium gasoline) (wt%)	C <sub>10+</sub> (diesel range) (wt%)
Fresh FCC	52	35	15
Mild steaming	25	38	40
Severe steaming	5	20	70

Severe steaming of FCC catalyst produced more of diesel range oil and lower yield of gas fractions, while fresh FCC catalyst produced fewer diesel fractions and higher gas fractions (Table 2.9). Moreover, the use of this catalyst is cost effective since it is a waste product from petroleum refining [6].

Marcilla et al. observed that maximum degradation temperature of single HDPE was 415 °C and the maximum degradation temperature of single PP was 369 °C on the application of FCC catalyst. For the mixtures, of different ratio, the maximum degradation temperature was reported to be 412 °C. They concluded that FCC was the most efficient for separation of degradation processes compared to the other zeolite catalysts (HZSM-5 and HUSY) used in their study [33].

Effect of other catalysts that has been studied by other researchers on catalytic pyrolysis of plastic waste is summarised in Table 2.10.

Table 2.10: Yield of other catalysts reported by some authors

Catalyst	Polymer	Temperature (°C)	Residence time	Reactor	Liquid yield (wt%)	Gas yield (wt%)	Solid yield (wt%)	Ref
Shwedaung clay	HDPE +LDPE	210-380	1.5 hour	Fixed bed reactor	65.81	21.78	11.34	[4]
Mabisan Clay	+PP +PS+				67.06	19.92	12.43	
Bentonite clay	PET				64.92	21.86	12.11	
Dolomite					63.96	28.52	6.87	
Zinc oxide					63.76	28.01	8.23	
Alumina (powder)	HDPE	450	30 min Heat rate 5-8 °C/min	Batch reactor	82.0	15.90	2.10	[50]
Bentonite clay	HDPE	475-525	95 min 10 °C/min	Lab scale setup	79.1 + Wax 11.4	5.2	4.3	[32]

#### 2.4.6 Effect of Heating Rate

The effect of heating rate on the degradation of polymers has not been extensively studied. Karisathan et al. have reported the effect of heating rate on the yield and reaction time of polymers during pyrolysis at different heating rates (5, 10, 15, 20 °C/min) on the degradation of HDPE. At 5 °C/min, a longer residence time was observed, which could lead to a prolonged initiation reaction. In the presence of a catalyst (Bentonite clay) and high residence time, the liquid produced was crack further to the gaseous product. At 10 °C/min, a high liquid yield was obtained because of reduced residence time, achieving primary catalytic cracking condition and the production of low molecular weight fractions. At 15 °C/min, shorter residence time was observed, leading to the yield of gases, more wax and lower liquid yield due to incomplete cracking. At 20 °C/min, lighter fractions were produced due to the  $\beta$ -scission reaction occurring at higher heating at the polymer chain end before radical transfer [32].

Panda et al. reported that higher heating rates favours the breaking of lighter fractions and enhances bond breaking. The decrease in production of aliphatic content was due to increase in temperature as heating rates increases [26]. Silvarrey and Phan reported that at higher heating rates, decomposition of MPW is distributed over wide temperatures range, resulting in the need for higher pyrolysis temperature to achieve the same conversion at an optimal heating rate [14].

## 3 Experimental

This experiment was performed at Norner AS laboratory, Asdalstrand Bamble, Norway.

### 3.1 Raw materials

High-density polyethylene (HDPE), low-density polyethylene (LDPE), and polypropylene (PP) in the form of a pellet, manufactured by Borealis, Norway, were used as the experimental material. Physical properties of the plastics used in this study are presented in Table 3.1. These properties are imperative to know when processing any plastic.

Table 3.1: Physical properties of polyolefins

Plastic	Type	Density (Kg/m <sup>3</sup> ) – ISO 1183	Melt flow rate (g/10 min)- ISO 1133	Melt temperature (°C)	Origin
HDPE	VS5580	945	0.3 (190°C / 2.16 kg)	129 (DSC)	Borealis
LDPE	FB2230	923	0.2 (190°C / 2.16 kg)	124 (DSC)	Borealis
PP	HE125MO	905	12 (230 °C / 2.16 kg)	220-260	Borealis

Two different catalysts obtained from Hulteberg Chemistry & Engineering AB, Sweden, were chosen for this study. They were stored in a glove box to prevent absorption of moisture from the atmosphere. Their selectivity for cracking of polymers is not known. A C<sub>7</sub>-C<sub>40</sub> Saturated Alkanes standard solution used for the identification of hydrocarbons was obtained from Sigma Sigma-Aldrich (St Louis, MO, USA). Hexane, heptane and rectifying spirit were locally available in the laboratory. Hexane was used for the dilution of the standard and the liquid product for GC analysis while heptane rectifying spirit was used for the cleaning of pyrolysis equipment.

### 3.2 Analytical technique

These samples (HDPE, LDPE, PP) were shredded to a smaller particle size of 1.5 mm using a Retsch shredder (Type ZM 100, Retsch GmbH & Co.KG Germany). Liquid N<sub>2</sub> was subsequently added to freeze the samples before adding to the shredder to prevent degradation of samples. The catalysts were also grounded to powder, to a smaller particle size (< 1.5 mm) using laboratory pestle and mortar, before TGA analysis and pyrolysis in the autoclave reactor.

The samples and the pyrolysis product obtained were analysed using the following techniques.

#### 3.2.1 Thermogravimetric analysis (TGA) and procedure

Before the pyrolysis experiments, the samples (HDPE, PP, PS and LDPE) were subjected to thermogravimetric analysis using a Thermogravimetric Analyzer (TA Instruments, TGA Q500) controlled by a PC to get the input data for the autoclave reactor. TGA analysis was

### 3 Experimental

carried out to determine the degradation (decomposition) rate of the polymers and influence of temperature (Process Variables). A Mettler Toledo weighing balance (Type: NewClassic MF, Model: MS204S /01, Switzerland) was used to weigh the samples before loading the TGA sample pan. The sample amount used was 20 mg loaded in a 4 mm platinum pan. The TGA recorded the initial weight before the thermal decomposition reaction (change in mass of the samples were monitored as temperature increases). The process was purged for 5 min with nitrogen to ensure pyrolysis condition by displacing air and oxygen in the furnace to avoid oxidation of the samples. The experiment was performed in a Nitrogen (N<sub>2</sub>= 99.999%) atmosphere with a flow rate of 60 mL/min continuously under the experimental conditions of Series A (Table 3.2).

Three dynamic (Non-isothermal) runs for each sample at the different heating rates were performed to test for repeatability of the results. 10 °C/min was chosen as the optimal heating rate, which corresponds to findings from literature [13, 32, 39].

A similar experiment was performed to assess the thermal stability of the catalysts at the same conditions of Series A. However, a heating rate of 10 °C/min (optimal heating rate) was used. The experiments were performed by mixing the grounded polymer (20 mg) with the catalysts in a petri dish, to have an almost homogeneous mixture and good heat and mass transfer at a catalyst feed ratio of 1:10 [36] (CAT-2). For CAT-3, catalyst feed ratio of 0.3:1 (since the origin is unknown, pillared clay catalyst was assumed) [57] was used after series of experiment with catalyst ratio of 1:10 without any significant change from the thermal analysis. The samples mass changes over the course of the experiment were measured. Three dynamic runs for each sample at the optimised heating rate (10 °C/min) were performed to test for repeatability of the results.

Table 3.2: Experimental scheme for TGA analysis

S/N	Sample	Experimental conditions
Series A		
1	HDPE	Non- isothermal (dynamic runs) from ~25 to 600 °C. The heating rate of 5, 10, 20, 30 °C/min and a total sample weight of 20 mg (± 1). Catalysts screening.
2	LDPE	
3	PP	
Series B		
	Mixture ratio	Experimental conditions
1	50/50 LDPE/PP	Non- isothermal (dynamic runs) from ~25 to 600 °C. The heating rate of 10 °C/min and a total sample weight of 20 mg (± 1). Catalyst screening.
2	75/25 LDPE/PP	
3	66/34 LDPE/PP	
4	34/66 LDPE/PP	



### 3 Experimental

Sample mixtures of LDPE/PP were analysed (Thermal and catalytic) using mixture ratios of 75/25 (%) and 50/50 (%) adopted from Marcilla et al.[33], and a mixture ratio of 66/34 % and 34/66 % adopted from Norner AS. The samples were mixed properly in a petri dish to obtain a representative homogeneous mixture after weighing, and the experiment was performed using experimental conditions of Series B (Table 3.2).

The data presented in this paper corresponding to the different operating conditions (Series A and B) are the values of one of the same runs carried out. The results obtained in all cases were very similar with a standard deviation of  $\pm 1$  to  $\pm 3$ .

#### 3.2.2 Analysis of pyrolysis products

A gas chromatograph coupled with a flame ionisation detector (GC-FID, Hewlett Packard, HP 6890 Series GC System, G1530A, USA) was used to analyse the pyrolysis products (liquid and gas). Table 3.3 shows the characteristics of the methods employed. The hydrocarbon contents were identified by comparison of their retention time with that of the calibration sample (standard solution) on a computer.

Table 3.3: GC method characteristics

Method	ISO 3924:2016 Determination of hydrocarbon range distribution (liquid oil/wax product)
GC	HP 6890 Series
Column	DB-1 HT
Column length	15
Column ID (mm)	0.32
Stationary Phase thickness	0.1
Carrier gas	He/H <sub>2</sub>
Total flow rate (mL/min)	68.9
Initial column temperature (°C)	40
Final column temperature (°C)	350
Detector	FID
Injection temperature (°C)	340
Injection volume (µL)	1
Detector temperature (°C)	360
Heating rate (°C/min)	10

### 3.3 Pyrolysis equipment and procedure

A closed batch reactor was used to validate the results obtained from TGA. Pyrolysis runs were conducted using TGA optimised condition (Heating rate of 10 °C/min). The setup comprises of a muffle furnace (Heraeus Instruments, Type M110, D-6450 Hanau, Germany), which was used to heat up the reactor. The reactor used in this study is a batch pressurised autoclave reactor, made of 253MA steel; manufactured by Promet AS, Risavika Havnering 109, 4056 Stavanger, Norway. It is equipped with rupture disc (Type B18rn 10-01, by Berstsheiben Schlesinger, Germany) which can hold a pressure of about 11 bar at 500 °C and 23.49 bar at 20 °C. The autoclave reactor was fitted with a nitrogen inflow and product outflow pipe. A pressure gauge was installed to measure the pressure of N<sub>2</sub> flowing into the furnace and through the autoclave reactor (Figure 3.1).

The experiment scheme/conditions designed for the pyrolysis experiment is as shown in Table 3.4 (Series A and B) to help understand the interaction of LDPE and PP, catalyst effect, and the effect of the mixture ratios on pyrolysis products.

