**ÇUKUROVA UNIVERSITY**
**INSTITUTE OF NATURAL AND APPLIED SCIENCES**

**MSc THESIS**

**Ceyla GÜNGÖR**

# PRODUCTION OF WASTE PLASTIC FUELS AND INVESTIGATIONS OF INFLUENCE OF WASTE PLASTIC FUELS ON PERFORMANCE AND EXHAUST EMISSIONS OF DIESEL ENGINE

**DEPARTMENT OF MECHANICAL ENGINEERING**

**ADANA, 2011**

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We certify that the thesis titled above was reviewed and approved for the award of degree of the Master of Science by the board of jury on 03.01.2011.

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## ABSTRACT

## MSc THESIS

**PRODUCTION OF WASTE PLASTIC FUELS AND INVESTIGATIONS OF INFLUENCE OF WASTE PLASTIC FUELS ON PERFORMANCE AND EXHAUST EMISSIONS OF DIESEL ENGINE**

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The overall objective of this study was to explore the utility of waste plastics as a potential source of diesel fuel. Waste plastics were produced by thermal and catalytic cracking method. The thermal and catalytic cracking reactions were carried out in a pilot cracking reactor equipped with contact thermometer. Waste plastic fuels were blended with diesel fuel at the volumetric ratio of 5%, 10%, 15%, 20%. Fuel properties of waste plastics and blends were analyzed by the standards of American Society fir Testing and Materials (ASTM) method. In addition to fuel properties, engine performance and exhaust emission studies of 5% waste plastic fuel-diesel blends were performed.



**Key Words**: Emissions, Fuel Properties, Performance, Thermal and catalytic cracking, Waste Plastics,

# ÖZ

**MSc THESIS**

**ATIK PLASTİK YAKITLARIN ÜRETİMİ VE DİZEL MOTORLARDA PERFORMANS VE EGZOZ EMİSYONLARINA ETKİLERİNİN İNCELENMESİ**

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Bu çalışmada, atık plastik yakıtlarının alternatif dizel yakıtı olarak kullanılabilirliği araştırılmıştır. Atık plastik yakıtları pilot ölçekli kraking reaktörde termal ve katalitik parçalanma yöntemleriyle elde edilmiştir. Elde edilen atık plastik yakıtları dizel yakıtı içerisine hacimsel olarak % 5, % 10, % 15 ve % 20 oranlarında karıştırılmıştır. Atık plastik yakıtlarının ve dizel karışımlarının yakıt özellikleri standart Amerikan Test ve Malzeme Enstitüsü (ASTM) metotlarına uygun olarak analiz edilmiştir. Yakıt özelliklerine ek olarak % 5 karışımlar için motor performans ve egzoz emisyon deneyleri de gerçekleştirilmiştir.

**Anahtar Kelimeler**: Atık Plastik, Emisyonlar, Performans, Termal ve Katalitik Parçalanma, Yakıt Özellikleri,

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## LIST OF ABBREVIATIONS AND NOMENCULATURE

| | |
|---|---|
| MT | : Million tones |
| HPDE | : High density polyethylene |
| LPDE | : Low density polyethylene |
| PP | : Polypropylene |
| PET | : Polyethylene terephthalate |
| PMMA | : Poly methyl methacrylate |
| PTFE | : Polytetrafluoroethylene |
| PS | : Polystrene |
| PVC | : Polyvinyl chloride |
| BTX | : Benzene, toluene, xylene |
| PE | : Polyethylene |
| FCC | : Fluid-bed catalytic cracking |
| BPD | : Boiling point distribution |
| GC/MS | : Gas chromatography mass spectrometry |
| $BaCO_3$ | : Barium carbonate |
| $MgCO_3$ | : Magnesium carbonate |
| Zr | : Zirconium |
| Mo | : Molibden |
| bTDC | : Before top dead center |
| DI | : Diesel Engine |
| ◦CA | : Crank angle |
| NOx | : Nitrogen oxide |
| CO | : Carbon monoxide |
| TG | : Thermogravimetry |
| DSC | : Differential scanning calorimetry |
| EGR | : Exhaust gas recirculation |
| HC | : Hydrocarbon |
| BSU | : Bosch smoke unit |
| WPO | : Waste plastic oil |

LPG : Liquid petroleum gas

UV : Ultraviolet

$AlCl_3$ : Aluminum (III) chloride

ASR : Automotive shredder residues

GPE : Granule Polyethylene

MG : Mixed Granule

CPE : Catalyzed polyethylene

LPP : Light polypropylene

WPE : Waste polyethylene

LP : Light phase

HP : Heavy phase

# 1. INTRODUCTION

Plastics are ‘‘one of the greatest innovations of the millennium’’ and have certainly proved their reputation to be true. There are a numerous ways that plastic is and will be used in the years to come. The fact that plastic is lightweight, does not rust or rot, low cost, reusable and conserves natural resources is the reason for which plastic has gained this much popularity. Plastics save energy and $CO_2$ emissions during their use phase. Constant developments in polymer technology, processing machineries, know-how and cost effective production is fast replacing conventional materials in every segment with plastics.

Continuous innovation explains that, plastics production has increased by an average of almost 10% every year on a global basis since 1950. The total global production of plastics has grown from around 1.3 million tonnes (MT) in 1950 to 245 MT in 2006. Plastics continue to be a global success story with Europe (EU25 + Norway (NO) and Switzerland (CH) remaining a major manufacturing region, producing about 25% of the total estimated worldwide plastics production of 245 million tonnes during 2006. An analysis of plastics consumption on a per capita basis shows that this has now grown to over 100 kg/y in North America and Western Europe, with the potential to grow to up to 130 kg/y per capita by 2010. The highest consumption of plastics among different countries is found in USA which is equal to 27.3 MT against 170 MT world consumption in 2000 and is expected to reach to 39 MT by 2010. The highest potential for growth can be found in the rapidly developing parts of Asia (excluding Japan), where currently the per capita consumption is only around 20 kg/year. In the European context, it is the new member states such as Poland, Czech Republic and Hungary which are expected to see the biggest increase as their economies development. Their current average per capita consumption of 55 kg is a little more than half of that of the old Member State. Significant growth rate in Asia and Eastern Europe expected, however in 2010 demand per capita in Asia and Eastern Europe is still much below the rate of the ‘‘traditional markets’’ like America and Western Europe. The average Indian consumption of virgin plastics per

capita reached 3.2 kg in 2000/2001 (5 kg if recycled material is included) from a mere 0.8 kg in1990/1991 and 1.8 kg in 1998/1999. However, this is only onefourth of the consumption in China (12 kg/capita, 1998) and one sixth of the world average (18 kg/capita). The Fig. 1 gives the comparison of per capita consumption of plastics over three different periods. This plot represents a clear picture of growth of plastic consumption in world.

**Per capita consumption of plastics in k g/year**

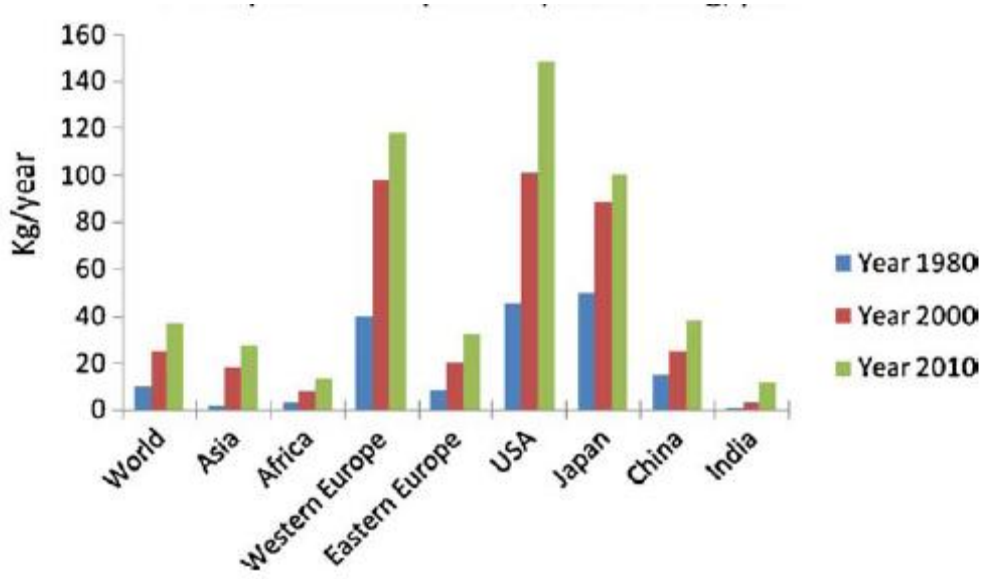



Figure 1.1. Comparison of per capita consumption of plastics over three different periods ( Panda et al. 2010).

The publics concern over the environmental impact caused by polymeric wastes, and the economic interest for a profitable use of such abundant source of chemicals and energy, are the main driving forces of the current research activities aimed at the development of plastic recycling processes (Aguado et al., 1997).

Different alternatives are currently being considered for reducing the environmental impact of plastic wastes. Plastic items start to be manufactured by thinking of their necessary future recycling. Thus, the easy identification of their components starts to be favored through ecolabels. Recycling of plastic wastes may proceed through two main alternatives: mechanical and feedstock recycling. Mechanical recycling is aimed at the reintroduction of the plastic materials in the

consumption cycle, although usually in secondary applications because goods made of recycled plastics are of lower quality. On the contrary, feedstock recycling involves the transformation of the plastic wastes into valuable chemicals or fuels, which exhibit properties similar to those of their counterparts prepared by conventional methods (Serrano et al., 2000).

Catalytic degradation of plastic waste offers considerable advantages as compared to pure thermal degradation, as the latter demands relatively high temperatures and its products require further processing for their quality to be upgraded. Catalytic degradation occurs at considerably lower temperatures and forms hydrocarbons in the range of motor engine fuel, eliminating the necessity of further processing. In such a recycling process, the most valuable product is obviously liquid fuel. Although gaseous products are useful too, as their burning can contribute to the energy demand of an endothermic polymer cracking process, excess gas production is not desirable. Gaseous products are considered of low value because of their transportation costs. Consequently, the target of a commercially viable recycling process should be an increase of the liquid product yield (Akpanudoh et al., 2005).

There are two main types of plastics; thermoplastics, (more than 80 %) which physical behaviour depends on the external temperature. They are soft when heated and becomes harder by cooling. Most common thermoplastics are HDPE for detergents bottles, LDPE for flexible containers, PP used in automotive parts, PET used in bottles, PVC for pipes etc. The other main type is the thermosets plastics. They are hardened by a curing process and can not be remelted or re-moulded. Different examples of thermosets plastics are PU, epoxy and phenolics (Zorriqueta, 2006). Two types of polymers were widely investigated, polyethylene and polypropylene, because they represent 60–65% of all plastic wastes (Miskolczi et al., 2004).

The overall objective of this study was to explore the utility of waste plastics as a potential source of diesel fuel. Waste plastics oils were produced by thermal and catalytic cracking method. The thermal and catalytic cracking reactions were carried out in a pilot cracking reactor equipped with contact thermometer. Waste plastics were blended with diesel fuel at the volumetric ratio of 5%, 10%, 15% and 20% and

fuel properties such as density, flash point, viscosity, pour point, cetane number and calorific value of blends were measured in the name of EN 590 diesel standards. In addition to fuel properties, engine performance and exhaust emission studies of 5% waste plastic fuel-diesel blends were performed.

## 2. PRELIMINARY WORK

The huge amount of waste plastics that resulted from the dramatic increase in polymer production gives rise to serious environmental concerns, as plastic does not degrade and remains in municipal refuse tips for decades. Plastic waste being more voluminous than the organic waste takes up a lot of landfill space that is becoming scarce and expensive. Incineration is not an acceptable solution to the problem, as toxic gases are produced and a solid waste problem becomes air pollution. The only sustainable solution is polymer recycling. Between various polymer recycling methods, thermal and/or catalytic degradation of plastic waste to fuel show the highest potential for a successful future commercial process, especially as plastic waste can be considered as a cheap source of raw materials in times of accelerated depletion of natural resources (Akpanudoh et.al., 2005).

Thermal Process comprises the thermal treatment of the plastic waste at 400-800 °C under an inert atmosphere. Thermal degradation leads usually (e.g., HDPE, LDPE, PP) to a broad hydrocarbon distribution of reaction products, except for certain plastics, wherein the recovery of the monomer is feasible (poly(methyl methacrylate) (PMMA), PS, polytetrafluoroethylene (PTFE)).

The most-known thermal treatment is the Hamburg process, which was developed by Kaminsky and co-workers; the core of the process is comprised of a fluidized-bed reactor, which promotes mass and heat transfer, ensuring a uniform temperature throughout the reactor. This system avoids the appearance of temperature gradients inside the reactor, in contrast to that it occurs, e.g., when rotary kilns are present, which usually promotes a wider product distribution. The process is designed for laboratory scale with an output of 1-2 kg/h. The reactor consists in a 1.5-m-wide stainless steel tube with a height of 6.7 m, which is filled with millimeter-grain-size sand. The reactor is heated with a filament, and the fluidizing gas enters at the bottom, through a steel plate distributor. Two screw conveyors feed the plastics into the reactor, wherein they are quickly converted. The products are caught in separation units that consist of a cyclone, coolers, and an electrostatic precipitator. Different strategies have been applied with this system:

(1) The cracking of plastics at 500-650 °C to produce waxes and oils, that constitute potential feedstocks in refineries.

(2) Pyrolysis of plastics in a steam stream at 650-800 °C to attain mostly light olefins, such ethene, propene, and butadiene.

(3) Pyrolysis at 600-800 °C, using liquid-free pyrolysis gases as a fluidizing agent and leading mainly to BTX oils.

(4) Monomer recovery from certain plastics (such as PS, PMMA, and PTFE) by heating at 450-550 °C.

Thus, in the pyrolysis of mixed plastics (polyolefin, polystyrene, and PVC) at 685-740 °C with a residence time of 2-3 s, a compostion of 44 wt% of gases and 50 wt% of oil was obtained, with the latter containing 40% of BTX (≈10% of benzene). In contrast, the pyrolysis at 510 °C of a plastic mixture of PP, PE, and PS led to 90 wt % of oil/waxes with a low aromatic content (0.1-0.3 wt %), showing the role of temperature in promoting the aromatic formation. The use of steam as fluidizing medium allows one to obtain high yields of ethene and propene. Thereby, at temperatures of 700-750 °C, high yields of olefins were achieved (21-29 wt % ethene, 16-21 wt % propene, and 5.6-6.6 wt % butadiene). On the other hand, poly(methyl methacrylate) (PMMA) was depolymerized at 450 °C into >98% of the monomer. Similarly, for the case of polystyrene at 520 °C, a 75% of styrene was achieved, as well as 10% of oligomers. However, the presence of fillers (such as alumina trihydrate) in PMMA was observed to decrease the amount of recovered monomer (just 58%) (Aguado et.al., 2008).

Williams et al.(1999) performed the pyrolysis of low-density polyethylene in fluidized-bed reactors, which led to a mixture of wax, oil, and gas products. An increase of reaction temperature improved the yield of gases, reaching 71% at 700 °C, and their main components were methane (11.7%), ethene (26.8%), and propene (18.6%). Similarly, the share of aromatics in oils was augmented in parallel with the temperature (Williams and Williams, 1999).

The use of catalysts allows the plastic degradation pathway to be modified, with regard to pure thermal cracking. Initially, two positive effects are to be expected by the incorporation of a catalyst into the reaction medium: (i) a reduction of the

cracking temperature, and (ii) suitable control of the selectivity, which enables the formation of more-valuable products (Aguado, et al., 2008).

Miskolczi et al. (2004) reported thermal and thermo-catalytic cracking of a commercial high-density polyethylene (HDPE) waste in temperature range of 400–450 °C in a laboratory scale Pyrex batch reactor using fluid catalytic cracking catalyst (FCC), HZSM-5 and a clinoptilolite containing rhyolite tuff as catalysts. At 450 °C, the liquid yield from 74.5% to 82.5% was obtained for thermal and catalytic (FCC) degradation processes respectively.

Lin et al. (2004) studied the pyrolysis of HDPE over various catalysts using a laboratory fluidised-bed reactor at ambient pressure. They discovered that ZSM-5 catalyzed degradation resulted in much larger amounts of volatile hydrocarbons as compared with degradation over non-zeolitic catalysts (MCM-41 and SAHA). A maximum conversion of 95.48% was achieved with zeolitic ZSM-5 catalyst where 94.21% gaseous product was produced with a nominal liquid product of 1.26%.

Garcia et al. (2005) applied hybrid ZSM-5/MCM-41 materials for the catalytic degradation of HDPE and compared it with the Standard Al-MCM-41 and HZSM-5 and obtained a high content of $C_3$–$C_5$ olefins in the products. The batch reactions were carried out at a lower temperature of 380 °C just to compare the activity of the catalysts. The results demonstrated that hybrid zeolitic–mesoporous show promising properties to be used as catalysts in the cracking of HDPE. HZM materials exhibit higher degradation activity than both Al-MCM-41 and HZSM-5 samples having similar aluminum content. Significant HDPE conversions were achieved in a batch reactor over the HZM samples in spite of working at low temperature and high plastic/catalyst ratio. Under these conditions, no activity was detected over the Al- MCM-41 material, whereas just a 5% conversion was observed for the pure HZSM-5 sample.

Aguado et al. (2007) investigated a zeolite catalyst for polyethylene cracking. It was reported that over n-HZSM- 5, 77 wt % of product was a gasoline fraction compared to only 56 wt% without the catalyst.

Angyal et al. (2009) investigated thermal and catalytic cracking of polyethylene waste in continued tube reactor system. They tested HZSM-5 and

equilibrium FCC type catalysts. They studied both the resistance to deactivation and the regeneration process of the catalyst. They used during the cracking treatment reaction temperature of 545$^{o}$C and residence time of 20 min. They analyzed the reaction products and they also determined the textural properties of catalysts. They found that after the first reaction run the FCC catalyst lost 75% of its cracking activity, in case of HZSM-5 the rate of deactivation was higher. The cracking activity of catalyst could be improved by regeneration process with only 2–3% compared to the coked catalyst. They observed the isomerisation effect of the catalysts and the effect of coked FCC catalyst could be improved by the regeneration process with 50% in case of HZSM-5 it was only 25%.

Miskolczi et al. (2009) investigated a pilot scale pyrolysis process. They decomposed waste plastics in a tube reactor at 520$^{o}$C, using hourly feed rate of 9 kg. They used horizontal gas heated tube reactor. They tested high-density polyethylene (HDPE) and polypropylene (PP) from agriculture and packaging sectors and they used ZSM-5 catalyst. They found that the yields of gases, gasoline and light oil could be considerably increased in the presence of ZSM-5 catalyst.

Jan et al. (2010) degraded waste high-density polyethylene (HDPE) thermally and catalytically using $BaCO_3$ as a catalyst under different conditions of temperature, cat/pol ratio and time. They collected the oil at optimum conditions (450 °C, 0.1 cat/pol ratio and 2 h reaction time) was fractionated at different temperatures and fuel property of the fractions and parent oil was evaluated by their physicochemical parameters for fuel tests. The results were compared with the standard values for gasoline, kerosene and diesel oil. Boiling point distribution (BPD) curves were plotted from the gas chromatographic study of the samples and compared with that of the standard gasoline, kerosene and diesel. The oil samples were analyzed using GC/MS in order to find out their composition. The physical parameters and the composition of the parent oil and its fractions support the resemblance of the samples with the standard fuel oils. The light fractions best match with gasoline, the middle fractions match with kerosene and the heavier fractions match with diesel oil in almost all of the characteristic properties.

Jan et al. (2010) degraded high-density polyethylene (HDPE) thermally and catalytically using $MgCO_3$ at 450$^oC$ into liquid fraction in a batch reactor. They optimized different conditions like temperature, time and catalyst ratio for the maximum conversion of HDPE into liquid fraction. Catalytic degradation yielded 92% liquid fraction whereas 90% wax was obtained with thermal degradation. The catalytic liquid fraction consisted of high concentration of $C_8$–$C_9$, $C_{13}$–$C_{14}$ and $C_{17}$–$C_{18}$ hydrocarbons. The distillation data showed that 50% of the fraction has boiling point in the range of gasoline and 50% in the range of diesel oil.

Walendziewski et al. (2005) carried out experiments of waste polymers cracking in a continuous flow tube reactor. He realized cracking process at the temperature range 420-480 °C and raw material feeding rate from 0.3 up to 2.4 kg/h. The principal process products, gaseous and liquid hydrocarbon fractions, were similar to the refinery cracking products. They were unstable due to the high olefins content (especially from polystyrene cracking) and their chemical composition and properties strongly depend on the applied feed composition, i.e. shares of polyethylene, polypropylene and polystyrene. The material balance experiments showed that the main products, liquid or solid materials in ambient temperature, contain typically 20–40% of gasoline fractions (range of boiling point 35–180.8$^{\circ}C$) and 60–80% of light gas oil fractions (initial boiling point >180.8$^{\circ}C$). The solid carbon residues were similar to coal cokes and contain even of 50% mineral components. Their calorific values attained 20 MJ/kg and they were solid fuels of quality similar to brown coals.

General results concluded from this study can be summarized as follows:

- Continuous flow tube cracking reactor equipped with the internal screw mixer can be satisfactorily applied to thermal cracking of waste polyolefines.
- Large reactor loading, i.e. the short reaction time, favors larger yields of higher boiling liquid or semi-solid products, especially higher boiling light gas oil fraction.
- From the point of view of the cracking plant operation efficiency polypropylene wastes are viewed as the best feed due to the factors like the

highest yield of liquid, low temperature freezing products as well as small solid carbon residue and gas yields

- In comparison with commercial “fresh” plastics the cracking process of the mixture of waste plastics gives considerably lower yield of the most valuable liquid products, 80-85 instead of ca. 92-93 wt.% and respectively higher gas and solid carbon residue yields.
- Liquid products of waste plastics cracking products. They were also unstable because of high olefins content (especially from polystyrene cracking), with low freezing temperature (< -20 ◦C) in case of cracking of larger shares of PP and PS containing wastes and high freezing temperature (>30◦C) in the presence of cracking polyethylene wastes.
- In the well selected process parameters, the solid carbon residues can contain up to 50% mineral components.
- Catalytic hydro-refining of liquid hydrocarbon fractions enables obtaining of good uality liquid fuel components.

Ji et al. (2006) pyrolysed low density polyethylene at high temperature in the presence of metal salts and they observed an increase in the formation of aromatics with increase in the temperature.

Marcilla et al. (2009) studied the catalytic pyrolysis of low-density polyethylene (LDPE) and high-density polyethylene (HDPE) over the HZSM5 catalyst in a batch reactor and an analysis of the evolution of the products generated with temperature was presented. As expected, the catalyst favored the formation of gaseous compounds. They obtained the composition of the products depended upon the polyethylene structure, especially at the beginning of the degradation process. Initially during the catalytic cracking of LDPE, olefins were the major compounds obtained in both the gaseous and condensed phases. As the temperature was increased, the composition of the gases remained constant, whereas in the condensed fraction, the olefins yield decreased, resulting in aromatics being the compounds predominantly generated. With HDPE, a greater quantity of paraffins and aromatics formed at the beginning of the decomposition process in the gaseous and condensed

products, respectively, as compared to LDPE. As the temperature was increased, however, a more similar composition to that for LDPE was obtained.

