

Formation of Diesel Product from Polyethylene Terephthalate and Polymer

Submitted in partial fulfilment of the requirements for the award of Bachelor of
Engineering degree in Mechanical Engineering

by

Ananth. M Reg. no. 39150006

Nanda Vardhan. C Reg. no. 39150026



DEPARTMENT OF MECHANICAL ENGINEERING

SCHOOL OF MECHANICAL ENGINEERING

SATHYABAMA

INSTITUTE OF SCIENCE AND TECHNOLOGY

(DEEMED TO BE UNIVERSITY)

Accredited with grade “A” by NAAC

JEPPIAAR NAGAR, RAJIV GANDHI SALAI, CHENNAI – 600119

APRIL 2023



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Jeppiaar Nagar, Rajiv Gandhi Salai, Chennai 600119

www.sathyabama.ac.in

DEPARTMENT OF MECHANICAL ENGINEERING

BONAFIDE CERTIFICATE

This is to certify that this Project Report is the bonafide work of Ananth.M (Reg.No.39150006) and Nanda Vardhan. C (Reg.No.39150026) who carried out the project entitled **Formation of Diesel Product From Polyethylene Terephthalate And polymer** under our supervision from December 2022 to April 2023.

Internal Guide

Dr.B.Kanimozhi M.E., Ph.D.,

Head of the Department

Dr. G. ARUNKUMAR, M.E., Ph.D.,

Submitted for Viva voce Examination held on **10/05/2023**

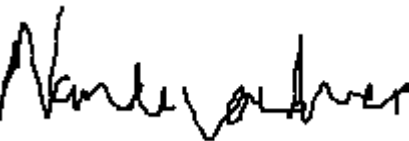
Internal Examiner

External Examiner

DECLARATION

We M. Ananth (Reg.No.39150006) and C.Nanda vardhan (Reg.No.39150026) hereby declare that the Project Report entitled **Formation of Petroleum Product From Polyethylene Terephthalate And polymer** done by us under the guidance of Dr. **B.Kanimozhi M.E., Ph.D** is submitted in partial fulfilment of the requirements for the award of Bachelor of Engineering degree in Mechanical Engineering.

1. 

2. 

Signatures of the Candidates

DATE:10.05.2023

PLACE: CHENNAI

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ABBREVIATIONS

SPI - Society of Plastic Industry

PE - Polyethylene

HDPE- High density polyethylene

LDPE - Low density polyethylene

PP - Polypropylene

PS - Polystyrene

PVC - Polyvinyl Chloride

PET - Polyethylene Terephthalate

GC - Gas chromatography

MS - Mass spectrometry

TGA - Thermo gravimetric analysis

LPG - Liquefied petroleum gases

MW - Molecular weight Micro-GC Micro gas chromatography

SEM - Scanning electron microscope

EDS - Energy-dispersive x-ray spectrometer

Abstract

This review study looks into how the world's excessive usage of fossil fuels and the dumping of waste plastic have affected the environment. Plastics and fuels made from petroleum are both hydrocarbons that include the elements hydrogen and carbon. The carbon chains in plastic molecules are longer than those in LPG, gasoline, and diesel fuels, which is how they differ from each other. When organic material is thermochemically decomposed at temperatures between 400 °C and 900 °C without the use of oxygen or other chemicals, the process is known as pyrolysis. The pyrolytic degradation of wood results in the production of several chemical compounds. Some of these substances can be used in place of traditional fuels.

PET materials were chemically recycled using pyrolysis in a fluidized bed reactor at temperatures between 510 and 730 °C. Numerous PET polymers, both with and without fillers, degraded satisfactorily. Products were mostly gases and solids. The gas output ranged from 38 to 49wt%. The main components of pyrolysis gas were CO₂ and CO. Small yields of other gases, including hydrogen, ethane, and methane, also occurred. The other significant portion was made up of solid items. Above all, the temperature rise had a significant impact on the organic residues in the reactor. At 510°C, just 5wt% of organic residues were discovered in the reactor; but, at 730°C, 40% were. Due to the breakdown of terephthalic acid and benzoic acid with rising temperature, the amount of compounds containing oxygen reduced.

Chapter-1

1.1 Introduction

Nearly 280 million tonnes of plastic are produced by people each year, much of it ending up in the environment and damaging other wildlife and marine life ecosystems. Plastic is extremely durable due to chemical bonding, which also make it resistant to deterioration caused by normal biotic processes. The removal of discarded plastics from the environment is highly challenging because plastics are not biodegradable in nature. 1 billion tonnes of plastic have been dumped since the 1950s, and some of it may remain for hundreds or perhaps thousands of years. Around US\$ 2 billion is spent annually on the disposal of plastic waste throughout the world. Even a small nation like Hong Kong invests over \$14 million on the activity each year [1].

1. Thermoplastics and thermosetting polymers are the two primary categories of plastics. If enough heat is used, thermoplastics can repeatedly soften and melt. As they cooled, they solidified, enabling the creation of new plastic items. Polyethylene, polystyrene, and polyvinyl chloride are a few examples.

2. A thermosetting can only melt and take shape once. Since they cannot withstand repeated heating, once they have formed, they remain solid.

1.2 Focus on Used Plastic:

Due to the high heat of combustion and growing availability in local communities, waste plastics are one of the most promising sources for the generation of fuel. Plastics do not readily absorb moisture like paper and wood, and their water content is significantly lower than the water content of biomass, such as plant material and food scraps. The techniques used to turn waste plastic into fuel rely on the polymers that will be used as well as the characteristics of any additional waste that may be used in the process. Additionally, choosing the right technology in accordance with regional economic, environmental, social, and technological features is necessary for an effective conversion.

In general, non-hazardous and combustible feedstock are needed for the conversion of waste plastic into fuel. Each kind of waste plastic conversion technique, in particular, has a unique feedstock that works well. The polymers used as feedstock might have extremely diverse compositions, and certain plastic products may have unfavourable additives like flame retardants made of bromine and antimony compounds or plastics made of nitrogen, halogens, or sulphur or any other potentially dangerous compounds) that endanger both people and the environment. The types of plastics and their makeup will affect the conversion process and will determine the pretreatment needs, the combustion temperature needed for the conversion and consequently the energy consumption needed, the fuel quality output, the composition of the flue gases (for example, the formation of hazardous flue gases like NO_x and HCl), the composition of the fly ash and bottom ash, and the possibility of chemical corrosion of the equipment. Consequently, the following are the main quality issues to consider while turning waste plastics into fuel resources:

Smooth feeding to conversion equipment:

Waste plastics are pre-treated using a variety of techniques before being converted into fuel resources to facilitate the subsequent conversion process's quick and painless handling. The pre-treatment machinery used for each form of plastic (crushing or shredding) varies frequently depending on their structures (such as rigid, films, sheets, or expanded (foamed) material).

2) Effective conversion into fuel products:

In the manufacturing of solid fuel, thermoplastics serve as binders that melt and solidify to produce pellets or briquettes. Sticking to other non-melting materials including thermosetting plastics, paper, and wood. Pellets made from woody materials can be created using a pelletizer, however combining plastics with wood or paper makes the process more difficult. Pellets made from thermoplastics and other flammable trash must be heated appropriately. Thermoplastics with liquid hydrocarbon content can be utilised as feedstock in the manufacturing of liquid fuel. Both the processing speed and the product yield are influenced by the kind of plastic being utilised. Moisture and unwanted contamination increase energy consumption and encourage the creation of byproducts during the fuel manufacturing process.

3) Clean flue gas and well-controlled combustion in fuel user facilities:

To enhance performance, it is critical to match the type of fuel and its quality to the burner effectiveness of heat recovery. The composition of the flue gas and the amount of ash produced, for example, can be impacted by contamination from nitrogen, chlorine, and inorganic species. It must be ensured that the flue gas composition conforms with regional air quality standards while using fuel made from waste plastic. Similarly, when disposed of at the landfill, ash quality must also be in accordance with local laws. In the absence of pertinent legislation, recycled fuel manufacturers and customers should both monitor the quality of the fuel and the emissions produced during combustion.

- Fuel Demand

The current pace of economic growth cannot continue. Unless fossil fuels like crude oil and natural gas are conserved coal or gas. Reports from the International Energy Outlook 2010 consumption of liquid and petroleum around the world increases from 86.1 million barrels per day in goods compared to 92,1 million barrels per day in 2020 and Natural gas and 110.6 million barrels per day in 2035 from 108 trillion cubic feet in usage to 156 trillion cubic feet by 2035 from 2007. Consequently, the oil and the gas supply can only support between 43 and 167 people. decades afterwards. Therefore, humanity must rely on the renewable energy alternatives, such as biomass, hydroelectric, geothermal, wind, and solar energy power, nuclear power, etc.

1.3 Background:

Plastic is a high molecular weight material that was invented by Alexander Parkes in 1862. [1] Plastics are also called polymers. The term polymer means a molecule made up by repetition of simple unit. For example, the structure of polystyrene can be written in a form as shown in Figure 1-1 or in Figure 1-2.

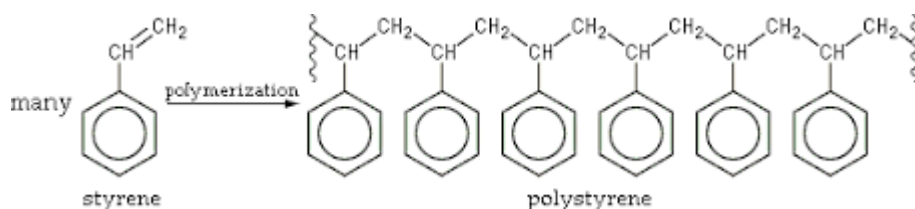


Fig. 1.1 Common expression of polystyrene molecular structure

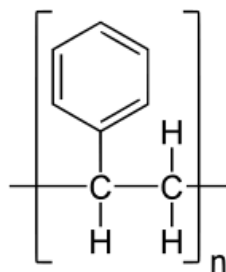


Fig. 1.2 A simplified expression of polystyrene molecular structure

The repeating unit of the polymer is in the brackets with a subscript, n , to represent the number of the unit in this polymer molecule. Plastic is one of the most commonly used materials in daily life which can be classified in many ways such as based on its chemical structure, synthesis process, density, and other properties. In order to assist recycling of the waste plastic, Society of Plastic 2 Industry (SPI) defined a resin identification code system that divides plastics into the following seven groups based on the chemical structure and applications:

PET (Polyethylene Terephthalate)

HDPE (High Density Polyethylene)

PVC (Polyvinyl Chloride)

LDPE (Low Density Polyethylene)

PP (Polypropylene)

PS (Polystyrene)

Other The above seven types of plastics are marked on various plastic products as follows



Fig. 1.3 Marks of the seven types of plastics on various plastic products

Due to the convenience to manufacturing and use, the world plastic production has been increasing since it was firstly commercially manufactured, from 1.5 million tons in 1950 to 260 million tons in 2007 as shown in Figure 1.4. One of the major concerns for extensive use of the plastics is the disposal of the waste plastic. In addition, the plastics are produced from non-sustainable oil or coal, and thus it is a non-sustainable product. There were 30.7 million tons of waste plastic generated in the U.S. in 2007, which accounts for 12.1% of the total municipal solid wastes. In U.K., 4.9 million tons of plastics were consumed in 2007. Europe consumes about 25% of the global plastic production, which is equivalent to 60 million tons per year.

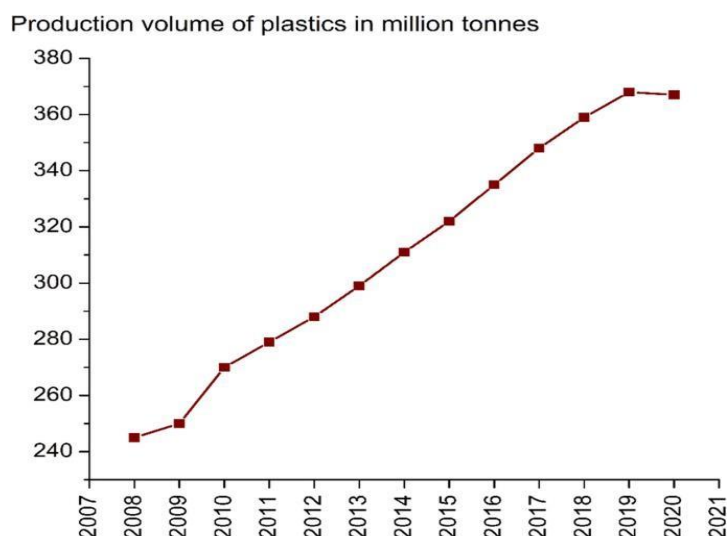


Fig.1.4 Plastic production in the world and in Europe from 1950 to 2007

In New Zealand, 262,904 tonnes of virgin plastics were imported for processing in 2004 and at least 71.3% (187,451 tonnes) of the plastic products were consumed domestically with the remaining being exported. The type and the quantity of the imported plastics were given in Table 1-1. It was found that over 30% of manufactured plastics were LDPE and 20% were HDPE. Most cities in New Zealand have plastic collection and recycling systems, however, only 13.5% of these post-consumed plastics (35,442 tonnes) were recovered in 2004 as shown in Table 1-2. The majority of the recovered plastics were PE that accounted for 60% in total recovered plastics, including 35% for LDPE and 25% for HDPE. In Table 1-2, the proportions of PET and HDPE in the recycled plastics are relatively higher than those in the imported plastic materials because these two types of plastics are identified and separated in recycling

of the municipal solid waste (MSW) in New Zealand. On the contrary, PVC is widely used in construction that has a longer lifespan than other packaging plastics, and there is no public recycling system for PVC. Therefore, the proportion of the recovered PVC is relatively low

1.4 Economic value to the community

The technology helps to save land resources by utilizing waste plastics to generate valuable energy. Currently, a majority of the waste plastic is land filled and it is not sustainable because waste plastic takes very long time to decay. However, it seems that New Zealand has no other choices but continues to do so in the foreseeable future. New Zealand is an island country and given its limited land resources, the society as a whole has to pay increasing attention to the environmental sustainability for the next generations. The world's annual consumption of plastic which was five million tones in the 1950's has skyrocketed to a global production of 245 million tones in 2008 and waste plastic generation is rapidly increasing. Plastic waste is the third largest contributor to municipal and industrial waste systems after food and paper. Christchurch produced 243054 tons of municipal refuse between July 2003 and Jun 2004 of which 15% was plastic waste. PE, PS and PP account for over 70% of this plastic waste according to the Christchurch City Council. Therefore, significant amount of energy can be produced with this technology. This could be an alternative energy resource for substituting fossil fuels. The New Zealand government could reduce the reliance on the imported oils. The community may also reduce the reliance on the hydrolic power generation.

The fuels produced from this process do not contain sulphur content because there is no sulphur in the waste plastic feedstock. This is an advantage compared with the classic fossil fuels such as diesel because sulphur content in the fuels could form SO₂ after combustion. SO₂ is a pollutant causing severe air pollutions, which affects people health and damages the concrete structure. Therefore, this technology is environmental friendly and has significant positive impact on the local government and community

1.5 The pyrolysis of Plastic Materials

Pyrolysis is a thermal cracking reaction of the large molecular weight polymer carbon chains under an oxygen free environment and produces small molecular weight molecules. [9-12] Traditional treatments for post-consumed plastics were landfills or incineration. However, landfill of the post-consumed plastics has potential problems because of limited land resource and high durability of plastics. Incomplete incineration may generate poisonous substances and causes serious health problems. Other methods like gasification and bioconversion are mainly used for organic materials.

HDPE, LDPE, PP and PS are all hydrocarbons consisting entirely of carbon and hydrogen, which are similar to hydrocarbon fuels such as liquefied petroleum gas (LPG), petrol and diesel. [14-16] Plastics are derived from petroleum and have calorific values in a similar range as those of LPG, petrol and diesel as given in

Comparison of energy density of plastics and different types of fuel

Some commercial plastic pyrolysis plants have been in operation in which all types of post-consumed plastics accepted need to be treated using hydrochloride scrubber which is for PVC cracking and is not preferable in the fuel product because chloride is not desirable in the fuels. [17-18] Those plants are sophisticated and not suitable for relatively small scale production.[17] In these plants, catalysts are also used to improve the quality of pyrolysis products in many existing equipments. Those equipments with catalysts have some weakness in terms of long material resistance time, undesired contact between plastics and catalysts, required high heat transfer rate, and cost of the catalysts[19]

In order to understand and optimise the pyrolysis of waste plastic and to investigate the impacts of different types of the plastics, extensive research has been conducted in the past decade. Kaminsky, Scheirs and their colleagues [17, 20-23] investigated the effects of reaction conditions on the pyrolysis product. Williams studied the products from pyrolysis of different individual and mixed plastics. [10-11, 24-27] Aguado et.al. investigated the effect of catalysts on the pyrolysis reactions. [28-32] In these studies, the lab-scale pyrolysis reactors were either batch type or semi-batch type rather than continuous type. Most studies focused on the effects of operation temperature, heating rate, and catalysts on the product yield. However, there are few researches in the literature review investigating the cracking process of the pyrolysis products during the pyrolysis which is believed to be complex. In addition, the final products are also very complicated. There could be over a hundred of components in the hydrocarbon products including paraffin, olefin and their isomers. Normally, the PONA system, which is an abbreviation for paraffin, olefin, naphthene and aromatic compounds, is used to describe those petroleum hydrocarbons. [17] Paraffins are saturated hydrocarbons with straight or branched carbon chain, which are also called “alkane”. Olefins have similar chain as paraffins, but they have one or more multiple bonds between carbon atoms in their chains. Naphthenes are saturated hydrocarbons like paraffins but their chains merge to a ring in their structure. Aromatics contain a benzene ring in the structure. Another common way to describe the hydrocarbons is based on the carbon numbers in their molecule structure. It is particularly applied to petroleum fuels. The complex pyrolysis products may also be grouped as petroleum gases, petrol, kerosene, diesel and 10 wax. The above fuels contain hydrocarbon group with different carbon chain lengths as given in. [33] There are also other ways

to describe the hydrocarbons such as boiling range, phase of products at room temperature etc.

1.6 Objectives of the Investigation

The main objectives of this study were to understand and optimize the processes of plastic pyrolysis for maximizing the oil products, and to design a continuous pyrolysis apparatus as a semi-scale commercial plant. The materials to be tested in this study are HDPE, LDPE, PP and PS which account for 70% of the plastics used in packaging. PVC and PET are not studied due to health concerns.

This study was divided into three stages following an extensive literature review on plastic pyrolysis. The first stage of the study focused on understanding of the thermal cracking process and identifying key factors that affect the pyrolysis process and the quality of the plastic pyrolysis products. From the literature review, reaction temperature was the most important factor that influenced the whole process, however, this study have also investigated the secondary cracking process and other significant factors such as temperature, heating rate, type of plastic, catalysts, interaction between different plastics, pyrolysis process, etc.. The effects of secondary cracking were investigated. This work has not been found in other researches.

In the final stage, a continuous pyrolysis apparatus were designed and manufactured based on the results and the information collected from the work performed during the first two stages. The aim of this continuous apparatus was to convert LDPE and mixture of PE, PP and PS into gas and liquid fuels with maximizing the diesel range product. The apparatus consists of a feeding section, a pyrolysis reactor, and a separation section, which separated diesel, wax, petrol and non-condensable gases.

CHAPTER-2

2. Literature Review on Plastic Pyrolysis

Several studies have investigated the effect of plastic pyrolysis oil composition of biodiesel on its performance and emission characteristics. Here are some of the key findings from these studies:

A study by (Adhvaryu, A., Erhan, S. Z., & Liu, 2007) found that biodiesel derived from soybean oil, which has a high percentage of polyunsaturated fatty acids (PUFAs), resulted in higher NO_x emissions compared to biodiesel derived from other feedstocks. This was attributed to the formation of free radicals during combustion of PUFAs, which react with nitrogen in the air to form NO_x.

Another study by (Lapuerta et al., 2017) investigated the effect of different fatty acid compositions on the combustion characteristics of biodiesel. The study found that biodiesel derived from saturated fatty acids (SFAs) had higher ignition delay and lower heat release rate compared to biodiesel derived from unsaturated fatty acids (UFAs). This was attributed to the higher cetane number of SFAs, which leads to better ignition quality.

A study by (Banapurmath, N. R., Tewari, P. G., & Hosmath, 2010) investigated the effect of different fatty acid compositions on engine performance and emissions. The study found that biodiesel derived from palm oil, which has a high percentage of SFAs, resulted in lower emissions of CO, HC, and NO_x compared to biodiesel derived from other feedstocks. This was attributed to the lower oxygen content of SFAs, which leads to more complete combustion.

A study by (Chen, Y., Shuai, S., Yu, Y., & Wang, 2011) investigated the effect of different fatty acid compositions on the combustion characteristics and emissions of a diesel engine. The study found that biodiesel derived from canola oil, which has a high percentage of monounsaturated fatty acids (MUFAs), resulted in lower emissions of CO and NO_x compared to biodiesel derived from other feedstocks. This was attributed to the lower reactivity of MUFAs, which leads to slower combustion and less formation of pollutants.

Overall, these studies suggest that the fatty acid composition of biodiesel can have a significant effect on its performance and emission characteristics. Biodiesel derived from feedstocks with a high percentage of SFAs may result in lower emissions of CO, HC, and NO_x, while biodiesel derived from feedstocks with a high percentage of MUFAs may result in lower emissions of CO and NO_x. However, biodiesel derived from feedstocks with a high percentage of PUFAs may result in higher NO_x emissions due to the formation of free radicals during combustion.

In the study conducted by (Huang, K.-C., Wei, C.-C., & Chang, 2013), they proposed a novel method for the determination of FFA in oils and using UV spectroscopy and copper soap colorimetry. The authors synthesized copper soap by reacting copper acetate with stearic acid, and the resulting copper soap was used as a colour reagent

for the FFA determination. The UV absorbance of the FFA-copper soap complex was measured at a wavelength of 320 nm, and the FFA content was calculated based on the standard curve. The authors optimized the experimental conditions, such as the concentration of copper soap and the reaction time, to improve the accuracy and sensitivity of the method. The results showed that the method had a high accuracy and sensitivity, and it could be applied to different types of oils and fats.

A study by (Győrik et al., 2006) presented a new analytical method for determining the total FFA concentration of thermally processed pyrolysis oil. The technique used a 632.8 nm He-Ne laser as the radiation source and relied upon the colorimetric coppersoap technique paired with the idea of the optothermal window. When results from this method and those from conventional spectroscopy were examined, they showed a strong concordance for FFA values greater than 2 μmol per mL [59].

In another study by (Xu, Y., Li, Y., Li, B., & Yang, 2016), a modified method for FFA identification using UV spectroscopy and copper soap colorimetry was reported. The authors used copper (II) chloride instead of copper acetate as the copper source to synthesize the copper soap, and the FFA-copper soap complex was measured at a wavelength of 340 nm. The authors also optimized the experimental conditions, such as the concentration of copper (II) chloride and the reaction time, to improve the accuracy and sensitivity of the method. The results showed that the modified method had a lower detection limit and a wider linear range than the traditional method.

The properties of biodiesel fuel, such as density, viscosity, flash point, and cetane number, are largely influenced by the composition of FAME. Different feedstocks can result in varying compositions of FAME, which can impact the fuel's properties. (Ahmad, M., Mamat, R., Ali, O. M., & Najafi, 2018) conducted a study to investigate the influence of different feedstocks on the physio-chemical properties of biodiesel. The study found that FAME composition significantly affects fuel properties such as density, viscosity, and flash point.

Furthermore, FAME can have an impact on the durability of fuel system components. (Ali, A., Al-Azawi, H., & Al-Rashed, 2019) evaluated the effect of FAME on the corrosion of aluminium alloys and found that FAME blends can accelerate corrosion. The study also found that the degree of corrosion depends on the composition of FAME.

Furthermore, the effect of FAME on the stability of biodiesel fuel is a critical consideration for its storage and transportation. Biodiesel is susceptible to oxidative degradation, which can cause fuel quality deterioration and negatively impact engine performance. Several studies have investigated the stability of biodiesel fuel with varying FAME compositions. For example, a study by (Liu, Y., Cheng, S., Li, S., & Li, 2021) found that blends of biodiesel with high stearic acid methyl ester (SAME) content exhibited better oxidative stability than blends with high oleic acid methyl ester (OAME) content.

Overall, the literature survey highlights the significant influence of FAME composition on the properties of biodiesel fuel. Optimizing FAME composition is crucial for improving fuel performance and reducing its impact on the environment. Also, UV

spectroscopy and copper soap colorimetry are reliable methods for the identification and quantification of FFA in oils and fats. These methods have the potential to be widely used in the food industry for the quality control of oils and fats. However, further research is needed to validate these methods for different types of oils and fats, and to investigate their applicability to complex food matrices.

CHAPTER-3

AIM AND SCOPE

AIM:

This review study looks into how the world's excessive usage of fossil fuels and the dumping of waste plastic have affected the environment. Plastics and fuels made from petroleum are both hydrocarbons that include the elements hydrogen and carbon. The carbon chains in plastic molecules are longer than those in LPG, gasoline, and diesel fuels, which is how they differ from each other. When organic material is thermochemically decomposed at temperatures between 400 °C and 900 °C without the use of oxygen or other chemicals, the process is known as pyrolysis. The pyrolytic degradation of wood results in the production of several chemical compounds. Some of these substances can be used in place of traditional fuels. PET materials were chemically recycled using pyrolysis in a fluidized bed reactor at temperatures between 510 and 730 °C. Numerous PET polymers, both with and without fillers, degraded satisfactorily. Products were mostly gases and solids. The gas output ranged from 38 to 49wt%. The main components of pyrolysis gas were CO₂ and CO. Small yields of other gases, including hydrogen, ethane, and methane, also occurred. The other significant portion was made up of solid items. Above all, the temperature rise had a significant impact on the organic residues in the reactor. At 510°C, just 5wt% of organic residues were discovered in the reactor; but, at 730°C, 40% were. Due to the breakdown of terephthalic acid and benzoic acid with rising temperature, the amount of compounds containing oxygen reduced

SCOPE:

Pyrolysis is the thermal degradation of plastic waste at different temperatures (300-900°C), in the absence of oxygen, to produce liquid and gaseous fuel. In pyrolysis, feedstock such as waste plastic is heated in the absence of oxygen or low-oxygen environment and, instead of burning, breaks down into a mixture of simpler hydrocarbons. This process is simply thermal depolymerisation, plastics are made from small building blocks (monomers) through a process known as polymerization. Pyrolysis is a process that reverts used, discarded plastics into a valuable resource in the form of monomers, fuel and other useful resources. Pyrolysis presents several advantages over other conventional waste plastic management approaches. For instance, most waste plastics during recycling are down-cycled; plastics are used in producing articles of lower quality and application. This is because the plastic tends to lose properties such as clarity, strength and flexibility as they are recycled again and again. On the other hand, in pyrolysis techniques, both thermoset and thermoplastic can be used as feedstock. Pyrolysis technique can also be used to treat waste of many novel materials, such as composites, especially in the emerging technology where polymer composites are replacing traditional materials in most engineered applications. Finally, depending on the feedstock composition, process condition (temperature, heating rate, reaction gas) and presence of catalyst (catalytic pyrolysis) or absence of catalyst (thermal pyrolysis), the product and yield composition can be varied.

CHAPTER-4

MATERIALS AND METHODS

4.1. Factors affecting Plastic pyrolysis

The major factors influencing the plastic pyrolysis process and pyrolysis product molecular distribution include chemical composition of the feedstock, cracking temperature and heating rate, operation pressure, reactor type, residence time and application of catalyst. These factors are summarized in this section as follows

4.2. Chemical composition of feedstock

The pyrolysis products are directly related to the chemical composition and chemical structure of the plastics to be pyrolyzed. In addition, the chemical composition of the feedstock also affects the pyrolysis processes. In reality, waste plastics are possibly contaminated before recycling which could also have effects on the pyrolysis process and products. As mentioned in Chapter 1, PE, PP and PS are most commonly used polymeric hydrocarbons and were selected as the investigated materials in this study. Polyethylene is formed from ethylene through chain polymerization which is shown in Formula.

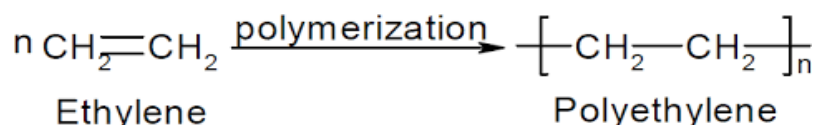


FIG. 4.1 Polymerization of ethylene to polyethylene

Plastics can be classified, according to structural shape of polymer molecules, as linear, branched, or cross-linked in Figure. The units in linear polymer are linked only to two others, one to each ends. The polymer is termed branched when branches extend 13 beyond the main polymer chain randomly. Regularly repeating of side groups are considered to be part of the unit but not considered as branches. Based on the above description, polystyrene is called linear polymer although it contains functional groups as part of the monomer structure. In branched polymers, at least one of the monomers is connected to more than two functional groups due to the branching points produced from the polymerization process. The functional side group and the branch structure have significant effects on the pyrolysis product. For example, the dominant component in PS pyrolysis products is styrene that is the side group come off from PS carbon backbone.

There is a significant relationship between the density and the branching intensity of polymers. The PE with more branches has relatively lower density. This has been found in McMurry's study. The branched polyethylene is also called low density polyethylene (LDPE), which is different from linear polyethylene that is called high density polyethylene (HDPE).

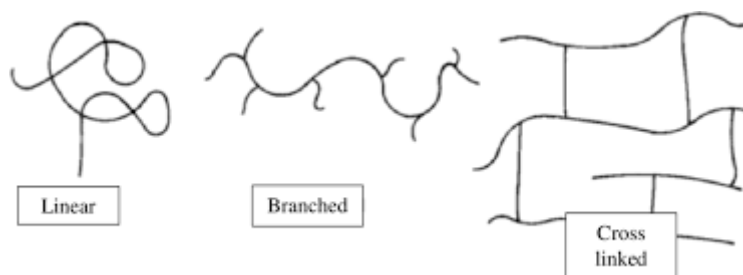


Fig. 4.2 Polymer structure, linear, branched and cross linked

A cross linked polymer can be described as an interconnected branched polymer with all polymer chains are linked to form a large molecule. Thus, the cross linked polymer constitutes large molecule. Theoretically, the molecular weight of a cross linked polymer can be infinite. In reality, the molecular weight of a cross linked polymer will be limited due to breaking down of the molecular inter-connections during the processing or the weight of the polymer sample. The cross linked polymer cannot be dissolved in solvents or be melted by heat because of their network structure. For example, PEX, a common abbreviate of cross-linked polyethylene, is widely used in oil and water piping. In pyrolysis process, cross linked polymer will crack rather than melt or evaporate. This is different from the reactions of linear or branched polymers in pyrolysis process.

4.3 Cracking temperature and heating rate

Temperature is one of the most important operating variable, since the temperature dominates the cracking reaction of the polymer materials. Not all of the polymer materials can be cracked by increasing the temperature. Van der Waals force is the force between the molecules, which attracts molecules together and prevents the collapse of molecules. When the vibration of molecules is great enough, the molecules will evaporate from the surface of the object. However, the carbon chain will be broken if energy induced by van der Waals force along the polymer chains is greater than the enthalpy of the C-C bond in the chain. This is the reason why high molecular weight polymer is decomposed rather than is boiled when it is heated. In theory, the temperature of thermal breaking the C-C bonds should be constant for a given type of plastic (polymer). However, this temperature has been found to differ in different studies. For example, the temperature when PP starts cracking was reported at 380 °C in Ciliz et al.'s result but it is measured to be 650 °C in Demirbas's result. Both of them used similar batch process reactor and thermo gravimetric analysis. According to the provided schemes, the most likely reason is the difference in the temperature measurement location where the temperature sensors were located. There was significant temperature gradient along the apparatus in which the melted plastic at the bottom of a fix-bed batch reactor had much lower temperature than that on the top surface of the reactor. It was also found that the space temperature in the pyrolyzer was strongly influenced by the product vapour. Different locations of the temperature sensors in different studies are believed to be one of the most important factors on the

different cracking temperature reported. Karaduman et al. investigated the temperature profile along a tube heated by external furnace. Large temperature variation was observed between the ends and the centre of the tube. (Figure 2-2) Clearly, there was significant heat loss at both ends of the tube reactor.

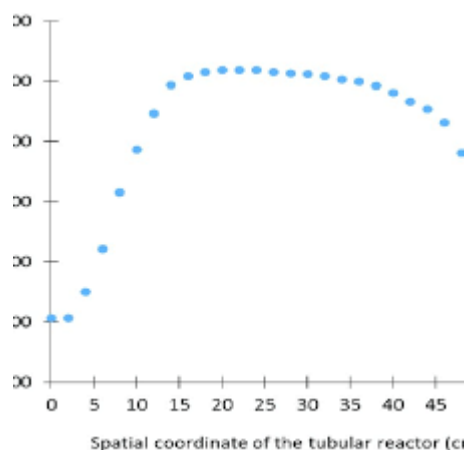


Fig. 4.3 Temperature profile along the tube reactor

The difference of the temperature on the surface in contact with the plastic and the temperature of the plastic close to the surface was measured by Karaduman, A., et al. for comparison, which is measured relatively minor and constant in this research study. Therefore, the temperature at the reaction surface is selected for monitoring the cracking temperature of plastics. In Shah et al.'s study, mixture of post-consumed plastics of PE, PP and PS was pyrolyzed in a fixed-bed batch reactor at different temperatures for one hour. It was found that higher reaction temperature favours the gas production and production of heavy molecular weight products in the liquid. (Fig 2.3 and Fig 2.4) Fig 2.3 shows the gas chromatography (GC) analysis results of the liquid products with the temperature on the curves indicating the cracking temperature. It is seen that the liquids produced at higher cracking temperatures have lower flash-off percentage at the same GC temperature during the analysis. This shows higher proportion of heavy molecular weight components in the liquid. Similar conclusion was also found in other research using virgin plastics and fluidized-bed, semi-batch reactor

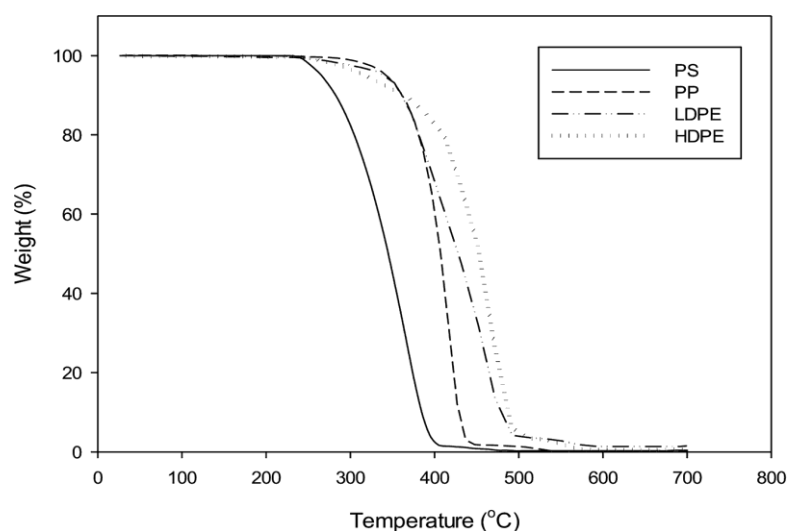


Fig. 4.4 GC analysis results of plastic pyrolysis liquid

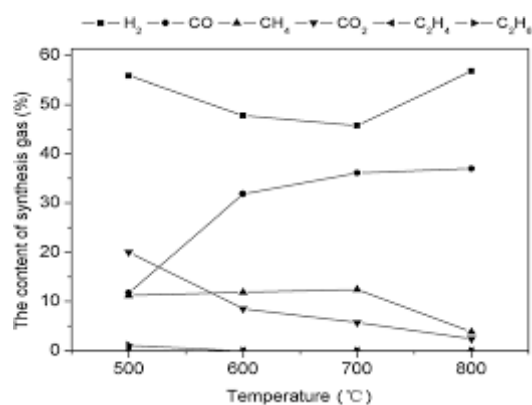


Fig. 4.5 Influence of temperature on product distribution

However, the overall gas proportion of gas product increased with increasing cracking temperature up to 730°C while the liquid product proportion decreased with the cracking temperature in the full range of temperature used. (Fig 2.4)

The other operating thermal dynamic parameter is heating rate. The term “heating rate” in this field means the increase of temperature per unit time. The influence of the heating rate on the plastic pyrolysis process and product distribution varies in different studies due to the differences in the pyrolysis reactor, operation conditions (temperature and pressure), and temperature measurement location. Normally, in a fast or flash pyrolysis, heating rate refers to the temperature change of the plastic from it dropped on the hot surface till decomposed and vaporized. The hot surface remains the temperature while the amount of plastic dropped on to it is relatively small. In this situation, the heating rate is very high, up to 10,000 K/s. [26, 45-47] This is hard to be measured precisely. Therefore, the surface temperature is normally applied as the reaction temperature indicator rather than heating rate in the flash and fast pyrolysis process. In a batch process, the plastic is normally heated from room temperature to the cracking temperature in several minutes. It is a slow pyrolysis process. Once the plastic feedstock is heated to the cracking temperature, the temperature remains

relatively constant until all feedstock has been pyrolyzed. Therefore, heating rate is normally applied as the temperature indicator instead of reaction temperature in a slow pyrolysis process. It was found that heating rate usually varied from 10 to 100 °C/minute in previous slow pyrolysis researches. In Saha and Ghoshal's study on pyrolysis of CocaCola drink PET bottles, the influence of heating rate on the reaction process was investigated by using thermo gravimetric analysis (TGA) as shown in Fig 2.5. In the figure, $d\alpha/dT$, defined as the rate of reaction (K-1), is plotted as a function of absolute temperature for different heating rates from 10 to 25 K/min. It was found that higher heating rate promotes the rate of pyrolysis reactions.

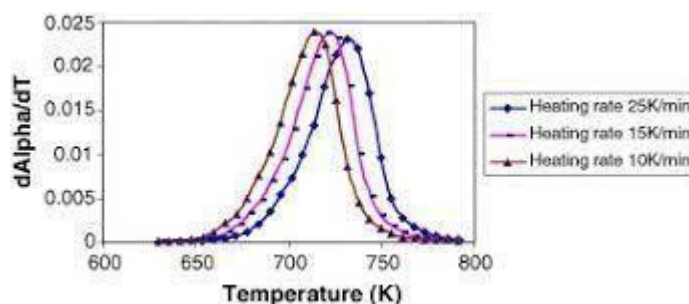


Fig. 4.6 Reaction rate as a function of temperature and heating rate in pyrolysis of Coca Cola soft drink PET bottle

4.4 Multi-factor effect on pyrolysis process

It is difficult to directly compare the product yields obtained for a specific plastic in different researches as the operating conditions and reactors can be very different. In general pyrolysis processes, thermal degradation occurs in the initial stages of the pyrolysis with absence of oxygen. The pyrolytic products immediately after the pyrolysis consist of solid residue, oil vapour and non-condensable gases among which the oil vapour will become liquid after cooling down. According to the residence time or the heating rate during the pyrolysis process, the pyrolysis can be classified into slow carbonization, slow pyrolysis, fast pyrolysis, and flash pyrolysis. The pyrolysis process and its target products are given in Table 2.1.

With slow heating rate (less than 10K/min), the carbonization occurs and the process proceeds from the outer surface to the core of the plastic particles with the local carbonization temperature of above 300 °C. The carbonization process is determined by the heat transfer rate to the material surface and the heat transfer rate within the material. At given temperature and heating rate, the residence time is also the most important variable to achieve the desired carbonization. [47] The residence time required is also related to the dimensions of the material. If the size of material is too large which needs much longer residence time, incomplete carbonization may occur at the centre of the plastic particles.

On the other extreme situation, if the operation temperature is very high, for example 800 to 1000 °C, gasification process occurs and in this case, the plastics are directly converted to short chain gases and the yield of non-condensable gases in the product is maximized. High heating rate is required to minimize the proportion of solid char production and rapid quenching favours the liquid production before further cracking into gaseous products.

In most practical pyrolysis processes, particularly those applied in industries, preheating and melting the plastic feedstock between 200 and 300 °C are applied in order to reduce the volume of the feedstock and to eliminate the oxygen from the feeding system. The melting temperature is also high enough for PVC to crack and form hazardous gases and acid. Therefore, a preheating chamber is commonly used in the commercial process to remove gases generated from the PVC degradation in the preheating.

- Quality Comparison of Pyrolysis Products and Petroleum Fuels
- Review of pyrolysis monitoring and product analysis



Fig. 4.7 pyrolysis monitoring

4.5 Pyrolysis process monitoring

In the plastic pyrolysis, plastic type and operation conditions applied in the researches and the industries varied largely. Consequently, the variation of the yield and the quality of the pyrolysis products are significant in the literature. However, when the same plastic is used and same operation conditions are applied, there are similarities in the product yield and production distribution. In most of the research work, the pyrolysis rate of feedstock plastics is measured by using thermogravimetric analysis (TGA) in fix-bed batch pyrolysis reactor. [9, 53] The percentage of gaseous products is measured simultaneously with the occurrence of the reactions. In fluidized bed reactor or continuous reactor, feeding rate is controlled and monitored to determine the reaction rate. Operation temperature is normally monitored by using thermocouples along the process line, which is used for estimating thermal reactions including heating-up, decomposition, cracking, and condensation. Some studies used high pressure pyrolysis in which pressure gauge is applied to control and monitor the operation pressure. With these monitoring devices, the processes can be controlled

by adjusting the operating factors such as heating power, feeding rate, pressure and carrier gas flow rate when needed.

4.6 Product analysis method

The pyrolysis products of plastics are mainly hydrocarbons presenting in gaseous, liquids and solid wax phases under standard conditions of temperature of 25 °C and pressure of 100 kPa. Minor amounts of char and hydrogen gas may be found in the products. The char product can be analyzed by elemental analyzer or electronmicroscope dispersive X-ray analyzer. In research, the hydrocarbon products can be firstly separated though gas chromatography (GC) and then identified by either comparing with hydrocarbon standards or passing through mass spectrometry (MS). The structure and the proportion of individual components are investigated in laboratory analysis.



Fig. 4.8 product analysis

Hydrocarbon products from industrial pyrolysis of waste plastics are used as a substitute for commercial fuels. Instead of investigation on individual components, the commercial fuel regulation requirements focus on the physical and chemical properties of fuels relate to engine performance. The New Zealand regulation requirements on the properties of petroleum fuels such as LPG, petrol and diesel adapted standard test methods from the American Society for Testing and Materials (ASTM) and institute of petroleum (IP) testing methods. The properties of plastic pyrolysis fuels are analyzed in some studies. It was found that the pyrolysis products from PE, PP, and PS are mainly hydrocarbons with molecular weights similar to the petrol and diesel range. A certain amount of non-condensable gases and insignificant amount of heavy wax were also found in the pyrolysis products. Heavy hydrocarbon wax can be processed into gases or light liquid by further high temperature treatments or catalytic cracking so that the yields of non-condensable gases and wax vary largely in different studies. The

plastic derived fuels were also found to have higher unsaturated hydrocarbon content and lower stability than those of commercial fuels.

4.7 Comparison of diesel with plastic derived fuels

The New Zealand diesel regulations have 18 requirements those can be characterized into four groups: thermodynamic properties, flowing properties, component distribution, and performance properties.

In the regulation for commercial diesels, one of the most important thermodynamic properties is cetane number or cetane index that can be a substitute as cetane number, which indicates the auto-ignition conditions of the fuel. Cetane index is calculated from fuel density and distillation range which is also listed in the regulation requirements. Therefore, cetane number, density, and distillation range are all important properties to diesel fuel. The next important properties are the fuel flow properties which include viscosity, cloud point, pour point, cold filter plugging point and flash point. The importance of these properties will depend on the extent of known information of fundamental properties mentioned above, e.g., density and distillation range. If all of the fundamental properties are well known, the flow properties are less critical.

Miscellaneous properties reflects the effects of the minorities in diesel fuels, including carbon residues, sulphur content, water content, ash content and polycyclic aromatic hydrocarbon content. The carbon residue is fine solid particles in the fuel that may form combustion chamber deposits. The sulphur content in the fuel above a certain level causes high engine wear and poisons catalysts. The water content can contribute to corrosion in tanks and fuel injection equipment whereas the ash content is the solid residue when fuel is burnt off. The polycyclic aromatic hydrocarbon content is used to increase the cetane number due to their low boiling point and high density. The properties of fuel performance consist of colour, particulate, filter blocking tendency, lubricity, oxidation stability and copper corrosion. These properties result from one or more effects of the fundamental and the miscellaneous properties. For example, the copper corrosion is an indicator mainly due to sulphur content in the diesel.

Based on the diesel regulation, the fundamental properties of plastic derived fuels are examined in most studies because the diesel fuel is produced from synthetic hydrocarbon polymers that do not contain any other elements except for carbon and hydrogen. Therefore, some of the miscellaneous properties are not important for the

diesel from plastic pyrolysis, such as sulphur content and water content. The quality of the liquid fuels from pyrolysis of plastics will vary with pyrolysis operation conditions, pyrolysis reactor type and types of plastic feedstock. However, comparison of the plastic pyrolysis fuels and petroleum derived fuels has both been found in the literature review and thus this study will investigate this in details.

The quality of plastic derived fuels varies largely based on the process and the feedstock. The diesel range products in the LDPE derived fuels contain the same linear chain alkanes as those in the fresh diesel. The content of alkene in LDPE derived products is much higher than that in diesel, which decreases the storage stability of fuel. [17] Compared to naphtha, aromatic compounds, and branched hydrocarbons, linear alkanes have relative higher cloud point with the same carbon number or density. Therefore, many catalysts and processes were used to reduce linear hydrocarbons and increase the proportion of others. It was found that plastic derived diesel contains high proportion of linear alkane that has low solubility in diesel. This can significantly increase the cloud point that is the temperature at which the first crystals appear in diesel. Dewaxing, hydrogenation, isomerization, and cyclization are normally used in the pyrolysis processes to change the chemical composition in the products. [25, 33, 70] Some other properties of plastic derived fuels are controlled in the producing processes such as distillation range and carbon residue in the fuel.

4.7.1 Pyrolysis

The description and classification of pyrolysis reactors are given in Section of this thesis and the existing commercial pyrolysis plants use various types of the reactors as summarized by Scheirs and Kaminsky.

Continuous pyrolysis process is applied on most commercial plants with capability to use catalysts in which the plastic retention time is relatively short. Very few of the commercial plants use high pressure operation condition and most of the plants operate at or slightly above atmospheric pressure. The operating temperature in the reactors varies largely from 250 °C (Mazda fixed-bed catalytic process in Japan) up to 800 °C (Compact Power fixed-bed pyrolysis in United Kingdom) but most of the pyrolysis reactors operate between 400 °C and 550 °C.

It must be noted that if the operation temperature is above 800 °C, the process becomes gasification and the products are mainly short chain hydrocarbons which remains as gases under room temperature and atmospheric pressure. All of the commercial plants are fast or flash pyrolysis. Three types of reactors including fixed-bed, fluidized-bed, and rotary kiln can be found in the literature review.

4.7.2 Product separation and collection

The products from the plastic pyrolysis are mainly combustible gases and liquids. The liquids can be either combusted for power generation or for further refining to produce high quality fuels. In some plants, the pyrolysis products are simply separated into liquid, gas and solid whereas others have a more complete separation system by feeding the mixture of liquid and gas into distillation columns. Diesel range products

can then be distilled out as in an oil refinery process. The non-condensable gases are mainly made of hydrocarbons, and a minor amount of hydrogen and carbon monoxide. The gases can be liquefied as fuels, or used as fuels to heat the pyrolysis reactor, or if the amount is insignificant, the non-condensable gases are sent to an incinerator flaring off with the air. Ash may present in the non-condensable gases so most commercial processes have a gas scrubber for cleaning the gases

The process is classified into four phases:

- Preparation of plastic pyrolysis oil.
- Properties of plastic pyrolysis oil and CNT particles blend with plastic pyrolysis oil.
- CNT particles are added to the plastic pyrolysis oil and diesel.
- Engine testing and analysis.

4.8 MATERIALS:

- PET Plastic
- Diesel
- Pyrolysis oil
- Carbon Nano Tube

Analysis of Plastic Pyrolysis Reaction Kinetics and Reaction Energies:

4.8.1 Theory of Pyrolysis Reactions

Plastic pyrolysis is a complex process of breaking the long polymer chains into short ones. In many books and researches, this thermal degradation process is usually considered as depolymerisation of polymers. In this chapter, the fundamental phenomena involved in the pyrolysis process are investigated from both physical and chemical point of view. Following further literature review on the reactions kinetics of the pyrolysis reactions, heat accompanied with the reactions and energy demand in the pyrolysis are analysed.

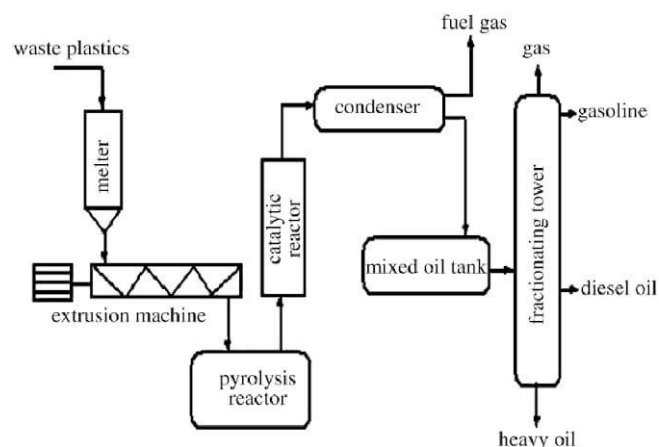


Fig. 4.9 pyrolysis process

Pyrolysis reaction progresses

The polymer cracking is an important reaction in the plastic pyrolysis; however, the complete process involves other reactions as well. In this section, the full pyrolysis reaction process will be investigated. There are numerous reactions in the plastic pyrolysis process, which can be considered to consist of four stages: initiation, propagation, hydrogen chain transfer and termination. The possible product species in the pyrolyzing process can be classified into two groups: molecules including alkane, alkene, and dialkene, etc; and free radicals which also contain unpaired electrons either at the ends or in the middle of the free radicals.

Initiation reactions

Initiation reactions break the carbon chain of polymer and form smaller free radicals and molecules. There are three types of initial crackings according to the side group of the plastic, which was mentioned in section . Initiation reactions occur randomly or at the end chain positions in PE pyrolysis. These two types of scission reactions are illustrated, respectively, the random scission reaction for end chain scission reaction in the plastic pyrolysis. In the figures, G represents the side group in the polymer unit, which can be H, CH₃ or others. Massive free radicals are produced in initiation reactions; accordingly, propagation and termination reactions are considered to be reactions of the generated free radicals.

Propagation reactions

Propagation is scission of the free radicals generated from the initiation reactions, which are intermediate reactions during the pyrolysis process. From the literature review, β scission was reported to be the main propagation reaction which also includes end chain scission reactions and mid-chain random scission reactions. These two types of propagation reactions are shown in Fig 4.1 for the mid-chain random scission reaction and in Fig 4.2 for end chain scission reaction. The products from the propagation reactions are mainly 1-alkenes.

Propagation reactions crack the large free radicals generated from the initiation reactions and produce alkene molecules and smaller free radicals. In macroscopic scale, longer chain free radicals in the vapour phase are further cracked to smaller products through the propagation reactions. This theory can be applied to explain the relationship between residence time and the molecular weight of the pyrolysis products.

4.8.2 Hydrogen chain transfer reactions

Hydrogen chain transfer is proton transfer to other locations. This type of reactions decreases the polymer molecular weight, which can be found in many polymerization systems. Hydrogen chain transfer reactions include intermolecular transfer reaction and intra-molecular transfer reaction. Intermolecular transfer reaction occurs between free radicals and other components. Saturated hydrocarbon molecules are formed from the corresponding radicals.

Most free radicals from the initiation are end chain free radicals, which have a positive charge at the ends. Some intermolecular transfer reactions on the mid-chain radicals are shown in. In the contrast, the intra-molecular transfer reactions transfer the free hydrogen proton from the end to the middle of the free radicals. This reaction encourages isomer production in the pyrolysis process.

4.8.3 Termination reactions

Termination reaction occurs by disproportionation of the free radicals or combining of two free radicals as shown in 2, This reaction directly affects the product chain length. As a result of the combination reaction, the final products vary largely when free radicals from different plastics are present in the pyrolysis process. According to the above reactions in the plastic pyrolysis, 1-alkenes are produced in β scission reactions (propagation) while the initiation and the termination reactions produce unsaturated compounds. Plastics like PE, PP, and PS can be considered as saturated alkene molecules due to their large molecular weight. Therefore, the number of unsaturated bonds in the product indicates the magnitude of initiation and termination reactions, and the amount of 1-alkenes indicates the magnitude of propagation β scission reactions.

The above reactions can also be described as the following reaction formula.

Initiation reaction:



Propagation (β -scission) reaction:



Termination reaction:



Where ,

R_n is a free radical with a chain length n .

O_j is an alkene (olefin) with a chain length j.

Pyrolysis of hydrocarbon polymers is a very complex process, which consists of hundreds of reactions and products. Several factors have significant effects on the reactions and the products. Based on previous research, this chapter investigated the fundamental plastic processes and reactions. With temperature increasing, plastic will go through glassy state, rubbery state, liquid state, and decomposition. Decomposition of plastic in an inert environment into liquid is called pyrolysis. There are four stages of reactions during the plastic pyrolysis process: initiation, propagation, hydrogen transfer, and termination reactions. In the initiation reactions, the polymer molecules undergo three types of cracking processes: random, end chain, and chain strip cracking; which is determined by the side functional group on the plastic molecular carbon backbone. In the propagation reactions, especially β -scission, the cracking of large molecular weight free radicals is an important process which produces smaller compounds. Hydrogen transfer reactions increase the variety of the free radicals and that of the final product. Termination is the reaction that combines all free radicals into molecules. Since the basic pyrolysis process and reactions are understood, a kinetic model was established for energy calculation of the reactions. According to the kinetic model and estimated product, the theoretical energy requirement for pyrolysis of PE was calculated, 1047.62 kJ/kg. The net energy gain of the process is 42.3 MJ/kg.

4.9 CARBON NANO TUBE:

Carbon nanotube as effective enhancer for performance and emission of diesel engine fueled with waste plastic pyrolytic oil/diesel blend and its combination with nanoparticle

KEYWORDS:

- Diesel Plastic
- pyrolytic oil
- Carbon nanotube

ABSTRACT:

The performance and emissions of diesel engines using titanium oxide (TiO₂) nanoparticles and carbon nanotube (CNT) as fuel-based nanoparticle additives in the plastic pyrolytic oil (PPO)-diesel mixture (B30) were investigated in this work. The fuel mixtures were prepared by adding 100 ppm TiO₂, 100 ppm CNT, and their combinations to B30, then mechanically stirring the mixtures at high speed and stabilizing them in an ultrasonic bath. Brake specific fuel consumption (BSFC), brake thermal efficiency (BTE), power, torque, carbon monoxide (CO), carbon dioxide (CO₂), hydrocarbon (HC), and oxygen (O₂) exhaust gas were all evaluated. The engine was run at full load in the 900 to 2400 rpm range. As CNT was added to B30, BTE increased by 7.01% than that of blank B30. Simultaneously, BSFC of B30 dropped with the addition of CNT, TiO₂ and their combination, with B30-CNT showing the greatest reduction of 16.00% than that of blank B30. CO₂ and HC emissions can be reduced by adding

CNT, TiO₂, and their combinations with B30. However, as compared to B30, B30-CNT emits the least CO₂ and HC, with 30.93 and 82.77% reductions, respectively. As a result, using CNT alone to increase performance and reduce emissions is the best option.

EXPERIMENTAL PROCEDURE:

Malaysian commercial diesel and PPO are procured from the local market and Kuala Lumpur-based Syngas Sdn Bhd. The present study utilized a mixture of PPO and commercial diesel to make the blend. TiO₂ and CNT, as well as commercially available nanoparticles with a size of 30 to 40 nm, were chosen as fuel additives. The composition of PPO was analysed using gas chromatography-mass spectrometry (GC-MS). In this test, 50 mg of liquid fuel was dissolved in 1 mL of n-hexane, then injected into the chromatographic inlet and processed for 42 minutes. Helium serves as the carrier gas, with a flow rate of 0.51 mL/min. The separation began at a temperature of 50 to 250 °C with a 5 °C/min heating rate (Juwono et al., 2018).

FUEL SAMPLE PREPARATION FOR ENGINE TEST RIG:

To make a B30 fuel combination (10% biodiesel + 20% plastic oil + 70% diesel), the purchased plastic oil was combined with Malaysian commercial diesel (B10). In order to produce a combination of nanoparticles and B30 fuel, an ultrasonic Q500 Sonicator (QSONICA, Newtown, USA) was utilized as shown in Figure 1. B30 fuels with additives as shown in Table 1 were produced on a magnetic stirrer at 700 rpm stirring speed for 30 min, and ultrasonic treatment was used to scatter the nanoparticles at a frequency of 20 Hz for 20 minutes with a 30% amplitude. Table 2 lists the properties that were measured according to ASTM standards.

Fuel sample code	Fuel sample composition
B0	100% PPO
B10	10% biodiesel + 90% diesel
B30	20% PPO + 10% biodiesel + 70% diesel
B30-TiO ₂	B30 + 100 ppm TiO ₂
B30-CNT	B30 + 100 ppm CNT
B30-TiO ₂ -CNT	B30 + 100 ppm TiO ₂ + 100 ppm CNT

Table 1: Composition of fuel blend samples

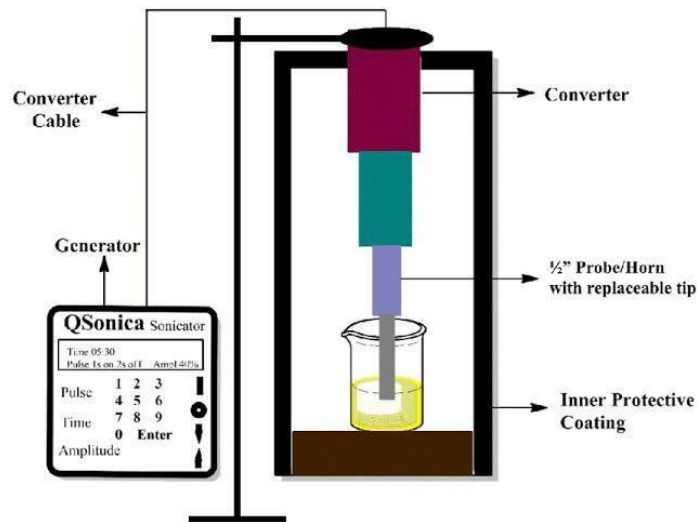


Figure 1: Ultrasound equipment for sonication of B30 fuel with additives.

EXPERIMENTAL SET-UP:

To examine the influence of fuel mixes on diesel engine performance and emission characteristics, a Yanmar (TF 120M) single-cylinder and radiator cooled diesel engine was used, as illustrated in Figure 2. Maximum power (7.7 kW), compression ratio (17.7), maximum rpm (2400 rpm), injection timing (17° before top dead centre), and injection pressure (200 kg/cm²) were the diesel engine specifications. The BOSCH BEA 350 gas analyser was used to analyse the engine exhaust gases (HC, CO, CO₂, and oxygen (O₂)). Due to a restriction in the gas analyser, NO_x could not be measured. Table 3 displays the measurement accuracies for diesel engine characteristics. These methods were adapted from Mujtaba et al. (2020).

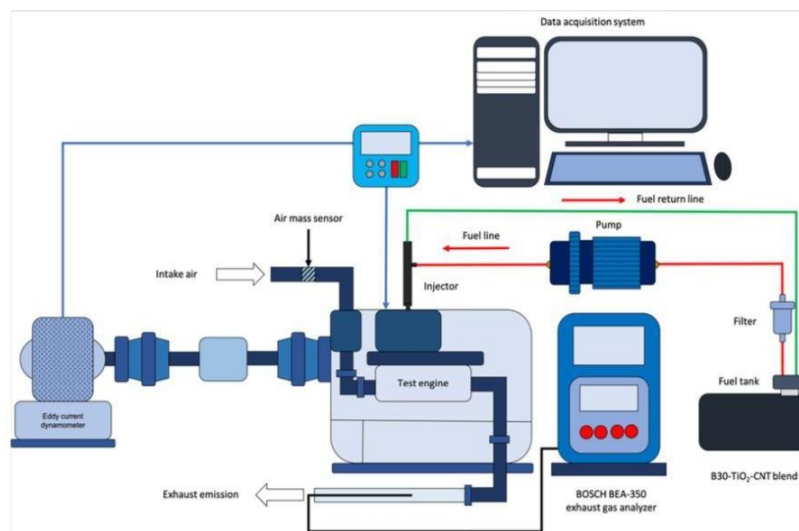


Fig 2: Schematic view of diesel engine set-up.

CHAPTER-5

RESULT AND DISCUSSION:

The readings are taken from the single cylinder 4 stroke engine under the running speed of 1500 rpm, brake power 3.5 KW, Injection pressure 200 bar, 3 tests are taken

There are;

	Diesel	Bio-diesel
Sample test 1	270ml	30ml
Sample test 2	240ml	60ml
Sample test 3	210ml	90ml

5.1 SAMPLE TEST 1:

5.1 ICEngine Test Report

5.1.1 Engine Details :

ICEngine set up under test is Research Diesel having power 3.50 kW @ 1500 rpm which is 1 Cylinder, Four stroke , Constant Speed, Water Cooled, Diesel Engine, with Cylinder Bore 87.50(mm), Stroke Length 110.00(mm), Connecting Rod length 234.00(mm), Compression Ratio 18.00, Swept volume 661.45 (cc)

5.1.2 Combustion Parameters :

Specific Gas Const (kJ/kgK) : 1.00, Air Density (kg/m³) : 1.17, Adiabatic Index : 1.41, Polytrophic Index : 1.34, Number Of Cycles : 1, Cylinder Pressure Referance : 6, Smoothing 2, TDC Reference :-12

5.2.2 Performance Parameters :

Orifice Diameter (mm) : 20.00, Orifice Coeff. Of Discharge : 0.60, Dynamometer Arm Legnth (mm) : 185, Fuel Pipe dia (mm) : 12.40, Ambient Temp. (Deg C) : 27, Pulses Per revolution : 360, Fuel Type : Diesel, Fuel Density (Kg/m³) : 830, Calorific Value Of Fuel (kj/kg) : 42000

IP, BP & FP

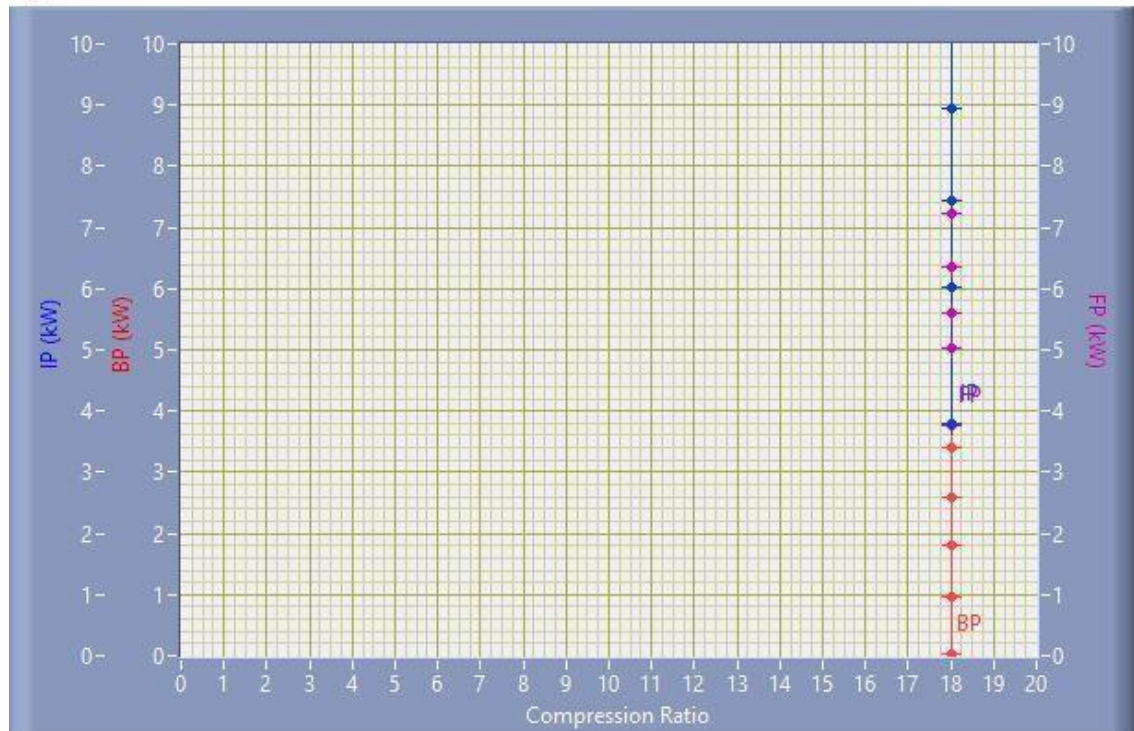


FIG. 5.1 IP, BP & FP

FIG. 5.2 IMEP, BMEP & FMEP

IMEP, BMEP & FMEP

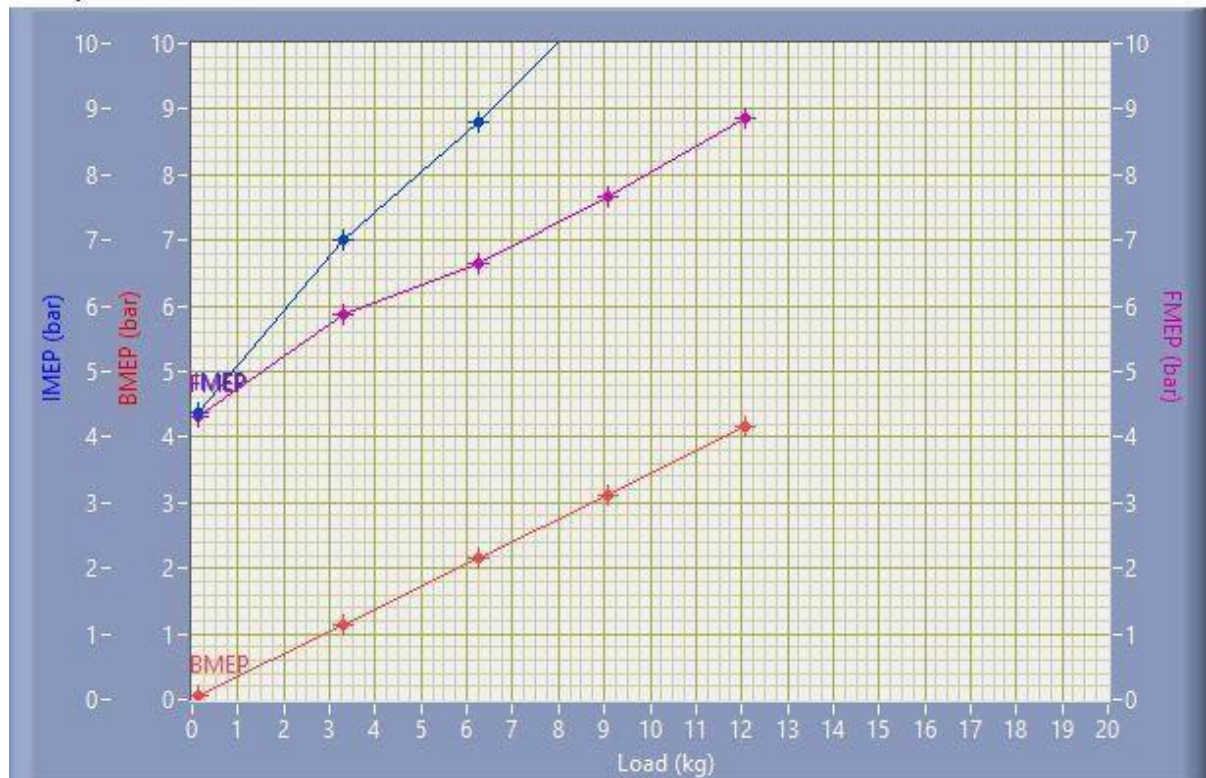


FIG. 5.3 TORQUE,MECHANICAL AND VOLUMETRIC EFFICIENCY

TORQUE, Mechanical & Volmetric Efficiency

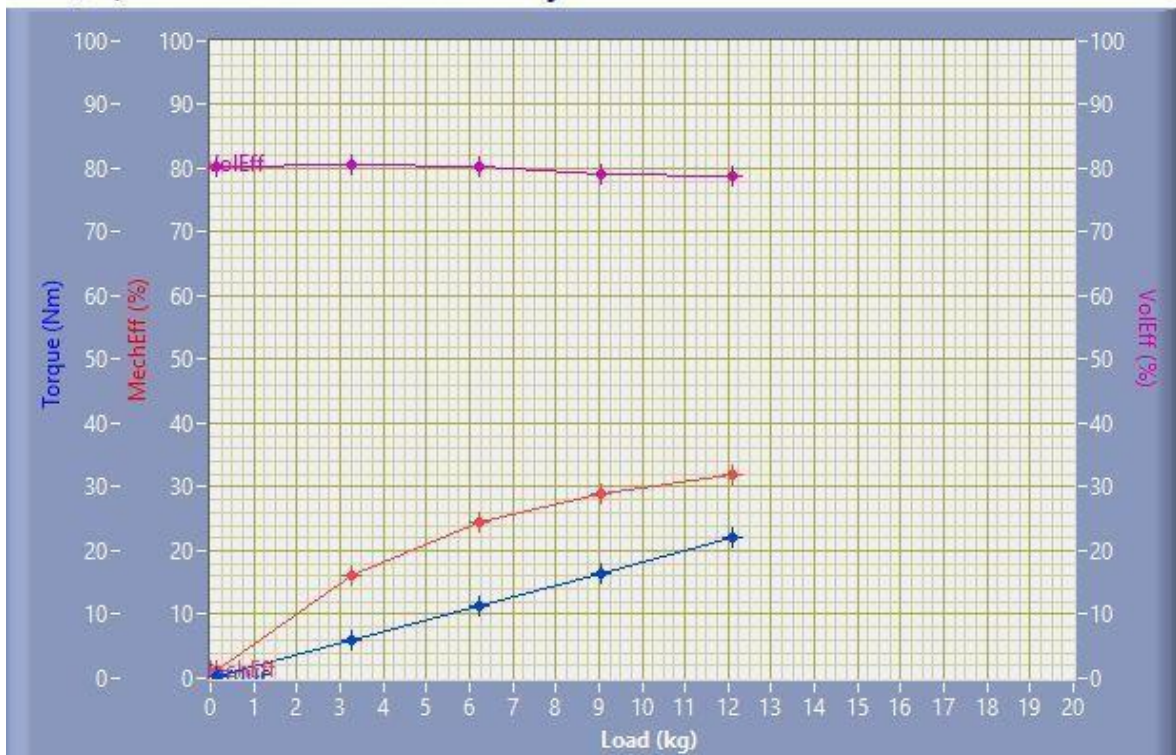


FIG 5.4 AIR & FUEL FLOW

Air & Fuel Flow

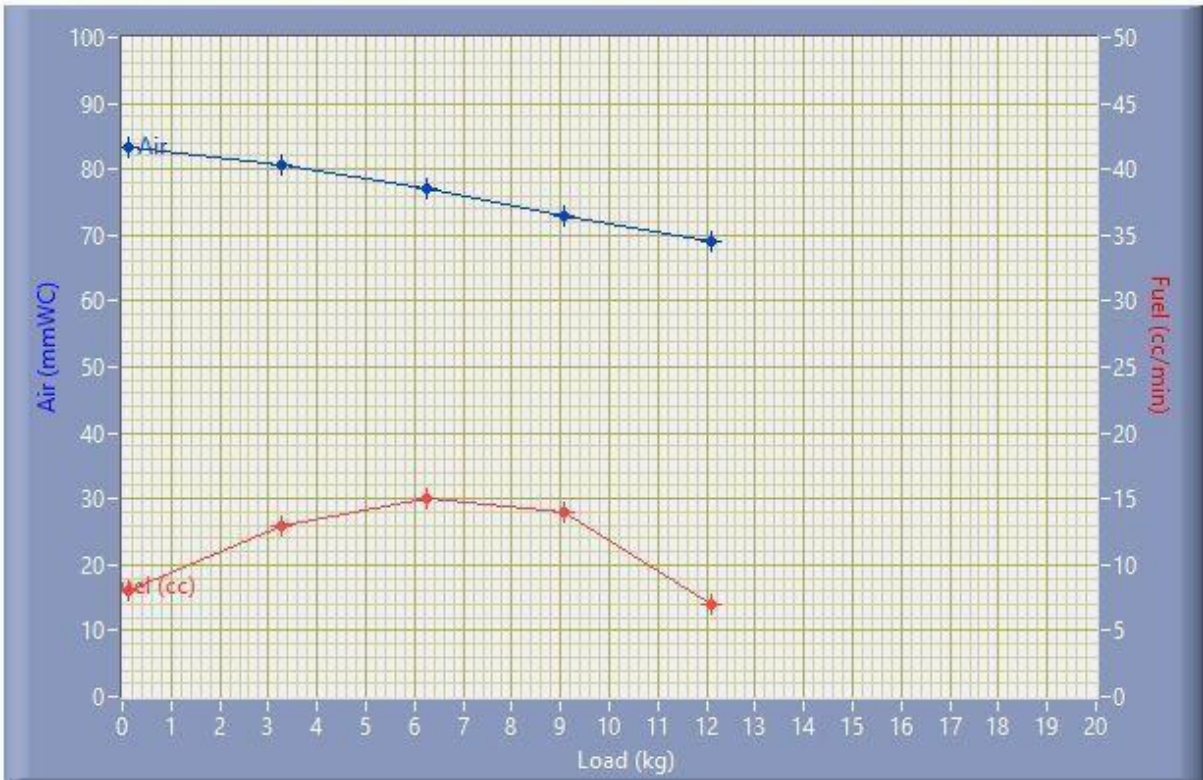


FIG. 5.5 INDICATED & BREAK THERMAL EFFICIENCY

Indicated & Brake Thermal Efficiency

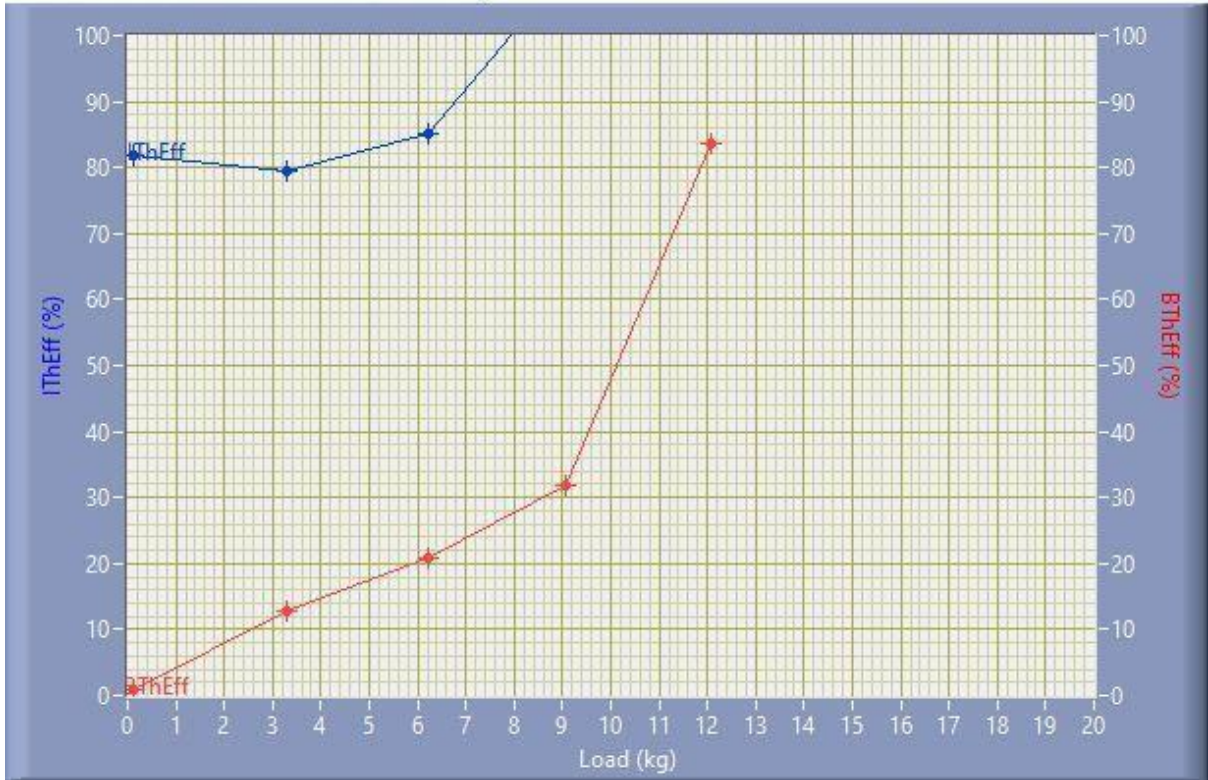
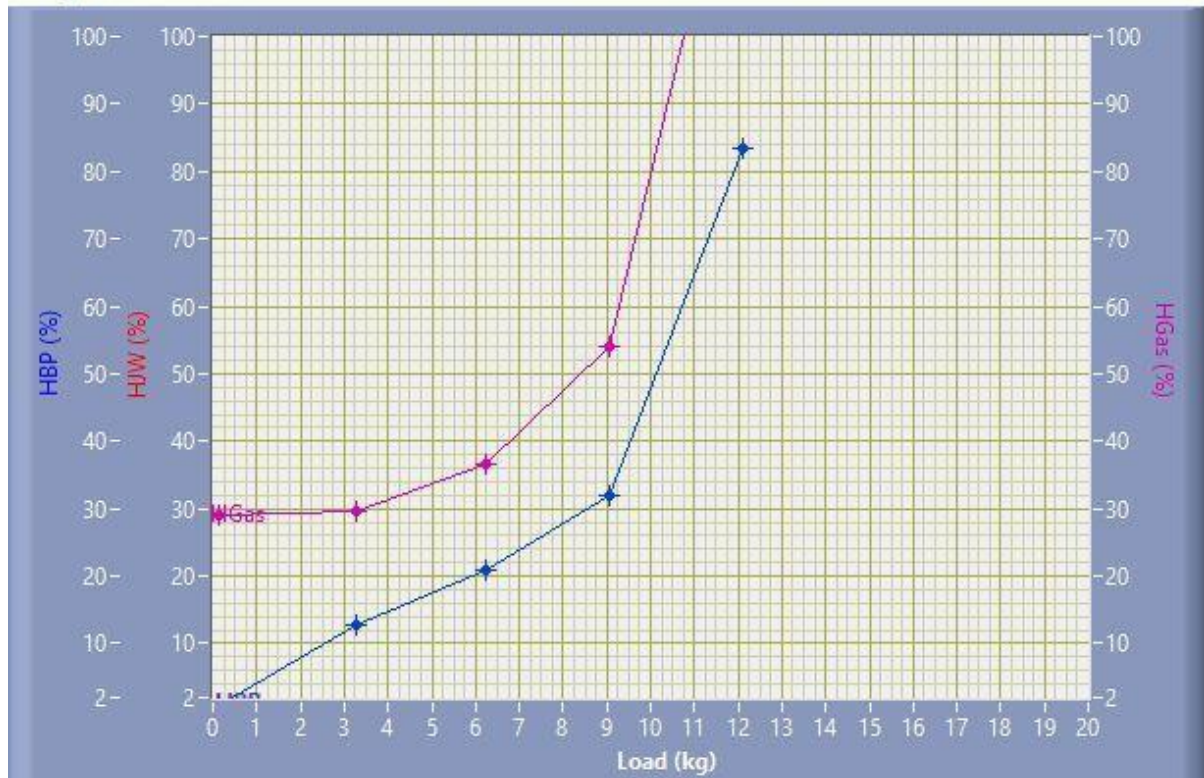


FIG 5.6 HBP,HJW&HGas

HBP,HJW & HGas



Observation Data :

Speed (rpm)	Load (kg)	Comp Ratio	T1 (deg C)	T2 (deg C)	T3 (deg C)	T4 (deg C)	T5 (deg C)	T6 (deg C)
1586	0.14	18.00	38.36	40.09	38.36	38.20	168.53	137.94
1558	3.28	18.00	38.20	39.25	38.20	37.34	165.59	132.71
1530	6.23	18.00	38.14	39.41	38.14	37.30	181.95	140.75
1506	9.06	18.00	38.09	40.69	38.09	37.97	233.03	170.70
1478	12.09	18.00	38.05	41.79	38.05	38.77	284.83	202.12

Table. 5.1: observation data 1

Air (mmWC)	Fuel (cc/min)	WaterFlow Engine (lph)	WaterFlow Cal (lph)
83.24	8.00	0	0

80.52	13.00	0	0
77.20	15.00	0	0
72.85	14.00	0	0
69.15	7.00	0	0

Table.5.2: observation data 2

Result data :

Torque (Nm)	BP (kW)	FP (kW)	IP (kW)	BMEP (bar)	IMEP (bar)	BTHE (%)	Mech Eff. (%)
0.25	0.04	3.77	3.81	0.05	4.36	0.89	1.09
5.95	0.97	5.04	6.01	1.13	7.00	12.86	16.16
11.31	1.81	5.62	7.43	2.15	8.81	20.80	24.39
16.45	2.59	6.35	8.94	3.13	10.78	27.89	29.00
21.94	3.40	7.23	10.62	4.17	13.04	30.51	31.97

Table.5.3: result data 1

Air Flow (kg/h)	Fuel Flow (kg/h)	SFC (kg/kW h)	Vol Eff. (%)	A/F Ratio	HBP (%)	HJW (%)	HGas (%)	HRad (%)
29.71	0.40	2.58	80.42	74.58	0.89	0.00	28.01	71.09
29.22	0.65	0.67	80.52	45.14	12.86	0.00	16.75	70.39
28.61	0.75	0.41	80.28	38.30	20.80	0.00	15.95	63.25
27.80	0.70	0.27	79.23	39.87	31.89	0.00	22.05	46.05
27.08	0.35	0.10	78.66	77.69	83.51	0.00	53.13	0.00

Table.5.4:result data 2

5.2 SAMPLE TEST 2:

IP, BP & FP

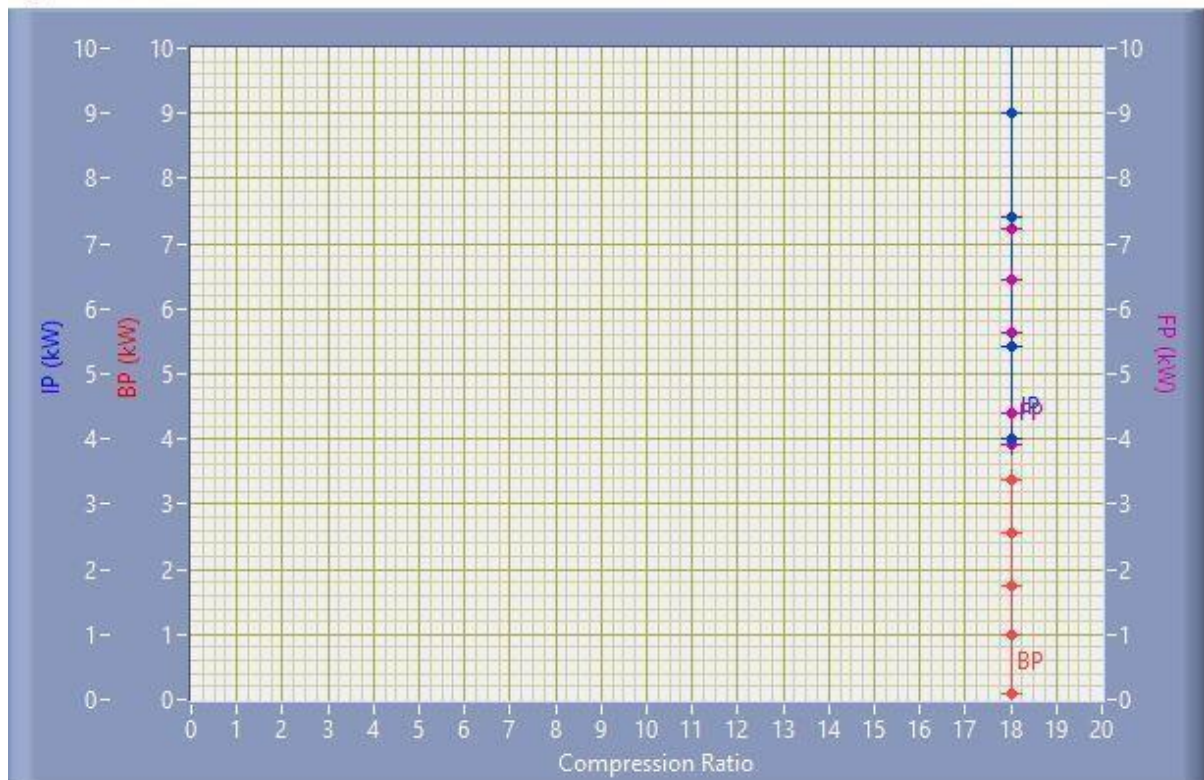


Fig. 5.2.1 IP,BP & FP

IMEP, BMEP & FMEP

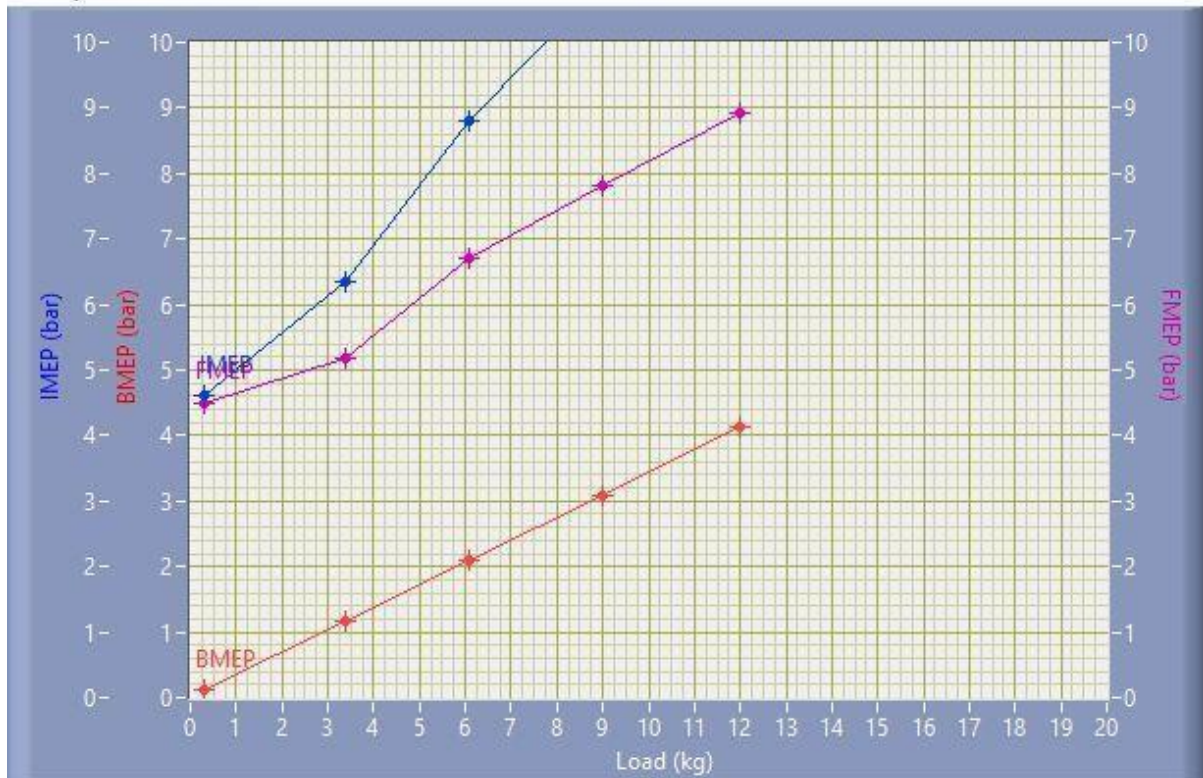


Fig. 5.2.2 IMEP, BMEP & FMEP

Air & Fuel Flow

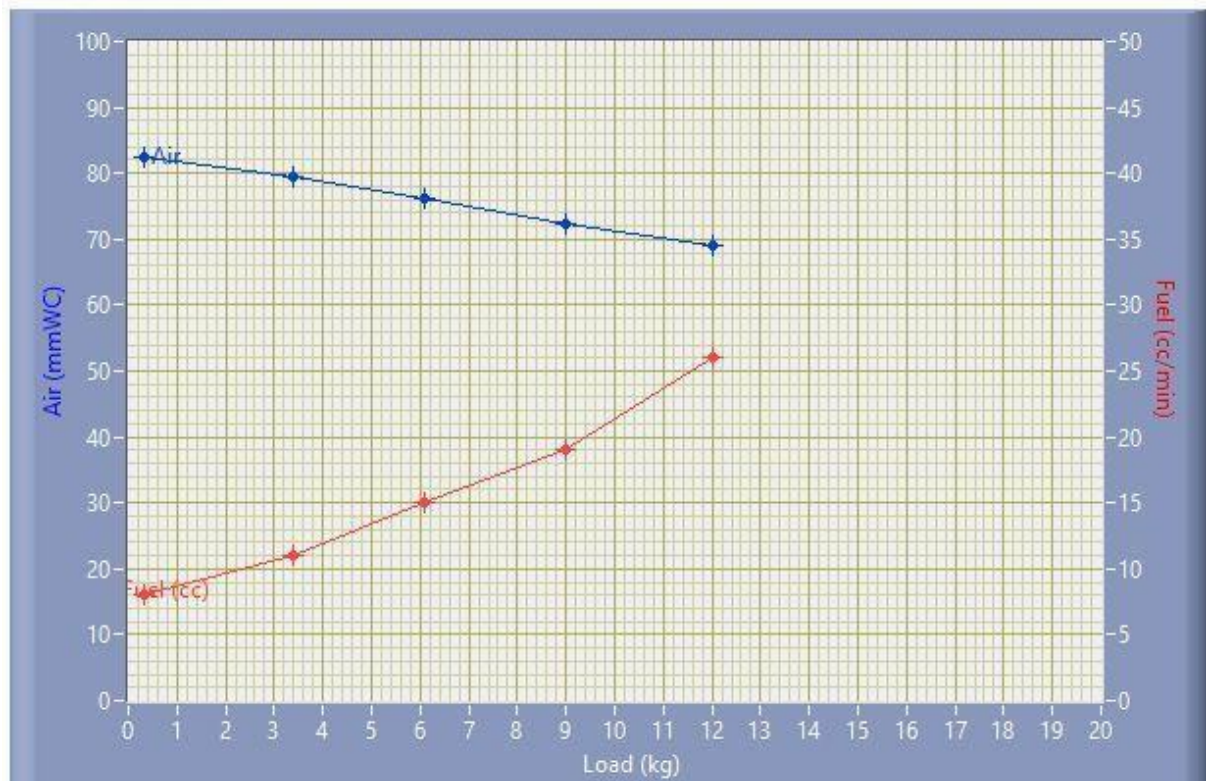


Fig. 5.2.3 Air & Fuel Flow

TORQUE, Mechanical & Volmetric Efficiency

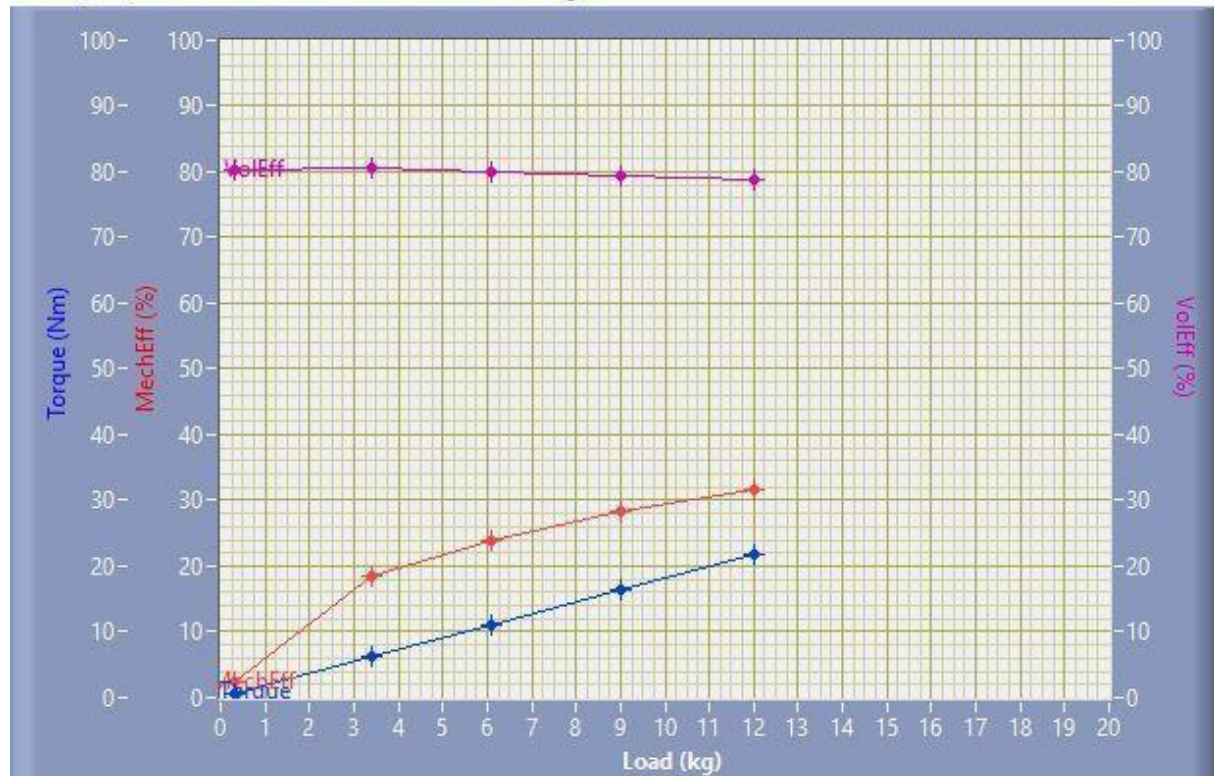


Fig. 5.2.4 Torque, Mechanical & Volmetric Efficiency

HBP, HJW & HGas

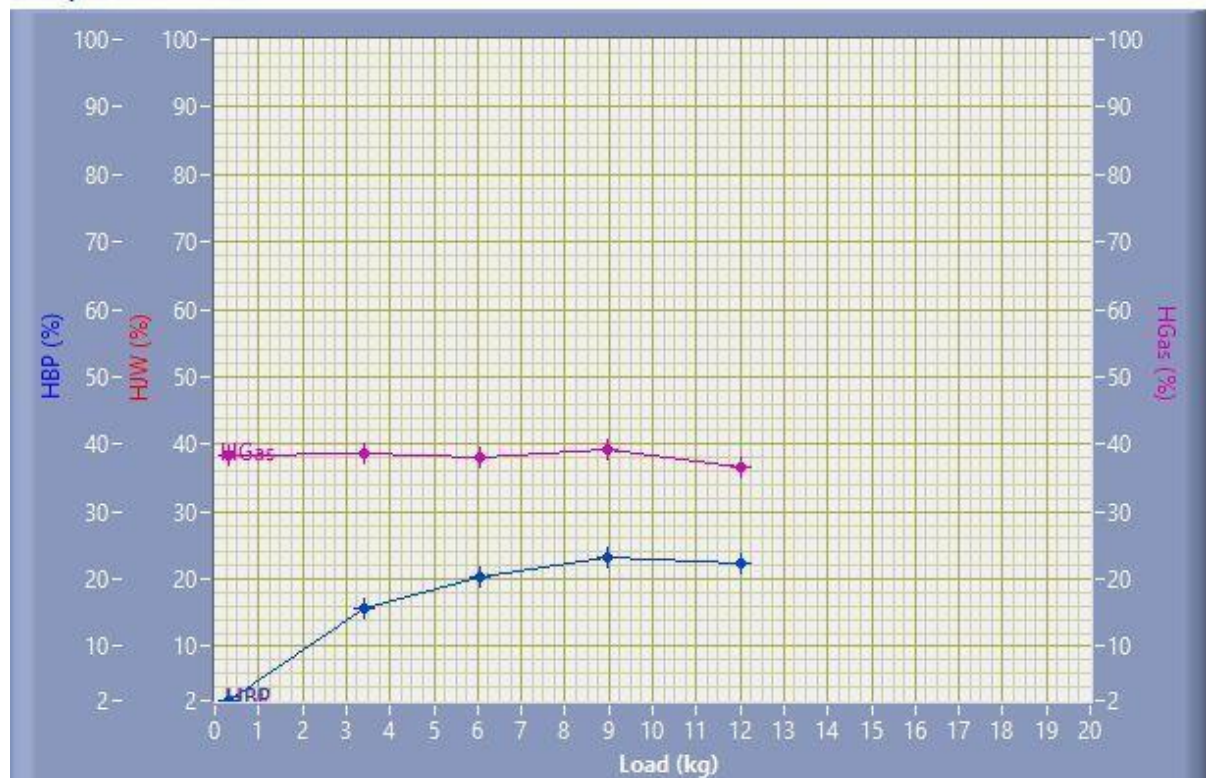


Fig. 5.2.5 HBP, HJW & HGas

Observation Data

Speed (rpm)	Load (kg)	Comp Ratio	T1 (deg C)	T2 (deg C)	T3 (deg C)	T4 (deg C)	T5 (deg C)	T6 (deg C)
1582	0.31	18.00	38.05	40.34	38.05	38.05	211.99	174.38
1547	3.39	18.00	38.03	39.13	38.03	37.34	189.72	155.36
1525	6.07	18.00	38.01	39.35	38.02	37.40	200.42	158.27
1500	8.99	18.00	38.01	40.13	38.01	37.74	228.19	171.32
1474	12.01	18.00	38.00	41.28	38.00	38.48	274.77	197.45

Table. 5.5 Observation data 1

Observation Data

Air (mmWC)	Fuel (cc/min)	WaterFlow Engine (lph)	WaterFlow Cal (lph)
82.29	8.00	0	0
79.35	11.00	0	0
76.21	15.00	0	0
72.34	19.00	0	0
69.02	26.00	0	0

Table. 5.6 observation data 2

Result Data

Torque (Nm)	BP (kW)	FP (kW)	IP (kW)	BMEP (bar)	IMEP (bar)	BTHE (%)	ITHE (%)	Mech Eff. (%)
0.56	0.09	3.92	4.01	0.11	4.60	1.98	86.33	2.29
6.16	1.00	4.41	5.41	1.17	6.34	15.61	84.60	18.45
11.02	1.76	5.64	7.40	2.09	8.81	20.20	84.94	23.78
16.31	2.56	6.46	9.02	3.10	10.91	26.21	81.69	28.41

21.79	3.36	7.24	10.60	4.14	13.05	31.27	70.18	31.73
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Table. 5.7 Result data 1

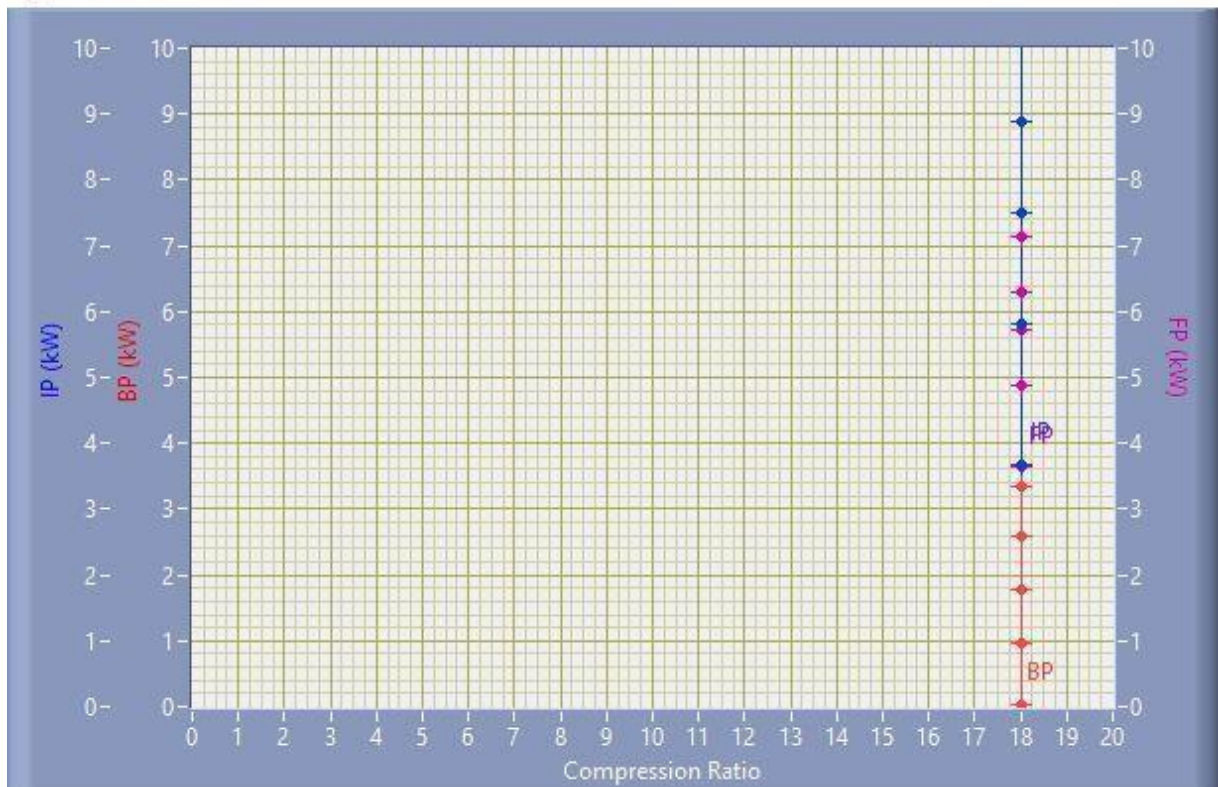
Result Data

Air Flow (kg/h)	Fuel Flow (kg/h)	SFC (kg/kW h)	Vol Eff. (%)	A/F Ratio	HBP (%)	HJW (%)	HGas (%)	HRad (%)
29.54	0.40	2.33	80.17	74.15	1.98	0.00	36.41	61.61
29.01	0.55	0.55	80.50	52.96	15.61	0.00	22.99	61.40
28.43	0.75	0.42	80.03	38.06	20.20	0.00	17.74	62.06
27.70	0.95	0.37	79.27	29.27	23.21	0.00	15.95	60.84
27.06	1.29	0.28	78.80	20.90	22.27	0.00	14.21	63.52