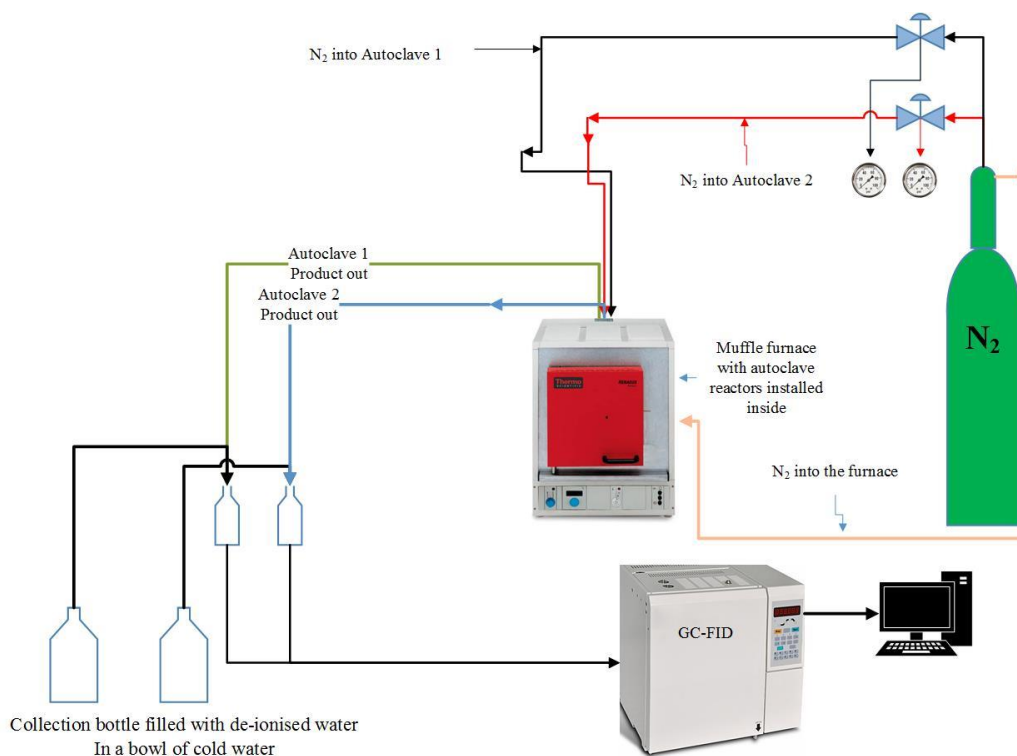


Figure 3.1: Pyrolysis equipment setup

Polymer samples of ~10 g (single and mixtures) were pyrolysed under the experimental conditions of Series A, and B (Table 3.4). The samples (single and mixtures) were poured into the autoclave reactor after weighing. It was stirred mechanically, tightened properly and assembled in the furnace (N<sub>2</sub> inlet and products outflow lines were connected). N<sub>2</sub> (99.9999%) was used to purge the reactor for 30 min to ensure an inert atmosphere (No air). The autoclave was heated slowly to the desired setpoint temperature using the programmable temperature

### 3 Experimental

controller (Thermicon P) of the muffle furnace. A hand-held thermometer (ANRITSU digital surface thermometer, HFT-80) was used to monitor the temperature in the furnace to make sure the temperature indicated by the furnace is approximately the same inside the furnace since N<sub>2</sub> was used to purge the furnace continuously. The sample was left in the reactor at the setpoint temperature until completion of reaction (no liquid product recovery). Time at the beginning and completion of the reaction was recorded.

Another run was conducted in the presence of catalysts. The catalyst was weighed on a Mettler Toledo balance (subchapter 3.2.1) and mixed in a glove box to avoid absorption of moisture from the atmosphere. CAT-2 was used for the pyrolysis process with a catalyst feed ratio of 1:10. The condensable products were collected in two collection bottles (Two autoclaves installed in the muffle furnace), after cooling down by another collection bottle filled with distilled water; placed in an ice bath, while the non-condensable product was vented. The liquid fraction obtained was analysed using GC-FID.

At the end of the reaction, the muffle furnace was switched off and allowed to cool to room temperature. The autoclaves were unmounted, products removed carefully from the collection bottle. The liquid product and the residue were weighed and recorded after each experiment. The bottles and the autoclaves were cleaned with heptane and rectifying spirit, dried in a vacuum dryer before another experiment.

Table 3.4: Pyrolysis experiment scheme

Run	Temperature	LDPE	PP	Catalyst / Thermal
Series A				
	460	0	100	Thermal
	460	33	66	Thermal
	460	66	33	Thermal
	460	100	0	Thermal
Series B				
	460	0	100	CAT-2
	460	33	66	CAT-2
	460	66	33	CAT-2
	460	100	0	CAT-2

The percentage yield of the pyrolysis liquid and residue collected at the end of the reaction was calculated by the equation [5];

$$\text{Liquid yield (\%L)} = \frac{M_2 \times 100}{M_1} \quad (3.1)$$

and

$$\text{Residue yield (\%R)} = \frac{M_3 \times 100}{M_1} \quad (3.2)$$

NOTE: The mass of the liquid product is the sum of the liquid product and wax collected at the end of the experiments.

The total percentage of gas produced during the experiment was calculated by [5]:

$$\text{Gas yield (\%G)} = 100 - (\%L + \%R) \quad (3.3)$$

Where:

$M_1$ : Mass of the sample

$M_2$ : Mass of liquid product

$M_3$ : Mass of residue/char

### 3.4 HSE

Safety is the prevention of accidents using appropriate technology to identify the hazards of a process and eradicate them before an accident occurs. There are common hazards; chemical or mechanical, that cause injury from toxic substances, falling and explosion hazards [58].

At Norner, health safety and the environment (HSE) is given a high priority. The management strives to improve the health, safety and environmental performance through the employees in partnership with the visitors and customers. HSE is a pro-active tool in all laboratory process and must be in our minds and hearts at all time.

It was stated clearly at Norner that when planning for any experiment, safe job analysis (SJA) must be done to help identify the risk potentials in a job and plan to reduce or prevent the risks.

In this work, SJA was prepared with safety delegates for the use of the catalyst and the pyrolysis equipment. The risk associated with the utilisation of the catalyst is high. The operator or user might breathe in the dust in the process of grinding in a mortar or during the experiment. It also causes skin irritation on prolong exposure.

The risk associated with the use of the pyrolysis equipment is fire/explosion. Since gases are the first product of pyrolysis, there might be leakage from the autoclave into the oven leading to fire outbreak. To prevent the above risks, SJA was prepared for the pyrolysis process to identify the risks and have a control measure in place as shown in Appendix F.

## 4 Results and Discussion

### 4.1 TGA results

#### 4.1.1 Thermal degradation of single HDPE, LDPE and PP

Figure 4.1 shows the TG/DTG curves for virgin HDPE, LDPE and PP at the experimental conditions of series A (Table 3.2), respectively. The onset temperature ( $T_{\text{onset}}$ ), final degradation temperature ( $T_{\text{F}}$ ) and the maximum degradation temperature ( $T_{\text{M}}$ ) of the samples at the optimal heating rate (10 °C/min) are presented in Table 4.1. The results obtained at a heating rate of 5, 20 and 30 °C/min are presented in Appendix B.

From Figure 4.1, the weight loss curves of all the samples followed the same trend, which correlates to the same pyrolysis behaviour because of the possession of similar chemical bonds in their molecular structures and degradation mechanism [10]. The TG curves flattened out at a temperature range of 440 - 510 °C for all heating rates, showing complete decomposition of the samples (Negligible residue).

The thermal degradation of plastics is a one-step process as demonstrated by the presence of only one rising peak in the DTG curve ( Figure 4.1). A lateral shift to the right is seen on the DTG curves as heating rate increased from 5 °C/min to 30 °C/min, showing a broad range of temperature distribution. The DTG lateral shift to the right is also an indication of the accelerated rate of weight loss as heating rate increases (HDPE > LDPE > PP), which conform to the result obtained by Silvarrey and Phan [14]. A similar phenomenon has been explained by different researchers [13, 39]. This change can occur because of change in the reaction mechanism of the polymers as many researchers argued. However, ineffective heat transfer from the furnace to sample can cause a significant temperature variation between the furnace and the sample, which increases with heating rate [35, 39]. Low thermal conductivity of polymers and the distribution of the polymers in the pan can also lead to this shift. It was observed from this analysis that the lower the heating rate, the longer the residence time and vice versa.

Table 4.1: Characteristic temperature of polymers at 10 °C/min

Plastics	Temperature (°C)		
	$T_{\text{onset}}$	$T_{\text{M}}$	$T_{\text{F}}$
HDPE	452	478	489
LDPE	437	473	486
PP	378	440	456

HDPE started decreasing in mass at temperatures of about 452 °C, the maximum degradation occurred at about 478 °C, and the degradation was complete at 489 °C. LDPE and PP followed a similar trend with their thermal decomposition occurring within a temperature range of 437-486 °C and 378-456 °C respectively. The maximum decomposition of LDPE and PP took place

## 4 Results and Discussion

at 473 and 440 °C respectively. The thermal degradation of all the polymers finished between the temperature range of 378 °C and 489 °C (Table 4.1). The result is similar to the result obtained by Demirbas Ayhan [10].

The decomposition temperature of the polymers increased in the following order: PP < LDPE < HDPE, corresponding with findings in the literature [13, 14, 39].