Lin and Yang (2007) used a laboratory catalytic fluidised-bed reactor to obtain a range of volatile hydrocarbons by catalytic degradation of polypropylene in the temperature range of 330-450◦C. The catalytic degradation of PP over spent FCC catalyst performed in fluidised-bed reactor was shown to be a useful method for the production of potentially valuable hydrocarbons. They used in the presence of the spent FCC commercial catalyst at 390 ◦C, conversion of PP polymer to volatile hydrocarbons in the catalytic fluidised-bed reactor was more than 87 wt% of feed in 20 min, while silicalite yielded less than 18 wt% of feed after 60 min. Their experiments carried out with FCC-s1 catalyst gave good yields of volatile hydrocarbons with differing selectivity in the final products dependent on reaction conditions. However, silicalite give very low conversions of polymer waste to volatile hydrocarbons compared with spent FCC catalyst (FCC-s1) under the same reaction conditions. The selectivity could be further influenced by changes in operating conditions; in particular, olefins and iso-olefins were produced by low temperatures and short contact times.

Xie et al. (2008) investigated catalytic cracking of polypropylene (PP) over MCM-41 modified by Zr and Mo. The relationship among structure, acidity and catalytic activity of Zr–Mo-MCM-41 was studied. The results showed that Zr–Mo-MCM-41 exhibited high activity for the cracking of PP and good selectivity for producing liquid hydrocarbons of higher carbon numbers. The results were compared with those obtained over HZSM-5, $SiO_2$–$Al_2O_3$ and other MCM-41 mesoporous molecular sieves. Moreover, the effect of different Zr sources on the reaction was examined. The results showed that both the conversion of PP and the selectivity to liquid product were greatly improved after introducing Zr.

Mani and Nagarajan (2009) investigated the influence of injection timing on the performance, emission and combustion characteristics of a single cylinder, four stroke, direct injection diesel engine using waste plastic oil as a fuel. They performed tests at four injection timings ($23^0$,$20^0$,$17^0$,$14^0$ BTDC). They compared tı the standart injection timing of $23^0$ BTDC the retarded injection timing of $14^0$ BTDC resulted in

decreased oxides of nitrogen, carbon monoxide and unburned hydrocarbon while the brake thermal efficiency, carbon dioxide and smoke increased under all the tests conditions.

Mani et al (2009) investigated the performance, emission and combustion characteristics of a single cylinder, four-stroke, air-cooled DI diesel engine run with waste plastic oil. The experimental results showed a stable performance with brake thermal efficiency similar to that of diesel. Carbon dioxide and unburned hydrocarbon were marginally higher than that of the diesel baseline. The toxic gas carbon monoxide emission of waste plastic oil was higher than diesel. Smoke reduced by about 40% to 50% in waste plastic oil at all loads.From the tests conducted with waste plastic oil and diesel on a DI diesel engine, the following conclusions are arrived:

- Engine was able to run with 100% waste plastic oil.
- Ignition delay was longer by about 2.5 ◦CA in the case of waste plastic oil compared to diesel.
- $NO_x$ is higher by about 25% for waste plastic oil operation than that of diesel operation.
- CO emission increased by 5% in waste plastic oil compared to diesel operation.
- Unburned hydrocarbon emission is higher by about 15%.
- Smoke reduced by 40% at rated power in waste plastic oil compared to diesel operation.
- Engine fueled with waste plastic oil exhibits higher thermal efficiency up to 75% of the rated power.

Coelho et al. (2010) studied the catalytic degradation of high and low density polyethylenes, using catalysts based on transition metals supported on zeolite Y, was analyzed using simultaneous thermogravimetry (TG) and differential scanning calorimetry (DSC). The results obtained in the catalytic degradation were compared with those that were obtained in the purely thermal degradation. The transition metals used, vanadium, zirconium and nickel, supported on NaY or HY were studied since they were found to be active, although with different degrees of efficiency, for

ethylene polymerization, which is, in a way, the reverse reaction of the one they were interested in. It was found that they are also able to promote the degradation process of polyethylene, also with varying efficiencies. A kinetic model capable to describe the performance of the catalytic degradation, and which has already been used to analyse its thermal degradation, has been applied. Fitting this model to the experimental results obtained by TG and DSC made it possible to estimate several kinetic parameters and to gain some insight into the processes involved.

Walendziewski et al. (2002) carried out two series of experiments of waste polymers cracking. He was carried out first series of polymer cracking experiments in a glass reactor of 0.5 $dm^3$ volume at atmospheric pressure and in a temperature range 350-420 $^{\circ}C$, the second one in autoclaves under hydrogen pressure (≈3-5 MPa) in the temperature range 380-440 $^{\circ C}$.

General results concluded from this study can be summarized as follows:

- Thermal and catalytic cracking of the most popular polymers, PE,PS, PP and their mixtures enable to convert them to liquid and gas fuels with over 95 % efficiency.
- Application of cracking catalysts results in lowering of polymers cracking process temperature as well as boiling temperature range and density of the obtained liquid products.
- Application of catalysts increases gas product yields but no visible influence of catalyst on gas composition was found. Gas composition depends on feed composition and process conditions.
- In comparison to the atmospheric process, the pressure cracking of waste plastics in autoclaves at long contact time and high temperature resulted in larger conversion level, larger gas and gasoline fraction yields and relatively lower boiling and lower freezing points however lower cetane number of diesel fuel fractions.
- Products of polymers cracking, are highly unsaturated, contain olefins and diolefins which can be hydrogenated over $Pd/Al_2O_3$ catalyst, bromine number lowers to lower than 0.5 g $Br_2$/100 g.

Gasoline fractions are characteristic by high octane number especially in the case when PS is the component of the reaction feed. For the same reasons, somewhat higher aromatic contents and low boiling temperature, diesel fuels from pressure system presents low cetane number while cloud point and ignition points respond to the suitable petroleum standards.

Mani et al (2010) investigated the effect of cooled exhaust gas recirculation (EGR) on four stroke, single cylinder, direct injection (DI) diesel engine using 100% waste plastic oil. Experimental results showed higher oxides of nitrogen emissions when fueled with waste plastic oil without EGR. $NO_x$ emissions were reduced when the engine was operated with cooled EGR. The EGR level was optimized as 20% based on significant reduction in NOx emissions, minimum possible smoke, CO, HC emissions and comparable brake thermal efficiency. Smoke emissions of waste plastic oil were higher at all loads. Combustion parameters were found to be comparable with and without EGR. Compression ignition engines run on waste plastic oil found to emit higher oxides of nitrogen.

Following are the major conclusions drawn from the experimental work conducted with diesel and waste plastic oil with and without EGR:

- The DI compression ignition engine was able to operate with 100% waste plastic oil. The brake thermal efficiency in waste plastic oil varies from 14% to 30% without EGR compared to 13–29% with 20% EGR. At full load the brake thermal efficiency decreases with increase in EGR flow rate due to high EGR percentages that result in larger replacement of air.
- At all loads, exhaust gas temperature decreases marginally with increase in EGR percentages. The exhaust gas temperature is higher by about 298 K in WPO operation without EGR throughout the load spectrum as compared to dieseloperation.
- The $NO_x$ emission in waste plastic oil varies from 14.63 to 8.56 g/kWh without EGR compared to 10.97–8.2 g/kWh with 20% EGR. The $NO_x$ emission reduces with increase in EGR percentage, due to the presence of higher heat capacity gases that reduces the peak combustion temperature.

- Unburned hydrocarbon emission varies from 0.41 to 0.03 g/kWh without EGR compared to 20% EGR that varies from 0.51 to 0.10 g/kWh and 0.56 to 0.13 g/kWh in diesel. Unburned hydrocarbon increased with increase in EGR rate due to the reduction of oxygen in the inlet charge by the EGR into the cylinder.
- The CO emission varies from 15.12 to 7.5 g/kWh without EGR compared to 20% EGR from 14.83 to 6.32 g/kWh and from 15.3 to 5.7 g/kWh in diesel. CO emissions are lowest at full load with 20% EGR when compared to WPO operation without EGR due to the displacement of air by recirculated exhaust gas that results in incomplete combustion.
- The $CO_2$ concentration decreases with increase in EGR percentages, due to instability in combustion.
- The smoke emission reduces with increase in EGR percentage. The smoke varies from 0.07 BSU to 5.2 BSU without EGR compared to 20% EGR of 0.11 BSU to 5.5 BSU and 0.02 BSU to 5.3 BSU in diesel. Smoke emissions are higher with 20% EGR in WPO operation without EGR at rated power. This is attributed to lesser oxygen present in the engine cylinder that leads to poor combustion.
- The peak pressure reduces with 20% EGR by 5% compared to that of WPO without EGR. This is because the EGR acts as a heat absorbing agent that reduces the cylinder charge temperature in the combustion chamber during the combustion process.
- A diesel engine can be run successfully with WPO, however with higher $NO_x$ emission. The $NO_x$ emission can be reduced significantly by adopting EGR techniques.

Jeng et al (2003) investigated the effects of catalysts, dosage of catalysts, and temperature variation on yield ratios of liquid fuels and residues in the catalytic cracking and reforming process. The following were the major achievements of the study:

- The study indicated that applying catalysts and varying catalytic temperature would affect yield ratios of the liquid fuels, gasoline, and catalytic coking ratio in the catalytic process.
- The experiment identified the related optimal reaction conditions.
- The project designed and implemented a fluidized bed cracker with continuous feeding and discharging equipment to convert waste plastics into fuels.
- The technology solved some critical problems in the producing process with respect to unsafe and disrupting operation.
- The demonstrating project could convert mixed waste plastics into gasoline and diesel fuels. The fuel products met the Chinese national standard of gasoline and diesel for auto fuel.

# 3. PYROLYSIS OF WASTE PLASTICS

## 3.1. Plastics

Plastics are a generic group of synthetic or natural materials, composed of high-molecular chains whose sole or major element is carbon. In common usage the terms plastics, *polymers* and *resins* are roughly equivalent. A plastic material is any one of a large group of materials consisting wholly or in part of combinations of carbon with oxygen, hydrogen, nitrogen, and other organic or inorganic elements which, while solid in the finished state, at some stage in its manufacture is made liquid, and thus capable of being formed into various shapes, most usually through the application, either singly or together, of heat and pressure.' Plastics are manufactured from *monomers*, i.e. a repeatable molecular unit and building block, by means of various chemical processes, such as:

- A catalytic or peroxide-initiated polymerization of monomer(s), e.g. ethylene, propylene, or butadiene + styrene (copolymers);
- A polycondensation of dissimilar monomers (e.g. bifunctional organic acids and alcohols or amines);
- Polyaddition of reactive monomer molecules.

Especially the first group forms an attractive feedstock for pyrolysis processes. Important monomers are polymerization grade (i.e. very high purity) ethylene, propylene, butadiene, three products obtained by thermal cracking or pyrolysis of e.g. naphtha, light gas-oil, or liquefied petroleum gases (LPG = propane or butane) and purified by low-temperature, high-pressure distillation, up to polymerization grade chemicals. Adding hetero-atoms to the monomer, such as chlorine in vinyl chloride monomer, creates additional difficulties in pyrolysis processes and methods for separating waste plastics at the source or by mechanical means, e.g. sink/float, froth flotation, separation after identification on the basis of absorption or reflection spectra, or electrostatic sorting after tribo-electric charging,

is an important practical consideration. Before its conversion into plastic products the resulting resin is almost always compounded with various additives of different nature and constitution, meant to improve processing, stability, or mechanical specifications as a function of a given application (outdoors, i.e. UV-light exposed, oxidation, high-temperature processing). Such additives are regularly used as:

- Antioxidants (1%),
- Heat and light stabilizers (5%),
- Plasticizers (40%),
- Impact resistance enhancers (10%),
- Pigments, colorants and dyestuffs (5%),
- Flame retardants (15%),
- Mould-release agents,
- Foaming agents (2%),
- Fillers (40%)

(Maximum amount encountered, in weight percent). Other additives are used as antiblocker, anti-fogging and anti-static agents, bio-stabilizers, chemical blowing agents, cross-linking agents, high polymeric impact strength additives and processing aids, lubricants, metal deactivators, optical brighteners, property modifiers, reinforcements, smoke and afterglow suppressants, wetting agents, etc. Their presence, as well as chemicals used in initiating or terminating polymerization, is a complicating factor in feedstock recycling, also termed chemical recycling or, in a more restricted sense, pyrolysis or thermal cracking of waste plastics, since their nature, amount, and behavior during pyrolysis (thermal volatilization or breakdown) and eventual influence upon reaction products and mechanism are somewhat unpredictable, especially for waste plastics of unknown origin and formulation. PVC absorbs more additive volume than any other resin. Plastics can be classified on the basis of numerous criteria, e.g.:

- chemical composition, directly connected with the nature of the monomer(s) and the method of polymerization. Plastics are thus subdivided into classes,

e.g. polyolefins, vinyl polymers, styrenics, polyamides, polyesters, epoxy resins, polycarbonates, polyurethanes, etc.;

- chemical structure, e.g. linear (high-density polyethylene), branched (low-density polyethylene), cross-linked and three-dimensionally networked (thermosets, rubbers);
- stiffness: elastic, flexible, or rigid;
- type of application: commodity vs engineering, general purpose vs specialty plastics;
- processing method used (injecting moulding, extrusion, film blowing, blow moulding, thermoforming, casting, calendaring, and many other techniques) (Scheirs et.al.,2006).

### 3.1.1. Polyethylene

Polyethylene is the most widely used plastic, with an annual production of approximately 80 million metric tons. Its primary use is within packaging (notably the plastic shopping bag).

Polyethylene is a thermoplastic polymer consisting of long chains produced by combing the ingredient monomer ethylene; the name comes from the ingredient and not the actual chemical resulting. The ethylene actually converts to ethane as it takes its place in a polymer and straight sections of the polymer are the same structure as the simple chain hydrocarbons e.g. propane, decane and other straight single bonded carbon chains. As with any polymer, the structure of the resulting substance defies molecular description due to cross branching of the chains. The recommended scientific name polyethylene is systematically derived from the scientific name of the monomer. In certain circumstances it is useful to use a structure-based nomenclature; in such cases IUPAC recommends polymethylene (polymethanediyl) is an non-preferred alternative). The difference in names between the two systems is due to the opening up of the monomer's double bond upon polymerization.

The name is abbreviated to PE in a manner similar to that by which other polymers like polypropylene and polystyrene are shortened to PP and PS respectively. In the United Kingdom the polymer is commonly called polythene, although this is not recognized scientifically.

The ethene molecule (known almost universally by its common name ethylene) $C_2H_4$ is $CH_2=CH_2$, Two $CH_2$ groups connected by a double bond, thus:

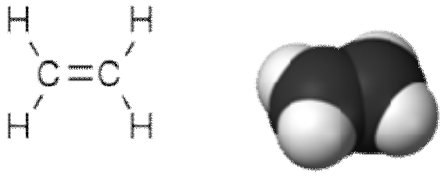


Figure 3.1. The ethene molecule

Polyethylene contains the chemical elements carbon and hydrogen. Polyethylene is created through polymerization of ethene. It can be produced through radical polymerization, aionic addition polymerization, ion coordination polymerization or cationic addition polymerization. This is because ethene does not have any substituent groups that influence the stability of the propagation head of the polymer. Each of these methods results in a different type of polyethylene.

### 3.1.1.1. Classification of Polyethylene

Polyethylene is classified into several different categories based mostly on its density and branching. The mechanical properties of PE depend significantly on variables such as the extent and type of branching, the crystal structure and the molecular weight. With regard to sold volumes, the most important polyethylene grades are HDPE, LLDPE and LDPE.

- Ultra high molecular weight polyethylene (UHMWPE)
- Ultra low molecular weight polyethylene (ULMWPE or PE-WAX)
- High molecular weight polyethylene (HMWPE)
- High density polyethylene (HDPE)

- High density cross-linked polyethylene (HDXLPE)
- Cross-linked polyethylene (PEX or XLPE)
- Medium density polyethylene (MDPE)
- Linear low density polyethylene (LLDPE)
- Low density polyethylene (LDPE)
- Very low density polyethylene (VLDPE)

#### 3.1.1.2. Physical Properties of Polyethylene

Depending on the crystallinity and molecular weight, a melting point and glass transition may or may not be observable. The temperature at which these occur varies strongly with the type of polyethylene. For common commercial grades of medium- and high-density polyethylene the melting point is typically in the range 120 to 130 °C (248 to 266 °F). The melting point for average, commercial, low-density polyethylene is typically 105 to 115 °C (221 to 239 °F).

Most LDPE, MDPE and HDPE grades have excellent chemical resistance and do not dissolve at room temperature because of their crystallinity. Polyethylene (other than cross-linked polyethylene) usually can be dissolved at elevated temperatures in aromatic hydrocarbons such as toluene or xylene, or in chlorinated solvents such as trichloroethane or trichlorobenzene.

When incinerated, polyethylene burns slowly with a blue flame having a yellow tip and gives off an odour of paraffin. The material continues burning on removal of the flame source and produces a drip (Anonymous, 2010).

### 3.1.2. Polypropylene

Polypropylene (PP), also known as polypropene, is a thermoplastic polymer, made by the chemical industry and used in a wide variety of applications, including packaging, textiles (e.g. ropes, thermal underwear and carpets), stationery, plastic parts and reusable containers of various types, laboratory equipment, loudspeakers, automotive components, and polymer banknotes. An addition polymer made from

the monomer propylene, it is rugged and unusually resistant to many chemical solvents, bases and acids.

### 3.1.2.1. Chemical and Physical Properties of Polypropylene

Most commercial polypropylene is isotactic and has an intermediate level of crystallinity between that of low-density polyethylene (LDPE) and high-density polyethylene (HDPE). Polypropylene is normally tough and flexible, especially when copolymerized with ethylene. This allows polypropylene to be used as an engineering plastic, competing with materials such as ABS. Polypropylene is reasonably economical, and can be made translucent when uncolored but is not as readily made transparent as polystyrene, acrylic, or certain other plastics. It is often opaque or colored using pigments. Polypropylene has good resistance to fatigue.

The melting of polypropylene occurs as a range, so a melting point is determined by finding the highest temperature of a differential scanning calorimetry chart. Perfectly isotactic PP has a melting point of 171 °C (340 °F). Commercial isotactic PP has a melting point that ranges from 160 to 166 °C (320 to 331 °F), depending on atactic material and crystallinity. Syndiotactic PP with a crystallinity of 30% has a melting point of 130 °C (266 °F).

The melt flow rate (MFR) or melt flow index (MFI) is a measure of molecular weight of polypropylene. The measure helps to determine how easily the molten raw material will flow during processing. Polypropylene with higher MFR will fill the plastic mold more easily during the injection or blow-molding production process. As the melt flow increases, however, some physical properties, like impact strength, will decrease.

There are three general types of polypropylene: homopolymer, random copolymer, and block copolymer. The comonomer used is typically ethylene. Ethylene-propylene rubber or EPDM added to polypropylene homopolymer increases its low temperature impact strength. Randomly polymerized ethylene monomer added to polypropylene homopolymer decreases the polymer crystallinity and makes the polymer more transparent (Anonymous, 2010).

### 3.2. Pyrolysis of Plastics

Pyrolysis is a process of thermal degradation in the absence of oxygen. Plastic waste is continuously treated in a cylindrical chamber and the pyrolytic gases are condensed in a specially-designed condenser system. This yields a hydrocarbon distillate comprising straight and branched chain aliphatics, cyclic aliphatics and aromatic hydrocarbons. The resulting mixture is essentially the equivalent to petroleum distillate. The plastic is pyrolysed at 370ºC - 420ºC and the pyrolysis gases are condensed in a series of condensers to give a low sulphur content distillate. The de-sulphur unit makes the process complete and turns the fuel into "green-diesel".

The essential steps in the pyrolysis of plastics involve:

- Purging oxygen from pyrolysis chamber.
- Evenly heating the plastic to a narrow temperature range without excessive temperature variations.
- Pyrolising the plastics.
- Passing the gases through a catalytic converter.
- Managing the carbonaceous char by-product before it acts as a thermal insulator and lowers the heat transfer to the plastic.
- Careful condensation and fractionation of the pyrolysis vapors to produce fuels of excellent quality and consistency (Anonymous, 2010i).

#### 3.2.1. Advantages of Pyrolysis

The advantages of pyrolysis of waste plastics into liquid fuels include:

- it allows the recycling of waste mixed plastics that cannot be efficiently recycled by alternative means;
- it permits the recycling of unwashed and soiled plastics (e.g. agricultural plastics, mulch/silage/greenhouse films and dripper/irrigation tube);

- it enables recycling of plastic laminates, coextrusions and multilayer packaging films, particularly those with aluminium foil layers that are difficult to recycle using traditional reprocessing technologies. Most commodity hydrocarbon plastics are suitable for pyrolysis. Generally the larger the substituent in the side chain, the easier the plastic can be degraded. The order of increasing side chain size is polyethylene<polypropylene<polyvinyl chloride<polystyrene.

Problems with many pre-existing plastic cracking technologies include:

- noncontinuous (batch) processes (not commercially viable);
- coking and carbon deposits on heat exchanging surfaces;
- stickiness of sand particles in fluidized-bed processes;
- unsatisfactory fuel quality; relatively high sulphur levels (100–700 ppm) in end product (Scheirs et.al.,2006).

### 3.3. Pyrolysis Reactors

The reactors used in pyrolysis processes are fluidized beds, melting pots, autoclaves, tubular reactors and rotary kilns.

#### 3.3.1. Fluidized Beds

The University of Hamburg has investigated the suitability of plastic wastes after the first oil crisis in 1975. For cracking plastics into oil the low heat transfer and the high heating energy needed as well as the different impurities such as inorganic fillers were problematic. One possibility to solve all those problems was the installation of a process that was able to use filled and dirty plastics in a fast pyrolysis process.

The plastics are fed into the reactor through a double flap screw. The fluidized bed consists of quartz sand and the reactor working temperatures are between 300 to 900 ºC. The fluidizer agent can be pyrolysis gas or a nitrogen stream preheated. The heat input takes place through fire pipes heated by pyrolysis or

propane gas. The exhaust gases are redirected to a heat exchanger. The product gases are separated from residual 15 carbon and fine dust in a cyclone. The gas flow is then directed through two packed condensation columns. Condensed oil fractions are distilled (fractions boiling from 135 to 145 ºC) in two columns. Also tar, with a high boiling point range, is produced as well as two fractions, toluene and benzene. The gases mostly stripped off liquid products, pass to an electrostatic precipitator where small droplets are removed. Subsequently, the gases are compressed in five membrane compressors connected in parallel and stored in 3 gas tanks. Part of the gases serve as fuel for the heating system and the remainder is used for fluidizing the sand bed. The excess gas is flared. The Hamburg process can be varied in some parameters such as pyrolysis temperature, type of fluidizing gas and residence time. This process has been used as well for oil and gas recovery from oil shale, oil sand and biomass (wood, lignin, bark, oil seed and fat).