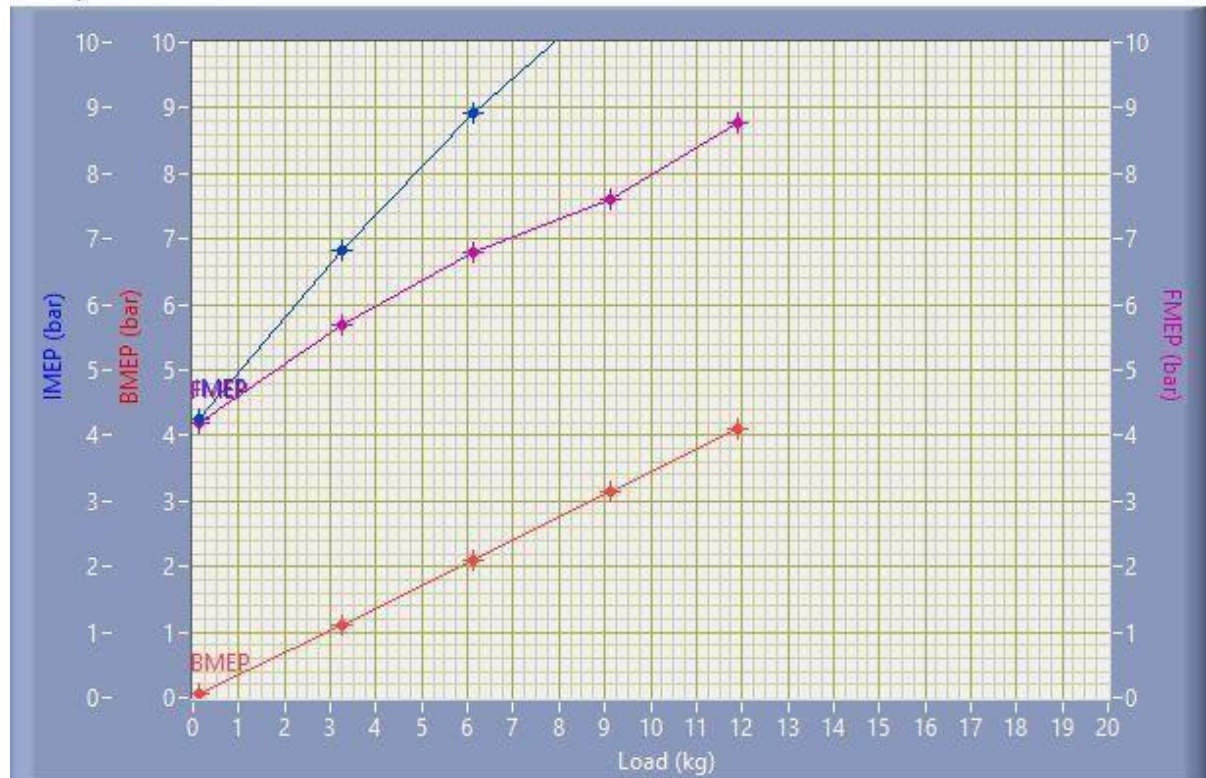
Table. 5.8 Result data 2

5.3 SAMPLE TEST 3:

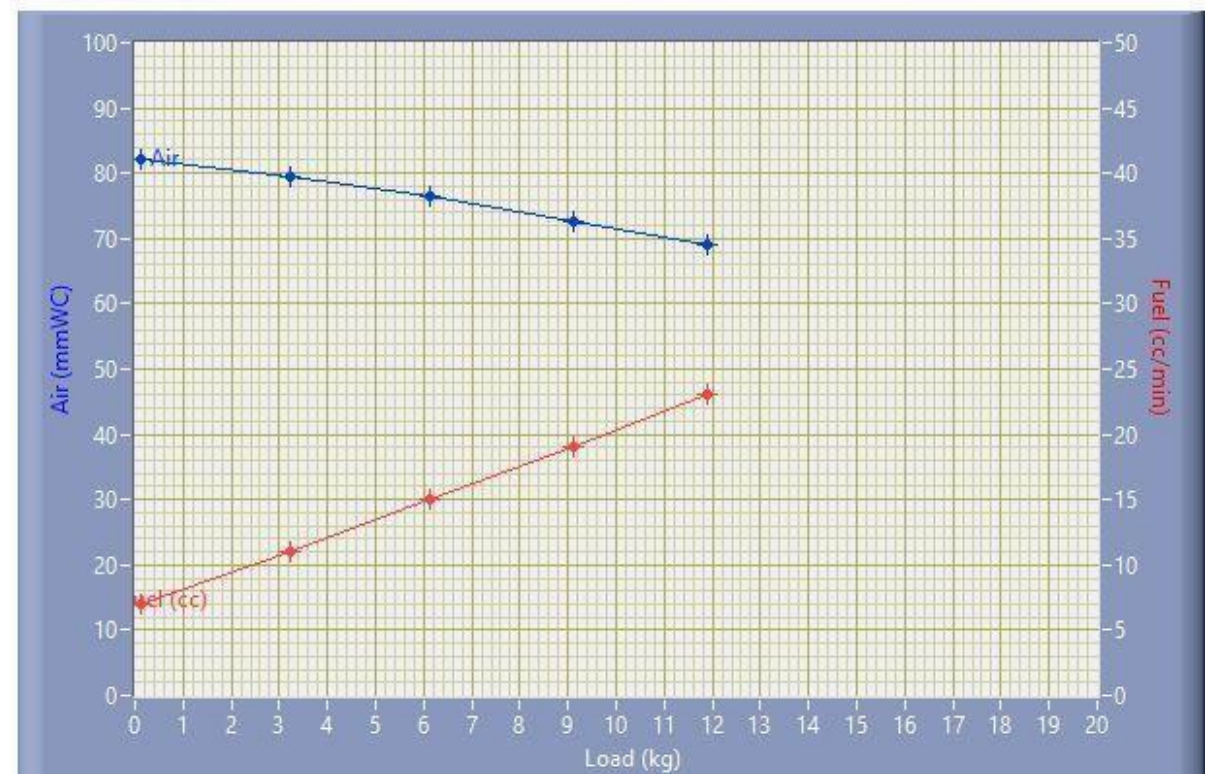
IP, BP & FP



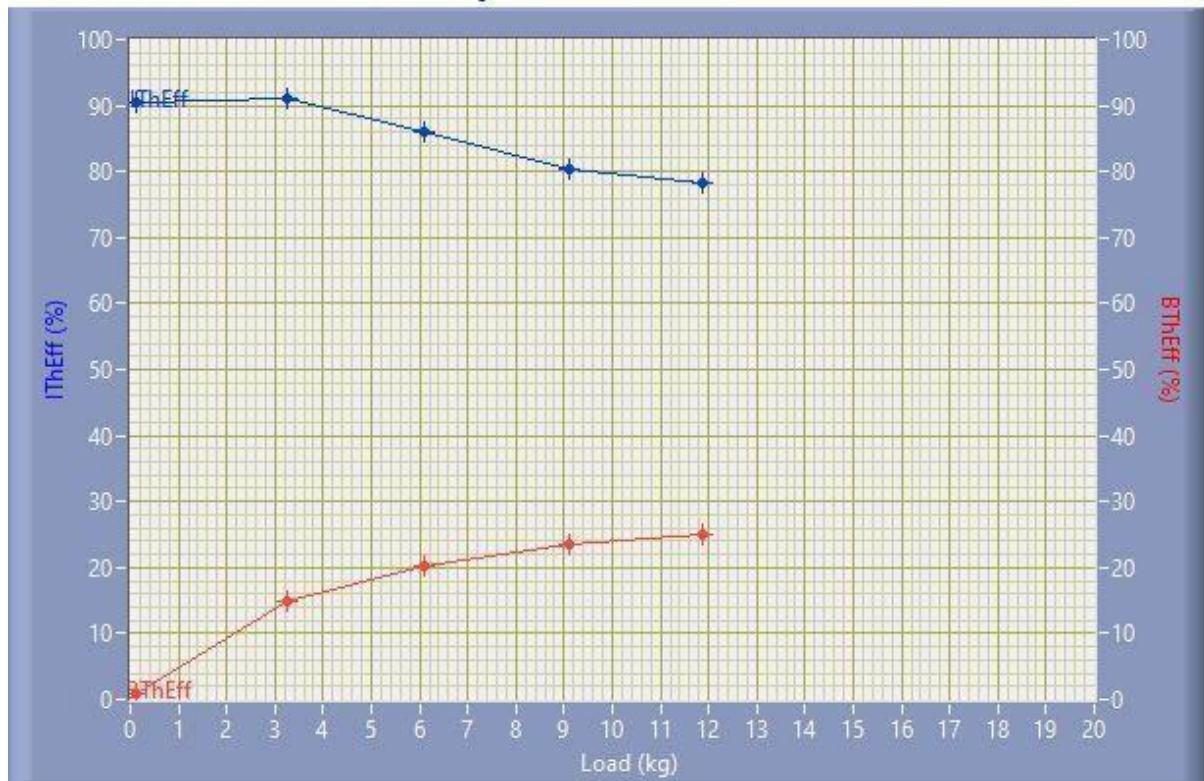
IMEP, BMEP & FMEP



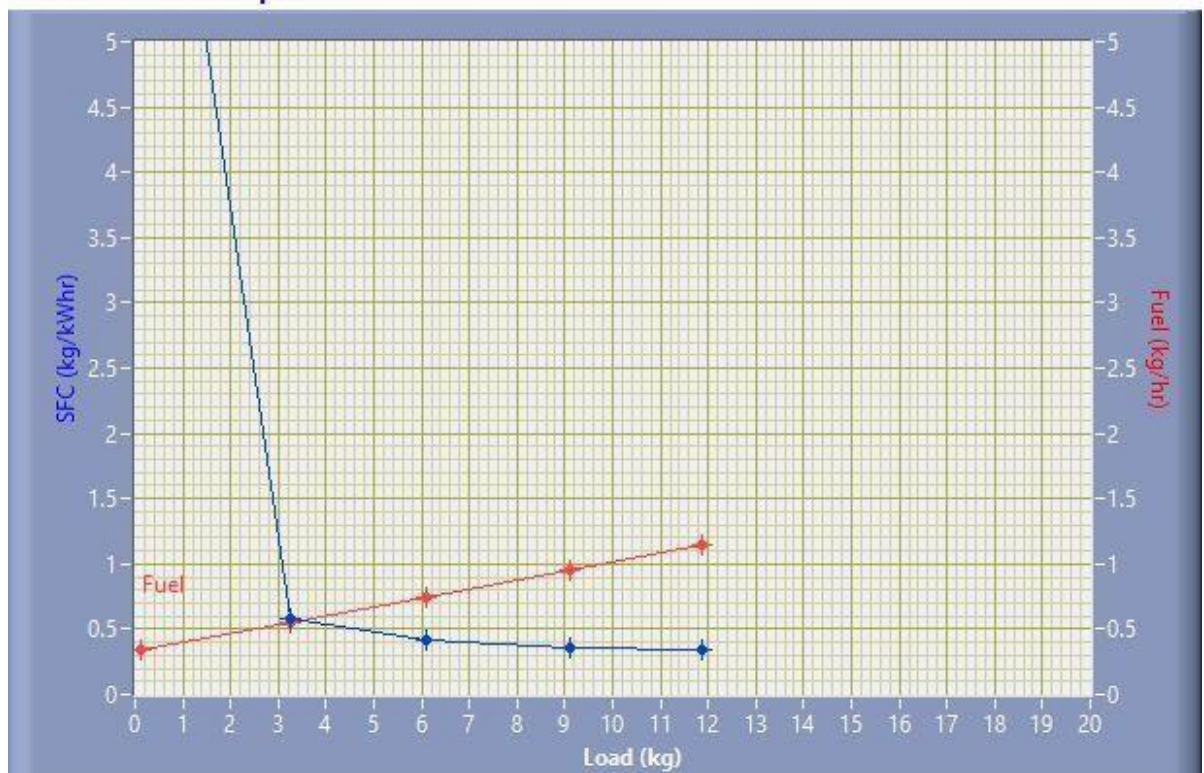
Air & Fuel Flow



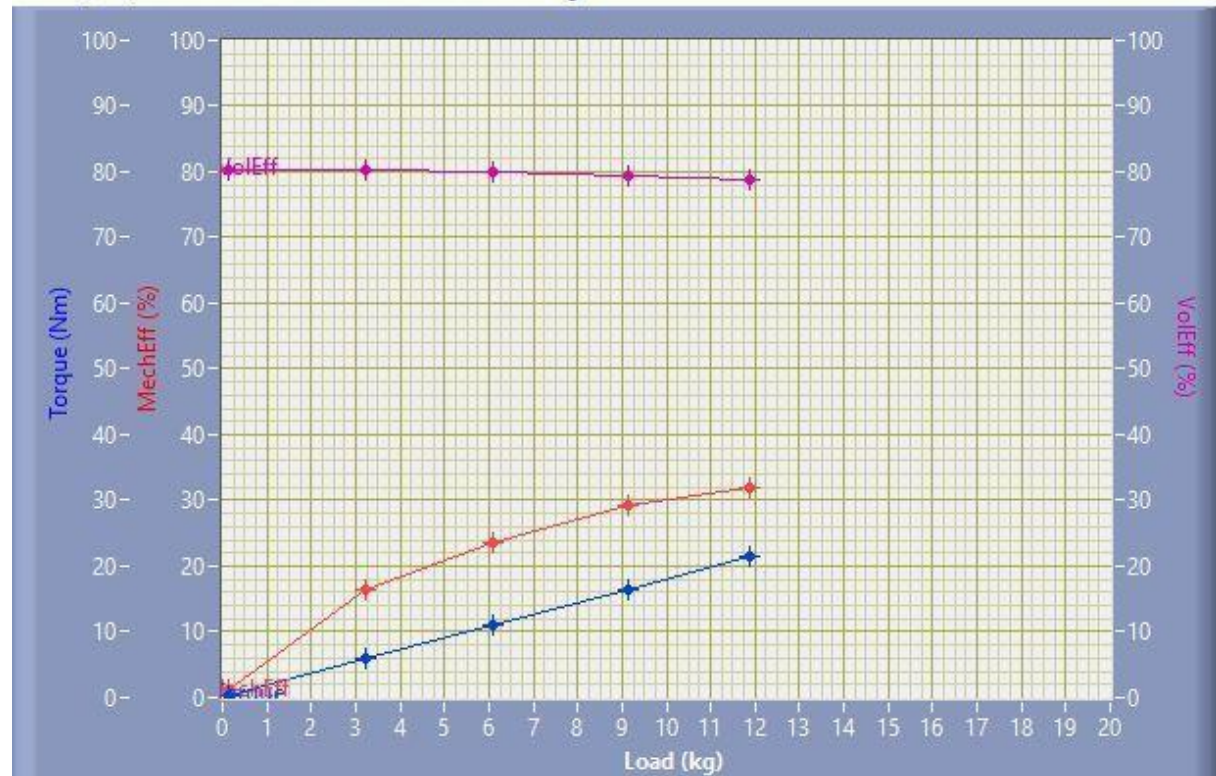
Indicated & Brake Thermal Efficiency



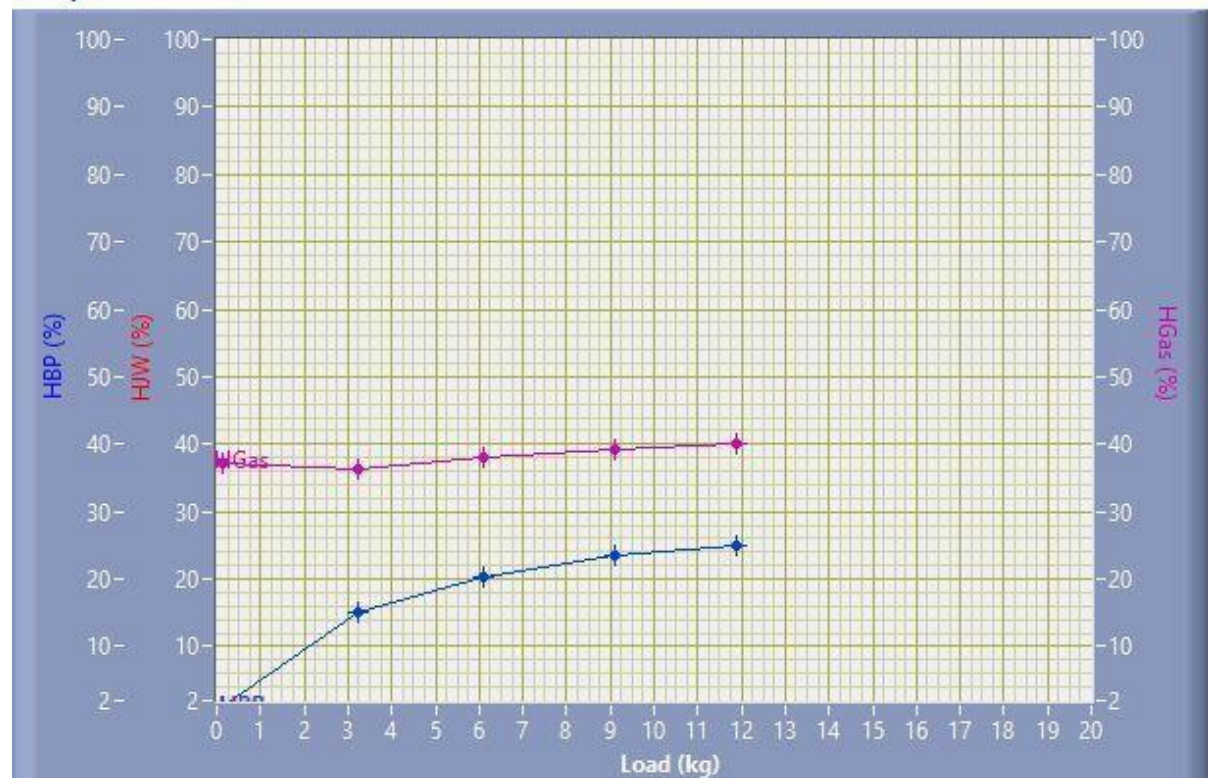
SFC & Fuel Consumption



TORQUE, Mechanical & Volmetric Efficiency



HBP, HJW & HGas



Observation Data

Speed (rpm)	Load (kg)	Comp Ratio	T1 (deg C)	T2 (deg C)	T3 (deg C)	T4 (deg C)	T5 (deg C)	T6 (deg C)
1574	0.14	18.00	38.01	39.33	38.01	37.52	188.80	159.13
1550	3.25	18.00	38.00	38.81	38.00	37.13	178.76	148.05
1528	6.11	18.00	38.00	39.34	38.00	37.37	199.36	155.71
1499	9.12	18.00	37.99	39.97	37.99	37.62	223.70	167.76
1476	11.89	18.00	38.00	40.89	37.99	38.18	260.59	187.97

Observation Data

Air (mmWC)	Fuel (cc/min)	WaterFlow Engine (lph)	WaterFlow Cal (lph)
82.03	7.00	0	0
79.47	11.00	0	0
76.55	15.00	0	0
72.48	19.00	0	0
69.13	23.00	0	0

Result Data

Torque (Nm)	BP (kW)	FP (kW)	IP (kW)	BMEP (bar)	IMEP (bar)	BTHE (%)	ITHE (%)	Mech Eff. (%)
0.25	0.04	3.64	3.68	0.05	4.24	0.0	90.47	1.12
5.89	0.96	4.87	5.82	1.12	6.81	14.96	91.08	16.42
11.09	1.77	5.73	7.51	2.11	8.92	20.36	86.16	23.63

16.56	2.60	6.29	8.89	3.15	10.76	28.54	80.50	29.25
21.58	3.34	7.14	10.47	4.10	12.87	32.96	78.38	31.84

Result Data

Air Flow (kg/h)	Fuel Flow (kg/h)	SFC (kg/kW h)	Vol Eff. (%)	A/F Ratio	HBP (%)	HJW (%)	HGas (%)	HRad (%)
29.49	0.35	2.44	80.44	84.61	1.02	0.00	36.28	62.71
29.03	0.55	0.57	80.41	53.00	14.96	0.00	21.46	63.58
28.49	0.75	0.42	80.05	38.14	20.36	0.00	17.67	61.97
27.73	0.95	0.36	79.40	29.30	23.54	0.00	15.61	60.85
27.08	1.15	0.17	78.75	23.64	24.96	0.00	15.07	59.97

5.3 Materials and apparatus:

As different types of plastics behave differently in pyrolysis process, the major three types of plastic, polyethylene (PE), polypropylene (PP) and polystyrene (PS) were investigated on the batch pyrolysis apparatus. The plastics used in this series of experiments were virgin plastic particles for the fundamental investigations thus the material variability can be eliminated.



Fig 5.3.1 samples

All of these particles were granular particles with dimensions of approximately 3 mm long and 3 mm wide. This chapter will discuss the pyrolysis of low density polyethylene (LDPE) with high density polyethylene (HDPE) is also pyrolyzed for comparison studies. In this chapter, effects of catalyst and reflux distillation are also presented. The low density polyethylene particles were produced by the state-of-the-art DSM Stamicarbon tubular process for blown film process. The chemical and physical properties of the LDPE were provided by PETLIN.

Physical properties	G811
Tensile strength at Break	11.8 MPa
Elongation	600%
Stiffness	180 MPa
Melting point	106°C

Fig. 5.3.2 Physical and chemical properties of LDPE (LD N103X)

In the experiments of this chapter and next chapter, the pyrolysis apparatus was modified to a vertical pyrolysis reactor in order to control the wax and to generate a distillation zone above the pyrolysis reactor. The modified apparatus is shown in Fig. 5.2, which consists of three major components: a furnace, a reactor with a distillation pipe and a condenser. The pyrolysis reactor and the distillation pipe are connected together and became two functional zones: the bottom zone for the pyrolysis and the top zone above the furnace for the distillation. The reflux rate in the distillation zone can be adjusted by changing the length of the pipe which is naturally cooled by the ambient air around the top part. Three different pipes were used which had lengths of 380 mm, 280 mm and 200 mm, respectively, corresponding to high, medium and low reflux rates in the pyrolysis tests. With high reflux rate in the process, the residence time of the heavy products will be longer than that with low reflux rate process.

Three thermowells were mounted on the apparatus for installing thermal couples. (Fig. 5.2.1) Thermal couple 1 (T1) is for measuring the space temperature over the pyrolysis reactor and below the distillation zone. The thermocouple locates 200mm below the top of the reactor pipe. Thermocouple 2 (T2) is located at the entrance of the condenser that also is the outlet of the distillation zone, which measured the temperature of the product flowing out of the distillation zone and into the condenser. Thermocouple 3 (T3) was inserted from the bottom of the furnace and fitted on the outer wall surface of the reactor, which measured the reactor outer wall surface temperature. As the temperature gradient from the outer wall to the inner wall (3 mm thick) is insignificant, the temperature measured by T3 can be regarded as the temperature of the reactor inner surface which is also close to the temperature of the feedstock in contact with the reactor wall.

In the experiment apparatus, a M303PY Gallenkamp electronic furnace was used to heat the reactor as an external heating resource. In the modified system, a 60 mm long stainless steel pipe was placed beneath the reactor pipe thus the reactor is located at the hottest position within the furnace. [12] In this way, char production is minimized by avoiding the relatively slow pyrolysis in the low temperature zone. In addition, the bottom empty 60 mm long pipe also reduced heat loss from the reactor.

In the experimental system, nitrogen bottle supplied the pure nitrogen to purge the air out of the system before the experiment started. The condenser is a tube-shell heat exchanger where the pyrolysis gases flow inside the tube and cooling water flow between the tube and the shell. The cooling water was directly from tap at a temperature of 10 to 15 °C. The condenser was effective enough to drop the temperature of the pyrolysis product to less than 30 °C. The temperature in the laboratory room was 15 °C. After the condenser, liquid and non-condensable gases were separated in a twoway beaker in which the liquid was collected and weighed after each run of the experiment. The non-condensable gases which were cooled down to less than 30 °C in the condenser were then collected by a water sealed cylinder which measured the volume continuously during the experiment. After the experiment, the non-condensable gases were collected by a balloon with an inner aluminium layer for gas analysis.

The non-condensable gases from the experiment were analysed using Agilent 3000A Micro Gas Chromatography (Micro-GC) which has two columns (A and B), thus, two streams of gases can be analysed simultaneously. (Figure 5-3) Column A used argon as a carrier gas, which measured hydrogen and relatively heavy hydrocarbon gases. In column B, helium was used as the carrier gas to measure nitrogen, oxygen, carbon monoxide, carbon dioxide and methane.

Liquid products were analyzed using a Varian Gas Chromatography (GC) CP-3800. (Figure 5-4) The column applied was a Varian CP-SIL capillary column of 15 mm long and 0.32 mm in diameter with 1 µm wall thickness and wax coating on the inner wall surface. This column was able to identify hydrocarbons from C5 to C45. An alkane standard mixture supplied by Sigma-Aldrich was used for the assay of the GC's performance. The standard mixture contained all even n-alkanes from C10 to C40 with 50 mg/L in n-heptane. The liquid samples were also analyzed by using Gas Chromatography-Mass Spectrometry (GC-MS) at Hill Laboratories, Hamilton, New Zealand.



Fig. 5.3.3 Agilent 3000A Micro Gas Chromatography

5.4 ENGINE SOFTWARE:

EngineSoft is a software package created by Apex Innovations Pvt. Ltd. that utilizes Labview technology for monitoring and analyzing engine performance. It offers a comprehensive range of functions, including data logging, reporting, and data entry, and is capable of assessing power, efficiency, fuel consumption, and heat release. EngineSoft can be customized to suit the specific configuration of an engine, and produces a variety of graphs for different operating conditions. During engine testing in RUN mode, the software captures and stores essential signals, which can be viewed graphically or in tabular format. The results and graphs can be printed, and the data can be exported in Excel format for further analysis. Temperature transmitter RTD PT100, Range 0-100oC,3 Nos; Thermocouple, Range 0- 1200 oC, 2 Nos Load indicator Digital, Range 0-50 Kg, Supply 230VAC Load sensor Load cell, type strain gauge, range 0-50 Kg Fuel flow transmitter DP transmitter, Range 0-500 mm WC Air flow transmitter Pressure transmitter, Range (-) 250 mm WC Software "EngineSoft" Engine performance analysis software Rotameter Engine cooling 40-400 LPH; Calorimeter 25-250 LPH Pump Type Monoblock Overall dimensions W 2000 x D 2500 x H 1500 mm Optional Computerized Diesel injection pressure measurement with injection variation 0-25 deg BTDC 27 Fig 4.10 Engine Software It is essential to verify that the nuts and bolts on the engine, dynamometer, propeller shaft, and base frame are securely fastened to ensure proper functionality.

Verify that there is an adequate amount of lubrication oil in the engine sump tank by referring to the level stick markings. Confirm that there is a satisfactory amount of fuel in the fuel tank and eliminate any air in the fuel line.. Turn on the electrical supply and verify that the PPU (Piezo powering unit AX-409), DLU (Dynamometer loading unit AX-155), load indicator, and voltmeter are activated. Power on the computer and launch the "ICEngineSoft" software by double-clicking on the respective desktop icon. From there, choose "File," followed by "Configure," and then select the product. Within the "Configure the product" window, opt for "Load Default." In the "Select File" section, pick your preferred setup from the provided drop-down menu. Review the parameters listed under the Engine, Sensors, Combustion, and Performance tabs within the "Set Parameters" section. Upon completion, click "OK. To modify any parameter, select the "New/Change" option and adjust the parameter within the corresponding tab. Once all changes have been made, select "Save & Apply" and then click "OK" to save the modifications. Click "OK" again to reconfigure changes. To adjust the graphs, you can reconfigure them. To configure the graphs, access the "Configure" option under the "File" menu, and then select "Graph". Within the resulting "Configure The Graphs" window, choose a configuration from the available options in the dropdown menu. Examine the pre-existing configuration of the X and Y axes, as well as the graph ranges for the chosen graphs.

Then, select "CLOSE & SET" and make 28 any necessary adjustments to the parameters and ranges. Once finished, select "SAVE" and then click "Close & SET" to apply the changes." There are three vertical tabs named Combustion, Performance, and Report. Under the Combustion tab, there are several horizontal tabs, including Combustion, Cylinder Pr., PV, Log PV, and RPR. Similarly, the other vertical tabs have additional horizontal tabs. To begin, activate the water pump and adjust the flow rate

of the "Rotameter (Engine)" to 900-1000 LPH and "Rotameter (Calorimeter)" to 200-250 LPH by using the globe valves provided at the rotameter inlet. Ensure that the water flows through the dynamometer at a pressure of approximately 0.5 to 1 Kg/cm². For hydraulic dynamometers, maintain a pressure of around 1.5 to 2 Kg/cm². Set the DLU knob to its lowest position. Adjust the fuel cock from "Measuring" to "Tank". Initiate the engine using the starter key switch and let it run at an idle state for approximately 4-5 minutes. To commence or end device communication, press the "Mode" toggle switch.



Fig. 5.3.4 Engine software

The color green denotes that the communication is active. Similarly, for starting or stopping data acquisition, use the "Measurement" toggle switch. The green color indicates that the data acquisition is in progress. It is essential to verify that the speed, temperature, and manometer readings are accurately displayed on the computer. These readings must match the readings shown on the engine panel. To validate the load reading on the indicator and computer, adjust the load on the engine by turning the knob on the DLU to increase it.

Ensure that the load reading on both the indicator and computer is the same. Increase the throttle gradually until it reaches the fully open condition while simultaneously loading the engine. Maintain the engine speed at around 2000-2500 RPM during this process. After reaching a steady state, which takes around 3 minutes, ensure that the RPM and load remain constant. Then switch the fuel cock position from "Tank" to "Measuring" and activate the fuel metering by clicking "Log on." It will be ON for the next 60 seconds. During the first 30 seconds, record the engine water flow and calorimeter jacket cooling water flow in LPH and press "OK." Save the initial reading data by naming the file. Finally, switch the fuel cock position back from "Measuring" to "Tank." Gradually decrease the load to the increase speed in steps of @500 RPM up to @ 4000 rpm maximum and repeat the data logging for each observation. Upon completion of all the readings, gradually decrease the load on the engine by using the DLU. Then slowly reduce the throttle until it reaches the fully down condition. To stop data acquisition on the PC, press the "Measurement" toggle switch. The green color indicates that it is currently ON. Similarly, to terminate device communication, use the "Mode" toggle switch. To close the data file, click on "File," followed by "Data," and then select "Close." Next, use the engine stop starter keys to shut down the engine.

Let the water circulate for approximately 5 minutes to cool the engine and then turn off the pump. To view the saved readings, click on "File," followed by "Data," and select "Open" on the PC. Then, choose the appropriate file under which the readings are stored and click "OK." To view the next set of readings, press "Next Data." The results will be displayed on all three screens. To generate the Performance and Combustion Reports, click on the "Report" tab. Next, enter a file name in the "Report File" field. Then, select the report requirements, which could be either Result Data, Observation Data, Graph Only, or Graph and Table. If the "Graph and Table" option is selected under the report requirements, the graph and table will be displayed in the report. If the "Graph and Table" option is selected for the Combustion Report, the output file size for printing may become too large. However, it can still be viewed in Excel. Once you have printed and checked the report, click on "File," followed by "Data," and select "Close." After that, click on "Exit" and shut down the computer.

Microstructure of the char produced from the plastic pyrolysis process was analyzed by using JEOL JSM 7000F high resolution scanning electron microscope (SEM) at the Department of Mechanical Engineering, University of Canterbury. (Figure 5-5) Element analysis in the scanning electron microscope and electron microprobe is performed by measuring the energy and the intensity distribution of the X-ray signal generated by a focused electron beam. When the electrons strike the sample, a variety of signals are generated, and it is the detection of specific signals which produces an image or a sample's elemental composition. [110] Standardless ZAF method was applied for SEMEDS (scanning electron microscope and energy-dispersive x-ray spectrometer).



Fig 5.4 JEOL JSM 7000F high resolution scanning electron microscope

5.5 Experiment method

At the beginning of the experiment, 20 grams of the LDPE particles were weighed using a four decimal place Mettler AE 200 balance and were filled into the pyrolysis reactor. Then, the system was sealed and purged using the nitrogen gas for one minute to create an oxygen free environment. After this, the furnace was turned on to full capacity with control scale at 100, equivalent to heating power of 881 W. During the experiment, three temperatures (T1, T2 and T3) and the volume of the collected

non-condensable gases were recorded every minute until temperature T3 rose above 800 °C when no product was left in the reactor. In order to investigate further cracking of the heavy pyrolysis product, three lengths of the distillation pipes (380 mm, 280 mm and 200 mm) were used separately in the experiments. The extra length above the furnace is cooled by the ambient air. Longer length of the reactor pipe leads to higher efficiency of condensation and higher reflux rate. In this section, only the results of high and low reflux tests (using 380 mm and 200 mm distillation pipes) are reported while the effects of the reflux distillation will be discussed in the following section.

The collected liquid, non-condensable gases and char were collected and analysed. The non-condensable gases were analyzed by using Agilent 3000A Micro Gas Chromatography (Micro GC). In the gas analysis, both of the columns A and B were set at 90 °C in the Micro GC. The injector temperature was set at 95 °C. (Table 5-2) The run time of column A is four minutes and that of column B is 10 minutes. This time setting allows hydrocarbon gases with the retention time less than n-butane to come out, such as hydrocarbons from C1 to C3 and butene and butane isomers. Some of the gases were identified by running a gas standard with this method.

The oils from low reflux rate process contained heavy molecular weight products and formed yellow cream; while the oils from high reflux rate process was clear liquid. (Figure 5-6) The cream product from low reflux rate process turned into clear liquid when it was heated to 60°C. The melted cream was able to be sucked by a one micro litre GC syringe for GC CP-3800 analysis injection.

In the liquid oil analysis, the liquid was firstly flash-vaporized at 320°C when it was injected into the GC. Then the vapour flow through the column which temperature was initially controlled at 80°C for two minutes. After this, the column temperature was increased to 300°C at a heating rate of 10°C/min. The temperature remained at 300 °C until no further peaks were observed. The total analysis time for the high reflux liquid product was 60 minutes and that for the low reflux product was 150 minutes. The GC allowed the hydrocarbons with carbon number between 7 and 40 to be separated and analyzed. In the analysis, the concentration of the liquid components was presented as molar percentage. Char from the LDPE pyrolysis were found at the bottom of the reactor, which were black fine powder and particles. The char microstructure was analyzed by using the JEOL JSM 7000F electron microscope.

In the experiments, HDPE was also used for pyrolysis; however, it was found that the process and products from the HDPE pyrolysis were identical to those of LDPE pyrolysis. Therefore, this thesis only presents the results of the LDPE pyrolysis

5.4.1 Process analysis:

During the pyrolysis experiments, the space temperature in the reactor (T1), the reactor outer wall surface temperature (T3) and the volume of the non-condensable gases were recorded every minute and the results are shown in Figure 5-7 for LDPE and in Figure 5-8 for HDPE. Both figures show the pyrolysis with high reflux rates. From the results of temperature profiles and non-condensable gas generation, the whole pyrolysis process can be divided into three stages: initial heating up stage (initial 18 minutes), fast pyrolysis stage (18 to 34 minutes) and decreasing pyrolysis stage (after 34 minutes). In the heating up stage, the space temperature (T1) remained low until about 18 minutes when no non-condensable gases were generated. However, the reactor wall temperature continued increasing during the heating up stage.

After about 18 minutes, the generation of non-condensable gases increased dramatically and the space temperature kept increasing. However, the temperature on the reactor wall surface stopped rising one minute after the massive non-condensable gases produced and then remained almost constant for about 16 minutes. As discussed in previous chapters, the initial gas production rate indicates the random cracking in the early fast pyrolysis stage. However, from the previous analysis, the energy required for the cracking reaction is not large; therefore, significant amount of energy must have been consumed in somewhere else as the reactor outer wall surface temperature remained constant indicating constant heat transfer rate from the furnace to the reactor. In this stage, the vapour from the primary cracking went up into the distillation zone, then, were condensed and refluxed back to the pyrolysis zone. This process of condensation and re-cracking consumed a significant amount of heat which was carried up by the vapour from the pyrolysis zone to the distillation zone. Therefore, it has been observed that reactor space temperature (T1) increased but reactor wall temperature (T3) remained constant after 18 minutes from the start. Through this reflux process, low boiling point products flew gradually into the condenser.

In the final termination pyrolysis stage, less vapour was produced and less energy was required thus the reactor wall temperature (T3) started increasing again. The high boiling point hydrocarbons were further pyrolyzed (secondary cracking) when the reaction surface temperature rose above 500 °C. This secondary cracking was indicated through the second rapid increase on the gas production curve. (Figure 5-7) However, the less high boiling point vapour was produced in this stage; the total vapour product from the pyrolysis zone was reduced although the non-condensable gases kept increasing as less condensate must have been generated at this time. This resulted in a decrease in the reactor space temperature.

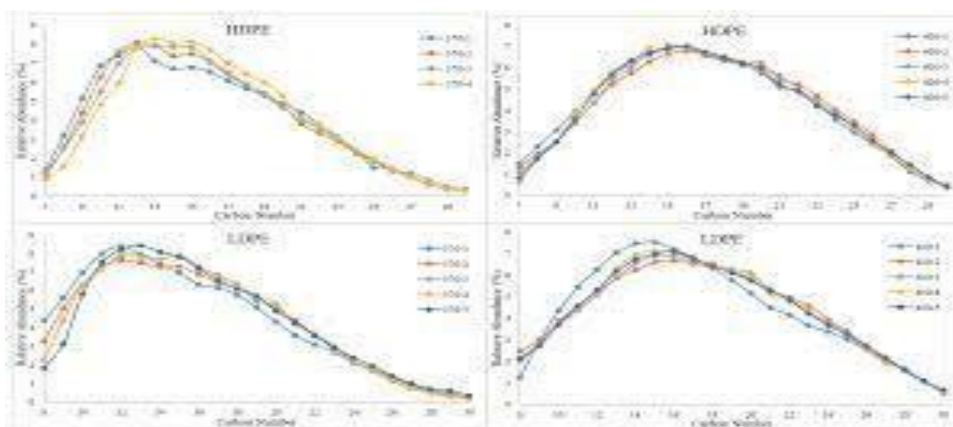


Fig. 5.5 High reflux rate LDPE pyrolysis process

In the low reflux rate pyrolysis, the secondary cracking was less intensive than the high reflux rate pyrolysis, thus higher boiling point hydrocarbons were generated as liquid product. Higher boiling point hydrocarbons have higher viscosity than that of lower boiling point hydrocarbons; [104] therefore, the viscosity of the liquid product from low reflux rate process is higher. (Figure 5-6) the effect of reflux distillation on the product distribution was further investigated in the following experiments.

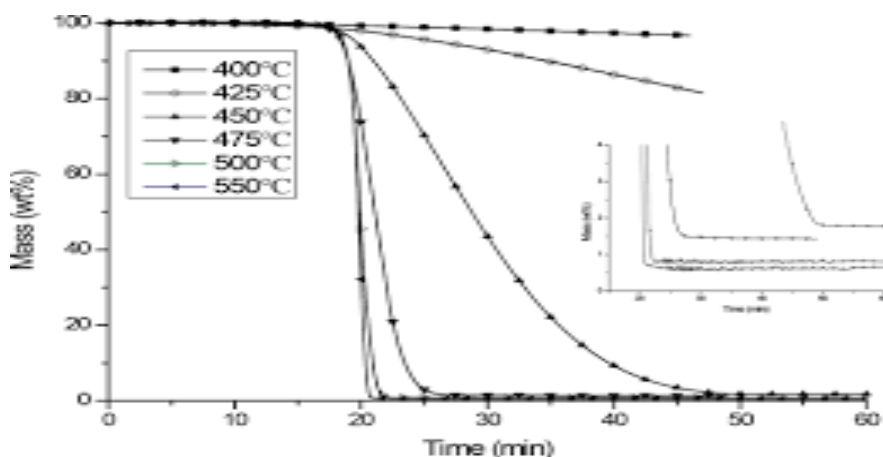


Fig. 5.6 High reflux rate process pyrolysis on HDPE

The temperature profiles of high reflux rate HDPE process are listed in Figure 5-8. There was no significant difference in the pyrolyzing process between HDPE and LDPE. The temperature profile and non-condensable gas production are identical between pyrolysis of LDPE and pyrolysis of HDPE indicating similar cracking processes. Both of the LDPE and HDPE underwent secondary cracking when the low boiling point hydrocarbons were removed. Because of the above similarity and the higher value potential for recycled HDPE to be used in other products, LDPE is the most suitable for energy production using the waste plastic stream. [7-8] Therefore, LDPE was intensively studied in this study as a typical polyethylene material.

The results of product distribution of high reflux rate process LDPE pyrolysis are given in Table 5-4 from the results, it can be seen that the conversion of LDPE to hydrocarbons was over 99% and very little char was produced in the experiment as fine black powers and particles found at the bottom of the reactor. The high reflux rate process experiments were repeated five times. The 95% confidence interval of the oil/wax mass was calculated, $16.7 \pm 0.1\text{g}$.

5.4.2 Non-condensable gas analysis:

A typical Micro-GC analysis result for the non-condensable gases is shown in Figure 5-9 with the top chart from Column A and bottom chart from Column B. By integrating each peak through the GC program, the composition of the corresponding gas species was determined and the results from Figure 5-9 are given in Table 5-5. In Table 5-5, 'Norm%' is the normal percentage of a component in the gas sample. From the above results, it is known that the non-condensable gases consisted of oxygen (O_2), nitrogen (N_2), methane (CH_4), ethene (C_2H_4), ethane (C_2H_6), propane (C_3H_8), butane (C_4H_{10}) and other four unidentified species (peak6, peak 8, peak 13 and peak 23). The oxygen, carbon dioxide and some nitrogen gases were likely to be from contamination of air during the gas sampling and sample collection process. The remaining nitrogen is believed to be due to the purge gas left in the system. There were four peaks (peaks 6, 8, 13, and 23) in the GC analysis chart which needed to be identified from further analysis.

According to the result, methane, ethene, ethane, peak8, propane, peak13, and butane are the major components in the non-condensable gases from LDPE pyrolysis. The retention time of peak 8 was between propane and ethane; therefore, peak 8 was believed to be propene. Peak 13 could be one of butene and butane isomers, which would come out between propane and n-butane. [65] According to liquid product analysis and other identified gas species, it was most likely to be 1- butene because most of 1-alkene could be generated in the β -scission reactions. [52, 83, 97] The 1-butene was also identified by other researchers. [32, 51, 58, 79, 83, 88, 111- 112] There was no H_2 detected in the gases. The hydrogen free radicals generated from initiation reactions may combine with alkenes and saturate the carbon double bonds. This has not been proven yet.

5.4.3 Identification of the components in liquid product:

The viscosity and colour of the LDPE pyrolysis oil varied with the pyrolysis condition as discussed in Section 5.1.2. It was clear yellow-brownish liquid from high reflux rate process but became creamy solid wax with low reflux rate process. (Figure 5-6) In analysis of the liquid product, a specially designed 1 μl GC syringe was used to transfer liquid product into the GC CP-3800. However, the syringe could only be used

for liquid but not for wax. Therefore, in order for the wax to be sampled by this syringe, the wax was preheated to 60 °C which turned into clear liquid for the GC analysis.

The GC analysis results for the LDPE pyrolysis liquid are shown in Figure 5-11 for high reflux rate (top) and low reflux rate (bottom). In total, 115 hydrocarbons were found in the high reflux process oil product and 121 peaks were detected in the low reflux rate pyrolysis. (Figure 5-11) The components from both the high and the low reflux rate processes had similar peak distribution in the first 60 minutes from the GC analysis. In the liquid from low reflux rate pyrolysis, the final 6 liquid peaks are high boiling point components (C37 to C42) which were not found in the high reflux process pyrolysis liquid product.

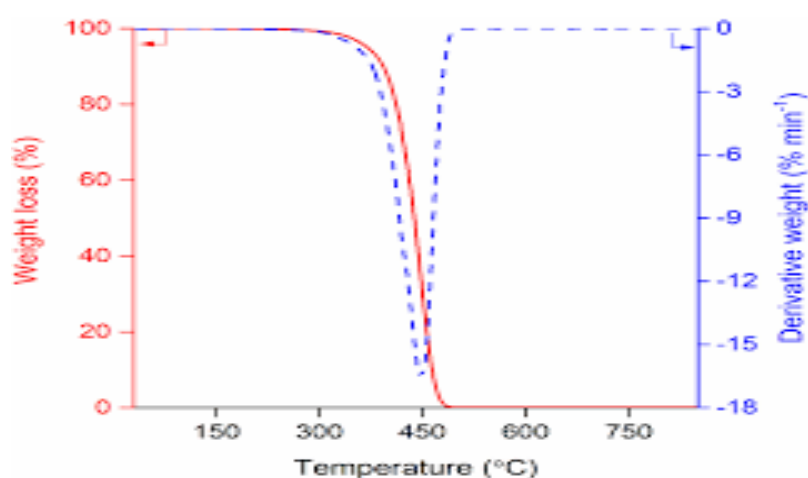


Fig 5.7. Distribution of low (top) and high (bottom) reflux rate LDPE liquid pyrolysis products

In the liquid product from the high reflux pyrolysis, the hydrocarbons chains ranged from C5 to C36 but those from the low reflux rate pyrolysis ranged from C5 to C42+. These results are in agreement with other studies. [18, 20, 27, 37, 49, 58, 60, 63, 86, 89, 98, 101, 103-106] Lee and Shin [50] found that the distribution of the oil product molecular weight ranges up to 500 which corresponds to C40. The molecular weight of the major components is between 200 and 400, which is from C14 up to C30. Aguado et al. [29] found that the carbon chain length in the products is up to C55.

From Figure 5-12, the components appeared on the GC analysis chart as peaks in subgroups. Each sub-group consisted of a small peak in the front and two major peaks behind. (Figure 5-11) According to the literature review [28, 31, 87], the small peak in the front of each group is α , ω -dialkene. The following two peaks are 1-alkene and nalkane, respectively, according to other studies. [58] This chromatogram obtained in this study is very similar to those obtained by other researchers. [27, 59, 88, 111-115] The oil products from both processes (high reflux and low reflux rate pyrolysis) had a

normal distribution with the maximum peak value at the 13.4 minute (C14 group). However, liquid from the high reflux rate pyrolysis contained lower proportion of the hydrocarbons with carbon chain length greater than 14 than that from the low reflux rate pyrolysis. On the other hand, the liquid from the high reflux rate pyrolysis contained lighter molecular weight hydrocarbons with carbon chain number less than 14 compared to that from the low reflux pyrolysis. (Figure 5-11) The heavy hydrocarbons with carbon number greater than 36 do not appear in the high reflux process product. This was due to the effect of secondary cracking of the liquid products, which was caused by the difference of reflux rates in the pyrolysis.

In order to identify the two major components in each sub-group, the liquid oil generated from the LDPE pyrolysis was firstly diluted in n-hexane with a ratio of 1:1000. Then, 1% v/v 1-Cetene (1-C16) and 1% v/v n-Cetane (n-C16) were added into the diluted oil, respectively. The GC results for these new samples are shown in Figure 5-12 with comparison with the only diluted oil. In theory, by adding known components in the liquid, the GC chromatogram will show a clear increase for the peaks of added components. On the word, the increased peaks are the known components. From the results shown in Figure 5-12, 1-C16 and n-C16 were identified on the sample GC analysis graph, which appeared at the 16th minute on the graph. The C16 group is the group with a clearly increased peak in the graph. (Figure 5-12 middle and bottom graphs) Therefore, it is determined that the front major peak in the group is 1-alkene and the second major peak is n-alkane. This technique was applied on all groups in the LDPE liquid product and thus the corresponding hydrocarbons were identified.

CHAPTER-6

Conclusion and reference

6.1 Conclusions

PE is one of the most commonly used plastic materials. According to the pyrolysis processes and the product distribution, there is no significant difference between LDPE and HDPE, therefore, LDPE was extensively investigated and reported in this chapter of the thesis. The LDPE products consist of non-condensable gases, liquid or wax hydrocarbons, and char. The proportion of each product can be changed by changing the reaction conditions. From this study, it is found that the product distribution was significantly influenced by reflux rate in the pyrolysis process. The products consisted of 83% oil/wax, 16% of non-condensable gases, and less than 1% char with high reflux rate pyrolysis. In the high reflux rate pyrolysis, heavy molecular weight hydrocarbons were refluxed into the pyrolysis zone and were further pyrolyzed into lighter hydrocarbons such as noncondensable gases and light liquid oil. Intensive secondary pyrolysis reaction was observed in the high reflux rate process. The char product was largely solid carbon with a small proportion of silica and calcium oxides.

The non-condensable gases (C1 to C4), oil and wax (C5+) were analysed to be hydrocarbons with carbon chain number ranged from C1 to C42+. The hydrocarbons with the same carbon chain number were grouped together on the chromatogram and the highest concentration for the liquid product had a peak value of at the C14 group. In order to determine the sub-group peaks, an innovative method was developed by diluting the sample and adding standard liquid with known carbon numbers. It was identified that the front major peak is 1-alkene and the other major peak is n-alkane in each group, respectively.

The influence of reflux rate on the products is very significant. In the high reflux rate pyrolysis, hydrocarbons above C36 were further pyrolyzed thus was not found in the liquid product. However, a significant amount of heavy hydrocarbons above C36 were found in the low reflux rate pyrolysis. The components in the liquid were also analyzed though GC-MS but the GC-MS method could not distinguish individual peaks in each sub-group. The effects of reflux rate and secondary cracking reactions on the products were further investigated in the following section.

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