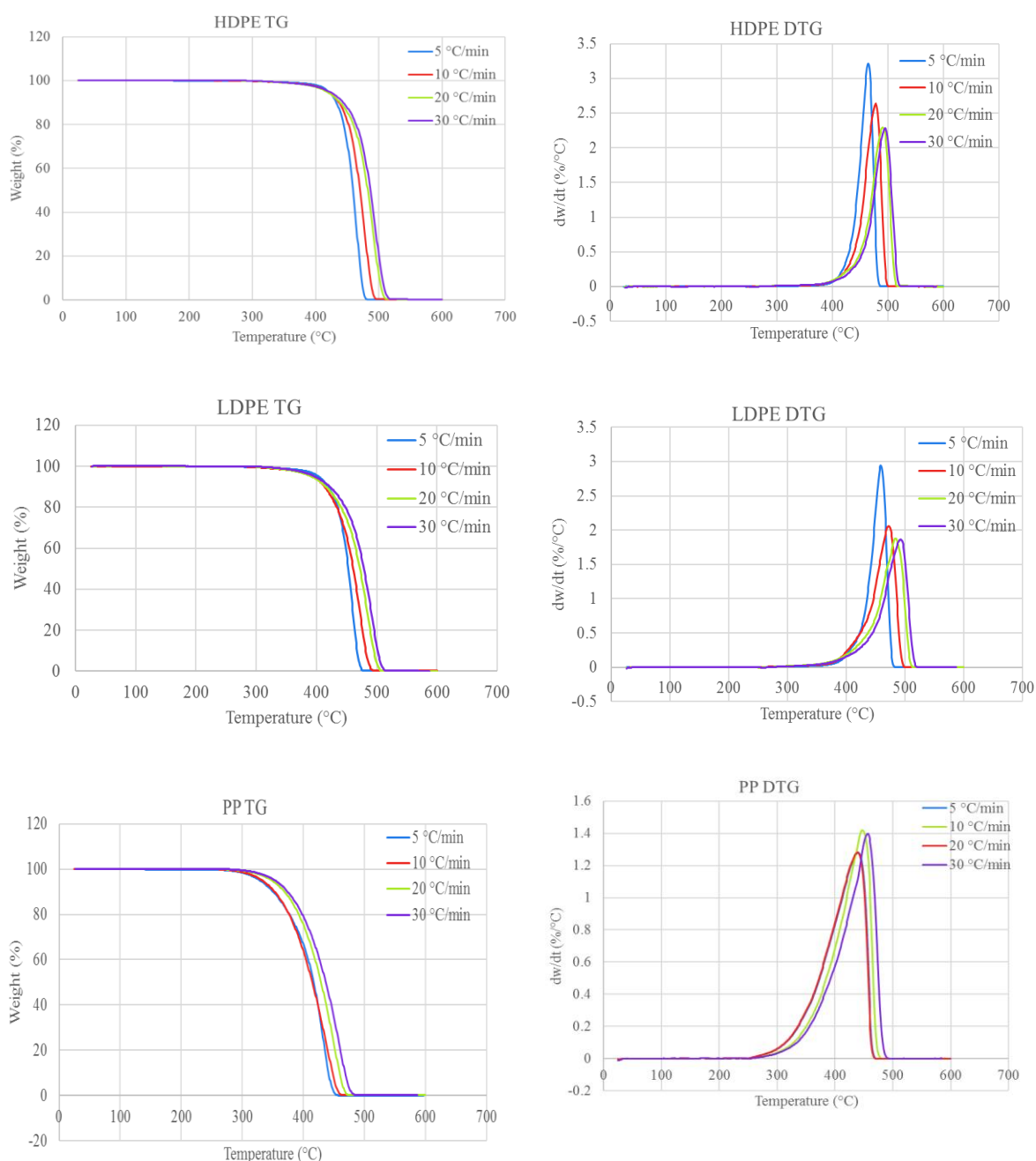


Figure 4.1: TG/DTG curve for HDPE, LDPE and PP at different heating rates (5, 10, 20, 30 °C/min)

## 4 Results and Discussion

The higher degradation temperature of HDPE and LDPE is likely due to their higher activation energy as seen in the literature [13, 14, 36, 39]. The decomposition of PP was faster compared to that of HDPE and LDPE. PP was observed to decomposed faster because of the branched chain that breaks off easily, while HDPE and LDPE were difficult because of the presence of linear chain; this is in line with a study by Sriraam et al. [36].

The differences in peak shape are as a result of the different reaction mechanisms. At higher heating rates ( $> 20$  °C/min), the mechanism of degradation differs, transforming the reaction from slow pyrolysis to fast pyrolysis [14] as seen in Figure 4.1. Moreover, as heating rate increases, the degradation temperatures increase.

### 4.1.2 Thermal degradation of Mixtures (LDPE/PP)

This study was performed to investigate the behaviour of different polymer mixtures (LDPE/PP) at a different ratio (Table 3.2). Thermal decomposition behaviour of LDPE/PP mixture was studied and compared to thermal decomposition behaviour of single LDPE and PP.

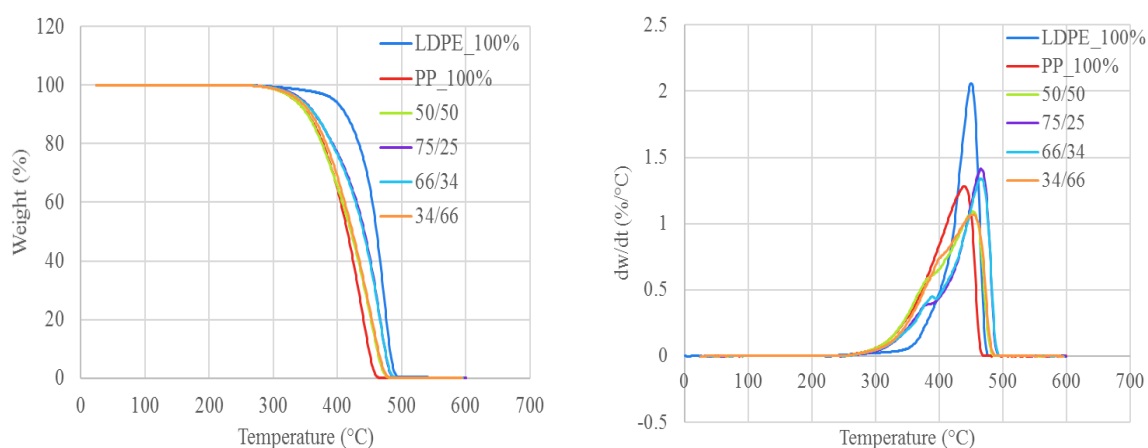


Figure 4.2: TG/DTG curve of LDPE/PP mixtures compared to single LDPE and PP

Figure 4.2 shows the thermogram (TG/DTG curve) of the weight loss behaviour of LDPE, PP and their mixtures during thermal degradation analysis. As stated earlier, PP has lower thermal degradation temperature compared to LDPE due to the presence of unstable branched chains that breaks off easily during pyrolysis.

The DTG curve has two partially overlapped peaks, implying that the decomposition of mixtures is a multiple step reaction as observed by Kaixin et al.[16] The peak of the DTG curve for the mixtures is wider compared to that of the single polymers. The peaks did not coincide with the peaks of the single LDPE and PP, indicating that there is an interaction between LDPE and PP, altering their thermal behaviour, as PP appeared to have catalysed the mixture.  $T_M$  of the mixtures was observed to be between  $T_M$  of single PP and LDPE (Table 4.1 and Table 4.2).

## 4 Results and Discussion

The mechanism of decomposition of LDPE and PP is a radical chain mechanism; the primary radical initiated by random chain scission of PP captures the hydrogen from LDPE, thereby enhancing the decomposition of LDPE at a lower temperature and amplifying decomposition of LDPE/PP mixture [16]. Ciliz et al. stated that the radical formation increases with increase stability of the polymers. They said that degradation of polymers depends on the stability of the formed radicals [18].

Table 4.2: Maximum degradation temperature of LDPE/PP mixtures

Plastics	Temperature (°C)		
	T <sub>onset</sub>	T <sub>M</sub>	T <sub>F</sub>
LDPE/PP			
50/50	378	453	471
75/25	409	467	481
66/34	406	466	481
34/66	378	453	473

### 4.1.3 Catalytic screening of pure HDPE, LDPE and PP

Dynamic runs were performed on the catalysts, to assess their thermal stability at a heating rate of 10 °C/min by observing their weight loss. Both catalysts showed weight loss around 40 °C which indicated moisture loss. The weight loss was more pronounced for CAT-2 than CAT-3. The TG curve shows that at 150 °C, the degradation of CAT-2 appears to be thermally stable while the weight loss of CAT-3 increases (Figure 4.3).

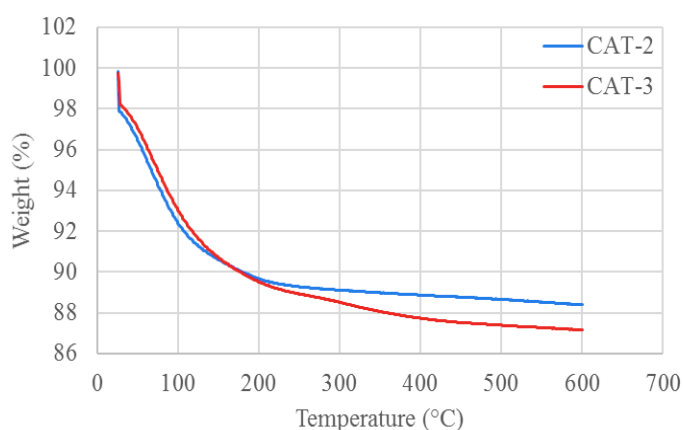


Figure 4.3: TGA analysis of the thermal stability of the catalysts

For the experiments, the catalysts were thoroughly mixed with the polymers (HDPE, LDPE and PP) in a petri dish after weighing, to have an almost homogeneous mixture. They were analysed using the TGA instrument.



## 4 Results and Discussion

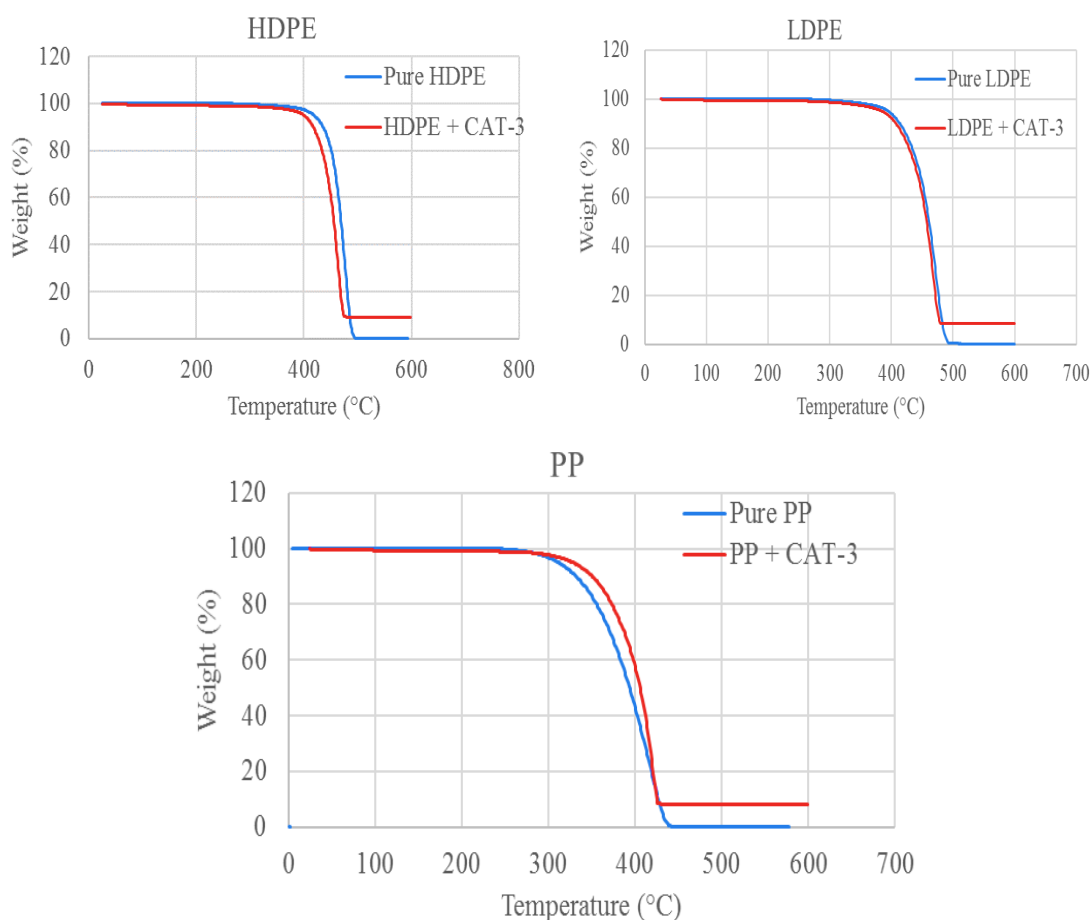


Figure 4.4: TG curve of HDPE, LDPE, and PP in the presence of CAT-3 (C/F 1:10)

Table 4.3: Maximum degradation temperature of HDPE, LDPE and PP; Pure and in the presence of catalyst (HR 10 °C/min)

	Maximum degradation Temperature $T_M$ (°C)		
	HDPE	LDPE	PP
Pure	478	473	440
CAT-2	424	452	395
CAT-3	453	457	404

Catalysts lowered the degradation temperature of the polymers (Figure 4.5).