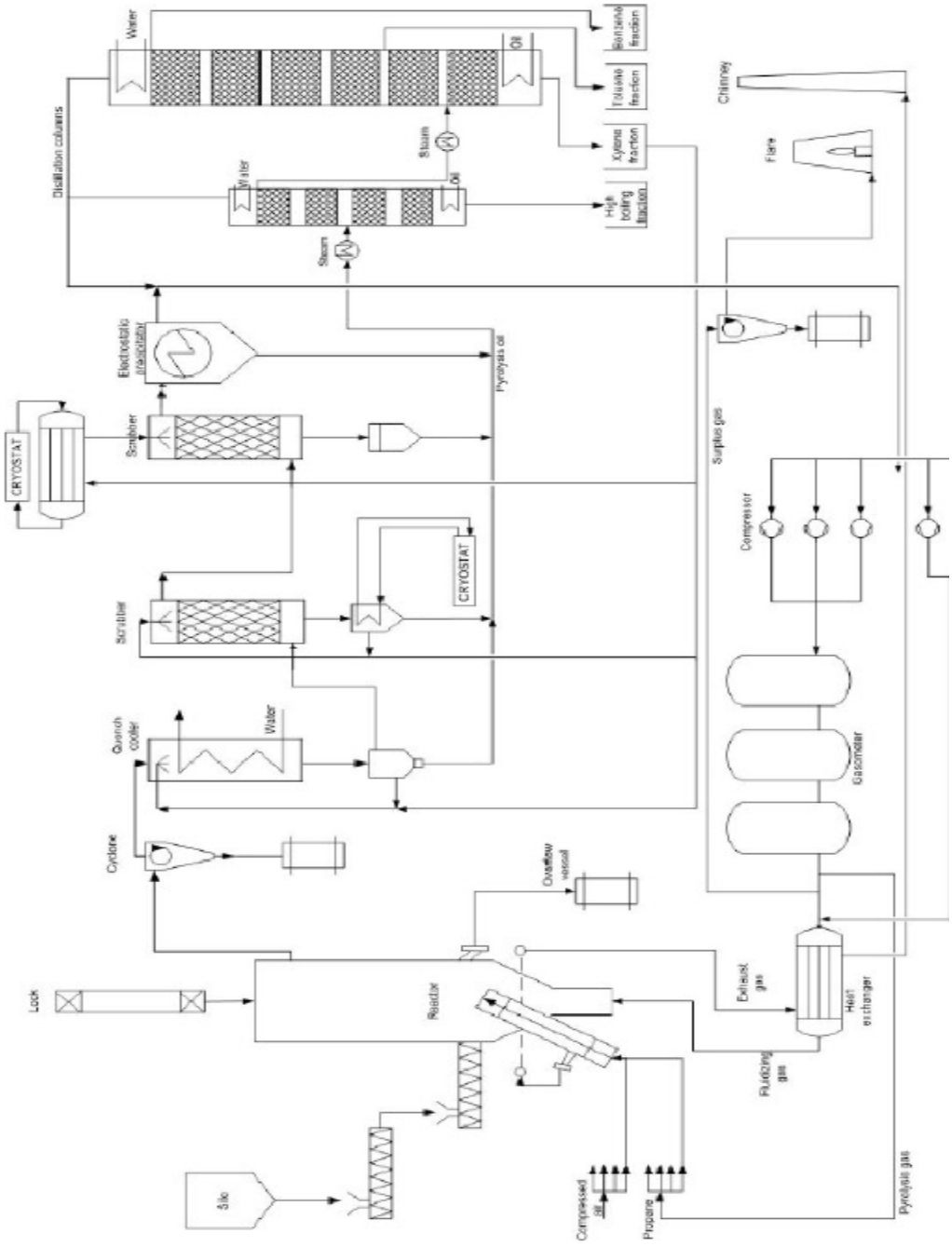



Figure 3.2. TWS pilot plant flow char of the Hamburg pyrolysis process

BP chemicals has investigated the conversion of waste plastics into petrochemicals. The “Polymer cracking process” was first tested on a lab scale and

later on a continuous pilot scale (400 t/y) at the BP's Grangemouth site in UK. Prepared mixed waste plastics, oxygen free and with a maximum of 5% of nonpolymeric impurities, are introduced into a bubbling fluidized bed reactor where the low temperature cracking takes place. The fluidized agent are nitrogen and recycled gas that fluidises the sand. Once the plastic is introduced into the reactor the pyrolysis reaction starts obtaining gases that leave the reactor with the fluidizing gas. The gaseous products are purified from residual carbon and fine dust first in a cyclone, and then in a successive guard bed which catches the chloride content, coming from PVC destruction, by the reaction of CaO with HCl. The main result is $CaO/CaCl_2$ that has to be landfilled. An intermittent withdrawal of material from both fluidized bed reactor and guard bed is necessary to purge the bed from accumulate unwanted materials.

The gas resulting from the process is collected in a two-stage process. A venture loop system partially condenses the gas turning it to a waxy hydrocarbon product. The not condensed gas stream is compressed, reheated and returned to the cracking reactor as fluidizing gas. Excess gas is continuously removed to keep the process operating at a pressure of 4 bar and partially used as fuel for indirect heating of the fluidized reactor. The Polymer Cracking Process has an efficiency of approximately 80 % conversion of plastic waste to petrochemical products with an additional 10 – 15 % used as fuel gas in the process itself. The obtained hydrocarbon feedstock is a high quality hydrocarbon while the waxy product can be used as feedstock material for steam crackers or can be fed into refinery units (FCC unit).

The most important variable in a pyrolysis process is the temperature. Depending on it and on the type of plastic different products will be obtained. For example, low temperature processes generally enhance liquid products whereas higher temperatures generate gas. Some polymers such as polystyrene and polymethylmethacrylate give high monomer yields, approaching 100 % when pyrolysed, while polypropylene yields only about 2 % of its weight.

As mentioned before, other variables in this process are residence time, reactor type, feeding arrangement and condensation arrangement. The fluidization technology allows to exalt the potential benefits of a pyrolysis process. Different

advantages can be listed for fluidised bed reactors utilised for thermal treatments of waste.

- Fast and good mixing of solids. Uniform temperature conditions throughout the fluidized bed.
- The well-mixed solids permit to keep constant the temperature resisting fast temperature changes and avoiding the formation of cold or hot spots. Constant process temperature gives uniform product and allow short residence time at moderate temperatures.
- The operating range of temperature is lower than that of other reactors.
- High heat and mass transfers between gas and particles.
- The liquid-like flow of particles allows continuous controlled operations with easy handling. The circulation of solids between two fluidized beds makes possible to remove or add the high quantities of heat produced or needed in large reactors as well as to substitute part of the sticky or agglomerated bed material with fresh solids.
- High process flexibility. Use of different fluidizing agents, operating temperatures and gas residence times, as well as the operation with or without catalysts.
- Lower maintenance cost, consequence of the absence of moving parts.

The main disadvantages are,

- Friable solids, bed materials, catalysts are pulverized and may be carried along with the gas.
- Agglomeration and sintering of fine particles, therefore. The process conditions can change, the temperature will be not constant in the whole reactor. The fluidised material has to be changed.
- The residence times are not uniform because of the fast solid mixing.
- Erosion of pipes and vessels b y abrasion of bed particles.
- Difficult scale –up (Zorriqueta, 2006).

### 3.3.2. Rotary Kiln

The rotary kiln with corresponding post-combustion chamber is the classical universal unit common in pyrolysis process for plastic wastes, rubber and scrap tires. The rotary-kiln reactor has a long, refractory-lined, slightly inclined cylindrical tube through which waste is moved continuously. Because of the very poor heat exchange the installation of a long cylinder kiln is a necessity. In the first section, the waste is dried. In the second section, the dried refuse is moved onto a rocking grate where it is partially pyrolysed. The third and last section is a cylinder where pyrolysis is completed. The cinders spill out at the end of the cylinder. A tall flue gas stack, fan, or steam jet supplies the needed draft. Ash drops through the grate, but many particles are carried along with the hot gases. The particles and any combustible gases are combusted in an "afterburner". The combustion product gases are further treated with acid gas scrubbers to remove hydrogen chloride, sulphuric acid and nitric acid emissions.

The rotary kiln technology is characterised by relatively long residence times (from 30 minutes up to 3 hours) of the material in the reactor obtaining a high conversion. The residence time is controlled by the rotational speed and the angle at which the kiln is positioned. The residence times of liquids and volatilised combustibles are controlled by the gas velocity in the pyrolysis system. The temperature profile is longitudinal as well as transversal (figure 3.5). One of the advantages is that it is not important the particle size. The material introduce can be relatively big compared with a fluidized bed reactor.

Other advantages of the rotary kiln for the pyrolysis of waste:

- minimum requirements with respect to sorting and preparation of waste
- wide variety of products
- continuous pyrolysis
- no moving parts inside the kiln
- waste can be fed directly, without preparation such as preheating or mixing

The main disadvantages are:

- Relatively low thermal efficiency

- The temperature gradient is big and not easy to control
- Spherical or cylindrical items may roll through the kiln before complete pyrolysis
- High maintenance costs.

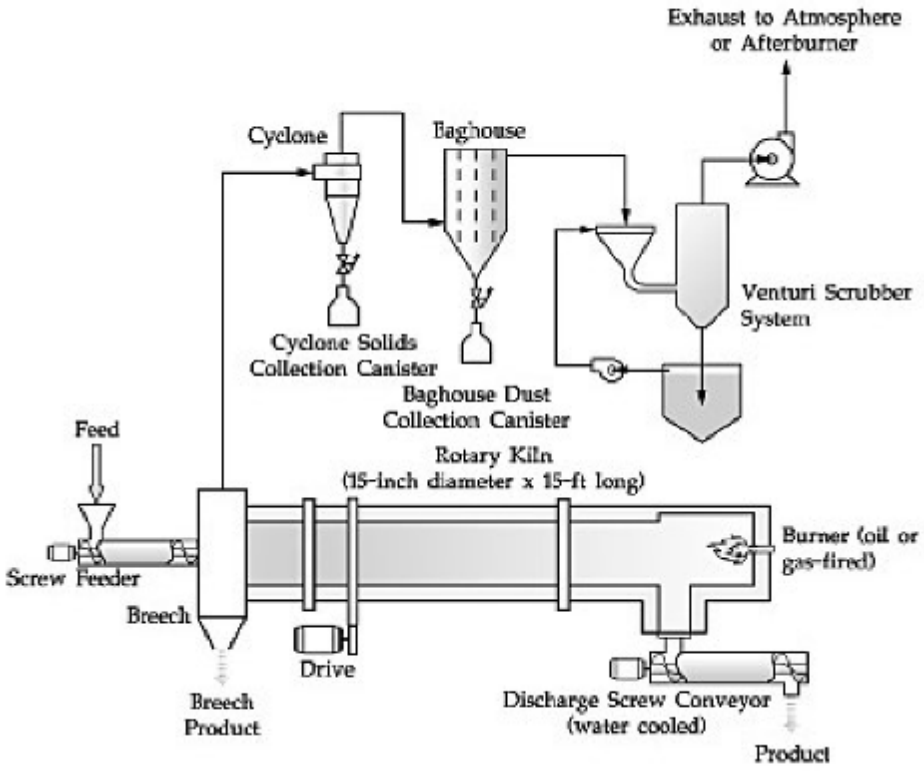



Figure 3.3 Rotary kiln reactor for pyrolysis (Zorriqueta, 2006).

### 3.3.3. Melting vessel

One example of an industrial melting vessel reactor is the BASF feedstock recycling process. It was designed to handle mixed plastic waste that needed a pre-treatment before entering the process. The conversion of pre-treated mixed plastic into petrochemical raw materials takes place in a multi-stage melting and reduction process, carried out under atmospheric pressure in a closed system. In the pre-treatment, the waste plastic is sorted based on physical properties such as hard, soft, films etc. and the plastic is separated from other materials. Size reduction of the

sorted feed is carried out using crusher, cutter and shredder and graded into uniform size using sieves. The sorted material is mixed and fed to the melting Vessel through a pre-heater feeder.

The first step of the conversion process is the melting of the plastic and the dehalogenation to preserve the plant's segments from corrosion. The impurities such as hard metal, sand, glass etc. settle out on the bottom of the reactor and are removed. In the subsequent stages the melted plastic waste is heated over 400 ºC under atmospheric pressure and cracked into components of different chain lengths. About 20-30 % of gases are produced. The gaseous products from the molten plastic can be separated into HCl gas and gaseous hydrocarbons. HCl gas is separated by absorption in a water column. The yield of oils is about 60-70 %. The oil is separated in a distillation column. Naphtha produced by the feedstock process is treated in a steam cracker and the monomers are recovered and used for the production of virgin plastic. High boiling oils can be processed into synthesis gas or conversion coke and then be transferred for further use. The residue consists of 5 % minerals at most. Disadvantageous is the really poor heat exchange of this kind of reactor presenting big temperature gradients and the difficulty to control. The residence times are always superior of 20 minutes. But the conversion efficiency is over 90 %. The range of products which can be obtained is wide and depends strongly on feed type and residence time. The quality of the products is not as high as the products produced by fluidized bed reactor. And, in the economic point of view really important, the processing cost exceed the value of the obtained products. Moreover, an installation like the melting vessel requires a full scale plant about 300.000 t/y of plastic waste to be convenient (Zorriqueta, 2006).

### 3.3.4. Mobile Grate

This process is a combination of a pyrolysis chamber and a smelting furnace. Von Roll has brought together both processes called the Von Roll process.

The reactor of the process (figure 3.6) is a reciprocating grate furnace as a pyrolysis chamber to convert the waste into pyrolysis gas and cokes. The waste is

pyrolysed at a bed temperature of about 500°C. The pyrolysis gas leaves the chamber at 900°C. The pyrolysis coke and any unused pyrolysis gas are drawn into a smelting furnace where additional oxygen injection creates high temperatures (1400°) to melt all solid materials. The use of oxygen reduces the volume of gases formed (compared to air). Heavy metals are concentrated and separated from the molten slag. The residual slag is pelletised and can be used as a cement additive or construction material. The hot gases from the smelting furnace are combusted in a circulating fluidised bed boiler at temperatures below 1400°C. Oxygen is again added to ensure complete oxidation of organic compounds. The flue gas and the circulating sand are separated in a hot cyclone. The gases are used to generate steam for electricity and heat.

The Von Roll process was developed for improved recycling of non-combustible fractions of waste by thermal treatment under total smelting conditions. Von Roll has a long history of utilizing conventional moving grate technology for MSW dating back to the 1930s. The first RCP (Recycled Clean Product) plant for the combustion of MSW began operations in 1997 in Bremerhaven, Germany. Although the moving grate furnace and smelting technologies are well known technologies, several years were required to bring the Bremerhaven facility up to full operation. During four operation periods between June 1997 and October 1998 the plant was for about 1000 hours operating under melting conditions. Since 1997, the plant was able to increase production processing to approximately 4,900 tons of material in 1999 and 8,600 tons of material in 2000.

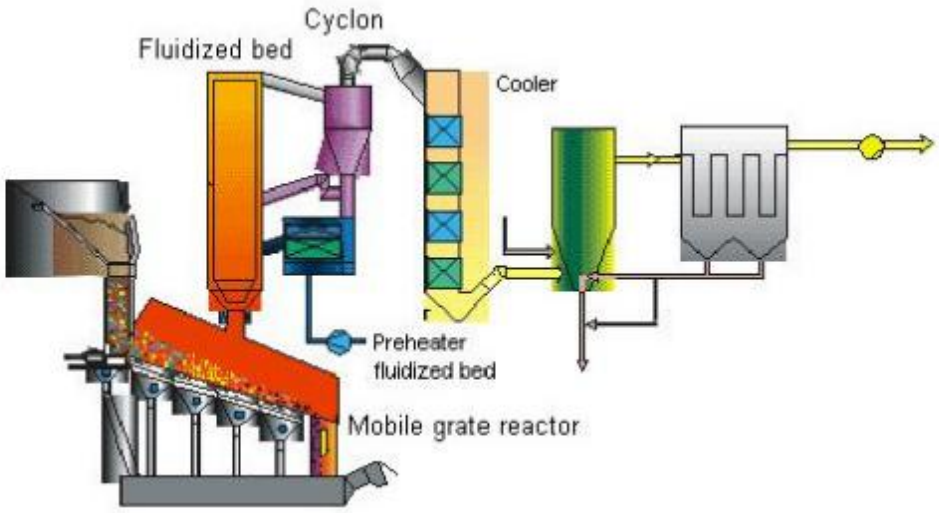



Figure 3.4. Mobile grate reactor for pyrolysis and process (Zorriqueta, 2006).

### 3.4. Pyrolysis Reaction Mechanism

#### 3.4.1. Thermal Cracking

Thermal cracking often yields a low-value mixture of hydrocarbons with a very broad volatility range that can extend from hydrogen to coke. It is therefore important to determine the optimal pyrolysis conditions and/or the most advantageous catalyst to obtain marketable products (e.g. diesel fuel) from mixed plastic wastes.

The pyrolysis product yield and composition are controlled not only by the temperature, but also by the duration of the residence time. As a general rule of thumb; the higher the pyrolysis temperature, the higher the yield of non condensable gaseous products and the lower the yield of liquid fuels such as diesel. The optimum temperature range for the production of diesel products from waste plastics is 390-425 ºC (Zorriqueta, 2006).

### 3.4.2. Catalytic Cracking

The use of catalysts allows the plastic degradation pathway to be modified, with regard to pure thermal cracking. Initially, two positive effects are to be expected by the incorporation of a catalyst into the reaction medium: (i) a reduction of the cracking temperature, and (ii) suitable control of the selectivity, which enables the formation of more-valuable products. Herein, the main aspects related to catalytic processes of plastic cracking are revised. These include the catalyst itself, the reactor type, the effect of chlorine from PVC, and the different pilot-plant and commercial-scale processes. (Aguado et.al, 1997).

Catalytic cracking has some distinct advantages over thermal cracking, such as, lowering the cracking temperature, increasing the reaction rate and increasing the production of iso-alkanes and aromatics which are desirable for diesel fuel. Suitable cracking catalysts have the ability to both substantially reduce the pyrolysis temperature and control the pyrolysis products.

Using catalysts does not only lower the activation energy, reduce the energy consumption and improve the process efficiency, but can also improve the selectivity and quality of the products produced.

The amount of the catalyst to be added to the waste plastic for catalytic cracking is at least 5% by weight (typically 5–10% by weight).

The problems associated with the use of a catalyst in the pyrolysis vessel are:

- the catalyst is a consumable and therefore adds to the running cost;
- the catalyst can have a short life-cycle due to poisoning/deactivation;
- the catalyst leads to increased levels of solid residue that requires disposal (Scheirs et.al., 2006).

#### 3.4.2.1. Catalysts

Both homogeneous and heterogeneous systems have been used in the literature for studying the catalytic cracking of polymers. In general, heterogeneous

catalysts are the preferred choice due to their easy separation and recovery from the reacting medium.

Homogeneous catalysts used for polyolefin degradation have mostly been classical Lewis acids such as $AlCl_3$, metal tetrachloroaluminates melts and more recently, new catalytic systems based on organic ionic liquids.

Catalytic systems over ionic liquids are gaining increased attention worldwide as benign solvents for green chemistry processes due to their low volatility and ease of product separation. Recently, catalytic cracking of polyethylene (HDPE, LDPE) has also been carried out using organic ionic liquids, such as 1-ethyl-3-methylimidazolium chloride-aluminum (III) chloride. Light alkenes ($C_3$–$C_5$), such as isobutene, and branched and cyclic alkanes were the major product components. The reported working temperatures are meaningfully lower (90–250◦C) than those used over conventional heterogeneous catalysts although times of 1–6 days of reaction were needed to obtain yields of 60–95 wt%.

A wide variety of heterogeneous catalysts have been tested for the catalytic cracking of polyolefins and polystyrene, which can be summarized as follows:

- conventional acid solids used in the catalytic cracking of hydrocarbon feedstocks:
- zeolites, silica–alumina, aluminas, fresh and spent FCC catalysts;
- mesostructured catalysts: MCM-41, FSM-16, Al-SBA-15;
- aluminium pillared clays;
- nanocrystalline zeolites (*n*-HZSM-5);
- superacid solids ($ZrO_2/SO_4^{2-}$);
- gallosilicates;
- metals supported on carbon;
- basic oxides (BaO, $K_2O$, etc.), mainly for polystyrene cracking.(Scheirs et.al., 2006)

Zeolites are, by far, the most-used catalysts. They are microporous aluminosilicates that are formed by the linkage of $SiO_4$ and $AlO_4$ tetrahedra. Zeolites show a monodimensional, bidimensional, or tridimensional pore channel system with pore sizes in the range of 0.4-1.0 nm, which turns them into molecular sieves (shape

selectivity). On the other hand, the presence of aluminum provides the zeolites with acid properties (Bronsted and Lewis) that vary from one zeolite to another, according to their topology. The zeolite structures HY, HZSM-5, and HBeta are the catalysts that are used industrially for the cracking of petroleum fractions (Aguado et. al. 1997).

# 4. MATERIAL AND METHOD

## 4.1. Experimental

### 4.1.1. Reactor

In this study, a pilot cracking reactor was designed for waste polymers cracking, which has a 20 liter maximum capacity (Figure 4.1.). Figure 4.2. shows the technical specifications of reactor. Reactor consists of heat exchanger, PT 100 type thermocouple in order to measure the variation of temperature inside the reactor, digital temperature indicator, filler cap, drain cover and manometer. Stainless still number 316 L is selected as the main material for reactor manufacturing.



Figure 4.1. Thermal and catalytic cracking reactor

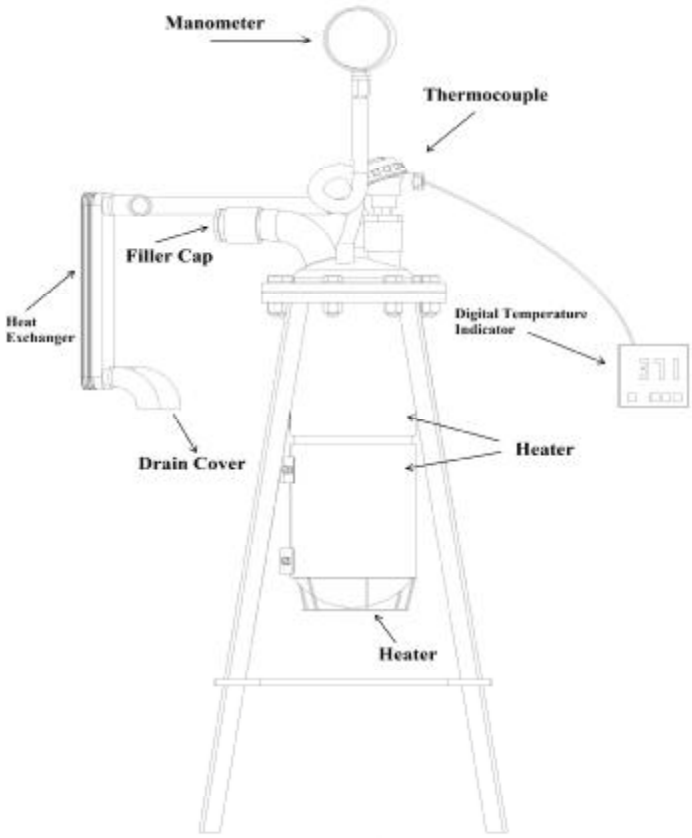



Figure 4.2. System reactor technical draw

### 4.1.2. The Properties of Polyethylene and Polypropylene

The properties of polyethylene and polypropylene that were used in the experiments are presented in Table 4.1, 4.2 and 4.3

Table 4.1. The properties of low density polyethylene

| | |
|---|---|
| Density at 20°C(kg/lt) | 0.920 |
| Hardness (Rockwell D) | 48 |
| Melting point (°C) | 120 |
| Elongation at break (%) | 400 |
| Strain at yield (%) | 19 |
| Tensile strength (MPa) | 10 |

Table 4.2. The properties of high density polyethylene (ANONYMOUS, 2010c)

| | |
|---|---|
| Density at 20°C(kg/lt) | 0.960 |
| Hardness (Rockwell D) | 68 |
| Melting point (°C) | 130 |
| Elongation at break (%) | 150 |
| Strain at yield (%) | 15 |
| Tensile strength (MPa) | 32 |

Table 4.3. The properties of polypropylene (ANONYMOUS, 2010d)

| | |
|---|---|
| Density at 20°C(kg/lt) | 0.910 |
| Melting Point °C, | 170 |
| Impact Strength (notched Izod) | 21 |
| Tensile elongation at rupture (%) | 600 |
| Tensile strength (MPa) | 29.3 |
| Vicat softening point ( °C) | 154 |

### 4.1.3. The Properties of Catalysts

There are 4 types of different chemicals were used as catalysts to decrease reaction temperature. The chemical and physical properties of these catalysts are listed in Table 4.4

Table 4.4. The chemical and physical properties of catalysts

| **Catalysts** | CAS number | Solubility (20 °C) | Bulk density ($kg/m^3$) | Melting point (°C) | Molar Mass (g/mol) |
|---|---|---|---|---|---|
| Aluminum Silicate | 1318-02-1 | insoluble | 700-750 | - | 282.21 |
| Sodium Aluminum Silicate | 1344-00-9 | insoluble | | Not determined | 305.19 |
| Aluminum Oxide | 1344-28-1 | insoluble | 370-900 | 2050 | 101.96 |
| Silica gel | 7631-86-9 | insoluble | 750-800 | 1710 | 60.08 |

### 4.1.4. The Production of Waste Plastic Fuels

Seven different types of base plastics were used as initial material in thermal and catalytic cracking processes. The processes are explained below in details.