Table 4.3 shows that CAT-2 and CAT-3 were very efficient in reducing the maximum degradation temperature of HDPE and PP. HDPE (pure) has a maximum degradation temperature of 478 °C, but on the application of CAT-2 a significant reduction was observed, showing that the catalyst has a strong cracking effect on the polymer. The maximum degradation temperature of LDPE (473-452 °C) and PP (440-395 °C) followed the same trend. Both catalysts had a slight effect on the degradation of LDPE, although CAT-2 had more effect

## 4 Results and Discussion

on the degradation temperatures as seen in the TG curve (Figure 4.5). CAT-2 was more efficient in the degradation of HDPE; reducing the maximum degradation temperature by 54 °C, followed by PP and LDPE, which indicates that the catalysts are polymer specific. Catalysts are selected based on the desired product and the feedstock [36].

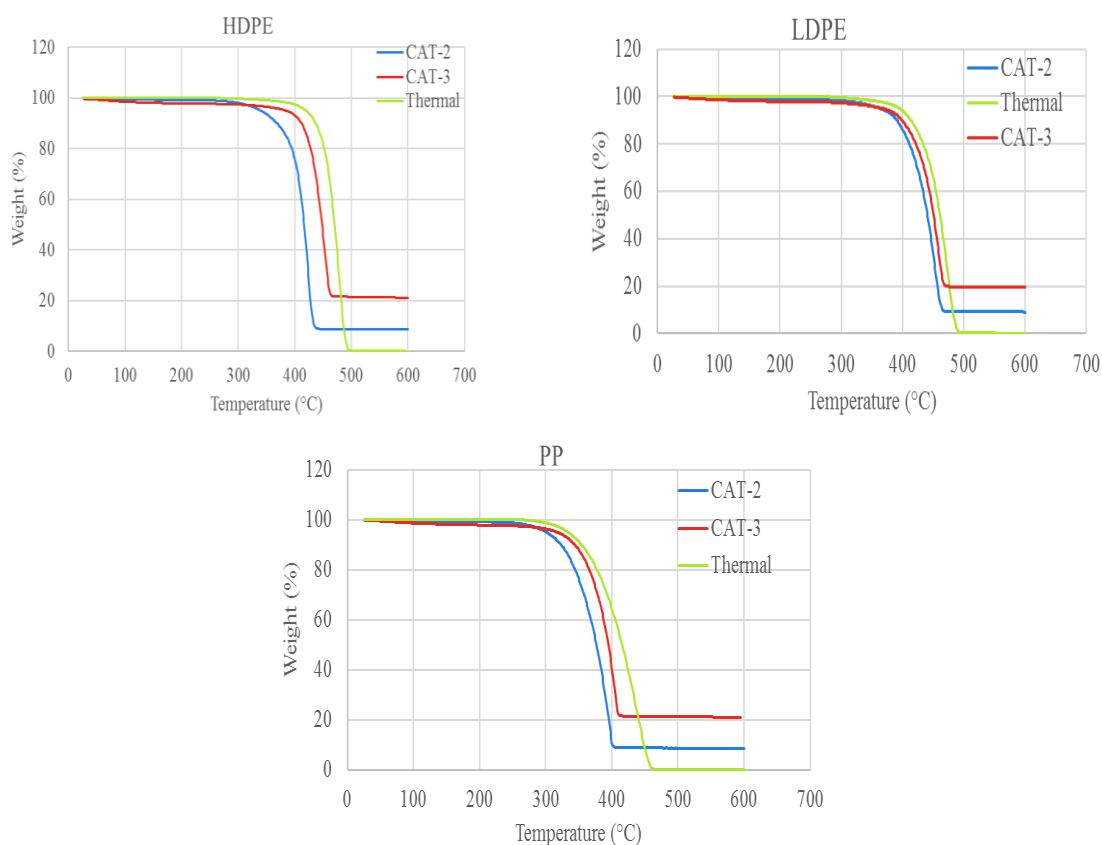


Figure 4.5: TG curve for catalytic degradation analysis of HDPE, LDPE and PP

On application of CAT-3, using catalyst feed ratio of 1:10 (Figure 4.4), it had no effect on the  $T_{\text{onset}}$  and  $T_M$  of LDPE. It increased the  $T_{\text{onset}}$  and  $T_M$  of PP. However, it lowered the final degradation temperatures compared to that of the pure polymers. CAT-3 has a slight effect on the degradation temperature of HDPE. This behaviour led to the increase in the quantity of CAT-3 used to 6mg (C/F = 0.3:1) for the rest of the analysis. As seen in Figure 4.4 and Figure 4.5, an increase in the quantity of CAT-3 had a significant effect on the degradation temperature of polymers. The application of CAT-3 to the samples lowered their maximum degradation temperatures. However, its effect is not significant as CAT-2.

The effect of the catalysts on the polymers depends on the acidity of the catalyst. The number of acid sites and pore size plays a major role in the catalytic degradation rate of polymers. This same observation was made by Sriraam et al. when they carried out TGA analysis of PP and PE using Zeolite catalysts. They concluded that the number of acid sites for cracking of polymers increases with the amount of catalyst used [36].

#### 4.1.4 Catalytic screening of plastic mixtures (LDPE/PP)

Figure 4.6 and Figure 4.7 shows the thermogram of the mixtures when the catalysts (CAT-2 and CAT-3) was applied. The catalysts lowered the  $T_{\text{onset}}$ ,  $T_M$  and  $T_F$  of the mixtures. A significant difference in the maximum degradation temperature was observed compared to the thermal analysis (Table 4.4). CAT-2 had a greater impact on the maximum degradation temperature of the polymers than CAT-3. It lowered the  $T_M$  of the mixtures (50/50, 75/25, 66/34, and 34/66) from 453, 467, 466, and 453 °C to 405 °C (50/50), 419 °C (75/25), 415 °C (66/34), and 411 °C (34/66) respectively.

Table 4.4: Maximum degradation temperature of Polymer mixtures (LDPE/PP) Pure and in the presence of catalyst (HR 10 °C/min)

Plastic	Maximum degradation temperature $T_M$ (°C)			
	50/50	75/25	66/34	34/66
Thermal	453	467	466	453
CAT-2	405	419	415	411
CAT-3	421	434	425	412

Moreover, both catalysts initiated the decomposition process at a lower temperature compared to the thermal analysis (Figure 4.2). The influence of CAT-3 on the maximum degradation temperature of 50/50 mixture and 75/25 was less pronounced than CAT-2. This is similar to Marcilla et al. observation using FCC, ZSM5 and HUSY catalysts in their study on catalytic pyrolysis behaviour of PE and PP mixtures [33].

The DTG curve appeared to be almost smooth without a peak on the application of CAT-3 (Figure 4.7). In Figure 4.6, the DTG curve seems to have a peak like a shoulder, which suggests that the decomposition of the mixture is a multiple step process. The wider area of the DTG curve (Figure 4.6) indicates more weight loss on the application of CAT-2.

From Figure 4.6 and Figure 4.7, it is evident that increase in the proportion of PP in the mixtures lowers the  $T_{\text{onset}}$  and  $T_M$  of the mixtures.

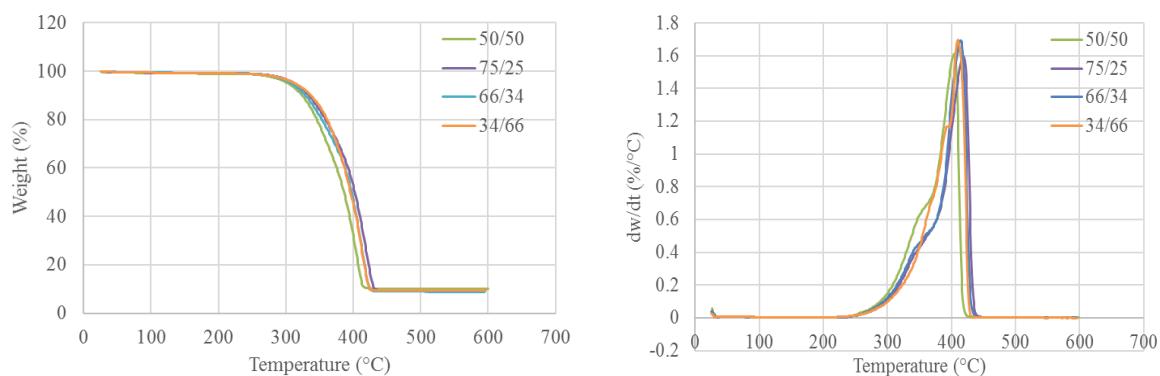


Figure 4.6: TG/DTG curve of CAT-2 degradation of LDPE/PP mixtures

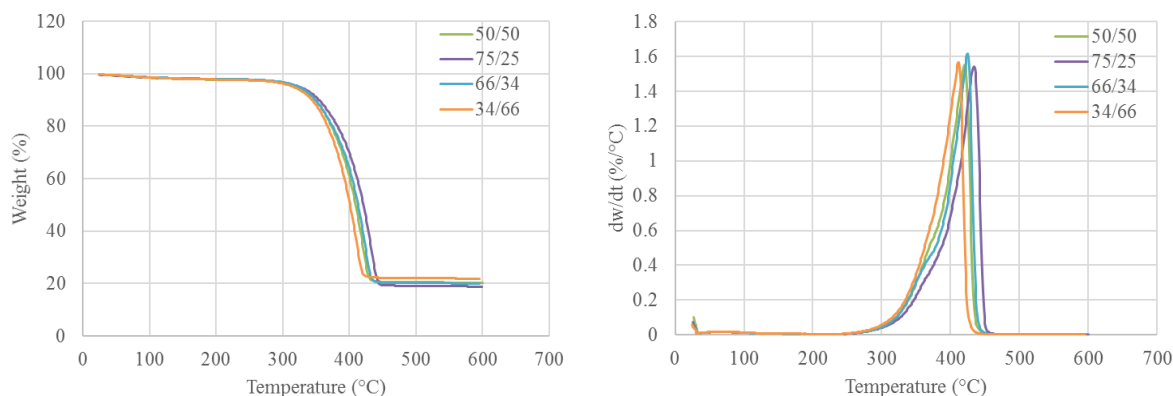


Figure 4.7: TG/DTG curve of CAT-3 degradation of LDPE/PP mixtures

## 4.2 Pyrolysis liquid yield

Thermal and catalytic cracking of single (LDPE and PP) and mixtures (LDPE/PP) of plastic waste has been performed in a batch reactor at conditions stated in Table 3.4 under atmospheric pressure. Gases that emerged from the reactors were condensed and collected as liquid fractions, while the gaseous fractions were calculated from equation 3.3. Thermal and catalytic pyrolysis yields at 460 °C are presented in Table 4.5 and Figure 4.8.

Table 4.5: Thermal cracking yield of LDPE, PP and LDPE/PP mixtures at 460 °C

Plastic	Liquid oil/wax (wt%)	Gas (wt%)
LDPE	94	6
PP	86	14
LDPE/PP (66/34)	63	37
LDPE/PP (34/66)	83	17

The yield of liquid oil/wax from thermal pyrolysis of single LDPE was significantly higher reaching about 96 wt % than the liquid oil produced from single PP which has a liquid oil yield of 86 wt %. The gas fraction obtained is very low in LDPE (6 wt%) but higher in PP (14 wt%), due to the secondary reaction as it appears that 460 °C is too high for the pyrolysis of PP (Table 4.5). Liquid oil was the main fraction obtained from thermal pyrolysis of PP while the product of LDPE pyrolysis was wax. A similar result was obtained by Sriraam et al. when they carried out the pyrolysis of PP at 450 °C and concluded that 450 °C is too high for the pyrolysis of PP because of high gas yield [36].

The yield of gases in the LDPE/PP (66/34) mixture was highest at about 37 wt % compared to LDPE, PP, LDPE (34/66), which produced 6, 14, and 17 wt % respectively. However, the difference in the yield of gases from cracking of PP and LDPE/PP (34/66) mixture was not

## 4 Results and Discussion

significant as it changed from 14 to 17 wt %. The residue obtained from this experimental Series A (Table 3.4) is negligible, which agrees with TGA results (chapter 4.1).

On pyrolysis of the mixtures (LDPE/PP); the mixture with a greater proportion of PP (LDPE/PP; 34/66) produced more liquid oil (83 wt%) than the mixture with a large proportion of LDPE (LDPE/PP; 66/34) (63 wt%). The gas fraction obtained was greater in the LDPE/PP (66/34) mixture, reaching 37 wt% (in Table 4.5 and Figure 4.8).

Table 4.5). The presence of PP in the mixture enhances the cracking of LDPE in the mixture at lower temperature leading to the production of more gas with an increase in reaction time, which corresponds to findings in the literature [16, 18, 28].

Table 4.6: Catalytic cracking yield of LDPE, PP and LDPE/PP mixtures at 460 °C

Plastics	Liquid oil (wt%)	Gas (wt%)
LDPE + CAT-2	51	49
PP + CAT-2	58	42
LDPE/PP (66/34) + CAT-2	69	31
LDPE/PP (34/66) + CAT-2	62	38

In the presence of a catalyst under the experimental conditions given in Table 3.4, gas production increased immensely and a reduction in liquid fraction yield. Products obtained from the catalytic cracking process were all liquid (Appendix C). PP gas yield increased from 14 wt% to 42 wt%, and LDPE increased from 6 wt% to 49 wt%. The mixtures followed the same trend. The liquid oil fractions obtained from the pyrolysis of LDPE/PP (66/34) and LDPE/PP (34/66) was 69 and 62 wt% respectively. Gas yield from LDPE/PP (34/66) increased significantly from 17 wt% (thermal) to 38 wt% (Figure 4.8). An unexpected result was observed in the gas yield from LDPE/PP (66/34), which decreased from 37 wt% (thermal) to 31 wt% in the presence of a catalyst (Table 4.5 and Table 4.6). Probably due to over cracking of PP, leading to the production of more gas in the reactor or uneven distribution of heat in the furnace. From literature [59], it is expected that when PP is co-pyrolysed with LDPE and the mass fraction of PP is higher than 20 wt%, the yield of gaseous product is supposed to increase. Figure 4.8 shows that CAT-2 has a strong cracking ability, which can be attributed to possession of strong acidity and high porosity, which often lead to secondary cracking of the primary pyrolysis product. Catalytic pyrolysis at a lower temperature would be beneficial, as it narrows product selectivity and improves cracking at a lower temperature.

The selectivity of the catalyst could be a contributing factor to the high gas yield. No residue was formed in this process, indicating a high conversion of the samples, which validates the TGA analysis results (Figure 4.5). CAT-2 improved gas yield and reduced the yield of liquid product. No wax was formed in comparison to the thermal pyrolysis of LDPE.

However, it is important to know that the quality and composition of liquid fraction would vary depending on the type of catalyst used [36].

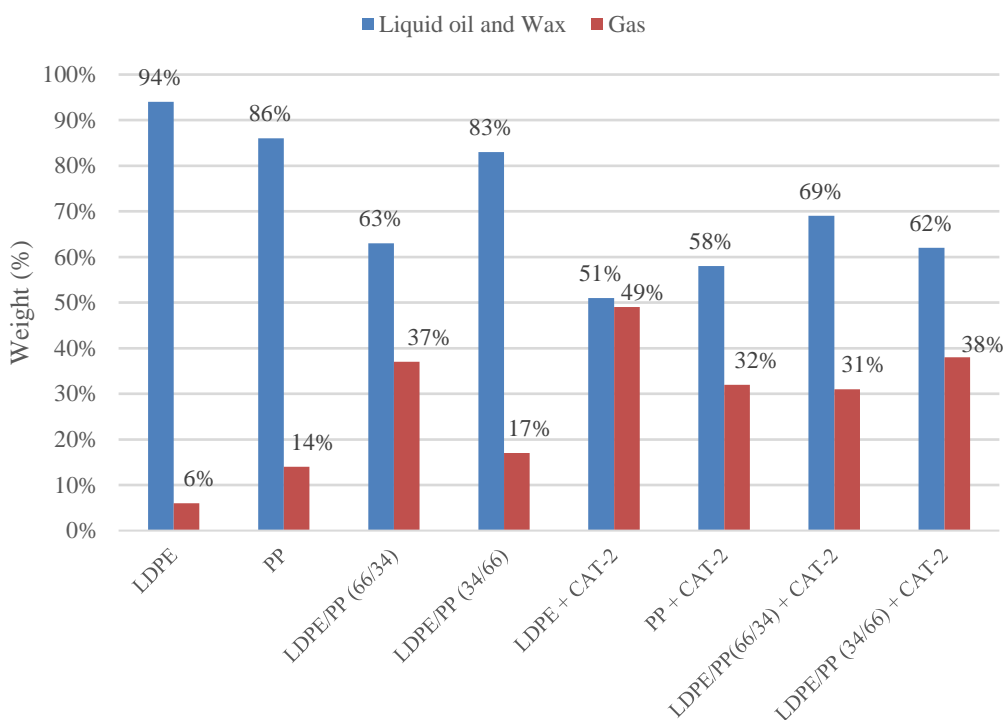


Figure 4.8: Thermal and catalytic pyrolysis yield of LDPE, PP and their mixtures

The difference in the pyrolysis yields obtained with thermal and CAT-2 could be attributed to the contact mode between the catalyst and the plastics. The increase in gas yield when the catalyst was introduced could be attributed to the mechanism of reaction during catalytic pyrolysis, as reported in the literature that thermal and catalytic decomposition are the two reaction mechanism in catalytic pyrolysis [30].

From Table 4.5, it can be concluded that thermal pyrolysis is the first step in the reaction since the liquid yield is higher in the absence of a catalyst. The second step is catalysis, whereby the liquid products of thermal pyrolysis moves freely into the acidic sites of the catalyst, leading to higher gas production. The role of catalyst in this work is consistent with findings in the literature [16, 40]. They reported that acidity and textural properties of a catalyst plays a significant role in the cracking of liquid oil/wax to gas.

#### 4.2.1 Analysis of pyrolysis liquid oil/wax

Figure 4.9 shows the carbon number distribution of the liquid oil/wax products which was identified using GC-FID. The carbon distribution obtained from analysis of LDPE liquid oil/wax (thermal pyrolysis) ranges from C<sub>7</sub>-C<sub>40</sub>, preponderated by heavy hydrocarbon fractions (C<sub>21</sub>-C<sub>40</sub>) which amounted to about 46%, followed by the diesel fractions (C<sub>13</sub>-C<sub>20</sub>) which were about 30% and 24% of gasoline fractions (C<sub>7</sub>-C<sub>12</sub>). The result showed that liquid wax fractions were enriched in diesel range hydrocarbons. The chromatogram (Appendix D) shows a series of second peaks, which could suggest the presence alkanes and alkenes respectively, distributed from C<sub>7</sub>-C<sub>28</sub>.

Table 4.7: Hydrocarbon distribution in PP and LDPE derived liquid oil/wax

Plastic	Hydrocarbon distribution (%)		
	C <sub>7</sub> -C <sub>12</sub>	C <sub>13</sub> -C <sub>20</sub>	C <sub>21</sub> -C <sub>40</sub>
LDPE	23.69	30.14	46.17
PP	43.88	32.64	23.48

Similarly, in the case of PP derived liquid fraction, the gasoline fractions, diesel fractions and heavy hydrocarbons fractions was 44%, 33% and 23% respectively (Figure 4.9). Moreover, from the chromatogram (Appendix D), it was observed that C<sub>8</sub> and C<sub>13</sub> were higher than the others as they make up about 42% of the oil (C<sub>13</sub> = 13% and C<sub>8</sub> = 29%). The diesel fraction percentage in this work is similar to the result obtained in the literature [13] at the same pyrolysis condition. The peaks of the chromatogram indicate that many compounds with double bonds and branched hydrocarbons are obtained during PP cracking than LDPE due to its structure (Figure 2.1). The proportion of hydrocarbon range component in the LDPE and PP derived fuel are presented in Table 4.7. The data showed that the percentage of gasoline range hydrocarbon in PP derived liquid fraction is higher than that obtained from LDPE.

66/34 LDPE/PP mixture also produced alkanes and alkenes as shown in the chromatogram (Appendix D). The hydrocarbon fractions obtained from 66/34 LDPE/PP mixture and 34/66 mixture are similar. However, in 34/66 LDPE/PP mixture, C<sub>8</sub> and C<sub>13</sub> were dominant recording 28% and 11% respectively, while in 66/34 LDPE/PP mixture, C<sub>8</sub> and C<sub>13</sub> also dominated but in smaller amount; 17% and 8% respectively (Appendix D). Moreover, 66/34 LDPE/PP thermal cracking showed no significant difference between the diesel and heavy hydrocarbon fractions, as both recorded about 31% and the gasoline fraction amounted to 37%. The heavy hydrocarbons (C<sub>21</sub>-C<sub>40</sub>) were present in small quantities; about 23% (Figure 4.9), indicating that the presence of a large proportion of PP in the mixture enhanced the production of shorter chain hydrocarbons (C<sub>7</sub>-C<sub>12</sub>).