#### 4.1.4.1. The Thermal Cracking Experiments

The plastics used in these experiments were granule polyethylene (GPE), mixed granule (MG) which is the mixture of 30% granule polypropylene and 70% granule polyethylene, granule polypropylene (GPP) and waste polyethylene (WPE). The thermal cracking reactions of these plastics were carried out particularly in a stainless steel batch reactor.

Firstly the reactor was heated up to the starting temperature of reaction for one and half hour, subsequently the reaction was started at 414 $^{\circ}C$ and finished at 480 $^{\circ}C$ and the reaction was carried out at atmospheric pressure for 1 hour. After thermal cracking reaction the product was distillated into a receiver and finally the final product was taken from the receiver for all of the experiments.

After thermal cracking reaction of granule polypropylene and waste polyethylene, the final products distillated again and the distillated part which are

volatile fractions are called light polypropylene (LPP) for granule polypropylene's final product and light phase (LP) for waste polyethylene's final product. The residue part of waste polyethylene is called heavy phase (HP).

#### 4.1.4.2. The Catalytic Cracking Experiments

In order to decrease the reaction temperature catalytic cracking process was carried out by using 4 types of catalysts, namely aluminium silicate, sodium aluminium silicate, silica gel and aluminium oxide. The catalysts were added at concentration of 5%. Waste polyethylene was used as plastic. For all catalysts, the catalytic reaction of waste polyethylene was carried out in stainless steel batch reactor over 400◦C and at atmospheric pressure for 1 hour. After catalytic cracking reaction the products were distillated into a receiver and finally the final products were taken from the receiver for all of the experiments.

### 4.1.5. Preparing the Waste Plastic Fuel Blends

In this study, seven different waste plastic blends were prepared by mixing euro diesel at volumetric rates of between 5 to 20% and blends were mixed in Yellowline OS 10 Basic circular shaker for half an hour (Figure 4.3).



Figure 4.3. Waste plastic fuel-diesel blends

Table 4.5. Waste plastic fuel contents of prepared diesel blends

| Sample Number | Samples | Waste Plastics (ml) | Diesel (ml) | Total (ml) |
|---|---|---|---|---|
| 1 | 5% GPE+95% D | 25 | 475 | 500 |
| 2 | 10% GPE+90% D | 50 | 450 | 500 |
| 3 | 15% GPE+85% D | 75 | 425 | 500 |
| 4 | 20% GPE+80% D | 100 | 400 | 500 |
| 5 | 5% MG+95% D | 25 | 475 | 500 |
| 6 | 10% MG+90% D | 50 | 450 | 500 |
| 7 | 15% MG+85% D | 75 | 425 | 500 |
| 8 | 20% MG+80% D | 100 | 400 | 500 |
| 9 | 5% CPE+95% D | 25 | 475 | 500 |
| 10 | 10% CPE+90% D | 50 | 450 | 500 |
| 11 | 15% CPE+85% D | 75 | 425 | 500 |
| 12 | 20% CPE+80% D | 100 | 400 | 500 |
| 13 | 5% LPP+95% D | 25 | 475 | 500 |
| 14 | 10% LPP+90% D | 50 | 450 | 500 |
| 15 | 15% LPP+85% D | 75 | 425 | 500 |
| 16 | 20% LPP+80% D | 100 | 400 | 500 |
| 17 | 5% WPE+95% D | 25 | 475 | 500 |
| 18 | 10% WPE+90% D | 50 | 450 | 500 |
| 19 | 15% WPE+85% D | 75 | 425 | 500 |
| 20 | 20%WPE+80% D | 100 | 400 | 500 |
| 21 | 5% LP+95% D | 25 | 475 | 500 |
| 22 | 10% LP+90% D | 50 | 450 | 500 |
| 23 | 15% LP+85% D | 75 | 425 | 500 |
| 24 | 20% LP+80% D | 100 | 400 | 500 |
| 25 | 5% HP+95% D | 25 | 475 | 500 |
| 26 | 10% HP+90% D | 50 | 450 | 500 |
| 27 | 15% HP+85% D | 75 | 425 | 500 |
| 28 | 20% HP+80% D | 100 | 400 | 500 |

### 4.1.6 Fuel Quality Measurement Methods

The development of internal combustion engines over the past century has resulted from the complimentary refinement of the engine design and fuel properties. As such, engines have been developed to utilize the properties of the fuels that were available. Replacement of existing fuels with new fuel formulations requires understanding the critical fuel properties to insure that the new fuels can be used. Discussed in this section will be some key fuel properties as well as the methods to measure these properties. The properties listed below will be specific gravity, kinematic viscosity, cetane number, flash point and pour point.

#### 4.1.6.1. Density Measurement

The density measurement was done using Kyoto Electronics DA-130 type densimeter. This densimeter uses the resonant frequency method to measure the densities. With the densimeter we can also measure the specific weight, API gravity, % Brix, volume and mass alcohol rates. The measurement interval of the device is 0 to 2 g/cm$^3$ and 0 to 40 ºC. The device has a sensitivity of ±0.001 g/cm$^3$, and a stability of 0.0001 g/cm$^3$. The device is measuring according to the standards of TS 6311, ASTM D 4052-96 (Abdulvahitoğlu et. al., 2008).



Figure 4.4. Kyoto electronics DA-130 portable densimeter

### 4.1.6.2 Viscosity Measurement

To define kinematic viscosity it is useful to begin with the definition of viscosity. Simply stated, viscosity, which is also called dynamic viscosity (η), is the ease with which a fluid will flow. Technically it is the ratio of the shear stress to the shear rate for a fluid. In contrast, the kinematic viscosity (ν) is the resistance to flow of a fluid under gravity (Garpen et al. 2004).

The viscosities of the blends are measured with Saybolt Universal Viscosimeter produced from Ubbelohde tube with ASTM D88 standards. The meaurement results were recorded in seconds. Then using a conversion table the results were converted from SSU (saybolt universal second) to centistokes (cSt) unit. The measurements were done at 40 ºC according to the TS EN 14214 standard (Abdulvahitoğlu et. al., 2008).



Figure 4.5. Saybolt universal viscosimeter

### 4.1.6.3 Cetane Number Measurement

Perhaps the most important measure of ignition characteristics of diesel and/or biodiesel fuels is the cetane number, since it directly pertains to ignition within compression ignition engines. The cetane number is the primary specification measurement used to match fuels and engines. It is commonly used

by refiners, marketers and engine manufacturers to describe diesel fuels (Gerpen et al. 2004).

The cetane number and indexes were measured by Zeltex ZX440 type device, which works under the close infrared spectrometer (NIR) principal. With the help of this principal the cetane number measurement experiement became very fast and cheap with only 3% error compared to the time consuming expensive motor tests (Abdulvahitoğlu et. al., 2008).



Figure 4.6. Zeltex ZX 440

#### 4.1.6.4 Flash Point Measurement

The flash point is the lowest temperature at which a combustible mixture can be formed above the liquid fuel. It is dependent on both the lean flammability limit of the fuel as well as the vapor pressure of the fuel constituents. The flash point is determined by heating a sample of the fuel in a stirred container and passing a flame over the surface of the liquid. If the temperature is at or above the flash point, the vapor will ignite and an easily detectable flash can be observed (Gerpen et al. 2004).

Flashpoints are measured with ASTM D93. Tanaka Automated Pensky-Martens Closed Cup Flash Point Tester is used for the flash point measurements during the tests which has a measurement range of 20-370 $^{o}$C. (Özcanlı, 2009).




Figure 4.7. Tanaka APM-7

#### 4.1.6.5. Pour Point Measurement

MPC-102 series has been designed for automatic determination of Pour Point (PP) and Cloud Point (CP) with small specimen size and shorter test cycle time while securing better test precision than the conventional manual methods. PP measurement is made utilizing a new ASTM D6749 on Standart Test Method for Pour Point of Petroleum Products test method namely Air Pressure Method, which yields eventually no bias against the conventional test method, repeatability/reproducibility of 1/2°C and 2-3 times faster determinations. The epochmaking high accuracy justifies PP determination at 1°C interval, which can help increasing the yields in the process. The CP/PP mode executes a CP determination and then PP determination consecutively, which further improves the test throughput in the lab. Multiple-tests versions with 6 test heads and 3 test heads are also available for higher volume tests.

The typical repeatability and reproducibility are 1°C and 2°C respectively, when PP is determined at 1°C intervals. This high precision attributes to the patented Air Pressure method, in which the disturbance to the formation of wax crystal structure through the test process is kept at a minimal and consistent level. With this high precision, PP can be determined at 1°C intervals for more precise process control, and therefore a considerable savings in the process can be realized.

Just set up a sample, select a test mode and then press the START key. The sample is cooled at the steepest possible rate without affecting the formation/ growth of wax crystal, which has been to be a critical factor for PP/CP determination. The test cycle time is typically 1/3 to 1/2 of that of the conventional tilting methods.

Since the required sample volume is a mere 4,5 ml and the sample cup is a test-tube type removable jar, the sample handling is extremely easy. Use of Peltier Cells for sample cooling/heating made this mini tester not only compact in design but energy efficient. Depending on the temperature range, air, tap water or small chiller with anti-freeze suffices the cooling requirement (Yilmaz, 2010).



Figure 4.8. Tanaka MPC-102 L

**4.1.6.6. Heating Capacity Measurement**

The heat capacities of liquid fuels can be measured automatically with IKA-Werke C2000 calorimeter. The working temperatures are between +15 ºC to +35 ºC. The combustion is done with a cotton wire instead of a tungsten wire. The results are measured in cal/gr units. The device can measure according to the TS 1740**,** ASTM 240 D, ISO 1928, DIN 51900, BSI standards (Abdülvahitoğolu et al., 2008).



Figure 4.9. IKA-WERKE C2000 calorimeter

### 4.1.7. Diesel Engine Test Rig

In the experiments, Mitsubishi Canter 4D34-2A (Figure 4.10.), four stroke diesel engine with four cylinders which has a maximum torque 295 Nm at 1800 rpm has been used. Note that the maximum torque value and maximum brake power values that obtained in the test engine could be change depending upon the fuel that used in engine. Specifications of the engine are presented in Table 4.7.

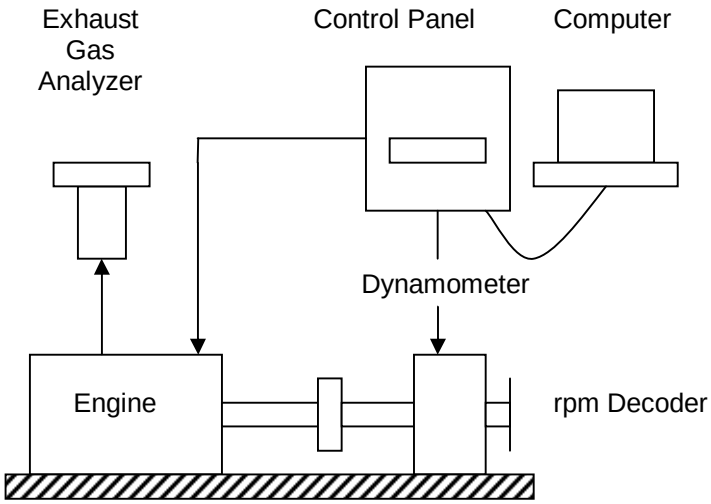



Figure 4.10. Layout of experimental setup

Table 4.6. Technical specifications of the test engine

| | |
|---|---|
| Brand | Mitsubishi Canter |
| Model | 4D34-2A |
| Configuration | In line 4 |
| Type | Direct injection diesel with glow plug |
| Displacement | 3907cc |
| Bore | 104mm |
| Stroke | 115mm |
| Power | 89kW @ 3200rpm |
| Torque | 295Nm @ 1800rpm |
| Oil Cooler | Water cooled |
| Weight | 325kg |

The engine torque was measured by the help of a hydraulic dynamometer.

Table 4.7 shows technical specifications of the dynamometer.

Table 4.7. Technical specifications of the dynamometer

| | |
|---|---|
| Torque range | 0-1700 Nm |
| Speed range | 0-7500 rpm |
| Body weight | 45 kgf |
| Total weight | 110 kgf |
| Body diameter | 350 mm |
| Torque arm length | 350mm |

The speed sensor used to detect prime mover speed is the magnetic pickup (MPU). When a magnetic material (usually a gear tooth driven by the prime mover) passes through the magnetic field at the end of the magnetic pickup, a voltage is developed. The frequency of this voltage is translated by the speed into

a signal which accurately depicts the speed of the prime mover. S type load cell is used to measure the torque of dynamometer (Stainless steel which has a sensivity of 1/3000. Dynamometer control unit was used for receiving and collecting all the data that was used by the system.

### 4.1.8. Exhaust Emission Measurements

TESTO 350 XL gas analyzer is used to measure exhaust emissions. Emission data was collected by the help of a computer program. Measurement accuracy of the gas analyzer is ±10 ppm for CO, 1% for $CO_2$ and ±1 ppm for $NO_x$. Measurement capacity of the device is 0-10000 ppm for CO, 0-50% for $CO_2$ emission and 0-3000 ppm for $NO_x$.

# 5. RESULTS AND DISCUSSION

## 5.1. Granule Polyethylene-Diesel Blended Fuels

### 5.1.1. Fuel Properties

Granule polyethylene has been blended into diesel with various blended rates (5%, 10%, 15%, 20%) the blends have been analyzed by the standard ASTM test methods and results are shown in Table 5.1. The "GPE" designates pure polyethylene and the number of next to GPE designates the percentage volume of pure polyethylene. The GPE5 means, 5% pure polyethylene was blended with 95% with diesel. Fuel property measurement results are shown in Table 5.1.

Table 5.1. Fuel Properties of Granule Polyethylene-Diesel Blended Fuels

| Properties | Diesel | GPE100 | GPE5 | GPE10 | GPE15 | GPE20 |
|---|---|---|---|---|---|---|
| Density (kg/lt) | 0.833 | 0.786 | 0.830 | 0.828 | 0.826 | 0.825 |
| Cetane Number | 54.580 | 58.3 | 54.880 | 55.543 | 55.700 | 55.821 |
| Pour Point ($^{o}$C) | -12.0 | 13.0 | -6.0 | -2.0 | 1.0 | 2.0 |
| Viscosity (cSt) | 2.52 | 2.17 | 2.48 | 2.44 | 2.42 | 2.40 |
| CalorificValue (kcal/kg) | 10 790 | 10 529 | 10 770 | 10 752 | 10 700 | 10 626 |
| Flash Point ($^{o}$C) | 58.5 | 58.5 | 58.5 | 58.5 | 58.5 | 58.5 |

The density of Granule Polyethylene (GPE) is lower than that of euro diesel, which are 0.786 g/lt and 0.833 kg/lt respectively. Due to the lower density of GPE in accordance with the euro diesel, blending with GPE was caused a reduction in the density values. Any increase in the percentage of the GPE caused a decrease in the blend density.

An adequate Cetane number is required for good engine performance. Higher Cetane numbers help ensure good cold start properties and minimize the

formation of white smoke. As it can be seen from Table 5.1 Cetane number can be improved by mixing GPE with diesel.

The temperature at which crystal formation is extensive enough to prevent free pouring of fluid is determined by measurement of its pour point (PP). If pour point of a fuel is not low enough, some concerns with storing, transferring and using in cold weather can occur. One of the major disadvantages of waste plastic fuels is their high pour points. And addition to GPE to the blends caused an increase in the pour point values.

Viscosity, which is a measure of resistance to flow of a liquid due to internal friction of one part of a fluid moving over another, affects the atomization of a fuel upon injection into the combustion chamber and thereby, ultimately, the formation of engine deposits. The general rule is; the higher the viscosity, the greater the tendency of the fuel to cause such problem. Fuel property experiments revealed that, GPE has lower viscosity value than euro diesel (2.17 and 2.52 $mm^2/s$ respectively), It is observed that, GPE addition to diesel caused a decrease in the viscosity values.

Diesel fuels with high percentages of aromatics tend to have high energy contents per liter even though the aromatics have low heating values per kilogram. Their high density more than compensates for their lower energy content on a weight basis. This is of a special importance for diesel engines because fuel is metered to the engine volumetrically. A fuel with lower energy content per liter will cause the engine to produce less peak power. The experiments showed that GPE has lower calorific value than diesel. It is observed that, GPE addition to diesel caused a decrease in the calorific values.

The flash point is the temperature at which the fuel will give off enough vapor to produce a flammable mixture. This is important information for the safe transportation, storage of the fuel. The experiments showed that GPE has same flash point with diesel so that all blends had same flash point with diesel.

### 5.1.2. Engine Performance

#### 5.1.2.1. Brake Power Output

Figure 5.1 shows the variation of brake power according to different engine speed values. As it can easily be seen in Figure 5.1 there were no noticeable differences in the measured engine power output between GPE5 and diesel fuel at low engine speeds. The characteristics of power curve were not changed, according to the type of fuel. It was observed that the maximum power values with GPE5 and diesel were obtained at an engine speed of 2400 rpm.

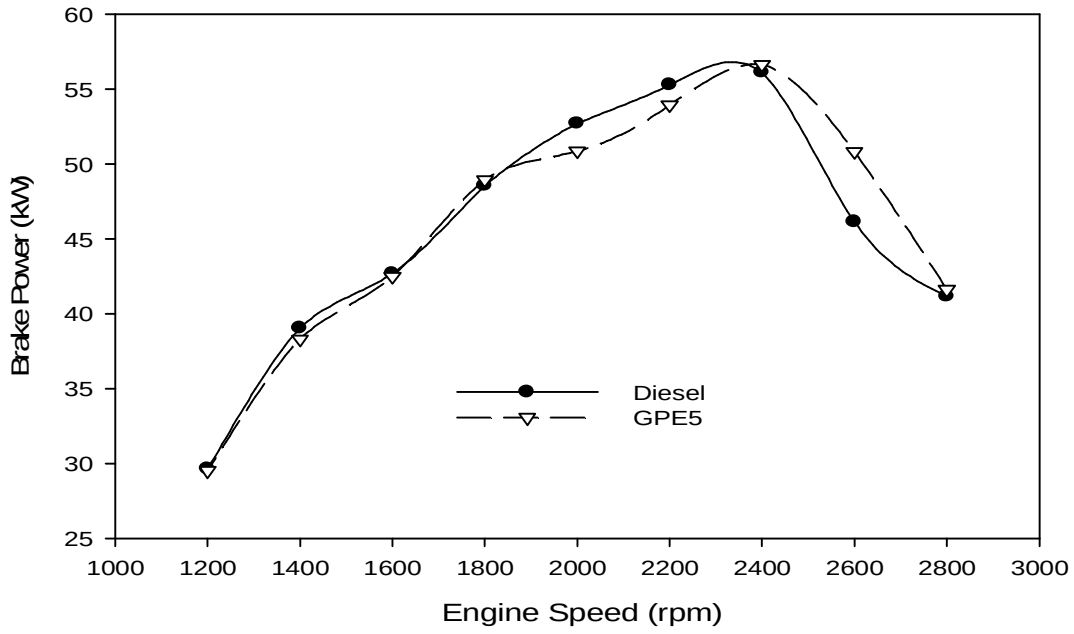



Figure 5.1 Brake power output versus engine speed for GPE5 and Diesel

#### 5.1.2.2. Torque Output

The torque output of test fuels is shown in Figure 5.2. The value of the torque output increase at low engine speeds, decrease at high engine speeds. The maximum torque values for diesel and GPE5 were obtained at an engine speed of 1400-1800 rpm. The torque output is reduced through higher engine speeds.

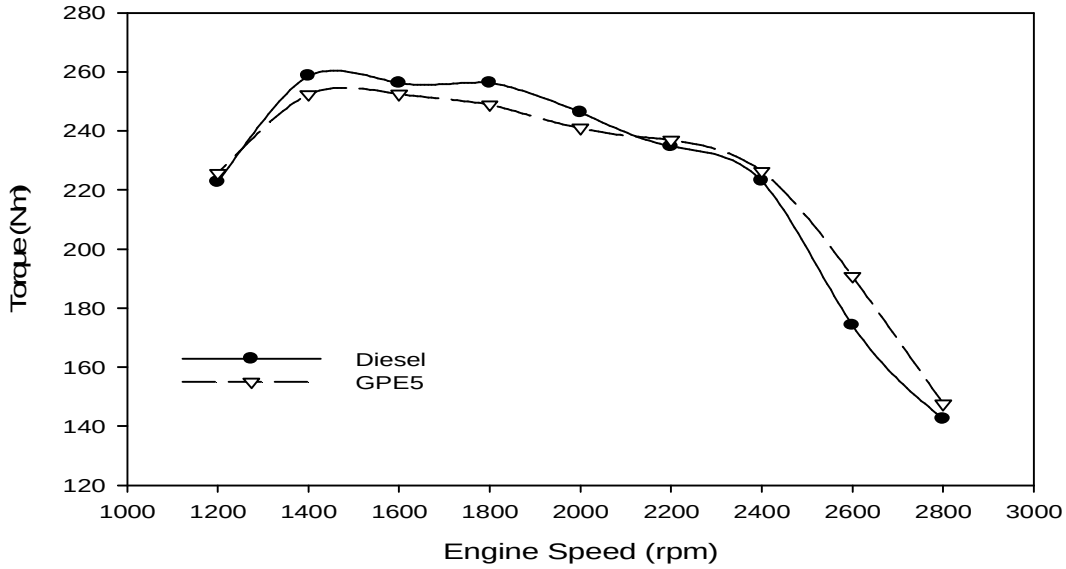



Figure 5.2 Torque output versus engine speed for GPE5 and Diesel

### 5.1.3. Exhaust Emissions

Generally, CI engine operates with lean mixtures and hence the CO emission would be low. CO emission is toxic and must be controlled. It is an intermediate product in the combustion of a hydrocarbon fuel, so its emission results from incomplete combustion. Emission of CO is therefore greatly dependent on the air fuel ratio relative to the stoichiometric proportions. Rich combustion invariably produces CO, and emissions increase nearly linearly with the deviation from the stoichiometry. The variation of carbon monoxide with engine speed is shown in Figure 5.3. It can easily be seen from the figure that there is an average of 19% reduction in CO emission values when GPE5 was used instead of diesel fuel. The reductions in CO emission could be due to the better combustion.