As shown in Figure 4.9, the hydrocarbon distribution of the liquid/wax pyrolysis product obtained from the thermal analysis of single and mixture of plastic waste was a mixture of C<sub>7</sub>-C<sub>40</sub> compounds.

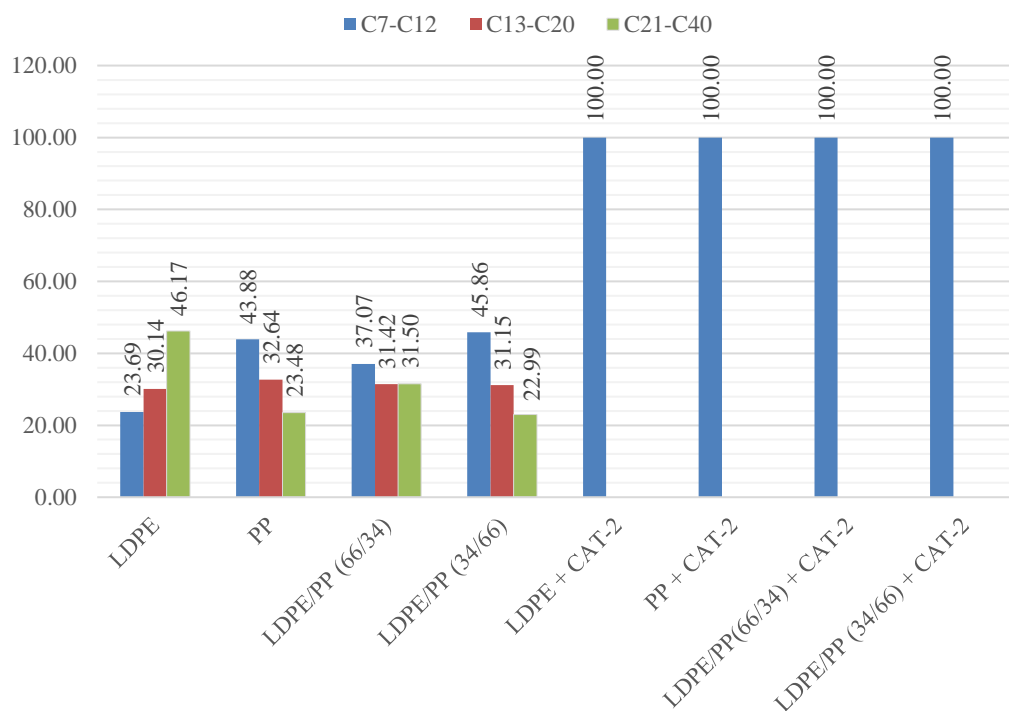


Figure 4.9: Carbon number distribution of liquid oil and wax products determined by GC-FID

CAT-2 produced a narrower carbon distribution range that is skewed towards the gasoline range (C<sub>7</sub>-C<sub>12</sub>) hydrocarbons (Appendix E). The results of GC-FID analysis agree with the low yield of liquid product and increased yield of gaseous (light hydrocarbon) fractions as shown in Figure 4.8, which confirms the strong cracking activity of CAT-2. CAT-2 proved to have an excellent high selectivity of gasoline (C<sub>7</sub>-C<sub>12</sub>) fractions since no diesel (C<sub>13</sub>-C<sub>20</sub>), and heavy fractions (C<sub>21</sub>-C<sub>40</sub>) were detected in the analysis of derived liquid oil/wax from LDPE, PP and their mixtures (Figure 4.9). CAT-2 can be a potential catalyst for gasoline production from plastic waste since the liquid products obtained on its application contains more of C<sub>7</sub>-C<sub>12</sub> hydrocarbons. However, its narrow carbon distribution might be a disadvantage to using this gasoline without upgrading. Catalytic pyrolysis occurred at a lower temperature than thermal pyrolysis and narrows product selectivity. However, the composition and quality of the liquid oil would vary depending on the reaction condition and the type of catalyst used.

Comparing the thermal and catalytic cracking hydrocarbon distribution, the diesel (C<sub>13</sub>-C<sub>20</sub>), gasoline (C<sub>7</sub>-C<sub>12</sub>) and heavy hydrocarbon (C<sub>21</sub>-C<sub>40</sub>) fraction content of the single, and mixed plastics were similar in all the thermal runs, whereas, only gasoline fractions (C<sub>7</sub>-C<sub>12</sub>) was obtained in the catalytic cracking process.



## 5 Conclusion and future work

In this study, CAT-2 was used as a catalyst for pyrolysis of single and mixed plastic wastes. Plastics such as HDPE, LDPE and PP were thermally decomposed in the presence and absence of catalysts using TGA. Thermogravimetric studies at different heating rates (5, 10, 20 and 30 °C/min) on the decomposition of plastic feedstock showed that HDPE, LDPE and PP shared a similar thermal behaviour. However, the LDPE/PP mixture presented a slightly different thermal behaviour from single LDPE and PP, implying an interaction between LDPE and PP (reduction in degradation temperature). It was also found that the residence time decreased as the heating rate increased (5 to 30 °C/min). TGA studies was an approach to identify the degradation temperature and residence time as they are the most important factors influencing product yield. On application of a catalyst, CAT-2 enhanced the degradation of HDPE and PP while CAT-3 was suitable for all the plastic sample (HDPE, LDPE and PP). Overall, the catalysts lowered the degradation temperature of the plastics, indicating energy saving and cost reduction in pyrolysis process. Similar observation was reported by López et al. [40]. Optimised reaction condition for pyrolysis was developed from the TGA studies.

Thermal and catalytic pyrolysis experiments were carried out in an autoclave reactor at 460 °C in a nitrogen atmosphere. In thermal cracking of PP and LDPE, total conversion of plastic to liquid oil/wax was about 86 wt% for PP and 94 wt% in case of LDPE. GC-FID results showed that the hydrocarbon distribution of the liquid products was distributed within C<sub>7</sub>-C<sub>40</sub> carbon range. The selectivity of diesel fraction which is the main aim of this study (subchapter 1.1) was 30%, gasoline fraction 24% and heavy fraction reached 46% in the liquid/wax obtained from LDPE. Comparing the liquid components of LDPE to PP, gasoline fraction amounted to 44%, heavy fraction 23%, and diesel fraction was 33% in the oil obtained from thermal pyrolysis of PP. Such results indicate that lighter fraction selectivity of liquid oil can be achieved in thermal cracking of PP at high temperature. However, diesel fractions obtained from LDPE and PP were not significantly different. Thermal cracking of the mixtures (LDPE/PP: 66/34 and 34/66) produced liquid oil/wax which is rich in diesel fraction (31% each). However, the LDPE/PP 34/66 mixture, gave 46% of gasoline fraction compared to LDPE/PP 66/34 which gave 37% of gasoline fractions. This is because of the increase in the proportion of PP in the mixture which enhanced the production of lighter fractions.

CAT-2 was used for pyrolysis of the plastic samples (single and mixed). The GC-FID analysis of the liquid oil/wax showed that the products obtained on application of CAT-2 have similar hydrocarbon fractions (gasoline) for both single and mixed plastics than the thermal runs. The use of catalyst has a significant influence on the product yield and hydrocarbon properties. It promoted gas production and narrowed the hydrocarbon distribution in the liquid oil to gasoline range fractions (C<sub>7</sub>-C<sub>12</sub>). The fuel properties were better in the gasoline range than in that obtained from thermal pyrolysis.

From the results, it can be concluded that the batch pressurised autoclave reactor can be used to degrade LDPE, PP, and LDPE/PP mixtures effectively, and could also be an efficient way of producing quality and usable fuel by varying pyrolysis parameters. Nevertheless, upgrading of the fuel might be required. CAT-2 lowered the pyrolysis temperature and exhibited an exceptionally high selectivity for gasoline fuel although, it was originally intended to enhance the selectivity and yield of diesel fuel.

## 5 Conclusion and future work

It is recommended from the observations made during this study that future work on this thesis should be focused towards the following investigations:

- Study on the determination of chemical compounds present in the liquid fuel and its comparison to EU fuel standard.
- A study of the effect of process parameters such as particle size, heating rate, temperature and residence time.
- A study on the energy consumption (energy balance) of the process and prevention of heat losses in the process.
- A study on the effect of additives in plastic waste pyrolysis.
- Improvement of the batch reactor to determine the temperature and pressure inside the autoclave during pyrolysis.
- Study on the effect of different catalysts on the pyrolysis of single and mixed plastics.

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# Appendices

## Appendix A Task Description



Faculty of Technology, Natural Sciences and Maritime Sciences, Campus Porsgrunn

### FMH606 Master's Thesis

**Title:** Experimental study of catalysis in plastic pyrolysis

**USN supervisor:** Prof. Lars-André Tokheim

**External partner:** Norner AS (Dr. Siw Fredriksen)

**Task background:**

*“Plastic has become the most common material since the beginning of the 20th century and modern life is unthinkable without it. Unfortunately, what makes it so useful, such as its durability, light weight and low cost, also makes it problematic when it comes to its end of life phase.”* (European Commission, 2016).

It is widely accepted that the CO<sub>2</sub> emission levels have to be reduced in order to prevent a climate change due to increased earth temperature. Norner is developing green solutions to its customers. This includes developing technology for thermal cracking of plastic waste, in order to produce environmental friendly fuel.

Norner is a global provider of R&D services in polymers for the industry, located in Grenland in Telemark. Norner has a comprehensive scientific laboratory, and the company competence and equipment covers a wide range of key technologies in the polymer and materials industry.

In this project, the student will make a literature review of plastic waste pyrolysis processes, identify and study catalysts for such processes. The student will carry out experimental work in Norner comprising catalytic pyrolysis of polyethylene and polypropylene to map catalyst performance.

**Task description:**

The aim of the project is to study experimentally the process of plastic waste pyrolysis in order to improve pyrolysis process by the use of catalyst, in order to produce environmental friendly diesel.

The specific tasks are:

1. A literature review on the plastic pyrolysis process including relevant catalysts
2. An experimental study of pyrolysis to investigate the effect of different catalysts
3. A complete report documenting the findings

**Student category:**

PT or EET

**Practical arrangements:**

Practical work is carried out at Norner and HSN.

**Address:** Kjølnes ring 56, NO-3918 Porsgrunn, Norway. **Phone:** 35 57 50 00. **Fax:** 35 55 75 47.

**References**

Ding et al. (2012), Kinetic study of low temperature conversion of plastic mixtures to value added products, *Journal of Analytical and Applied Pyrolysis*, **94**; 83–90, <https://www.researchgate.net/publication/256995981> Kinetic study of low-temperature conversion of plastic mixtures to value added products

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Kunwar et al. (2016), Plastic to fuel: a review, *Renewable and Sustainable Energy Reviews*, **54**, 421-428, <https://www.researchgate.net/publication/284131362> Plastics to fuel a review


Miandad et al. (2016), Catalytic pyrolysis of plastic waste: A review, *Process Safety and Environmental Protection*, **102**, 822-838, <http://www.sciencedirect.com/science/article/pii/S0957582016301082>

**Signatures:**

Student (date and signature):



Supervisor (date and signature):

27/1-17 



Appendix B Characteristic temperatures of plastics at three different heating rates (5, 20, and 30 °C/min).

Table B 1: Characteristic temperature of plastics at 5 °C/min

Plastics	Temperature (°C)		
	T <sub>onset</sub>	T <sub>M</sub>	T <sub>F</sub>
HDPE	444	465	475
LDPE	436	459	470
PP	388	432	446

Table B 2: Characteristic temperature of plastics at 20 °C/min

Plastics	Temperature (°C)		
	T <sub>onset</sub>	T <sub>M</sub>	T <sub>F</sub>
HDPE	460	491	507
LDPE	446	484	500
PP	392	448	470

Table B 3: Characteristic temperature of plastics at 30 °C/min

Plastics	Temperature (°C)		
	T <sub>onset</sub>	T <sub>M</sub>	T <sub>F</sub>
HDPE	465	495	510
LDPE	452	493	506
PP	402	458	475

Appendix C Product liquid oil (fuel) from single and mixed plastic wastes with catalyst (CAT-2)



Figure C 1: liquid oil produced from catalytic cracking; from left: PP, LDPE, LDPE/PP (3.4/6.6), and LDPE/PP (6.6/3.4)

## Appendix D Chromatogram of liquid oil/wax product from thermal cracking

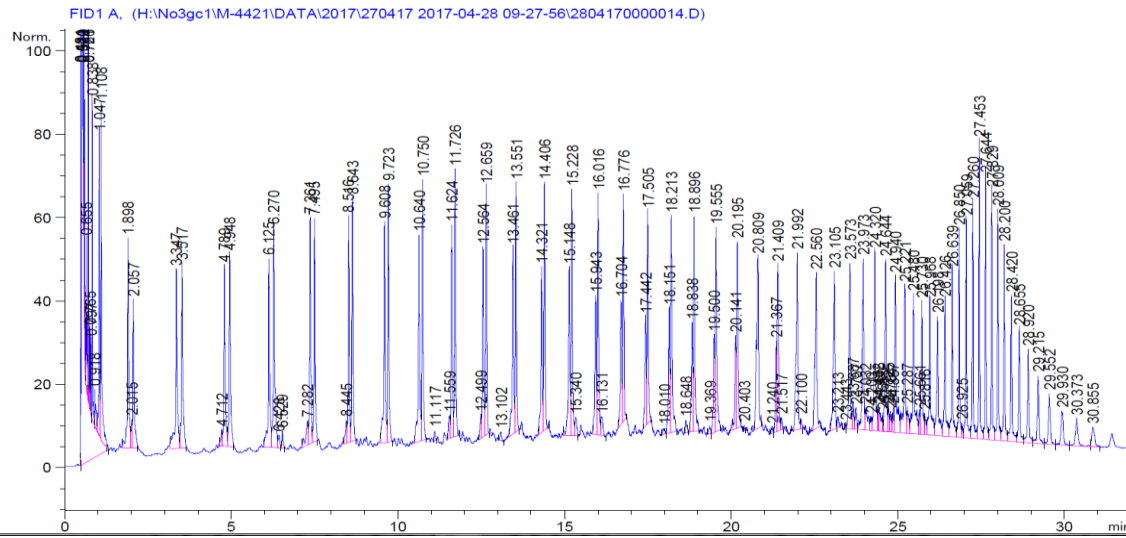


Figure D 1: Chromatogram of LDPE obtained wax

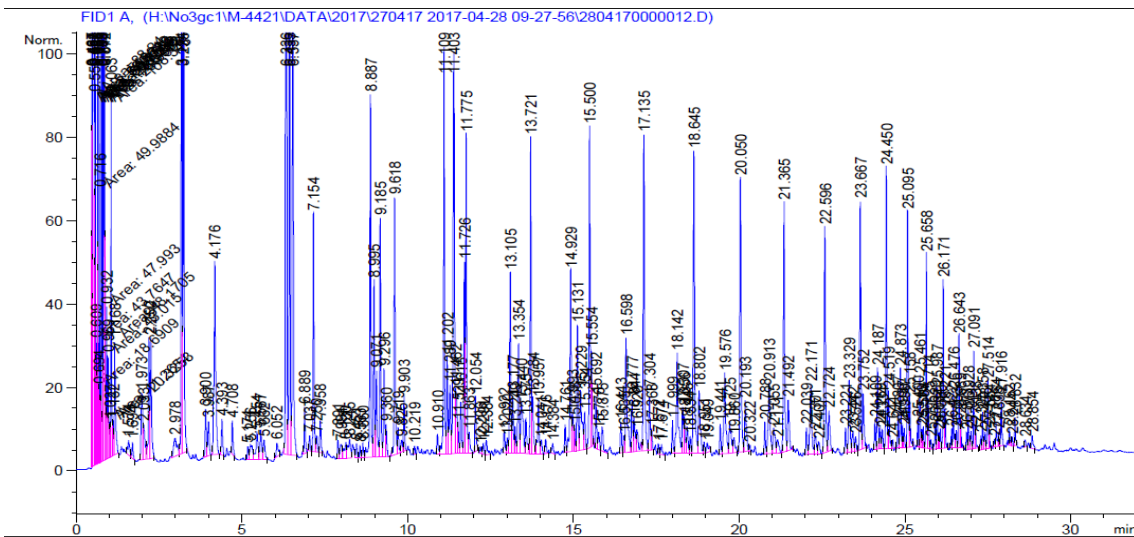


Figure D 2: Chromatogram of PP obtained liquid oil

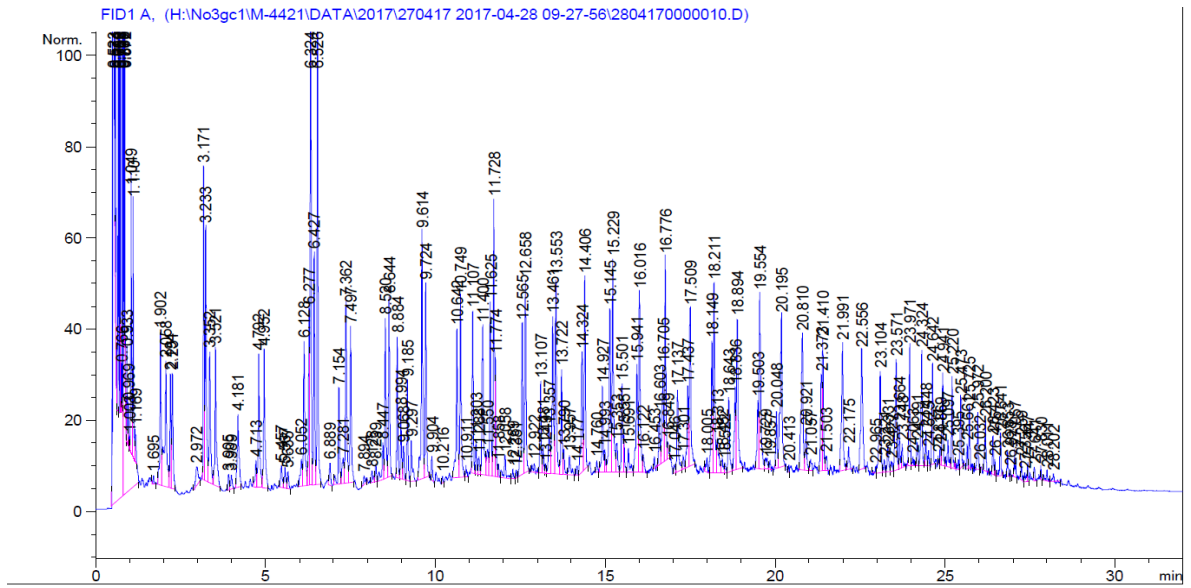


Figure D 3: Chromatogram of LDPE/PP (3.4/6.6) obtained liquid oil

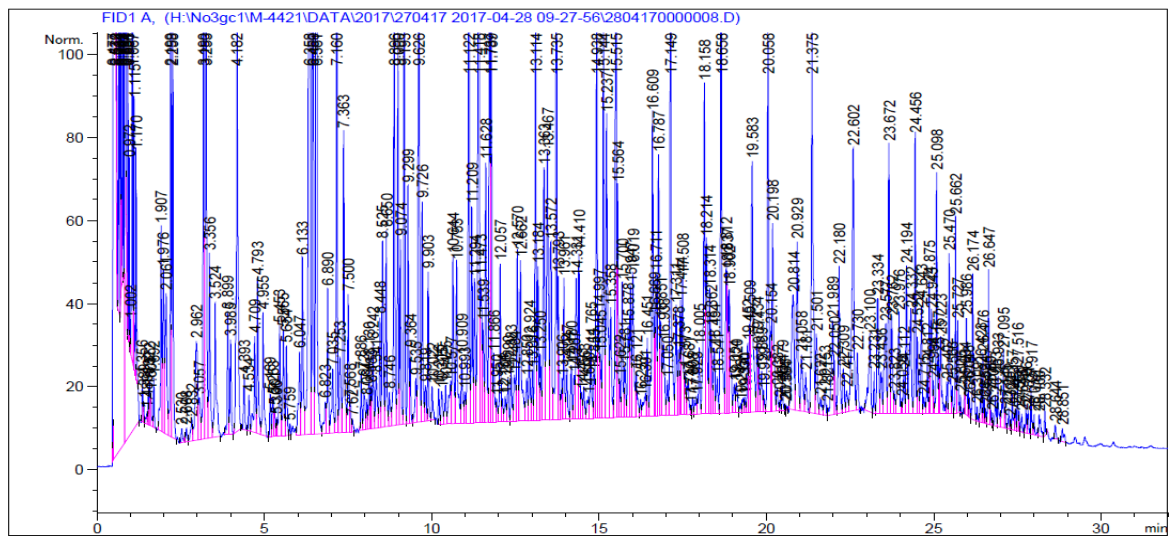


Figure D 4: Chromatogram of LDPE/PP (6.6/3.4) obtained liquid oil

Appendix E Chromatogram of liquid oil product from catalytic cracking

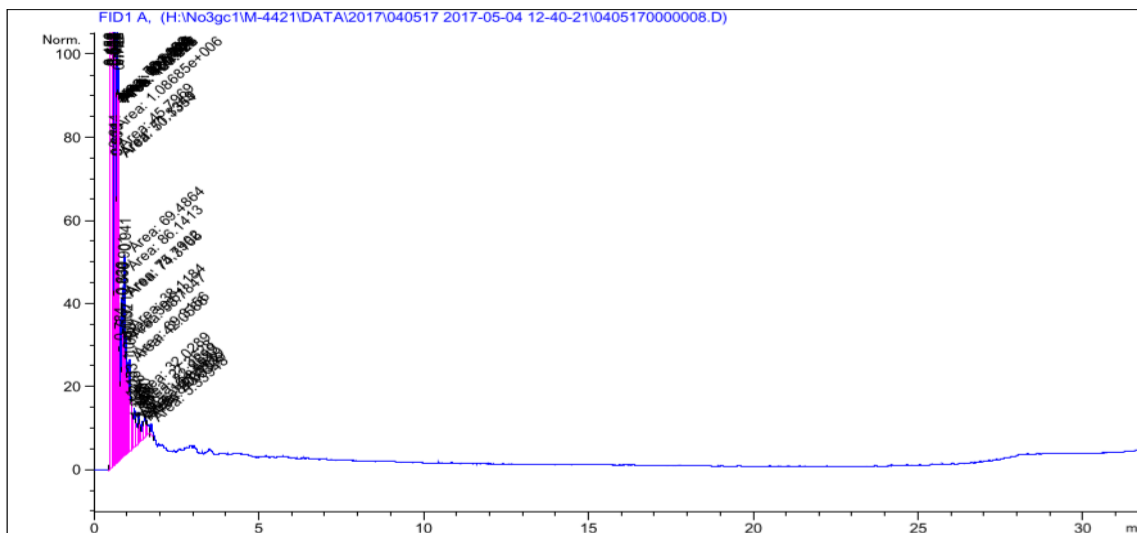


Figure E 1: Chromatogram of LDPE liquid oil

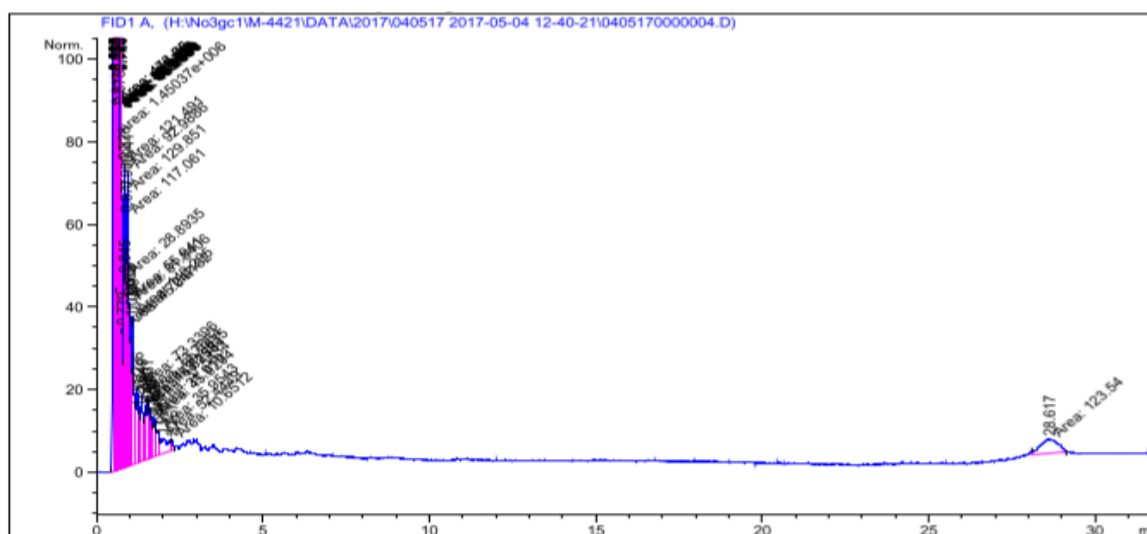


Figure E 2: Chromatogram of PP catalytic liquid oil

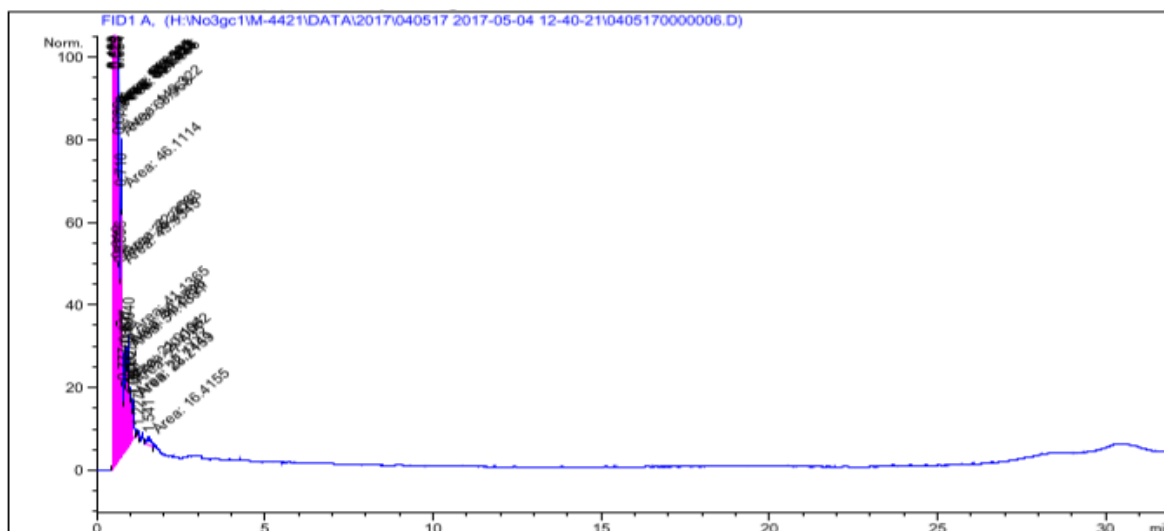


Figure E 3: Chromatogram of LDPE/PP (6.6/3.4) liquid oil

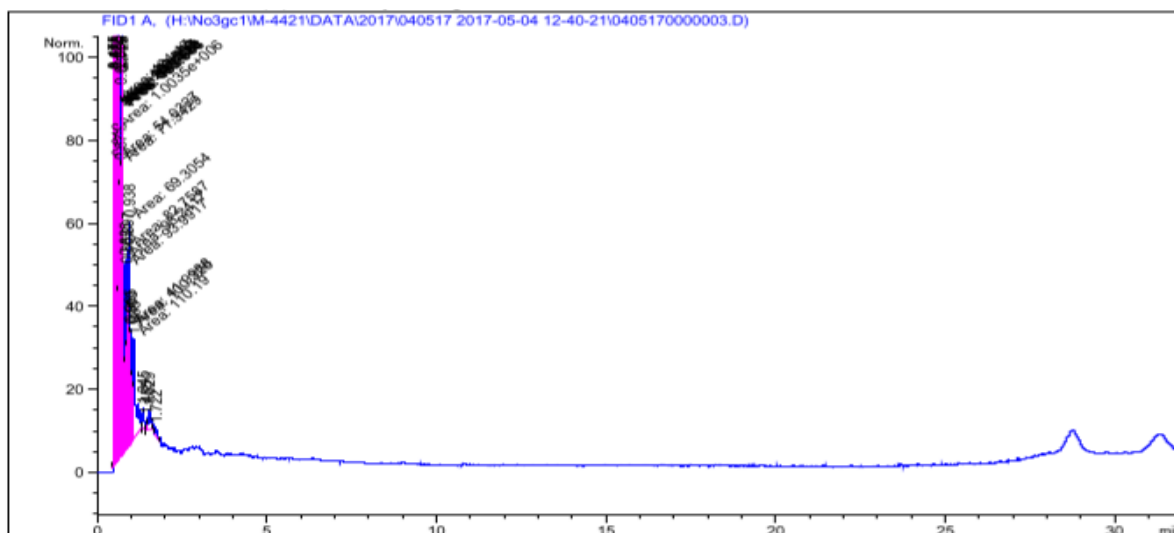


Figure E 4: Chromatogram of LDPE/PP (3.4/6.6) liquid oil

Appendix F Safe job analysis



**SAFE JOB ANALYSIS – Pyrolysis in muffle oven (PE,PP & catalyst 2&3)**

<b>ARB.TILL.NR:</b>	<b>Reviewed by:</b>					
	<b>Participants:</b>	<b>Department</b>	<b>SIGN</b>	<b>Participants:</b>	<b>Department</b>	<b>SIGN</b>
<b>DATO:</b> 23.03.2017	Azubuike F Anene	Student	<i>[Signature]</i>			
<b>BLIND LIST:</b> YES <input type="checkbox"/> NO <input checked="" type="checkbox"/>				Knut Fosse	R&D	<i>[Signature]</i>
<b>VALVE LIST:</b> YES <input type="checkbox"/> NO <input checked="" type="checkbox"/>	Kai Arne Sætre	R&D	<i>[Signature]</i>	Tore Dreng	R&D	<i>[Signature]</i>
<b>HSE-DATASHEET:</b> YES <input checked="" type="checkbox"/> NO <input type="checkbox"/>						

DESCRIPTION OF ACTIVITY	DESCRIPTION OF CRITICAL FACTOR	DESCRIPTION OF SAFETY ACTION
Overview: Pyrolysis of polymer in new reactors inside the muffle oven at up to 500C. Testing various PE, PP and catalysts. Max 15g polymer.		