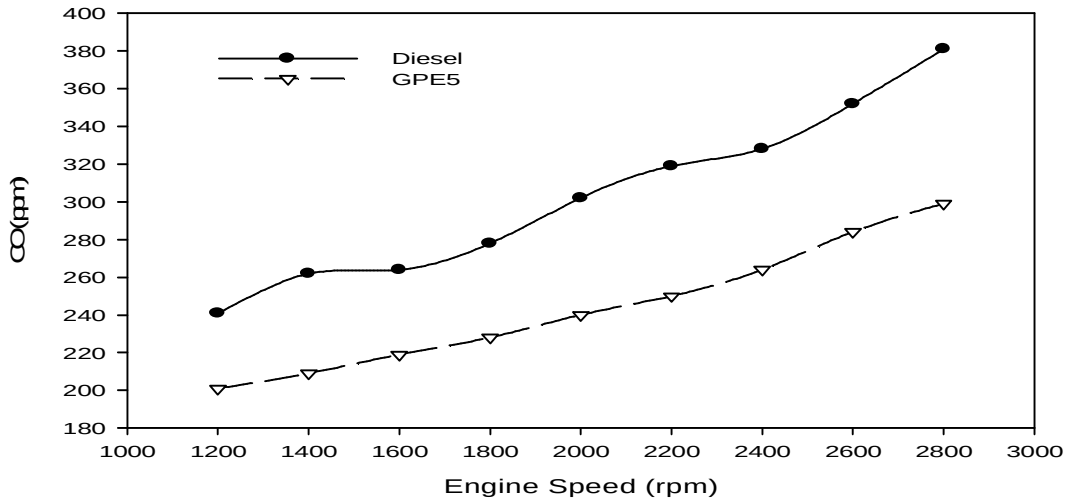



Figure 5.3 CO emission values of GPE5 and Diesel

Figure 5.4 shows the variation of measured $CO_2$ emission values of test fuels for different engine speeds. There is an average of 1.9% increment in $CO_2$ emission values when GPE5 is used instead of diesel fuel. For GPE5 and diesel, maximum $CO_2$ emission values were measured at about 1600 rpm where maximum torque values were obtained.

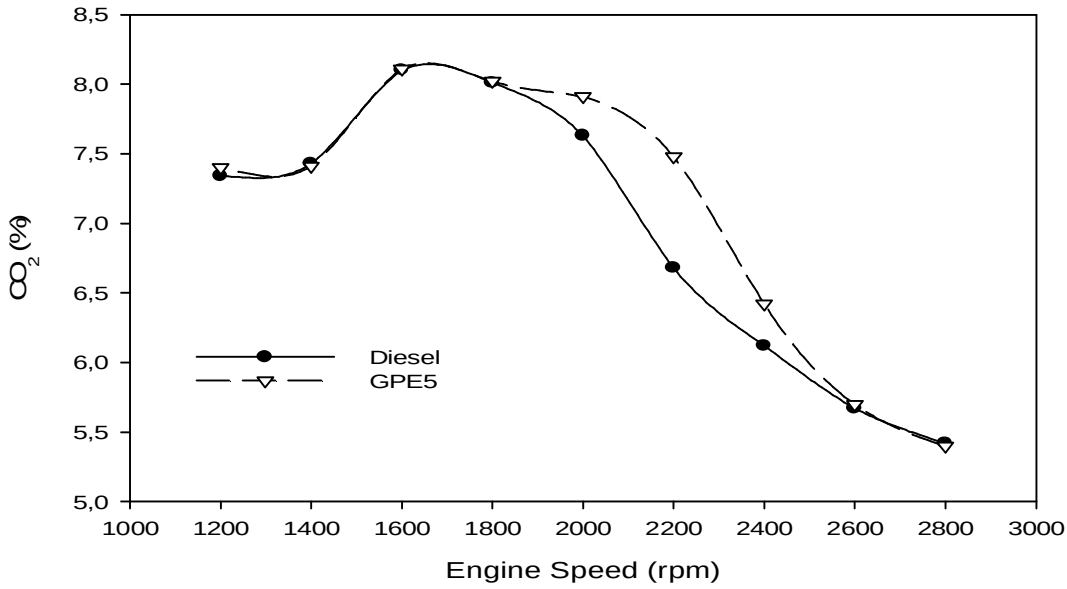



Figure 5.4 $CO_2$ emission values of GPE5 and Diesel

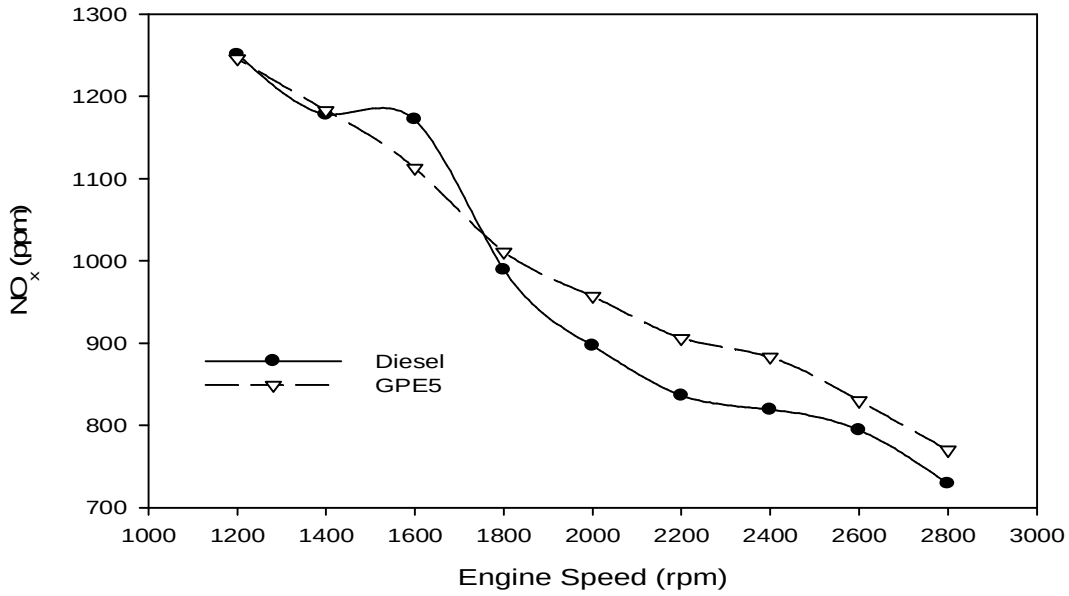



Figure 5.5 $NO_x$ emission values of GPE5 and Diesel

The oxides of nitrogen in the emissions contain nitric oxid (NO) and nitrogen dioxide ($NO_2$). The formation of nitrogen oxides ($NO_x$) is highly dependent on in-cylinder temperature, oxygen concentration and residence time for the reactions to take place. The nitrogen oxides ($NO_x$) emissions of tests fuels in shown in Figure 5.4 On an average of 3.4% increment in $NO_x$ was obtained for GPE5 and as compared to diesel. The reductions in $NO_x$ emission could be due to the higher combustion temperature.

## 5.2. Mixed Granule-Diesel Blended Fuels

### 5.2.1. Fuel Properties

Mixed granule (70% polyethylene-30%polypropylene) has been blended into diesel with various blended rates (5%, 10%, 15%, 20%) the blends have been analyzed by the standard ASTM test methods and results are shown in Table 5.2. The “MG” designates mixed granule and the number of next to MG designates the

percentage volume of mixed granule. The MG5 means, 5% mixed granule was blended with 95% with diesel.

Table 5.2. Fuel Properties of Mixed Granule-Diesel Blended Fuels

| Properties | Diesel | MG100 | MG5 | MG10 | MG15 | MG20 |
|---|---|---|---|---|---|---|
| Density ($g/cm^3$) | 0.833 | 0.788 | 0.831 | 0.829 | 0.827 | 0.826 |
| Cetane Number | 54.580 | 41.488 | 53.129 | 52.375 | 51.990 | 51.620 |
| Pour Point ($^oC$) | -12.0 | 15.0 | -8.0 | -5.0 | -3.0 | -1.0 |
| Viscosity (cSt) | 2.52 | 2.157 | 2.48 | 2.45 | 2.42 | 2.36 |
| CalorificValue (kcal/kg) | 10 790 | 10 946 | 10 812 | 10 823 | 10 845 | 10 877 |
| Flash Point ($^oC$) | 58.5 | 61 | 58.5 | 59.5 | 59.5 | 60 |

Densities of Mixed Granule-Diesel blends are decreasing related to MG contents clearly because of its lower density and this can be seen in Table 5.2. The density of MG which was used in this study 0.788 kg/lt at 16 $^\circ$C.

Cetane Numbers of Mixed Granule-Diesel blends are shown in Table 5.2. As it seen the table, cetane number is getting lower with addition of MG significantly. Pour points of Mixed Granule-Diesel blends are increasing up to -1$^\circ$C with MG additions. Kinematic viscosities of Mixed Granule-Diesel blends are decreasing by percentage volume of MG. Calorific values of Mixed Granule-Diesel blends are increasing by percentage volume of MG additions. Flash points of Mixed Granule-Diesel blends are increasing by percentage volume of MG additions.

### 5.2.2. Engine Performance

#### 5.2.2.1. Brake Power Output

Figure 5.6 shows the variation of brake power according to different engine speed values. As it can easily be seen in Figure 5.6 there were no

noticeable differences in the measured engine power output between MG5 and diesel fuel at low engine speeds. The characteristics of power curve were not changed, according to the type of fuel. It was observed that the maximum power values with all fuels were obtained at an engine speed of 2400 rpm.

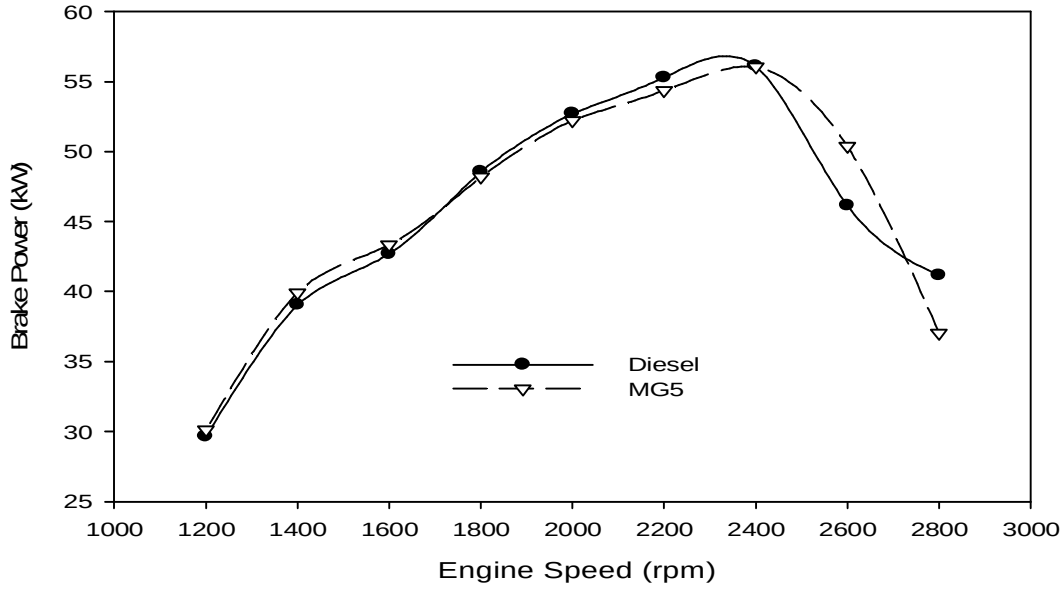



Figure 5.6 Brake power output versus engine speed for MG5 and Diesel

### 5.2.2.2. Torque Output

The torque output of test fuels is shown in Figure 5.7. The maximum torque values for diesel and MG5 were obtained at an engine speed of 1400-1800 rpm. There were no noticeable differences in the measured engine power output between MG5 and diesel fuel at 1200-2400 rpm. The torque output of MG5 was decreased about 8% at 2800 rpm. The torque output is reduced through higher engine speeds.

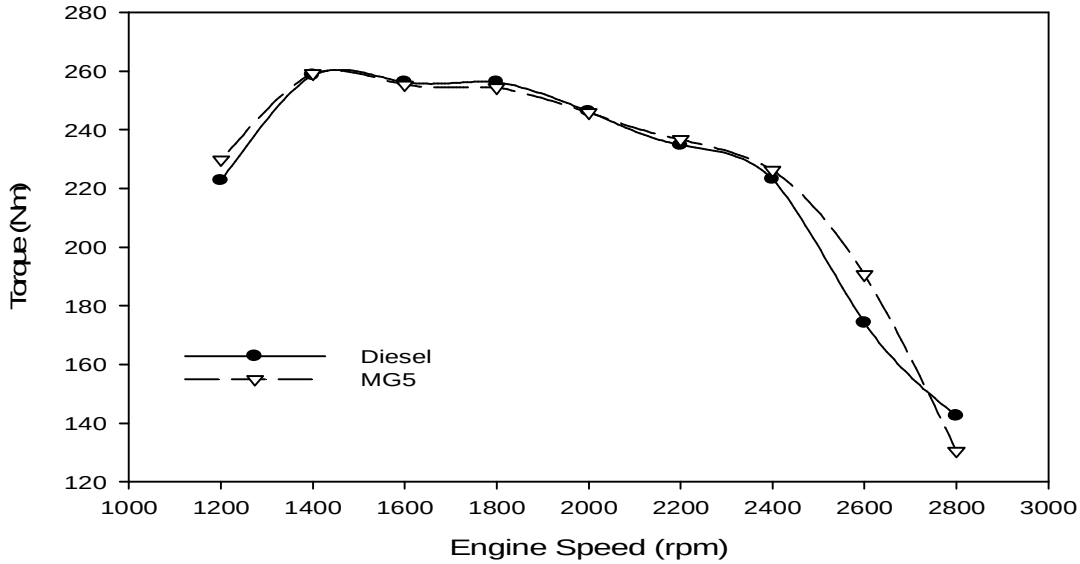



Figure 5.7 Torque output versus engine speed for MG5 and Diesel

### 5.2.3. Exhaust Emissions

The variation of carbon monoxide with engine speed is shown in Figure 5.8. It can easily be seen from the figure that CO emission were found decreased except 2800 rpm however, there is an average of 8% reduction in CO emission values when MG5 was used instead of diesel fuel.

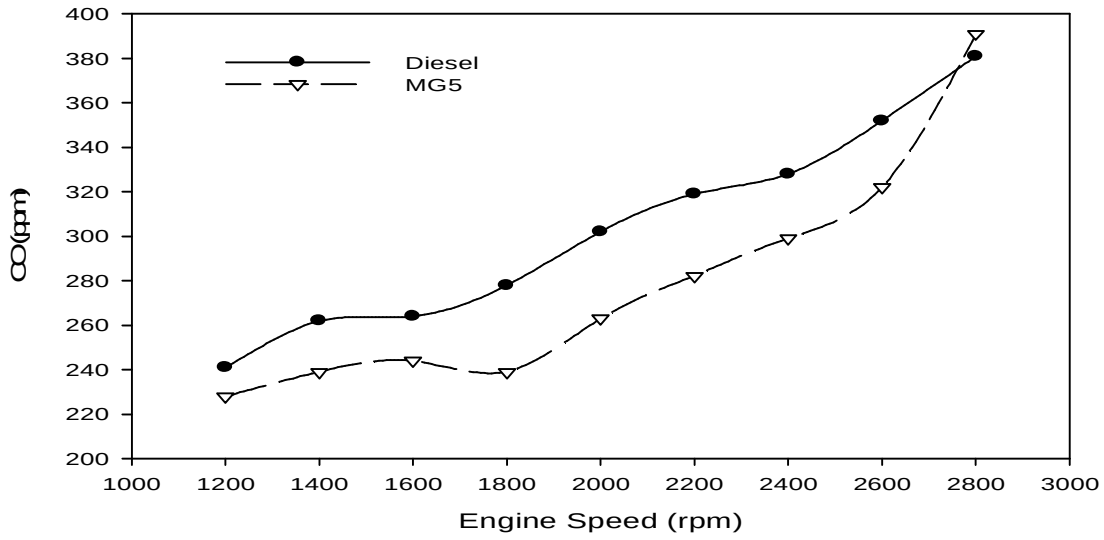



Figure 5.8 CO emission values of MG5 and Diesel

Figure 5.9 demonstrates the variation of measured $CO_2$ emission values of test fuels for different engine speeds. There is an average of 1.96% increment in $CO_2$ emission values when MG5 is used instead of diesel fuel. For MG5 and diesel, maximum $CO_2$ emission values were measured at about 1600-1800 rpm where maximum torque values were obtained.

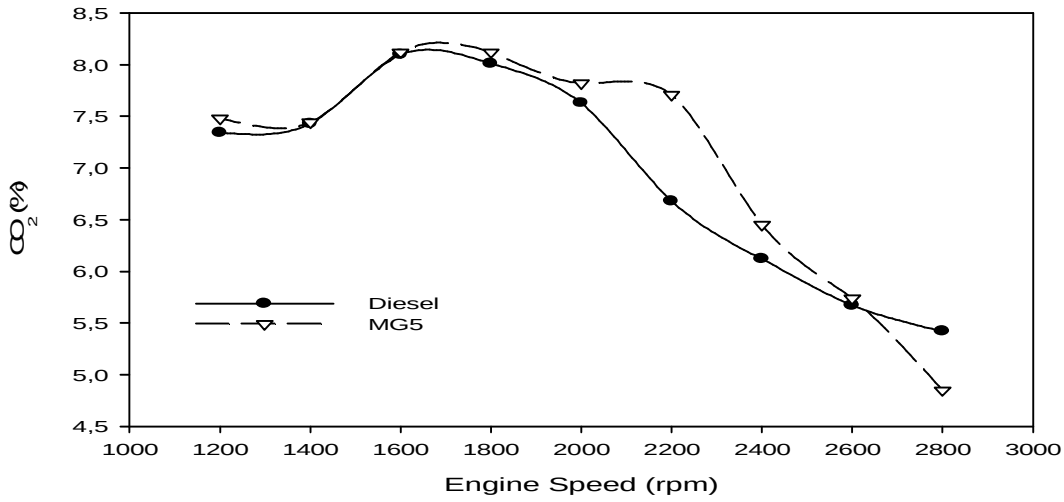



Figure 5.9 $CO_2$ emission values of MG5 and Diesel

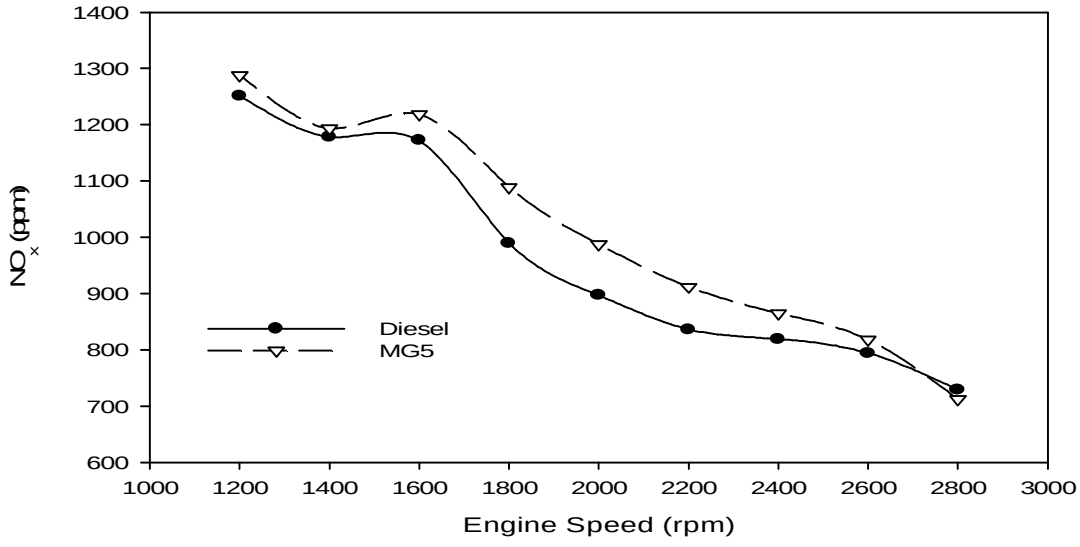



Figure 5.10 $NO_x$ emission values of MG5 and Diesel

The nitrogen oxides ($NO_x$) emissions of tests fuels in shown in Figure 5.10 On an average of 4.87% increment in $NO_x$ was obtained for MG5 and as

compared to diesel. The maximum $NO_x$ emission was measured at 1600 rpm where maximum torque values were observed.

### 5.3. Catalyzed Waste Polyethylene Diesel Blended Fuels

#### 5.3.1. Fuel Properties

Four different types of catalysts were used in order to decrease the reaction temperature however all catalysts did not decrease the reaction temperature as expected and all final products showed the similar specifications. Catalyzed waste polyethylene has been blended into diesel with various blended rates (5%, 10%, 15%, 20%) the blends have been analyzed by the standard ASTM test methods and results are shown in table 5.3. The "CPE" designates catalyzed waste polyethylene catalyzed and the number of next to CPE designates the percentage volume of waste polyethylene catalyzed with sodium aluminosilicate. The CPE5 means, 5% catalyzed waste polyethylene was blended with 95% with diesel.

Table 5.3. Fuel Properties of Catalyzed Waste polyethylene-Diesel Blended Fuels

| Properties | Diesel | CPE100 | CPE5 | CPE10 | CPE15 | CPE20 |
|---|---|---|---|---|---|---|
| Density ($g/cm^3$) | 0.833 | 0.789 | 0.830 | 0.828 | 0.827 | 0.825 |
| Cetane Number | 54.580 | 44.874 | 53.820 | 52.275 | 51.990 | 51.016 |
| Pour Point ($^oC$) | -12 | 11 | -8.0 | -6.0 | -4.0 | -1.0 |
| Viscosity (cSt) | 2.52 | 2.157 | 2.49 | 2.44 | 2.41 | 2.39 |
| Calorific Value (kcal/kg) | 10 790 | 10 593 | 10 765 | 10 746 | 10 716 | 10 700 |
| Flash Point ($^oC$) | 58.5 | >100 | 58.5 | 59 | 60 | 60 |

Densities of Catalyzed Waste Polyethylene-Diesel blends are decreased related to CPE contents clearly. Table 5.3 represents the trend of densities of Densities of Catalyzed Waste Polyethylene-Diesel blends.

Cetane Numbers of Catalyzed Waste Polyethylene-Diesel blends are shown in Table 5.3. Cetane number is getting lower with addition to CPE significantly. Pour points of Catalyzed Waste Polyethylene-Diesel blends are increasing up to -1◦C with CPE additions. Kinematic viscosities of Catalyzed Waste Polyethylene-Diesel blends are decreasing by percentage volume of CPE. Calorific values of Catalyzed Waste Polyethylene-Diesel blends are decreasing by percentage volume of CPE additions. Flash points of Catalyzed Waste Polyethylene-Diesel blends are increasing by percentage volume of CPE additions.

### 5.3.2. Engine Performance

#### 5.3.2.1. Brake Power Output

Figure 5.11 proves the variation of brake power according to different engine speed values. As it can easily be seen in Figure 5.11 there were no noticeable differences in the measured engine power output between CPE5 and diesel fuel at low engine speeds. The brake power output of CPE5 was decreased about 16% at 2800 rpm. The characteristics of power curve were not changed, according to the type of fuel. It was observed that the maximum power values with all fuels were obtained at an engine speed of 2400 rpm.

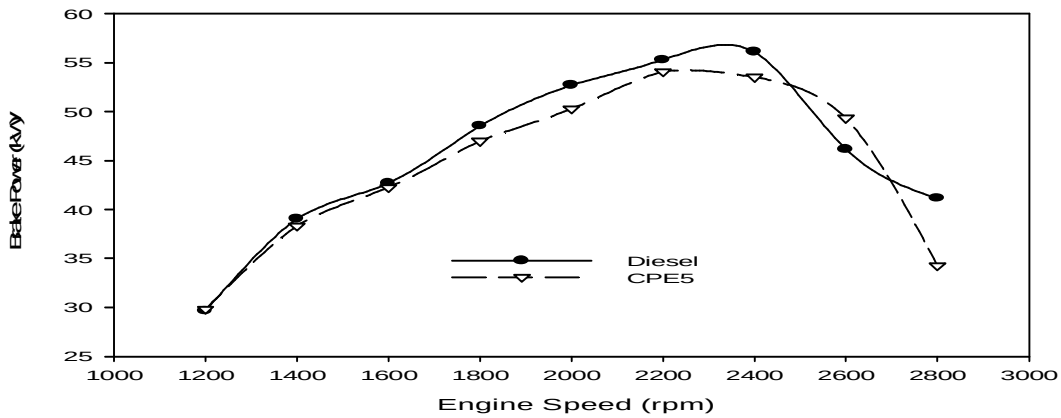



Figure 5.11 Brake power output versus engine speed for CPE5 and Diesel

### 5.3.2.2. Torque Output

The torque output of test fuels is shown in Figure 5.12. The maximum torque values for diesel and CPE5 were obtained at an engine speed of 1400-1800 rpm. There were no noticeable differences in the measured engine power output between CPE5 and diesel fuel at 1200-2400 rpm. The torque output of CPE5 was decreased about 16.5% at 2800 rpm. The torque output is reduced through higher engine speeds.

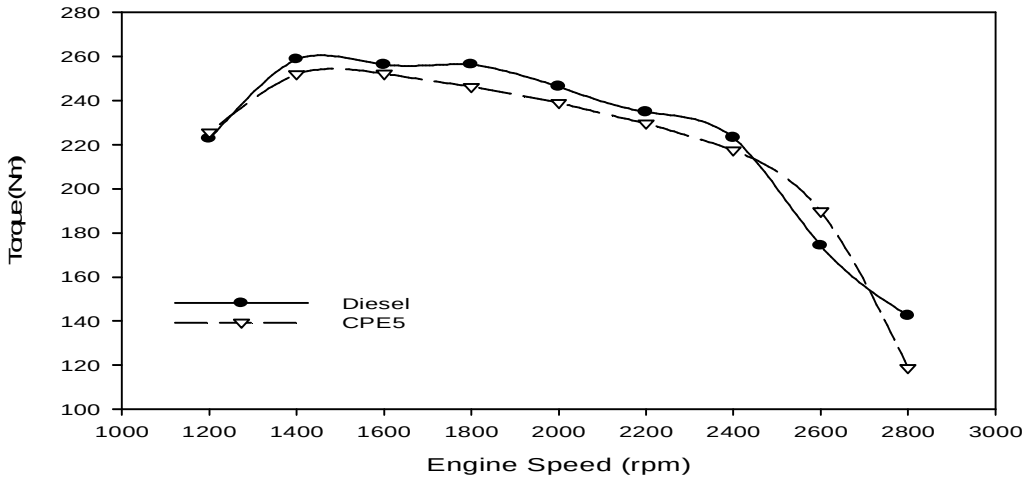



Figure 5.12 Torque output versus engine speed for CPE5 and Diesel

### 5.3.3. Exhaust Emissions

The variation of carbon monoxide with engine speed is shown in Figure 5.13. It can easily be seen from the figure that there is an average of 12% reduction in CO emission values when CPE5 was used instead of diesel fuel. The maximum CO emission reduction was measured at high engine speeds (1800-2200).

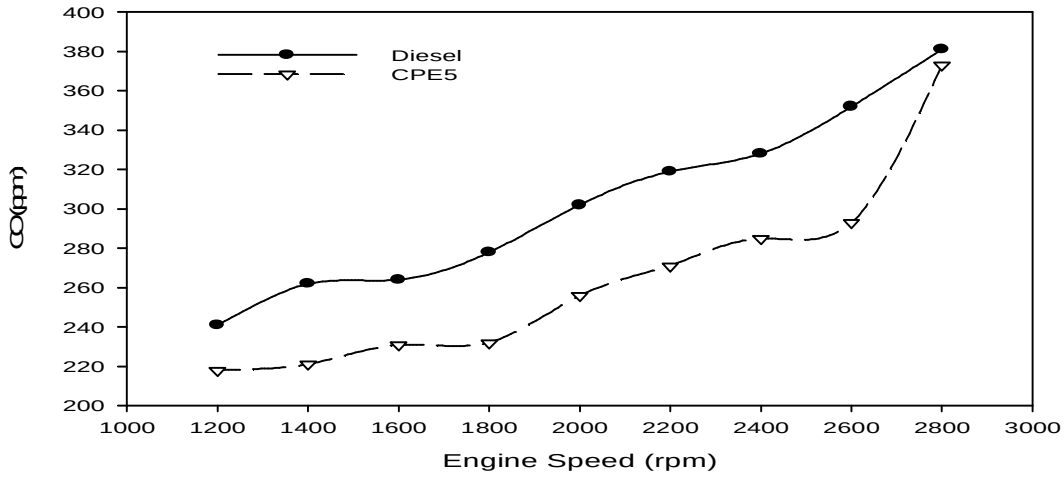



Figure 5.13 CO emission values of CPE5 and Diesel

Figure 5.14 presents the variation of measured $CO_2$ emission values of test fuels for different engine speeds. The maximum $CO_2$ emission reduction was observed at 2800 rpm. There is an average of 1.12% reduction in $CO_2$ emission values when CPE5 is used instead of diesel fuel. ForCPE5 and diesel, maximum $CO_2$ emission values were measured at about 1800 rpm where maximum torque values were obtained.

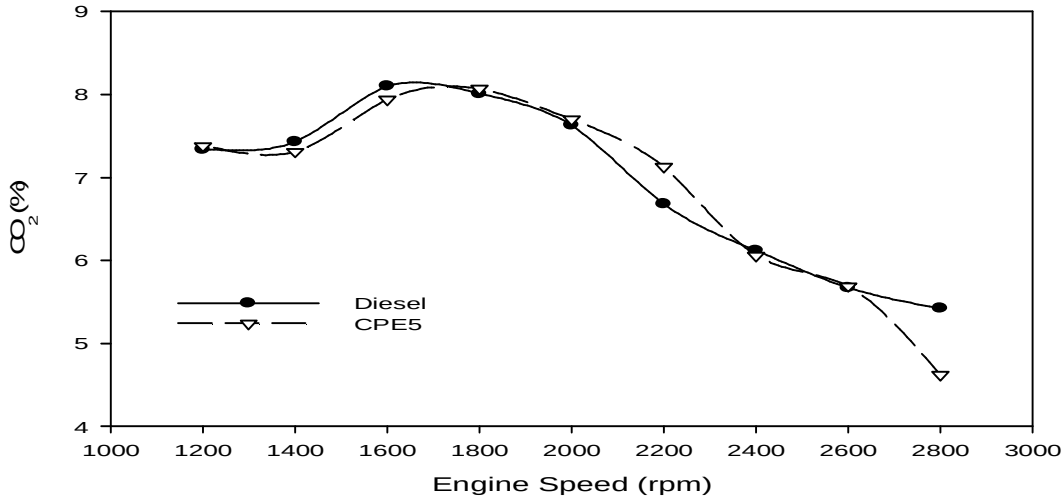



Figure 5.14 $CO_2$ emission values of CPE5 and Diesel

The nitrogen oxides ($NO_x$) emissions of tests fuels in shown in Figure 5.15 the maximum $NO_x$ emission value was observed at 1800 rpm. On an average 5% increment in NOx was obtained for CPE5 and as compared to diesel.

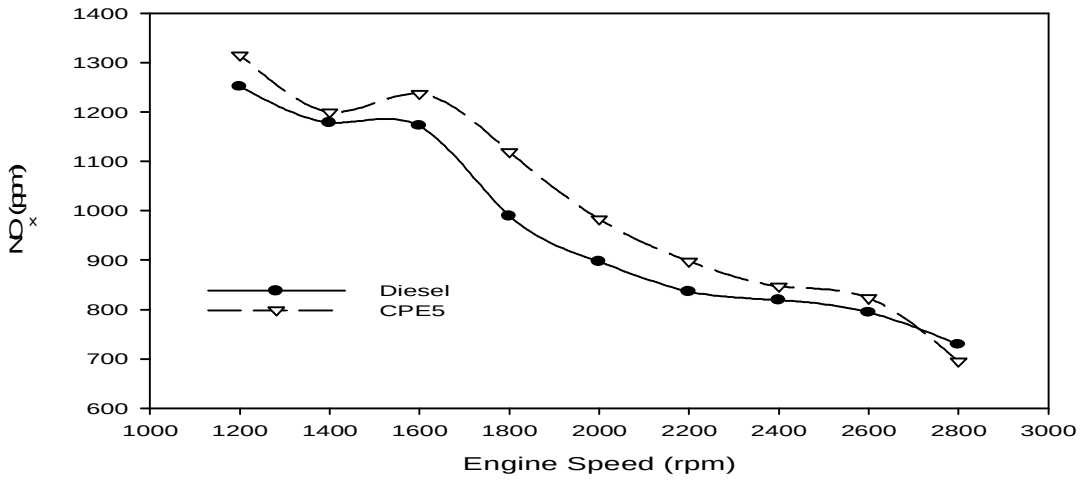



Figure 5.15 $NO_x$ emission values of CPE5 and Diesel

## 5.4. Light Polypropylene-Diesel Blended Fuels

### 5.4.1. Fuel Properties

Light polypropylene has been blended into diesel with various blended rates (5%, 10%, 15%, 20%) the blends have been analyzed by the standard ASTM test methods and results are shown in Table 5.4. The “LPP” designates waste polypropylene and the number of next to LPP designates the percentage volume of polypropylene. The LPP5 means, 5% light propylene was blended with 95% with diesel.

Table 5.4. Fuel Properties of Light Polypropylene-Diesel Blended Fuels

| Properties | Diesel | LPP100 | LPP5 | LPP10 | LPP15 | LPP20 |
|---|---|---|---|---|---|---|
| Density (g/cm$^3$) | 0.833 | 0.777 | 0.830 | 0.827 | 0.825 | 0.822 |
| Cetane Number | 54.580 | 47.910 | 52.999 | 52.894 | 52.500 | 52.316 |
| Pour Point ($^o$C) | -12 | 23 | -1.0 | 3.0 | 8.0 | 11.0 |
| Viscosity (cSt) | 2.52 | 3.896 | 2.55 | 2.65 | 2.69 | 2.74 |
| Calorific Value (kcal/kg) | 10 790 | 10 191 | 10 755 | 10 722 | 10 697 | 10 678 |
| Flash Point ($^o$C) | 58.5 | 58.5 | 58.5 | 58.5 | 58.5 | 58.5 |

Densities of Light Propylene-Diesel blends are decreasing related to LPP contents clearly and this can be seen in Table 5.4. Cetane numbers of Light Propylene-Diesel blends are decreasing related to LPP contents clearly and this can be seen in table 5.4. LPP showed the highest pour point among the waste plastic oils considered in this study and Pour points of Light Polypropylene-Diesel blends are increasing up to 11◦C with LPP additions. Kinematic viscosities of Light Polypropylene-Diesel blends are increasing by percentage volume of LPP. Calorific values of Light Polypropylene-Diesel blends are decreasing by percentage volume of LPP. The experiments showed that LPP has same flash point with diesel so that all blends had same flash point with diesel.

### 5.4.2. Engine Performance

#### 5.4.2.1. Brake Power Output

Figure 5.16 shows the variation of brake power according to different engine speed values. As it can easily be seen in Figure 5.16 there were no noticeable differences in the measured engine power output between LPP5 and diesel fuel at low engine speeds. The characteristics of power curve were not changed, according to the type of fuel. It was observed that the maximum power values with all fuels were obtained at an engine speed of 2400 rpm.

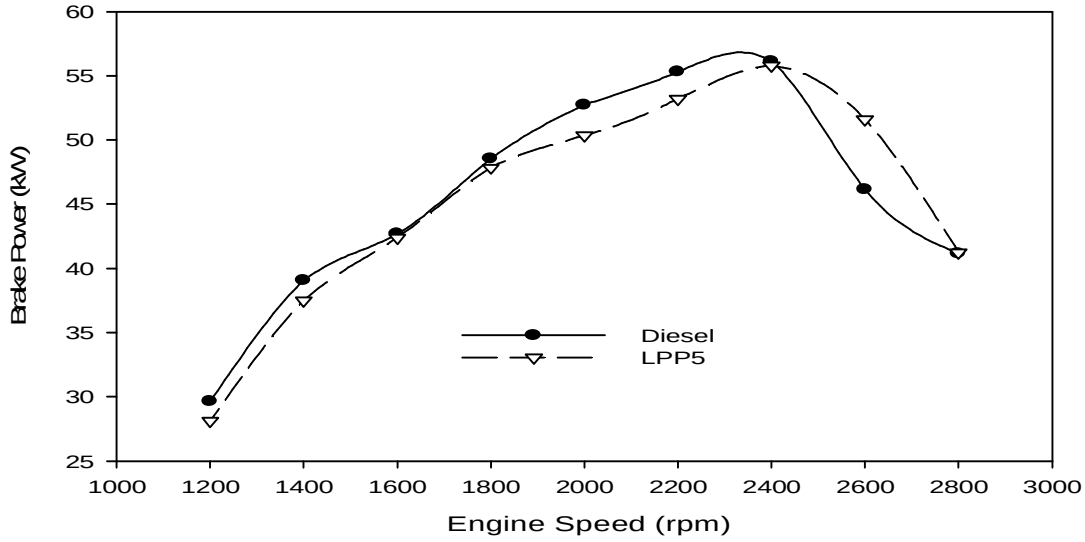



Figure 5.16 Brake power output versus engine speed for LPP5 and Diesel

### 5.4.2.2. Torque Output

The torque output of test fuels is shown in Figure 5.17. The maximum torque values for diesel and LPP5 were obtained at an engine speed of 1400-1800 rpm. There were no noticeable differences in the measured engine power output between % 5 LPP and diesel fuel at 1200-2400 rpm. The torque output is reduced through higher engine speeds.

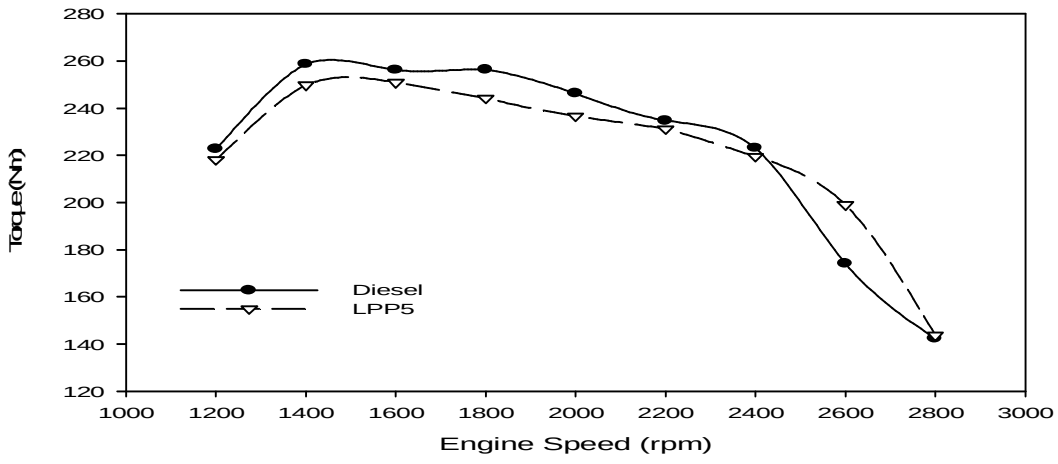



Figure 5.17 Torque output versus engine speed for LPP5 and Diesel

### 5.4.3. Exhaust Emissions

The variation of carbon monoxide with engine speed is shown in Figure 5.18. The maximum CO emission reduction value was measured at 2600 rpm. It can easily be seen from the figure that there is an average of 16% reduction in CO emission values when LPP5 was used instead of diesel fuel.

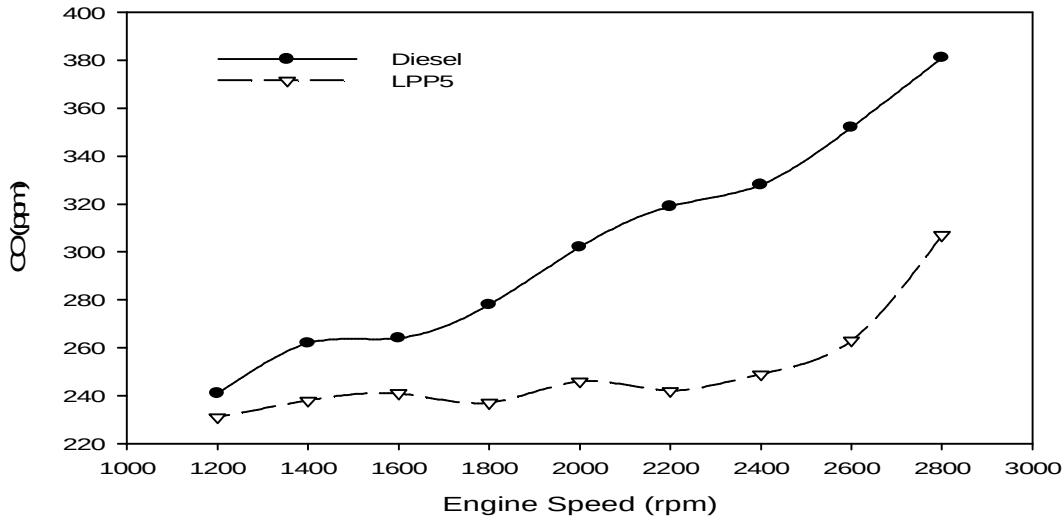



Figure 5.18 CO emission values of LPP5 and Diesel

Figure 5.19 proves the variation of measured $CO_2$ emission values of test fuels for different engine speeds. There is an average of 2.6% increment in $CO_2$ emission values when GPE5 is used instead of diesel fuel. For GPE5 and diesel, maximum $CO_2$ emission values were measured at about 1600 rpm where maximum torque values were obtained.

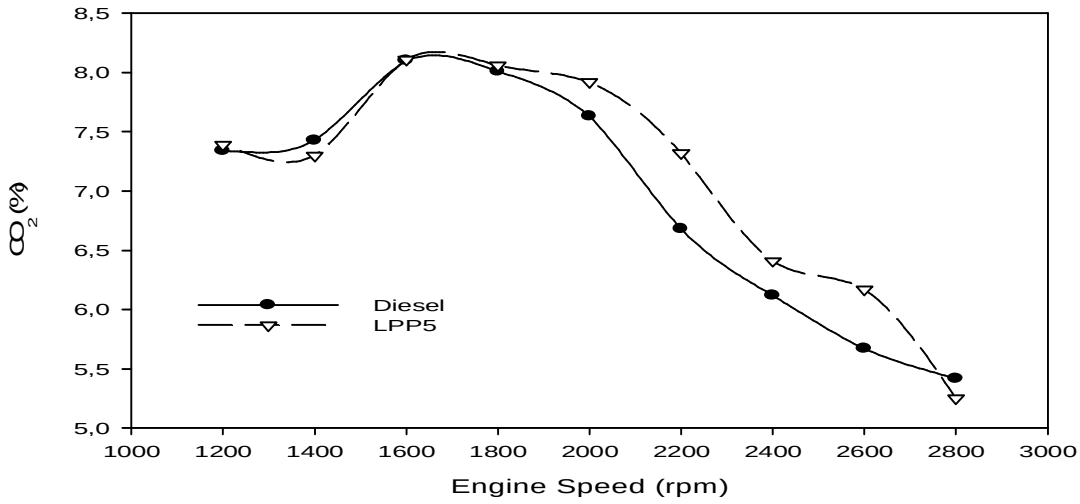



Figure 5.19 $CO_2$ emission values of LPP5 and Diesel

The nitrogen oxides ($NO_x$) emissions of tests fuels in shown in Figure 5.20 On an average of 5% increment in $NO_x$ was obtained for LPP5 and as compared to diesel. The maximum $NO_x$ emission increment value was measured at high engine speeds.

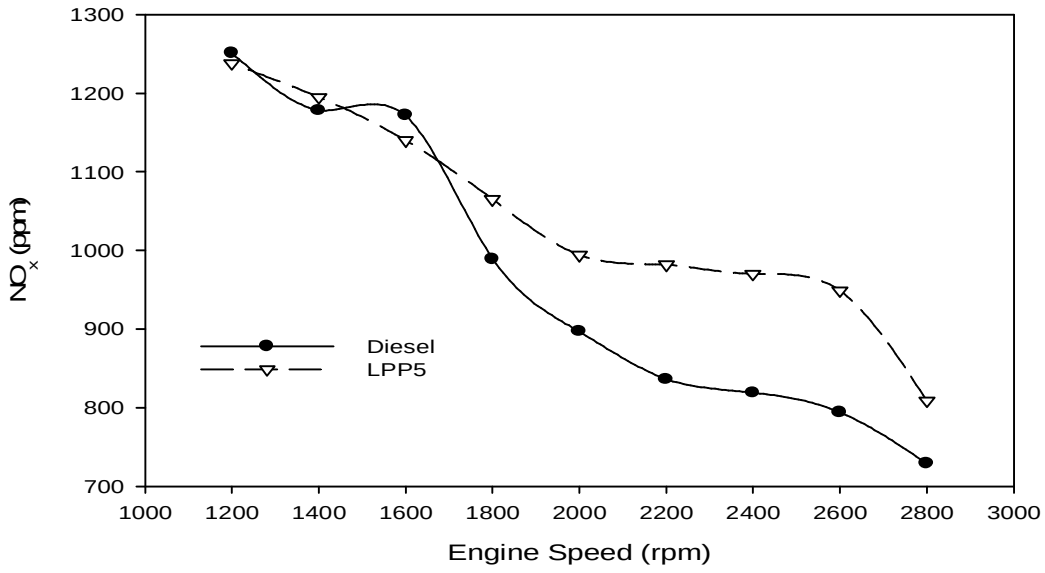



Figure 5.20 $NO_x$ emission values of LPP5 and Diesel

## 5.5. Waste Polyethylene-Diesel Blended Fuels

### 5.5.1. Fuel Properties

Waste polyethylene has been blended into diesel with various blended rates (5%, 10%, 15%, 20%) the blends have been analyzed by the standard ASTM test methods and results are shown in table 5.5. The "WPE" designates waste polyethylene and the number of next to WPE designates the percentage volume of waste polyethylene. The WPE5 means, 5% waste polyethylene was blended with 95% with diesel.

Table 5.5. Fuel Properties of Waste Polyethylene-Diesel Blended Fuels

| Properties | Diesel | WPE100 | WPE5 | WPE10 | WPE15 | WPE20 |
|---|---|---|---|---|---|---|
| Density ($g/cm^3$) | 0.833 | 0.788 | 0.831 | 0.828 | 0.826 | 0.824 |
| Cetane Number | 54.580 | 43.751 | 52.588 | 51.637 | 50.370 | 49.626 |
| Pour Point ($^oC$) | -12 | 18 | -8.0 | -4.0 | -2.0 | 1.0 |
| Viscosity (cSt) | 2.52 | 2.336 | 2.49 | 2.48 | 2.43 | 2.40 |
| Calorific Value (kcal/kg) | 10 790 | 10 867 | 10 800 | 10 807 | 10 812 | 10 818 |
| Flash Point ($^oC$) | 58.5 | >100 | 58.5 | 59 | 59.5 | 61 |

Densities of Waste polyethylene-Diesel blends are decreasing related to WPE contents clearly and this can be seen in Table 5.5. Cetane numbers of waste polyethylene-diesel blends are decreasing related to WPE contents clearly and this can be seen in Table 5.5. Pour points of waste polyethylene-diesel blends are increasing up to $1^{\circ}C$ with WPE additions. Kinematic viscosities of waste polyethylene-diesel blends are decreasing by percentage volume of WPE. Calorific values of waste polyethylene-Diesel blends are increasing by percentage volume of WPE. The experiments showed that flash point of waste polyethylene are increasing by percentage volume of WPE additions.

### 5.5.2. Engine Performance

#### 5.5.2.1. Brake power output

Figure 5.21 exposes the variation of brake power according to different engine speed values. As it can easily be seen in Figure 5.21 there were no noticeable differences in the measured engine power output between WPE5 and diesel fuel at low engine speeds. The characteristics of power curve were not changed, according to the type of fuel. It was observed that the maximum power values with all fuels were obtained at an engine speed of 2400 rpm.

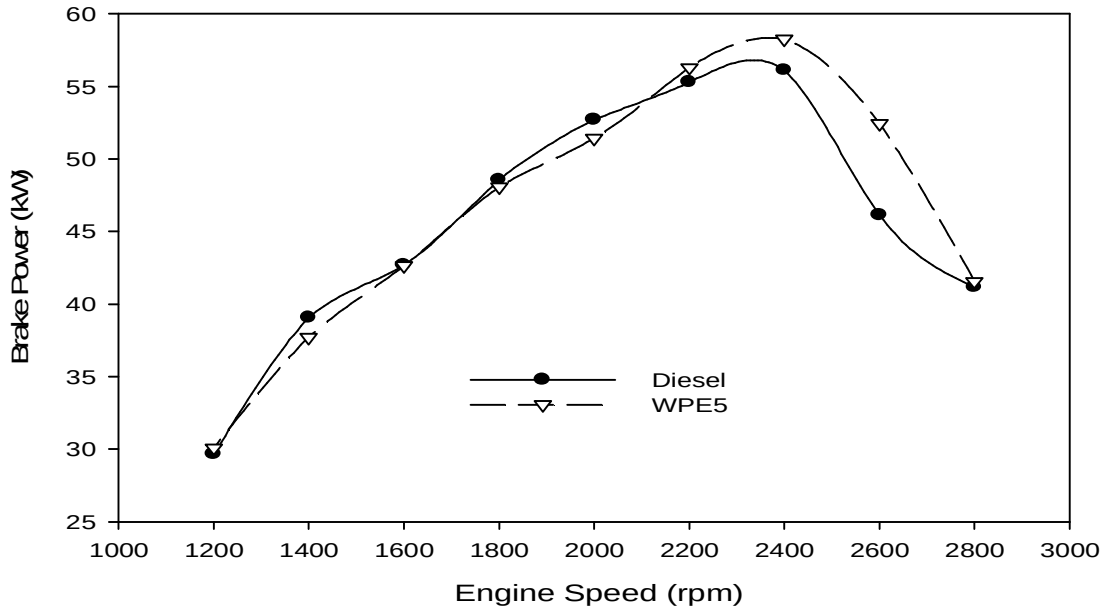



Figure 5.21 Brake power output versus engine speed for WPE5 and Diesel

#### 5.5.2.2. Torque Output

The torque output of test fuels is shown in Figure 5.22. The maximum torque values for diesel and WPE5 were obtained at an engine speed of 1400-1800 rpm. There were no noticeable differences in the measured engine power output between WPE5 and diesel fuel at 1200-2400 rpm. The torque output of

WPE5 was increased about 14% at 2600 rpm and about 5% at 2800 rpm. The torque output is reduced through higher engine speeds.

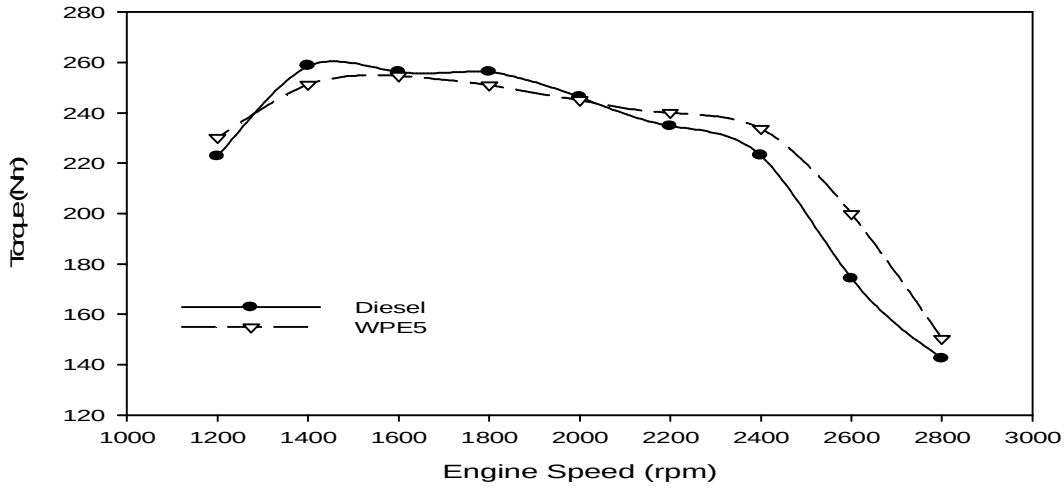



Figure 5.22 Torque output versus engine speed for WPE5 and Diesel

### 5.5.3. Exhaust Emissions

The variation of carbon monoxide with engine speed is shown in Figure 5.23. The maximum CO emission reduction values were measured at high speeds. It can easily be seen from the figure that there is an average of 20% reduction in CO emission values when WPE5 was used instead of diesel fuel.

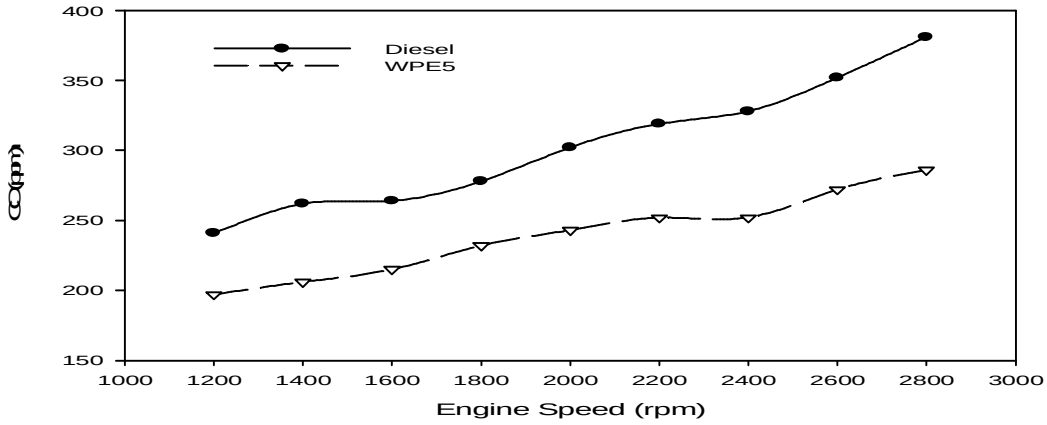



Figure 5.23 CO emission values of WPE5 and Diesel

As you can see in Figure 5.24 there is an average of 3.3% increment in $CO_2$ emission values when WPE5 is used instead of diesel fuel. For WPE5 and diesel, maximum $CO_2$ emission values were measured at about 1600-1800 rpm where maximum torque values were obtained.

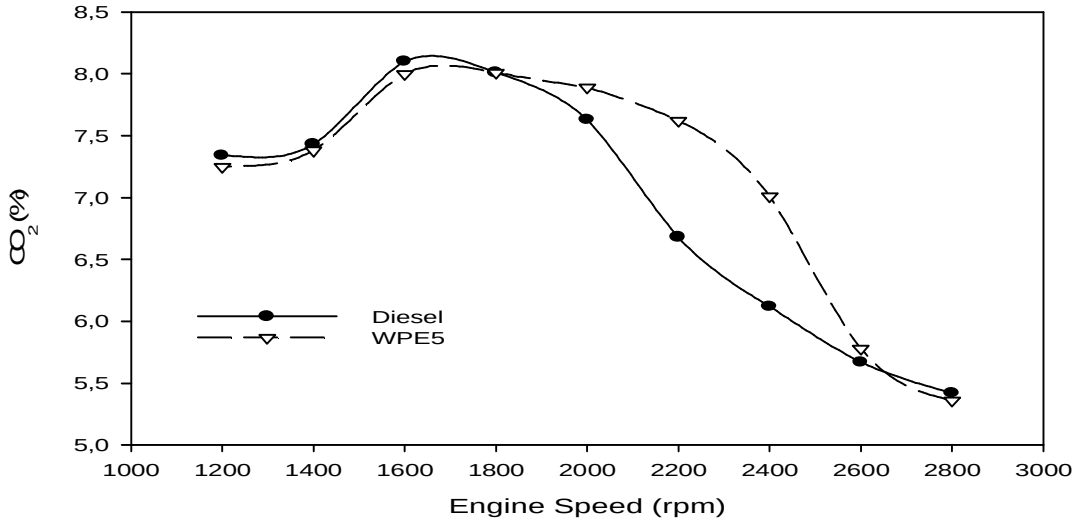



Figure 5.24 $CO_2$ emission values of WPE5 and Diesel

The nitrogen oxides ($NO_x$) emissions of tests fuels in shown in Figure 5.25 On an average of 9.1% increment in $NO_x$ was obtained for WPE5 and as compared to diesel. The maximum $NO_x$ emission value was observed at low engine speeds.

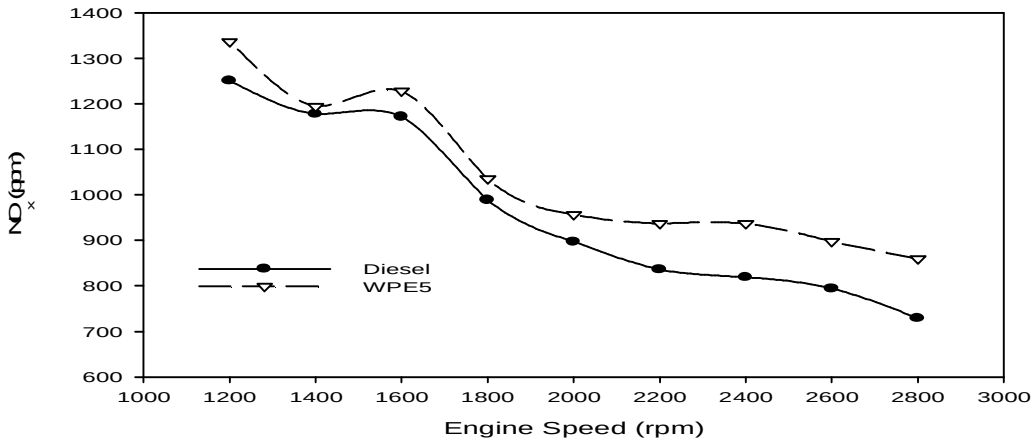



Figure 5.25 $NO_x$ emission values of WPE5 and Diesel

## 5.6. Light Phase-Diesel Blended Fuels

### 5.6.1. Fuel Properties

Light phase has been blended into diesel with various blended rates (5%, 10%, 15%, 20%) the blends have been analyzed by the standard ASTM test methods and results are shown in table 5.6. The "LP" designates thin phase and the number of next to LP designates the percentage volume of light phase. The LP5 means, 5% light phase was blended with 95% with diesel.

Table 5.6. Fuel Properties of Light Phase-Diesel Blended Fuels

| Properties | Diesel | LP100 | LP5 | LP10 | LP15 | LP20 |
|---|---|---|---|---|---|---|
| Density ($g/cm^3$) | 0.833 | 0.739 | 0.828 | 0.824 | 0.820 | 0.815 |
| Cetane Number | 54.580 | 51.100 | 53.367 | 53.117 | 53.010 | 52.795 |
| Pour Point ($^oC$) | -12 | -5.0 | -10.0 | -9.0 | -7.0 | -6.0 |
| Viscosity (cSt) | 2.52 | 2.0 | 2.40 | 2.36 | 2.33 | 2.30 |
| Calorific Value (kcal/kg) | 10 790 | 10 348 | 10 761 | 10 738 | 10 715 | 10 687 |
| Flash Point ($^oC$) | 58.5 | 58.5 | 58.5 | 58.5 | 58.5 | 58.5 |

Densities of Light phase-Diesel blends are decreasing related to LP contents clearly and this can be seen in Table 5.6. Cetane numbers of Light phase-Diesel blends are decreasing related to LP contents clearly and this can be seen in Table 5.6. Pour points of Light phase-Diesel blends are increasing up to -6$^\circ$C with LP additions. Kinematic viscosities of Light phase-Diesel blends are decreasing by percentage volume of LP. Calorific values of Light phase-Diesel blends are decreasing by percentage volume of LP. The experiments showed that LP has same flash point with diesel so that all blends had same flash point with diesel.

### 5.6.2. Engine Performance

#### 5.6.2.1. Brake Power Output

Figure 5.26 shows the variation of brake power according to different engine speed values. As it can easily be seen in Figure 5.26 there were no noticeable differences in the measured engine power output between LP5 and diesel fuel at low engine speeds. The brake power output of LP5 was decreased about 10% at 2800 rpm. The characteristics of power curve were not changed, according to the type of fuel. It was observed that the maximum power values with all fuels were obtained at an engine speed of 2400 rpm.

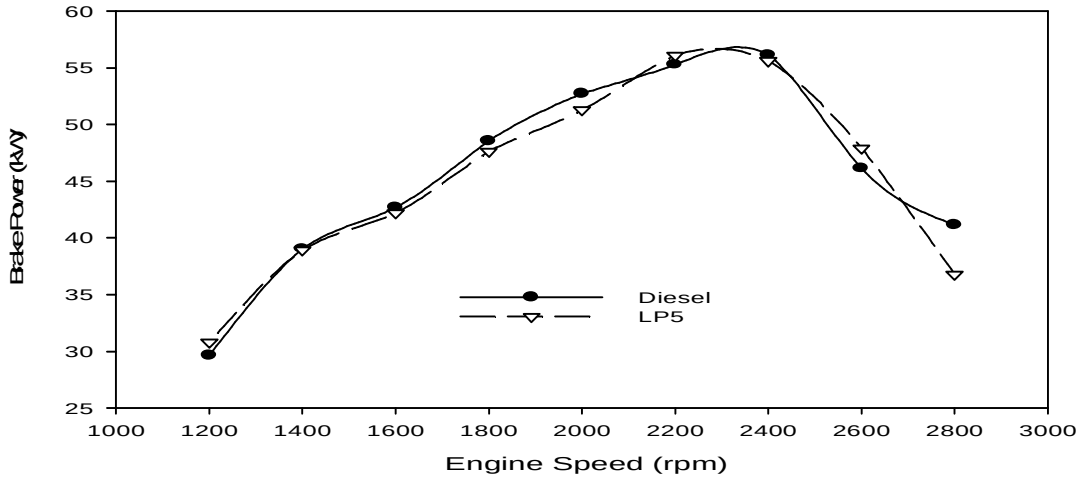



Figure 5.26 Brake power output versus engine speed for LP5 and Diesel

#### 5.6.2.2. Torque Output

The torque output of test fuels is shown in Figure 5.27. The maximum torque values for diesel and LP5 were obtained at an engine speed of 1400-1600 rpm. There were no noticeable differences in the measured engine power output between LP5 and diesel fuel at 1200-2400 rpm. The torque output of 5% LP was decreased about 9% at 2800 rpm. The torque output is reduced through higher engine speeds.

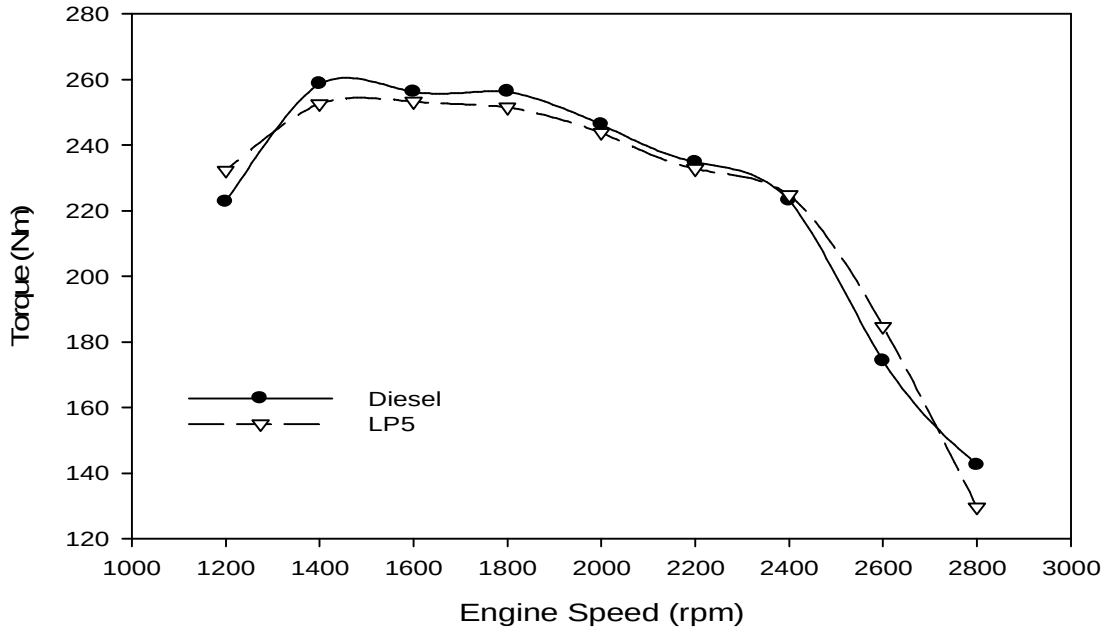



Figure 5.27 Torque output versus engine speed for LP5 and Diesel

### 5.6.3. Exhaust Emissions

The variation of carbon monoxide with engine speed is shown in Figure 5.28. It can easily be seen from the figure that there is an average of 18% reduction in CO emission values when LP5 was used instead of diesel fuel.

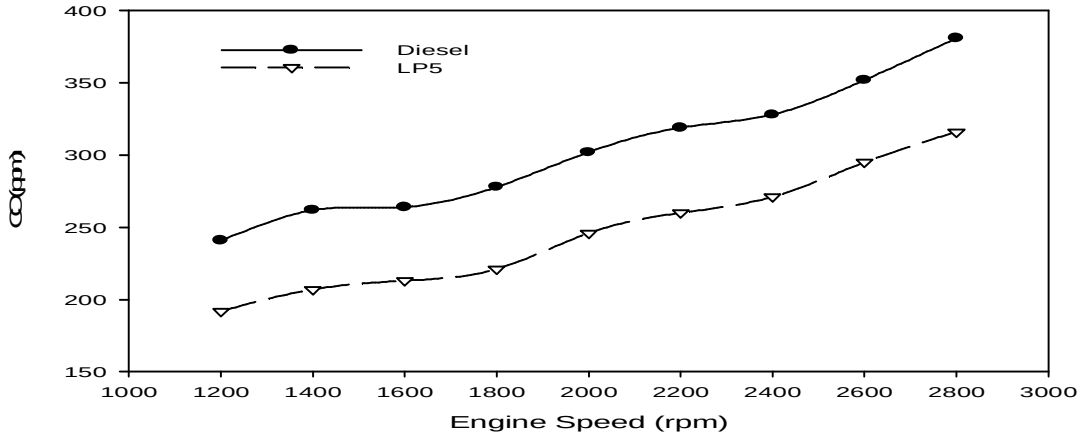



Figure 5.28 CO emission values of LP5 and Diesel

Figure 5.29 proves that there is an average of 1.78% reduction in $CO_2$ emission values when LP5 is used instead of diesel fuel. For LP5 and diesel, maximum $CO_2$ emission values were measured at about 1800 rpm where maximum torque values were obtained.

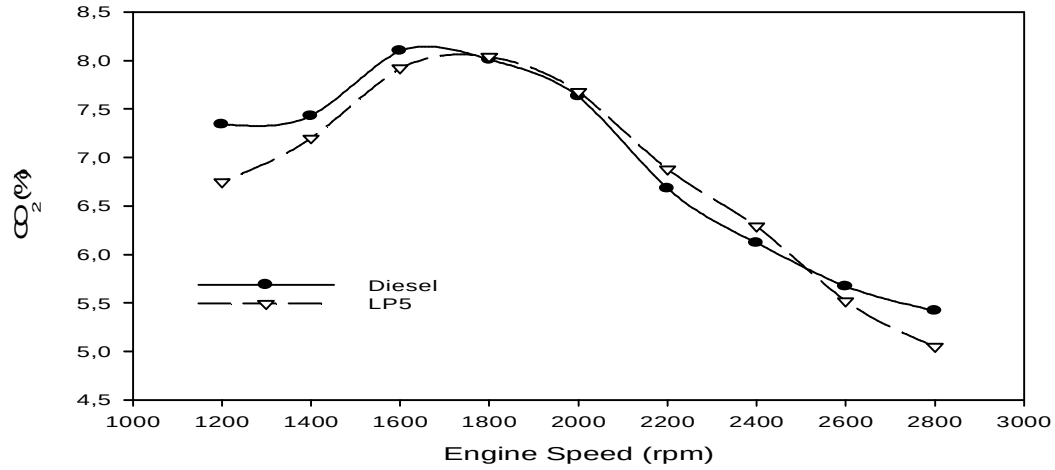



Figure 5.29 $CO_2$ emission values of LP5 and Diesel

The nitrogen oxides ($NO_x$) emissions of tests fuels in shown in figure 5.30. On an average of 4.11% increment in $NO_x$ was obtained for LP5 and as compared to diesel.

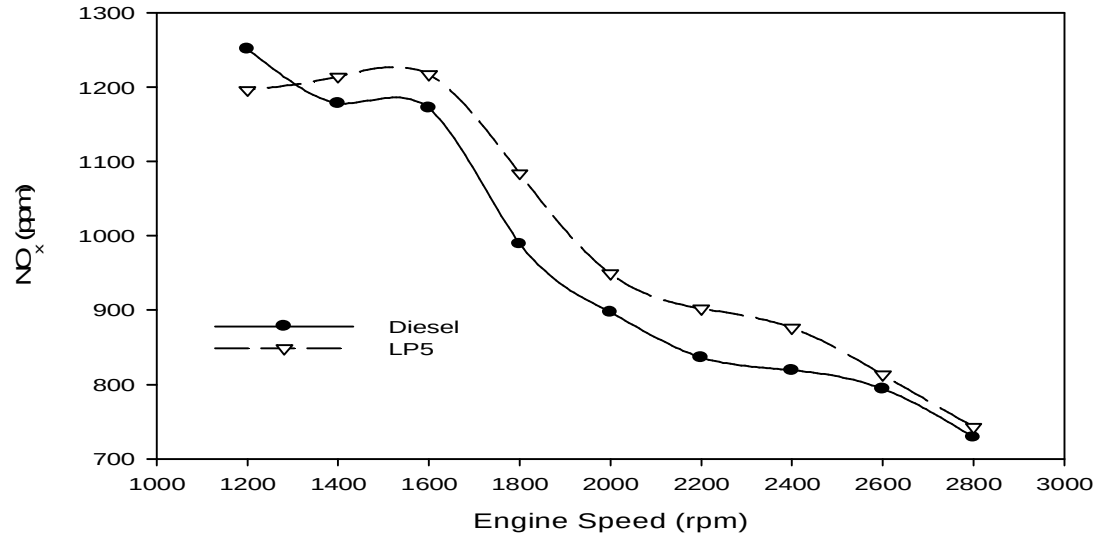



Figure 5.30 $NO_x$ emission values of LP5 and Diesel

## 5.7 Heavy Phase-Diesel Blended Fuels

### 5.7.1. Fuel Properties

Heavy phase has been blended into diesel with various blended rates (5%, 10%, 15% and 20%) the blends have been analyzed by the standard ASTM test methods and results are shown in Table 5.7. The "HP" designates thick phase and the number of next to HP designates the percentage volume of Heavy phase. The HP5 means, 5% Heavy phase was blended with 95% with diesel.

Table 5.7. Fuel Properties of Heavy Phase-Diesel Blended Fuels

| Properties | Diesel | HP100 | HP5 | HP10 | HP15 | HP20 |
|---|---|---|---|---|---|---|
| Density ($g/cm^3$) | 0.833 | 0.793 | 0.831 | 0.829 | 0.827 | 0.825 |
| Cetane Number | 54.580 | 54.821 | 54.693 | 54.760 | 54.783 | 54.799 |
| Pour Point ($^oC$) | -12 | -2 | -11.0 | -10.0 | -10.0 | -9.0 |
| Viscosity (cSt) | 2.52 | 2.03 | 2.37 | 2.32 | 2.30 | 2.25 |
| Calorific Value (kcal/kg) | 10 790 | 10 299 | 10 775 | 10752 | 10 722 | 10 700 |
| Flash Point ($^oC$) | 58.5 | 58.5 | 58.5 | 58.5 | 58.5 | 58.5 |

Densities of Heavy phase-Diesel blends are decreasing related to HP contents clearly and this can be seen in Table 5.7. Cetane numbers of Heavy phase-Diesel blends are decreasing related to HP contents clearly and this can be seen in Table 5.6. Pour points of Heavy phase-Diesel blends are increasing up to -9°C with HP additions. Kinematic viscosities of Heavy phase-Diesel blends are decreasing by percentage volume of HP. Calorific values of Heavy phase-Diesel blends are decreasing by percentage volume of HP. The experiments showed that HP has same flash point with diesel so that all blends had same flash point with diesel.

### 5.7.2. Engine Performance

#### 5.7.2.1.Brake Power Output

Figure 5.31 shows the variation of brake power according to different engine speed values. As it can easily be seen in Figure 5.31 there were no noticeable differences in the measured engine power output between HP5 and diesel fuel at low engine speeds. The brake power output of HP5 was decreased about 10% at 2800 rpm. The characteristics of power curve were not changed, according to the type of fuel. It was observed that the maximum power values with all fuels were obtained at an engine speed of 2400 rpm.

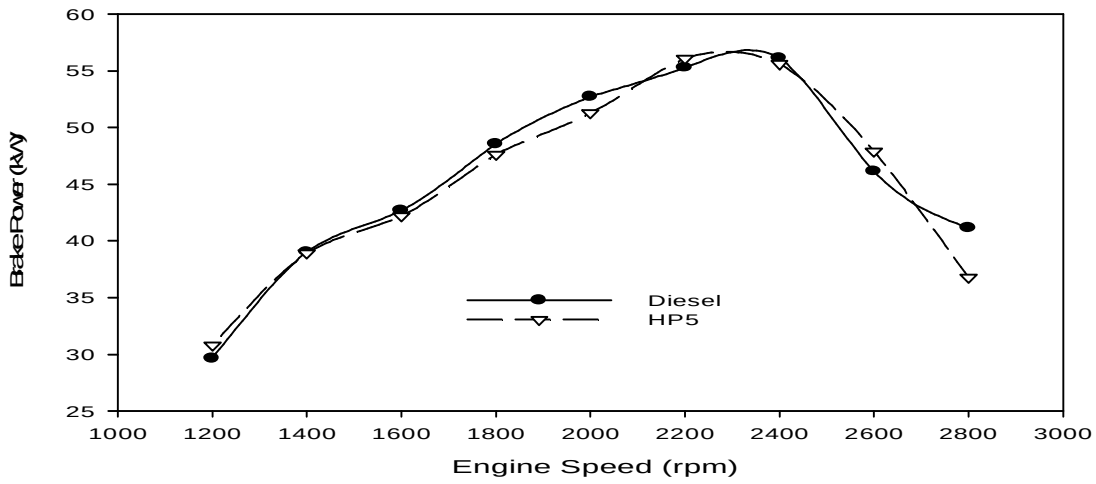



Figure 5.31 Brake power output versus engine speed for HP5 and Diesel

#### 5.7.2.2. Torque Output

The torque output of test fuels is shown in Figure 5.32. The maximum torque values for diesel and HP5 were obtained at an engine speed of 1400-1600 rpm. There were no noticeable differences in the measured engine power output between HP5 and diesel fuel at 1200-2400 rpm. The torque output of HP5 was decreased about 9% at 2800 rpm. The torque output is reduced through higher engine speeds.

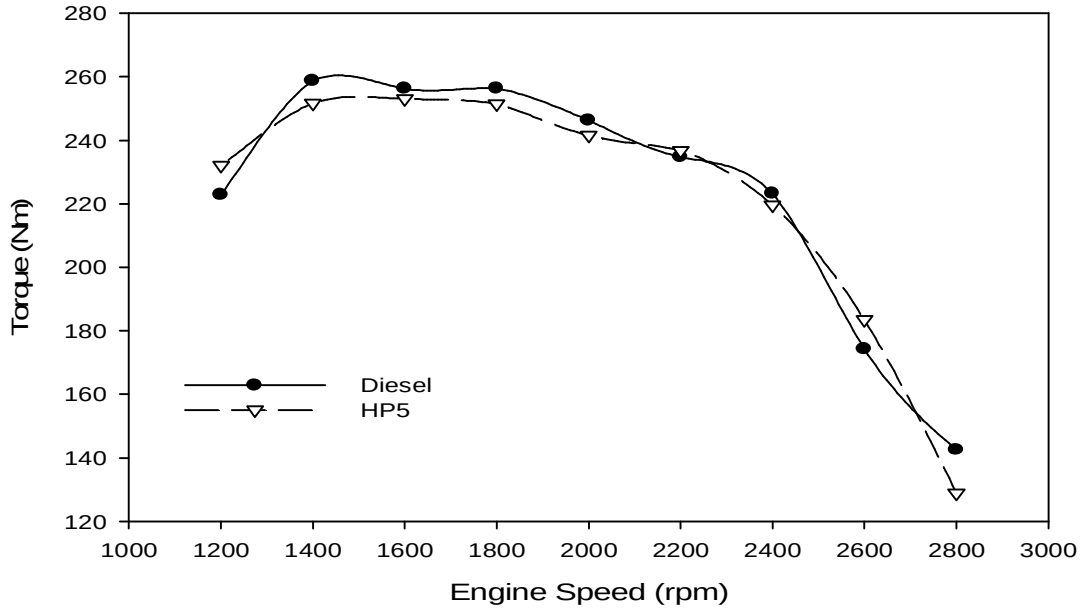



Figure 5.32 Torque output versus engine speed for HP5 and Diesel

### 5.7.3. Exhaust Emissions

The variation of carbon monoxide with engine speed is shown in Figure 5.33. The maximum CO emission reduction was measured at 1800 rpm where the maximum torque values were obtained. It can easily be seen from the figure that there is an average of 18% reduction in CO emission values when HP5 was used instead of diesel fuel.

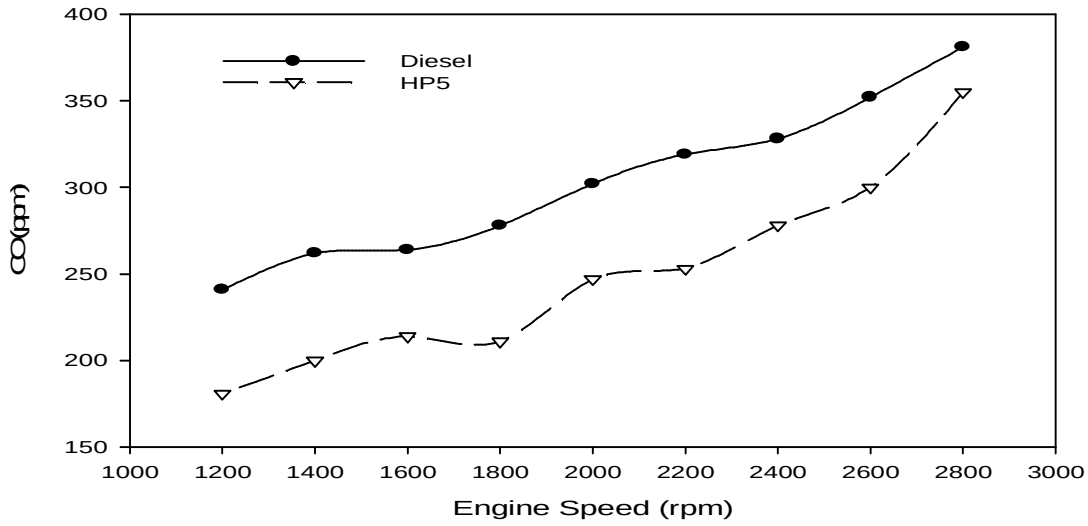



Figure 5.33 CO emission values of HP5 and Diesel

Figure 5.34 demonstrates the variation of measured $CO_2$ emission values of test fuels for different engine speeds. There is an average of 2.35% reduction in $CO_2$ emission values when HP5 is used instead of diesel fuel. For HP5 and diesel, maximum $CO_2$ emission values were measured at about 1800 rpm where maximum torque values were obtained.

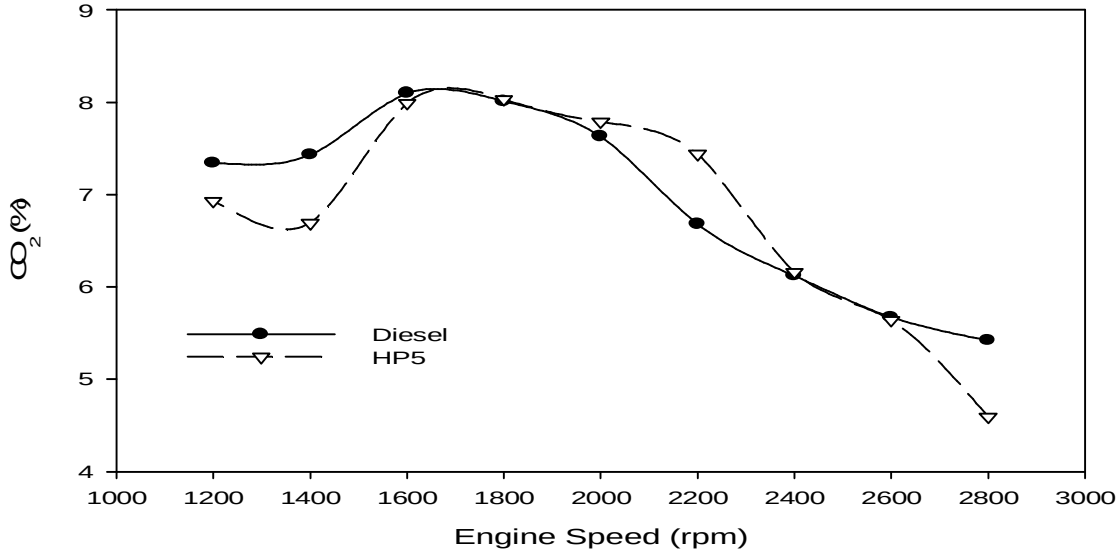



Figure 5.34 $CO_2$ emission values of HP5 and Diesel

The nitrogen oxides ($NO_x$) emissions of tests fuels in shown in figure 5.35. On an average of 4.11% increment in $NO_x$ was obtained for HP5 and as compared to diesel. The reductions in $NO_x$ emission could be due to the higher combustion temperature.

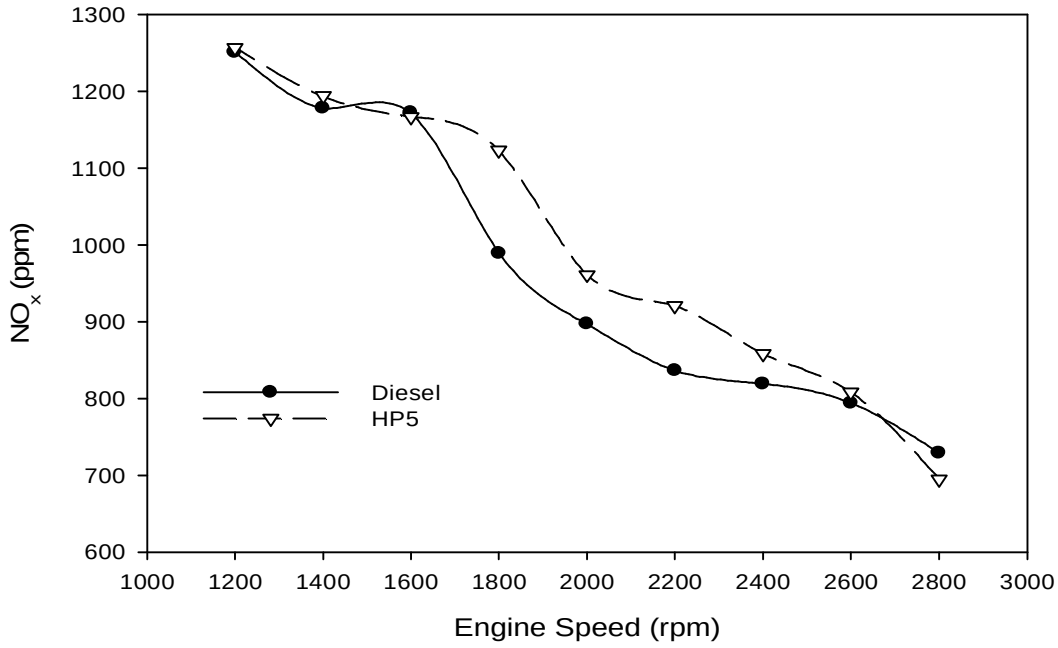



Figure 5.35 $NO_x$ emission values of HP5 and Diesel

# 6. CONCLUSION

In this study, granule polyethylene, mixed granule, catalyzed waste polyethylene, light propylene, waste polyethylene, light phase and heavy phase blend with the diesel different ratios (5%, 10%, 15%, 20%) and the effects of each blend on diesel's fuel properties were investigated. In addition to fuel properties, engine performance and exhaust emission experimental studies were performed.

Densities of waste plastic fuel-diesel blends decrease because of their low densities.

Cetane numbers of Granule Polyethylene (GPE) and Heavy Phase (HP) blends increases because of their high cetane numbers however cetane numbers of the other waste plastic fuel blends decrease because of their low cetane numbers. For cetane numbers, best cetane improver is Granule Polyethylene.

The variation in the kinematic viscosity of the waste plastic fuel blends depends on the density values of waste plastic fuel blends. Light Polypropylene (LPP) blends increase with addition of LPP on the other hand the kinematic viscosities of other waste plastic fuel blends decrease.

It is important to measure the pour point properties of the samples. One of the major disadvantages of waste plastic fuels is their high pour points. Light Polypropylene showed the highest pour point of the blends. For other waste plastic fuel blends the pour point results were acceptable according to the EN 590 diesel standards.

There are no noticeable differences observed for the flash point property for test fuels.

Calorific values of Mixed Granule and Waste Polyethylene blends increases because of their high calorific values.

The obtained results showed that WPE addition with 15% and 20% and LPP addition with 15% and 20% could not use in diesel engine however the other waste plastic fuel blends could use in diesel engine.

Power output of engine with blends increased maximum by 1.63% with WPE5 blend compared with diesel fuel. Torque output of blends decreased by 2.73% with WPE5 compared to diesel fuel especially at higher engine speeds.

While CO emission is decreased by 20.63% with WPE5 blend and $CO_2$ emission is increased by 3.34% with WPE5 blend. NOx emission is increased by 9.17% with WPE5 compared to diesel fuel.

Finally WPE5 blend can be the best alternative fuel blend for diesel engines not only for its performance characteristics but also for the environmental aspects.

## REFERENCES


ABDULVAHİTOĞLU, A., YILMAZ, A., AYDIN, K., 2008. Fuel quality investigation of diesel fuel, biodiesel and different hydrocarbon blends, University of Çukurova Faculty of Mechanical Engineering and Architecture, 30th Annual Symposium, 606-610.

AGUADO, J., SOTELO, J. L., SERRANO, D. P., CALLES, J. A., and ESCOLA, J. M., 1997. Catalytic Conversion of Polyolefins into Liquid Fuels over MCM-41: Comparison with ZSM 5 and Amorphous $SiO_2$-$Al_2O_3$, *Energy & Fuels,* 11:1225-1231.

AGUADO, J., SERRANO, D.P., MIGUEL, G.S., CASTRO, M.C., and MADRID, S., 2007. Feedstock recycling of polyethylene in a two-step thermo-catalytic reaction system, Journal of Analytical and Applied Pyrolysis, 79:415–423.

AGUADO, J., SERRANO, D.P. and ESCOLA, J.M., 2008. Fuels from Waste Plastics by Thermal and Catalytic Processes: A Review, Ind. Eng. Chem. Res, 47, 7982–7992.

AKPANUDOH, N.S., GOBIN, K., and MANOS, G., 2005. Catalytic degradation of plastic waste to liquid fuel over commercial cracking catalysts Effect of polymer to catalyst ratio/acidity content, Journal of Molecular Catalysis A: Chemical 235:67–73.

ANGYAL, A., MISKOLCZI, N., BARTHA, L., and VALKAI, I., 2009. Catalytic cracking of polyethylene waste in horizontal tube reactor, Polymer Degradation and Stability 94:1678–1683.

ANONYMOUS, 2010a, http://www.wikipedia.com

ANONYMOUS, 2010b, "Envosmart Technologies, Waste Plastics to Diesel Fuel http://www.envosmart.com

ANONYMOUS, 2010c, http:// www.azom.com

ANONYMOUS, 2010d, http://www.icis.com

BUEKENS, A.G., and HUANG, H., 1998. Catalytic plastics cracking for recovery of gasoline-range hydrocarbons from municipal plastic wastes, Resources, Conservation and Recycling, 23:163–181.

COELHO, A., FONSECA, I.M., MATOS, I., MARQUES, M.M., BOTELHO DO REGO A.M., LEMOS, M.A.N.D.A., and LEMOS, F., 2010. Catalytic degradation of low and high density polyethylenes using ethylene polymerization catalysts: Kinetic studies using simultaneous TG/DSC analysis, Applied Catalysis A: General 374:170–179.

GARCIA, R.A., SERRANO, D.P., and OTERO, D., 2005. Catalytic cracking of HDPE over hybrid zeolitic–mesoporous materials, Journal of Analytical and Applied Pyrolysis 74:379–386.

GARPEN, J.V., SHANKS, B., PRUSZKO, R., CLEMENTS, D. and KNOTHE., G., 2004, Biodiesel Analytic Methods, National Renewable Energy Laboratory, NREL/SR-510-36240.

JAN, M.R., SHAH, J., and GULAB, H., 2010. Catalytic degradation of waste high-density polyethylene into fuel products using $BaCO_3$ as a catalyst, Fuel Processing Technology, 91:1428-1431.

JAN, M.R., SHAH, J., and GULAB, H., 2010. Degradation of waste High-density polyethylene into fuel oil using basic catalyst, Fuel, 89:474–480.

JENG, G.M., YUAN, X. Z., HU, T. J., YAN, G., YIN, Y. Y., and LI, J. B., 2003. Manufacture of Liquid Fuel by Catalytic Cracking Waste Plastics in a Fluidized Bed, Energy Sources, Utilization, and Environmental Effects, Energy Sources, 25:577–590.

JI, L., HERVIER, A., and SABLIER, M., 2006. Study on the pyrolysis of polyethylene in the presence of iron and copper chlorides, Chemosphere, 65:1120–1130.

LIN, Y.H., YANG, M.H., YEH, T.F., and GER, M.D., 2004. Catalytic degradation of high density polyethylene over mesoporous and microporous catalysts in a fluidized bed reactor, Polymer Degradation and Stability, 86:121-128.

LIN, Y.H., and YANG, M.H., 2007. Chemical catalysed recycling of waste polymers: Catalytic conversion of polypropylene into fuels and chemicals over spent FCC catalyst in a fluidized-bed reactor, Polymer Degradation and Stability, 92:813-821.

LUO, G., SUTO, T., YASU, S., and KATO K., 2000. Catalytic degradation of high density polyethylene and polypropylene into liquid fuel in a powder-particle fluidized bed, Polymer Degradation and Stability 70:97-102.

MANI, M., SUBASH, C., and NAGARAJAN, G., 2009. Performance, emission and combustion characteristics of a DI diesel engine using waste plastic oil, Applied Thermal Engineering, 29:2738–2744.

MANI, M., SUBASH, C., NAGARAJAN, G., 2009. An experimental investigation on a DI diesel engine using waste plastic oil with exhaust gas recirculation, Fuel, 89:1826–1832.

MANI, M., NAGARAJAN, G., 2010. Influence of injecting timing on performance, emission and combustion characteristics of a DI diesel engine running on waste plastic oil, Energy, 34:1617–1623.

MARCILLA, A., BELTRAN, M.I., and NAVARRO, R., 2009. Thermal and catalytic pyrolysis of polyethylene over HZSM5 and HUSY zeolites in a batch reactor under dynamic conditions, Applied Catalysis B: Environmental, 86:78–86.

MISKOLCZI, N., BARTHA, L., DEAK, GY., JOVER, B., and KALLO, D., 2004. Kinetic model of the chemical recycling of waste polyethylene to fuel, Process Safety and Environmental Protection, 82:223–229.

MISKOLCZI, N., ANGYAL, A., BARTHA, L., and VALKAI, I., 2009. Fuels by pyrolysis of waste plastics from agricultural and packaging sectors in a pilot scale reactor Fuel Processing Technology, 90:1032–1040.

PANDA, A.K., SINGH, R.K., MISHRA, D.K., 2010, Thermolysis of waste plastics to liquid fuel A suitable method for plastic waste management and manufacture of value added products—A world prospective, Renewable and Sustainable Energy Reviews, 14:233–248.

ÖZCANLI, M., 2009. Development of biodiesel production processes and additives for improvement of biodiesel performance and emissions, Ç.Ü. Mechanical Engineering-Doctor thesis pp:129.

SCHEIRS, J. and KAMINSKY, W., 2006. Feedstock Recycling and Pyrolysis of Waste Plastics: Converting Waste Plastics into Diesel and Other Fuels. John Wiley & Sons, Ltd. Chichester, UK. 792 p.

SERRANO, D.P., AGUADO, J., and ESCOLA, J.M., Catalytic Cracking of a Polyolefin Mixture over Different Acid Solid Catalysts. 2000. Ind. Eng. Chem. Res. 39:1177-1184.

WALENDZIEWSKI, J., 2002. Engine fuel derived from waste plastics by thermal treatment, Fuel Processing Technology, 86:1265–1278.

WALENDZIEWSKI, J., 2005. Continuous flow cracking of waste plastics, Fuel, 81:473–481.

WILLIAMS, P.T., WILLIAMS, E.A., 1999. Fluidised bed pyrolysis of low density polyethylene to produce petrochemical feedstock, Journal of Analytical and Applied Pyrolysis. 51:107–126.

XIE, C., LIU, F., YU, S., XIE, F., LU, L.,ZHANG, S., and YANG J., 2008. Catalytic cracking of polypropylene into liquid hydrocarbons over Zr and Mo modified MCM-41 mesoporous molecular sieve, Catalysis Communications 10:79–82.

YILMAZ, A., 2010. Investigation of new oil additives, Ç.Ü. Mechanical Engineering-Master thesis pp:64.

ZORRIQUETA, I.J.N., 2006. Pyrolysis of polypropylene by ziegler-natta catalysts, Fachbereich Chemie Universität Hamburg-Doctor thesis pp:164.

## CURRICULUM VITAE

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