- Sample preparation: • Mixing of the catalyst and polymer to have a homogeneous mixture is done in the glove box. • The autoclaves (reactor) are loaded with the mixture inside the glove box.	•	• Mix the samples in the glove box  • The bolts of the autoclaves should be properly tightened before fixing in the muffle furnace. Use the nose mask also when checking the autoclaves bolts are properly tightened outside the glove box.
- Prepare the autoclave in the muffle oven • Mount the Nitrogen line in and product line out to the autoclaves • Purge the autoclaves with Nitrogen (99.99%)	• Catalyst is exposed to air • Carry over of powder if it is too high flow of Nitrogen	• Operator must use a nose mask when mounting the nitrogen line in and product line out. • Purge to remove air / oxygen from the reactor carefully



- Pyrolysis • Turn on the muffle furnace after fixing the autoclaves and purge the furnace continuously with Nitrogen. • Ramp the temperature to the desired temperature for the pyrolysis • Product stream from reactor to collection bottles (2 wash bottles in series, 1 dry and one with bubbling through distilled water)	- Risk of burning when the inner surface is touched at high temperature  - Pressure build up in reactor – leakage of hydrocarbons or explosion	• Avoid contact with the furnace. Protective gloves and goggles must be used by the operator. • Ensure adequate clearance between the inside wall of the furnace and the reactor. (Unload the reactor when the oven is cooled to a lower temperature)  • Small purge stream of Nitrogen through reactors during pyrolysis to avoid that product is settling in product line • Use blast disk (8.5-11.5bar at 550C) • Nitrogen purging of reactor during pyrolysis in case of leakage or ruptured blast disk. • The door to the meeting room is closed and marked with warning sign. And marking the other way. • Outlet valves should be open, and the handle should be removed when running test. • The fume hood should be closed to 25cm from the bottom so the glass won't break if the blast disk ruptures. Side glass can be used when needed. • Extinguisher should always be in close range. The phone number to Norward is on the fume hood.
- Gas sampling • Sample gas with sampling bag. • Using gas detector to see when we have hydrocarbons.		•
- Washing - Check the pipe after tests for fouling. - Wash the pipes (when cold) with toluen, heptane, isopropanol	Spill toluene, hydrocarbons, alcholes.	• Use gloves, and glasses. Avoid fumes.

NOTE: USE A LOG BOOK TO RECORD ANY TEST CARRIED OUT.

HSE-Datasheets: