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Effect of Catalytic Reforming on Pyrolytic Oil Production from Waste Plastics

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by

Mochamad SYAMSIRO

Tokyo, Japan
February, 2015

Summary

A significant growth of the plastic consumption and production has resulted in an increased generation of plastic wastes. Thus, plastic wastes have become a major stream in solid waste and caused significant environmental problems for nations worldwide. To minimize the environmental impact and to reduce damages caused by plastic wastes, they must be recycled and recovered. Feedstock or chemical recycling is an alternative method which involves pyrolysis of plastics not only to produce fuels but also to reduce the waste plastics. Treatment of waste plastics by separating pyrolysis and the catalytic reforming processes in different reactors is the preferred choice for the feedstocks. The overall objective of this study is to investigate the effect of the catalytic reforming on the pyrolytic oil production of waste plastics over commercial and modified natural zeolites in order to utilize the oil in a diesel engine.

There were significant influences of the reforming temperature and WHSV on the products yields for both HDPE and PS when utilizing Y-Zeolite catalyst. The maximum oil production for HDPE (70.0wt%) and PS (88.1wt%) were obtained at the pyrolysis temperature of 450°C and 400°C respectively and at the same reforming temperature of 450°C and WHSV of 4. The gasoline fraction is the highest yield since the higher activity of Y-Zeolite catalyst. The gaseous fraction of C_2, C_3 and C_{4+} (>75 mol %) and valuable aromatic and branched species in the gasoline range (C_5-C_{12}) (>70 wt %) were the main components of the gaseous and liquid products for HDPE, which were attributed to the molecule structure of HDPE, as well as the relatively moderate acidity and large hole size of the Y-Zeolite catalyst. In case of PS, C_2 and C_3 gases (>65 mol %) were the main components of the gaseous product.

To reduce the catalyst cost for small scale application in developing countries, preparation, modification and performance test of natural zeolites have been investigated. The mordenite-type natural zeolites, either with the calcinations treatment (A-NZ) or the HCl treatment (H-NZ) or the nickel impregnation (Ni-NZ) could be used as efficient catalysts for the conversion of PP and PS into liquid and gaseous fuels. Natural zeolites after the HCl treatment (H-NZ) showed an increase of the surface area and the Si/Al ratio compared with that of A-NZ catalyst. The presence of nickel in Ni-NZ increased the activity of the catalyst which enhanced the cracking reaction

of pyrolysis gas. For polypropylene, the use of H-NZ catalyst increased the gasoline fraction compared with A-NZ catalyst. The presence of nickel in Ni-NZ catalyst also increased the gasoline fraction. However, it was lower than H-NZ catalyst due to a lower surface area of the catalyst. A-NZ catalyst produced higher diesel fraction than other catalysts. It was found that the gaseous products was dominated by propene in all conditions. The presence of natural zeolite catalysts increased the yield of propene, ethane and propane. For polystyrene, H-NZ catalyst produced higher diesel fraction than other catalysts. Propane and propene were the main components of gases in the presence of Ni-NZ catalyst.

The use of municipal plastic waste to produce oil has also been studied. The results show that the feedstock types strongly affect the product yields and the quality of liquid and solid products. HDPE waste produced the highest liquid fraction. The highest diesel fraction has been produced in PE bag 2 (with crushing and washing) while PE bag 1 (without crushing and washing) produced the highest gasoline fraction. Pyrolysis with natural zeolite catalyst (A-NZ) produced higher liquid products and diesel fraction compared with Y-Zeolite catalyst. However, the presence of catalysts have slight effect on the product yields. This might be due to the presence of impurities in MPW. The quality of waste plastics oil (WPO) was still lower than those of commercial diesel fuels according to the oil properties. Blending of WPO and diesel fuels will obtain better quality of oil.

The performance of diesel engine have also been studied using blends of WPO produced over A-NZ catalyst with diesel fuel under different loads. Brake thermal efficiencies are slightly higher as compared to that of diesel. The lower viscosity will make the fuel easily to be injected into the combustion chamber and will be sprayed into the combustion chamber more uniform. The NO_x emission is found to be lower by blending diesel with WPO. This is due to the decrease of the in-cylinder temperature as the effect of non-homogeneity of WPO. The concentration of HC of WPO blends is higher than that of diesel. The higher HC emission in WPO-diesel blends compared to diesel may be attributed to the reason that the fuel spray does not propagate deeper into the combustion chamber. The increased CO emission is due to incomplete combustion as the effect of reducing the in-cylinder temperature, poor mixture preparation and local rich regions.

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Mochamad Syamsiro

February, 2015

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Chapter 1

1 Introduction

1.1 Motivation of the Research

Plastics are now becoming substantial materials in modern life and have wide range of applications. Plastic consumption has been growing rapidly in the last six decades due to their ability to be simply formed, its light weight together with non-corrosive behavior. These excellent properties often make plastics more economical to use than other materials. Therefore, plastics have been used to replace the use of wood, metal, glass and rubber. The world's annual plastic consumption has increased about 20 times today compared to 1950s (UNEP, 2009). According to Association of Plastics Manufacturers (PlasticsEurope, 2013), the global plastics production in 2012 rose to 288 million tonnes, 2.8% increase compared to 2011 as shown in Fig. 1.1.

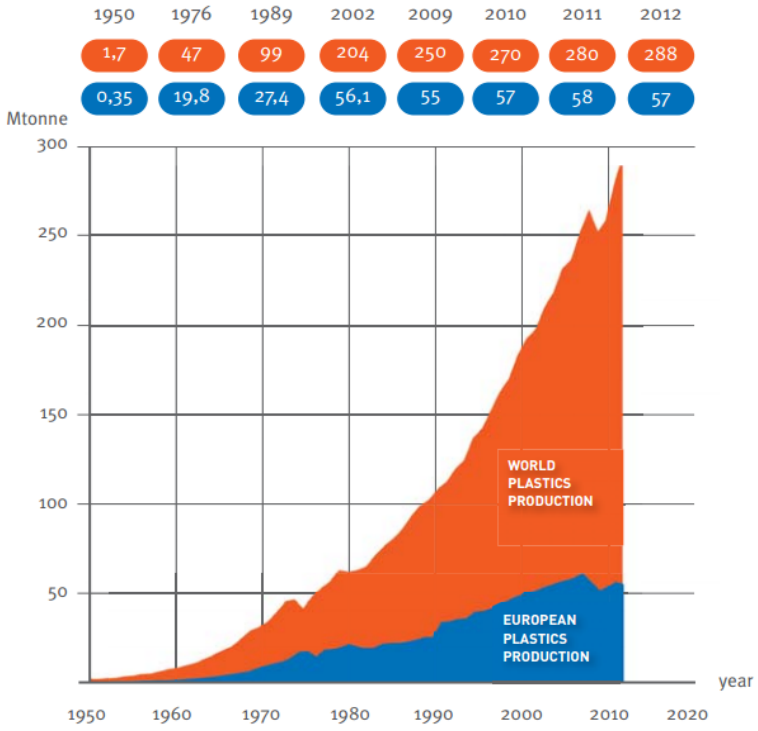

Fig. 1.1. World plastics production 1950-2012 (PlasticsEurope, 2013)

Plastics are polymers mostly containing carbon and hydrogen and few other elements like chlorine and nitrogen. Plastics can be classified based on its chemical structure, synthesis process, density and other properties. In order to facilitate waste plastics recycling, Society of Plastic Industry (SPI) has introduced the Resin Identifica-

tion Code (RIC) system since 1988 and began work with ASTM International to develop a new standard in 2008 (Industry, 2014; SPI, 2014). The code was developed to meet recyclers need while providing manufacturers a consistent, uniform system that could apply nationwide. The majority of plastics are made with one of six resins i.e. polyethylene terepthalate (PET), high density polyethylene (HDPE), polyvinyl chloride (PVC or vinyl), low density polyethylene (LDPE), polypropylene (PP) and polystyrene (PS). The RIC assigns each of these resins a number from 1 to 6. The coding system also includes a seventh code identified as "other". The above seven codes of plastics are marked on various plastic products as shown in Fig. 1.2.

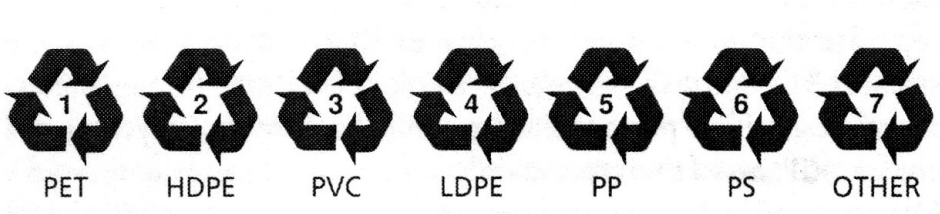

Fig. 1.2. Marks of the seven codes of plastics on various plastic products.

A significant growth of the plastic consumption and production has resulted in an increased generation of plastic wastes. Thus, plastic wastes have become a major stream in solid waste and caused significant environmental problems for nations worldwide. According to the United States Environmental Protection Agency (EPA, 2013), plastics contributed 12.7% to the total municipal solid waste (MSW) generated in the United States as shown in Fig. 1.3. In Asian countries, MSW composition strongly depends on the level of the economy which can be seen from Gross Domestic Product (GDP) for each country. For example, Japan as a developed country, plastics contributed 20% to the total MSW, while Indonesia as developing country, plastics contributed only 10% to the total MSW (Borongan and Okumura, 2010).

Disposing of plastic wastes by landfilling is not a suitable option due to slow degradation rates. The use of incineration technology has caused environmental problems since it generates several pollutants to the atmosphere. To minimize the environmental impact and to reduce damages caused by plastic wastes, they must be recycled and recovered.

Recycling of waste plastics can be divided into further important categories, such as mechanical recycling, feedstock recycling and energy recovery (Al-Salem et al.,

2009). Mechanical recycling is the process of recovering waste plastics for the re-use in manufacturing plastic product via mechanical means. This method can only be performed on single-polymer plastic. The contaminated waste plastics is difficult to recycle using this method. Feedstock recycling refers to advanced technology processes which converts plastic materials into smaller molecules, usually liquids or gases, to produce fuels or chemicals. Energy recovery is burning waste plastics to produce energy in the form of heat, steam and electricity.

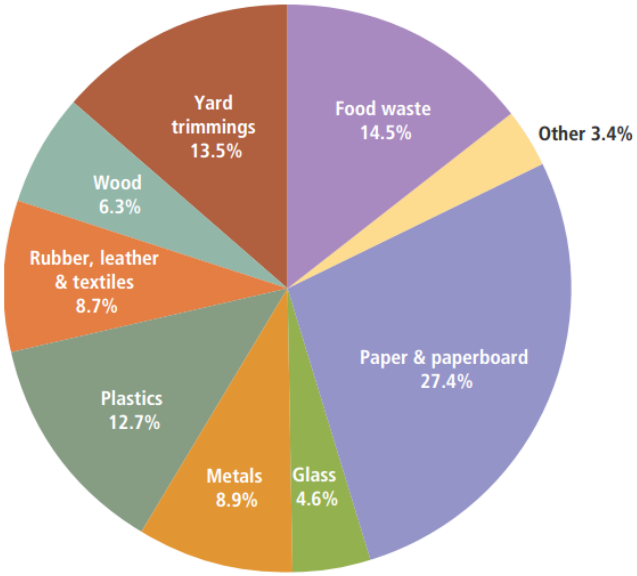

Fig. 1.3. MSW composition in the United States in 2012 (EPA, 2013)

Plastic materials possess a very high calorific value since they are derived from crude oil. Table 1.1 illustrates the calorific value of plastic materials compared with common fuels. At the same time, the world oil consumption grew very fast in recent years, while oil reserves have declined in several countries like Indonesia. Therefore, producing fuels such as diesel, kerosene and gasoline by using feedstock recycling is a very promising method to recycle waste plastics due to the vast amount of plastics that cannot be economically recovered by conventional mechanical recycling processes. Feedstock or chemical recycling is an alternative method which involves pyrolysis of plastics not only to produce fuels but also to reduce the waste plastics.

Feedstock recycling is virtually a thermal degradation method namely pyrolysis by which the long alkyl chains of polymers are broken into a mixture of lighter hydrocarbons. This is one of the prospective ways to utilize waste polymers (Ballice and

Reimert, 2002; Lee et al., 2002; Wong and Lam, 2002). Recently there are three degradation methods commonly developed by researchers, which are thermal degradation or pyrolysis, catalytic pyrolysis and combination of pyrolysis and the catalytic reforming.

Table 1.1. Calorific value of some major plastics compared with common fuels (Al-Salem et al., 2009)

Item	Calorific value (MJ kg^{-1})
Polyethylene	43.3-46.5
Polypropylene	46.50
Polystyrene	41.90
Kerosene	46.50
Gas oil	45.20
Heavy oil	42.50
Petroleum	42.30

1.2 Pyrolysis of Waste Plastics

Pyrolysis or thermal cracking involves the degradation of the polymeric materials at elevated temperatures in the absence of oxygen. The process is usually conducted at temperatures between 500-800^{o}C (Aguado et al., 2007). It involves the simultaneous change of the chemical composition and the physical phase and is irreversible. These pyrolytic products can be divided into a noncondensable gas fraction, a liquid fraction and solid residues (Buekens and Huang, 1998). Waste plastics can be decomposed as a single feedstock or mixed with other materials such as coal and biomass (Ishaq et al., 2006).

During pyrolysis, the macromolecular structures of waste plastics are broken down into smaller molecules, resulting in a wide range of hydrocarbons being formed. The thermal degradation of plastics may involve three different decomposition pathways (Aguado and Serrano, 1999) : (i) the random scission at any point in the polymer backbone leading to the formation of smaller polymeric fragments as primary products, (ii) the end-chain scission, where small molecules and long-chain polymeric fragments are formed, (iii) the abstraction of functional substituents to form small molecules. These different mechanisms are related to the bond dissociation energies, the chain defects of the polymers, and the degree of aromacity, as well as the presence of halogen and other heteroatoms in the polymer chains (Xingzhong, 2006).

In many cases, several of these pathways occur simultaneously. For instances, polyethylene and polypropylene are thermally degraded by both random and end-chain scissions. The type of the plastic feedstock for pyrolysis processes has a direct correlation on the quality of fuel products, especially the carbon atom distribution, the flash point, the cetane index and the low-temperature properties. Each polymer has different chemical structures and different reaction mechanisms. According to Plastic Waste Management Institute, Japanese waste plastics consist mainly of PE, PP and PS which contributed more than 60% to the total waste plastics (PWMI, 2014). Fig. 1.4 shows the different molecular structures of PE, PP and PS.

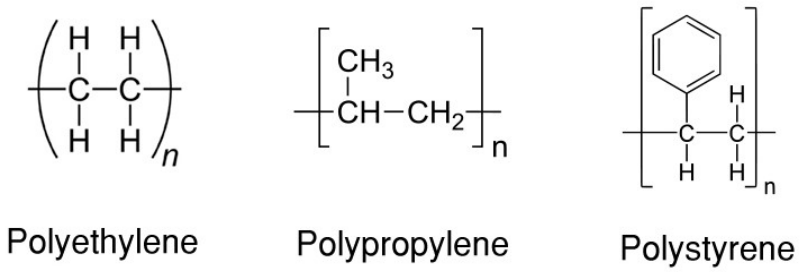

Fig. 1.4. The molecular structures of PE, PP and PS

PE is the major polymer present in waste plastics. Both low density and high density polyethylene are found in large quantities in waste plastics. PE is synthesized by the polyaddition of ethylene molecules, which leads to different types of PE depending on the reaction conditions. PP is synthesized by polymerization of propylene, which may result in two main types of PP. The liquid products of the pyrolysis of PP contain primarily olefins that resemble the molecular skeleton of PP. Compared with PE, PP produces less coke residue and more liquid products, but with a higher content of "lights" (Scheirs, 2006). PS is produced by the styrene monomer polymerization, which leads to an amorphous, non-flexible polymer having good electrical insulation properties. PS will depolymerise in a pyrolysis process to give predominantly styrene monomer, a liquid fuel with good energy content.

In addition, the quantity and quality of products in the thermal degradation process are also affected by several parameters, such as the type of a reactor, the temperature in a reactor and the residence time (Conesa et al., 1994; Miskolczi et al., 2004; Wallis and Bhatia, 2007). The thermal decomposition of plastic materials is an endothermic process,

thus, at least the dissociation energy of the C-C bond in the chain must be supplied to break down the plastics. Fig. 1.5 shows a direct relationship between dissociation energy and the decomposition temperature for different plastic materials (Aguado and Serrano, 1999). PE has higher decomposition temperature than PP and PS due to different molecular structures of each plastic as mentioned above.

The effects of the temperature in a reactor, the residence time of mixture of plastic wastes have been analyzed and showed that the yields of volatile products increased with the increase of both the residence time and the temperature in the case of each mixture of polymers. It could be caused by the differences in the thermal stability of polymer chains. The yield increasing effect of the residence time is due likewise to the thermal stability of C-C bonds. At the residence time of 1.2h, the melted polymer stayed longer under the thermal degradation conditions, therefore resulting in higher liquid and gas yields (Miskolczi et al., 2004).

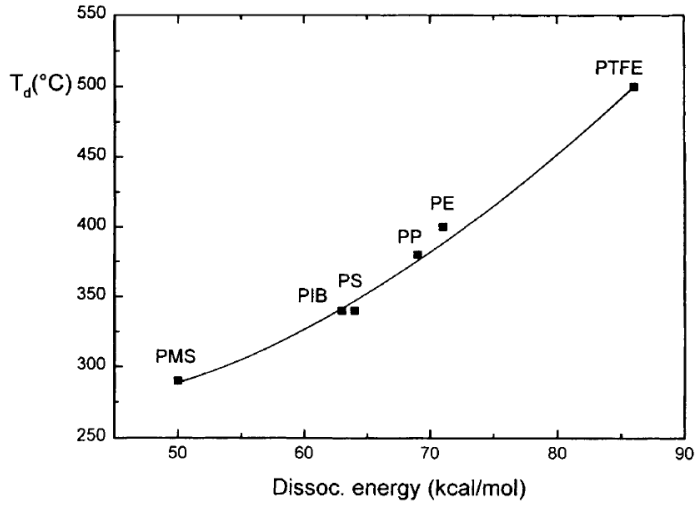

Fig. 1.5. Relationship between the dissociation energy of the C-C chain bonds and the decomposition temperature for different plastic materials (Aguado and Serrano, 1999).

However, the thermal degradation of plastics has a major drawback such as very broad product range and requirement of high temperature. These facts strongly limit their applicability and especially increase the cost of feedstock recycling for waste plastic treatment (Lin et al., 2010). The catalytic degradation therefore provides a means to address these problems. The use of catalyst is expected to reduce the reaction temperature, to promote decomposition reactions, and to improve the quality of the products.

1.3 Catalytic Pyrolysis of Waste Plastics

The catalyst plays an important role in a pyrolysis process. Pyrolysis in the presence of catalyst requires less energy than a noncatalytic process and results in the formation of more branched hydrocarbons. The catalyst also reduces the pyrolysis initiation reaction time and improves the output quality and quantity of the product. The comparison of the thermal and the catalytic degradation of plastics have been investigated by researchers using several catalysts such as silica alumina, fluid catalytic cracking (FCC) catalyst, HY zeolite, etc (Lee, 2009; Uddin et al., 1997; Walendziewski and Steininger, 2001). Both homogeneous and heterogeneous catalysts have been used for studying the catalytic cracking of plastics. In general, heterogeneous catalysts are the preferred choice due to their easy separation and recovery from the reacting medium (Aguado, Serrano & Escola, 2006).

The advantages of catalytic cracking process compared with simple thermal degradation process are summarized as follows :

- lowering the reaction temperature, which leads to a decrease of the energy consumed in the process
- the cracking reaction proceed faster, bringing about shorter residence times and lower reactor volumes
- selectivity may be tailored towards different valuable products by a judicious choice of both the catalyst and the process conditions
- in the case of polyolefins, the products derived from the catalytic cracking contain mainly cyclic, branched and aromatic hydrocarbons, which increase the quality of the potential fuels
- inhibiton of the formation of undesired products such as chlorinated hydrocarbons which is a feature especially interesting in the presence of PVC

A wide variety of heterogeneous catalysts have been tested by researchers for the catalytic cracking of polyolefins and polystyrene which summarized as follows (Aguado et al., 2006):

- Conventional solid acid catalyst : zeolites, silica alumina, FCC catalyst.
- 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
- Basic oxides : BaO, K_2O

The mechanism of the catalytic pyrolysis of waste plastics was proposed by Buekens using PE as an example which is described as follows (Buekens and Huang, 1998) :

- *Initiation* may occur on some defect sites of the polymer chains.
- *Depropagation.* The molecular weight of the main polymer chains may be reduced through successive attack by acidic sites or other carbonium ions and chain cleavage, yielding an oligomer fraction.
- *Isomerization.* The carbonium ion intermediates can undergo rearrangement by hydrogen or carbon atom shifts, leading to a double bond isomerisation of an olefin.
- *Aromatization.* Some carbonium ion intermediates can undergo cyclization reactions.

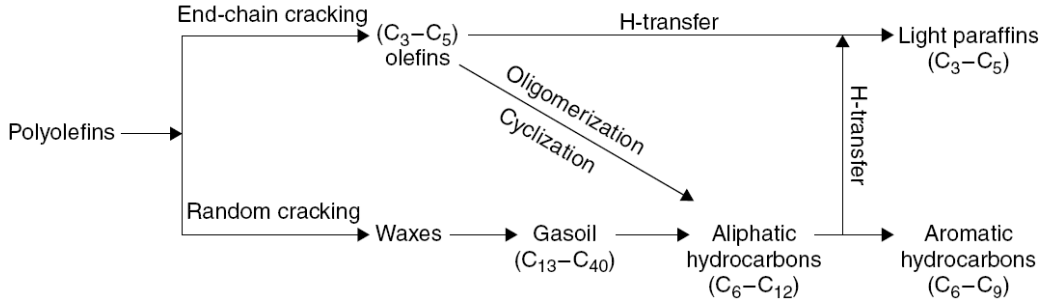

Fig. 1.6. Mechanism of the catalytic pyrolysis of polyolefins over acid solid catalysts (Aguado et al., 2006)

Products obtained in the catalytic pyrolysis of plastic materials depend on several variables. The possible products derived from pyrolysis of polyolefin plastic wastes mixture over acid solid catalysts are presented in the mechanism shown in Fig. 1.6. The pyrolysis proceeds mainly by either random (medium or weak acidity) or end-chain scission (strong acidity) giving rise to waxes and middle distillates (gasoil, gasoline) or light hydrocarbons (C_3-C_5 olefins), respectively.

However, the direct catalytic cracking of plastic wastes suffers from a number of drawbacks which have prevented its commercial success. The first relates to difficulty to recover the catalyst after use, which increases the operational cost. Furthermore, direct contact with plastic wastes will make catalyst deactivate rapidly due to the deposition of carbonaceous matter and the poisoning effect of extraneous elements and impurities such as chlorine, sulfur and nitrogen containing species that may be present in the plastic wastes (Aguado et al., 2007). Therefore, separation of the catalytic reforming reaction from the pyrolysis stage can be applied to overcome these problems.

1.4 Sequential Pyrolysis and Catalytic Reforming of Waste Plastics

Treatment of waste plastics by separating pyrolysis and the catalytic reforming processes in different reactors is the preferred choice for the feedstock containing a high proportion of components that may affect negatively the catalyst performance. This method has been tested by Bagri and Williams (Bagri and Williams, 2002; Williams and Bagri, 2004) for polyethylene and polystyrene using zeolite-Y and ZSM-5 catalysts. The use of other catalysts such as silica alumina and Al-MCM-41 have also been investigated by others (San Miguel et al., 2009; Wang and Wang, 2011). Preliminary assessment of plastic wastes valorization by using this method has been studied by Iribarren et al. (Iribarren et al., 2012). From a combined energy and environmental perspective, the results suggested the suitability of this system for plastic waste valorization. The energy performance of this system was deemed appropriate, based on the calculated cumulative energy demand and the net energy ratio values.

This method has also been developed in Yoshikawa Laboratory, Tokyo Institute of Technology, Japan as presented in Fig. 1.7. The main product of this system is liquid fuel with some additional products such as gaseous and solid fuels. This system consists of two reactors for pyrolysis and the catalytic reforming processes. The pyrolysis gas produced from a pyrolyzer will be sent to the catalytic reformer for further cracking reaction using catalysts to convert the pyrolysis gas into shorter chain hydrocarbons. The cracked gases will then condensed in a condenser to obtained liquid fuel. A non-condensable gas will be gaseous products which can also be used as a fuel. This gaseous fuel can be used either as a single fuel for gas engines or used together with diesel fuel

in dual fuel diesel engines. In a pyrolysis reactor, some solid residues will be left at the bottom of the reactor. This residues still have high calorific value which can be used as solid fuel for co-combustion with coal or biomass.

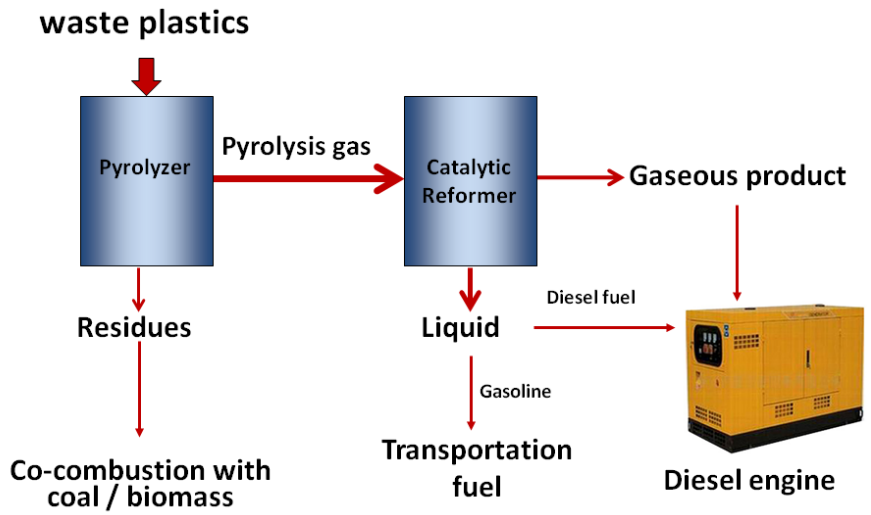

Fig. 1.7. A schematic diagram of the conversion system for waste plastics into fuels developed at Tokyo Institute of Technology

However, the use of catalysts is the main cost burden for recycling of plastic wastes by pyrolysis. Reducing the catalyst cost for small scale application in developing countries like Indonesia is very interesting challenges. Natural zeolites which can be found in many places worldwide including Indonesia might be used as a candidate for this purpose instead of the commercial catalysts. However, natural zeolites can not be used directly as a catalyst without pretreatment because the catalytic properties are not as good as commercial catalysts. Some preparation and modification can be done to natural zeolites such as calcination, acid and alkali treatment and metal impregnation (Cakicioglu-Ozkan and Ulku, 2005) to improve the properties and to enhance the catalytic performance of the catalyst.

Natural zeolite is naturally occurring zeolites which is formed from volcanic ash or other pyroclastics, by the reaction of the amorphous alumosilicate glass with pervading pore water (Chmielewska et al., 2002). More than 50 natural zeolites are discovered such as clinoptilolite, mordenite, chabazite, heulandites, etc. Natural zeolites found in Indonesia can be classified as mordenite type zeolite. The catalytic cracking of plastic

materials using natural zeolite catalysts have been investigated by several researchers (Fernandes et al., 1999; Hwang et al., 2002; Jeong et al., 2001; Lee et al., 2001; Park et al., 1999).

However, most of the research works have been done by the direct catalytic cracking which put the catalyst and plastic materials in the same reactor. Therefore, the use of modified natural zeolites in the sequential pyrolysis and catalytic reforming will be promising application. In addition, most of the researches have been done using clinoptilolite and chabazite zeolites which are different type with mordenite which is found in Indonesia. Furthermore, the researches have been done in laboratory scale using pure plastic materials. In our proposed research, mordenite type natural zeolite will be used as a catalyst in the sequential pyrolysis and catalytic reforming system in laboratory scale and pilot scale utilizing real waste plastics collected from disposal site in Indonesia.

Table 1.2. The change of properties of products (Miskolczi, 2006)

Property	**Presence of catalysts**	**Increasing temperature**
Density	⇓	⇓
Viscosity	⇓	⇓
Research Octane Number (RON)	⇑	⇑
Motor Octane Number (MON)	⇑	⇑
Cetane number	⇑	-
Pour point	⇓	-

In order to utilize the oil produced by pyrolysis of waste plastics, some parameters of the oil quality will be required to ensure the performance of the oil in engine. Therefore, the determination of the practical properties such as the density, the viscosity, the cetane number, the pour point of products obtained by pyrolysis of waste plastics is important. The change of some main properties of products is presented in Table 1.2.

1.5 Objective of the Study

The overall objective of this study is to investigate the effect of the catalytic reforming on the pyrolytic oil production of waste plastics over commercial and modified natural zeolites in order to utilize the oil in a diesel engine.

1.6 Thesis Contents and Chapter Outlines

The contents of this thesis have been divided into six chapters as follows :

Chapter 1: Introduction

In the first chapter, the discussion of plastics consumption and production as well as waste plastics generation and the method of waste plastics recycling have been presented. The energy potential of waste plastics has also been discussed in relation to converting waste plastics into fuels. Moreover, feedstock recycling of waste plastics which involves pyrolysis process has been discussed. The study on pyrolysis, the catalytic pyrolysis and the sequential pyrolysis and catalytic reforming of plastic materials are briefly reviewed to understand the mechanisms and characteristics of each system. The use of natural zeolite catalysts are also reviewed. The parameter of the oil quality for application in a diesel engine such as the cetane number, the viscosity, and the pour point have also been reviewed in order to study the quality of waste plastic oil.

Chapter 2: Pyrolytic oil production from plastic materials using a commercial catalyst

The sequential pyrolysis and catalytic reforming of plastic materials has been investigated in this chapter to produce liquid, gaseous and solid fuels over the Y-Zeolite catalyst. The fixed bed reactor was used as the pyrolysis reactor under the atmospheric pressure. High density polyethylene (HDPE) and polystyrene (PS) have been used as feedstock. The effect of the reforming temperature and the weight hourly space velocity (WHSV) on the product yields, the liquid characteristics and the gaseous composition have been investigated for both HDPE and PS samples.

Chapter 3: Pyrolytic oil production from plastic materials using a modified natural zeolite catalyst

In this chapter, modified natural zeolite catalysts obtained from Indonesia have been used for the catalytic reforming of polypropylene (PP) and polystyrene (PS). The natural zeolites have been prepared and modified by using the acid treatment and the metal impregnation. Pyrolysis and the catalytic reforming experiments were carried out using semi-batch two-stage reactors.

Chapter 4: Pyrolytic oil production from municipal plastic wastes in a pilot scale reactor

In chapter 4, the sequential pyrolysis and catalytic reforming of municipal plastic wastes (MPW) over Y-Zeolite and Indonesian natural zeolite catalysts have been investigated. The feedstock used for these experiments were three kinds of municipal plastic wastes, i.e. polyethylene bag with (PE bag 2) and without (PE bag 1) crushing and washing, and high density polyethylene (HDPE) waste after crushing and washing. They were obtained from the final disposal site and a small plastic recycling company in Yogyakarta city, Indonesia.

Chapter 5: Performance and emission analysis of blends of waste plastic oil and diesel fuel in a diesel engine

In this chapter, the performance and emission analysis of blends of waste plastic oil (WPO) and diesel fuel in a diesel engine have been investigated. WPO-diesel fuel blends of 10% and 20% WPO mixing ratio were used to test in the engine. The performance of diesel engine included the thermal efficiency and the specific fuel consumption while the emission included carbon monoxide, unburned hydrocarbon, nitrogen oxides and smoke opacity.

Chapter 6: Conclusions and Recommendations

In this chapter, major results and findings of the study are summarized. The recommendations for further research works are also presented in this chapter.

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Chapter 2

2 Pyrolytic Oil Production from Plastic Materials Using a Commercial Catalyst

Abstract

This chapter deals with the potential of using the sequential pyrolysis and catalytic reforming process for the conversion of plastics materials i.e. polyethylene and polystyrene into liquid and gaseous fuels using a commercial catalyst (Y-Zeolite) for the catalytic reforming of pyrolysis gas generated in a pyrolyzer. The effect of the reforming temperature and the weight hourly space velocity (WHSV) on the product yields, liquid and gaseous compositions have been investigated for each feedstock. The experiments were carried out at the pyrolysis temperature of 450°C, the reforming temperature of 400, 450, and 500°C and WHSV of 2, 3, and 4 g-sample g-catalyst^{-1} h^{-1}. The results show that increasing the reforming temperature and decreasing WHSV have resulted in an increase of gaseous and solid products while the liquid product decreased. The maximum oil production for high density polyethylene (HDPE) (70.0wt%) and polystyrene (PS) (88.1wt%) were obtained at the pyrolysis temperature of 450°C and 400°C respectively and at the same reforming temperature of 450°C and WHSV of 4. The gasoline fraction is the highest yield since the higher activity of Y-Zeolite catalyst. The C_2, C_3 and C_{4+} gases (>75 mol %) were the main components of the gaseous and liquid products for HDPE. In the case of PS, the C_2 and C_3 gases (>65 mol %) were the main components of the gaseous product. The residues also produced high calorific value solid products that can be utilized as a fuel as well.

2.1 Introduction

Plastics are substantial materials that stand for modern society. These materials are comodities among other products that have caused the rapid and huge development of the consumer society. Furthermore, plastics are materials which have lower energy consumption in their manufacturing compared with glass, steel, ceramics. However, plastic materials also have some drawbacks. They are nonbiodegradable materials which bring about environmental problems. There are about 288 million tonnes of plastics produced worldwide in 2012 and the amount of resulting plastic wastes is therefore an enormous quantity (PlasticsEurope, 2013). Thus, plastic wastes have become a major stream in solid waste and caused significant environmental problems for nations worldwide.

Waste plastics are normally landfilled or incinerated, however, both treatment methods have their respective negative environmental consequences. To overcome the negative impact of those treatments, waste plastics must be recycled and recovered. Feedstock recycling which converts waste plastics into fuels or chemicals is one of the emerging treatment option both for treating waste plastics and producing fuels. This method has become very promising technology since plastics have a high calorific value of more than 40 MJ/kg which is similar to those of common liquid fuels such as gasoline, diesel, kerosene, etc (Al-Salem et al., 2009).

Pyrolysis is the thermal degradation of the polymeric materials by heating in the absence of oxygen at elevated temperatures. The products of pyrolysis process can be divided into a gas fraction, a liquid fraction and solid residues (Buekens and Huang, 1998). Waste plastics can be decomposed as a single feedstock or mixed with other materials such as coal and biomass (Ishaq et al., 2006). Co-pyrolysis of plastic and coal has indicated that there was significant synergistic effect between plastic and coal, especially in the high temperature region (Zhou et al., 2009).

Nevertheless, the thermal degradation of waste plastics has some demerits which strongly limit their applicability and especially increase the cost of feedstock recycling such as very broad product range and requirement of high temperature (Lin et al., 2010). Therefore, the catalytic pyrolysis provides a means to address these problems since the use of catalyst is expected to reduce the reaction temperature, to promote decomposition reactions, and to improve the quality of the products. The catalytic degradation of waste

plastics has been investigated extensively by many researchers using Y zeolite, ZSM-5, mordenite, FCC catalyst and silica alumina (Lin and Yang, 2009; Mikulec and Vrbova, 2008; Seo et al., 2003; Wang and Wang, 2011). However, direct catalytic cracking of waste plastics has several drawbacks related to difficulty to recover the catalyst after use and rapid deactivation due to the impurities such as chlorine, sulfur and nitrogen containing species that may be present in the waste plastics (Aguado et al., 2007). Therefore, separation of the catalytic reforming reaction from the pyrolysis stage must be applied to overcome these problems.

The sequential pyrolysis and catalytic reforming (SPCR) system has been investigated by several researchers for some plastic materials using Y zeolite, silica alumina, Al-MCM-41 and ZSM-5 catalysts (Aguado et al., 2007; Bagri and Williams, 2002; San Miguel et al., 2009; Wang and Wang, 2011; Williams and Bagri, 2004). Preliminary assessment of plastic wastes valorization by using this method has also been studied to assess the environmental and energy performance of the SPCR system using a life cycle assessment approach (Iribarren et al., 2012). The result showed that the energy performance of this system was deemed appropriate, based on the calculated cumulative energy demand (CED) and the net energy ratio (NER) values. The environmental performance of the SPCR system was also found to be appropriate, although improvement actions aimed at minimizing both the thermal energy demand and direct emissions to the air should be taken into consideration.

The Y-Zeolite catalyst has been studied by Bagri and Williams (Bagri and Williams, 2002; Williams and Bagri, 2004). However, the Y-Zeolite used in their experiments has different properties such as lower surface area and different binder material. They also studied only the effect of the reforming temperature. In this chapter, we investigated not only the effect of the reforming temperature but also the effect of the catalyst loading on the liquid and gaseous products characteristics.

In this chapter, the sequential pyrolysis and catalytic reforming (SPCR) of plastic materials has been proposed to produce liquid and gaseous fuels over the Y-Zeolite catalyst. The fixed bed reactor was used as the pyrolysis reactor under the atmospheric pressure. Our proposed system will utilize all of products as fuels including liquid, gaseous and solid products as shown in Fig. 1.7. This novel system will utilize diesel fuel and gaseous products together with fueling a dual-fuel diesel engine to generate

electricity. This power can be utilized for supplying the electricity to the plant itself and the excess power will be sent to outside of the plant. The solid products will also be investigated in terms of the energy content to assess the feasibility as a fuel for co-combustion with coal and biomass.

2.2 Materials and Methods

2.2.1 Materials

The feedstocks used in these experiments were high density polyethylene (HDPE) and polystyrene (PS) granules manufactured by Tosoh Co. in Japan. The catalyst employed in this study was commercial pelletized Y-Zeolite (CBV 780 CY) obtained from the Zeolyst International as shown in Fig. 2.1. The Y-Zeolite has SiO_2/Al_2O_3 mole ratio of 80, the unit cell size of 24.24 Å and the surface area of 780 m^2/g in the powder form. The diameter of the pellet was 1.6 mm which contained 20% of aluminum oxide.

Fig. 2.1. The photographs of feedstock samples (HDPE and PS) and Y-Zeolite catalyst.

2.2.2 Experimental Procedure

A schematic diagram of the experimental apparatus is shown in Fig. 2.2. The apparatus was composed of a feeder, a pyrolyzer, a packed-bed catalytic reformer, a condenser, an oil collector and gas scrubbing bottles. The pyrolyzer and the reformer were made of stainless steel (SUS316) and covered with electric heaters. The pyrolyzer's inner diameter and height are 30 mm and 280 mm, respectively. The reformer's inner diameter and height are 45 mm and 550 mm, respectively. The reaction temperatures in both the pyrolyzer and the reformer were controlled with K-type thermocouples

and heaters. A double-tube condenser was installed at the outlet of the reformer to separate gas and liquid products. The gas scrubbing bottles were installed after the condenser and isopropanol was used as the scrubbing absorbent to remove some light tar in the gaseous products.

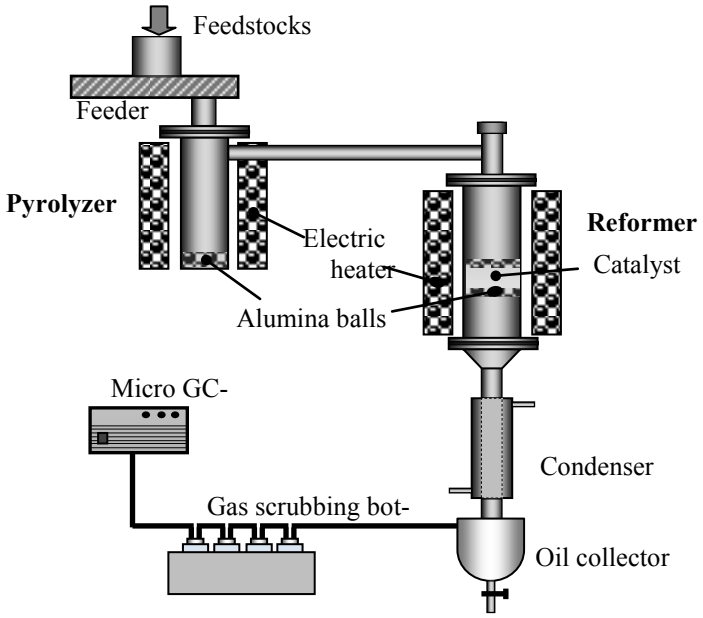

Fig. 2.2. A schematic diagram of the experimental apparatus

In these experiments, after the pyrolyzer and the reformer heated up to the preset temperatures and air in the reactors was replaced with N_2 carrier gas, plastic granules were fed into the pyrolyzer at the feeding rate of 1 g min^{-1}. The feeding time of each experiment was 2 hours. The N_2 carrier gas flow rate was 1 L min^{-1} controlled by using a mass flow controller (Model CR-300, KOJIMA Instruments Inc. Kyoto, Japan). The catalyst was loaded into the reformer with the weight hourly space velocity (WHSV) range of 2, 3 and 4 g-sample g-$catalyst^{-1}$ h^{-1}. The calculation of WHSV is based on the equation below (Park et al., 2010) :

$$WHSV = \frac{60\,x\,G}{W_{cat}} \tag{2.1}$$

where G = sample feed rate, g min^{-1}; and W_{cat} = weight of catalyst filled in the reformer, g.

The first experiments were carried out at the pyrolyzer temperature of 450°C, WHSV of 4 g-sample g-$catalyst^{-1}$ h^{-1} and the reformer temperature of 400, 450, and 500°C. The second experiments were conducted at the pyrolyzer temperature of 450°C, the reformer temperature of 450°C and WHSV of 2, 3, and 4 g-sample g-$catalyst^{-1}$ h^{-1}.

The gaseous and liquid products generated in the reformer were separated in the condenser and the liquid product was collected into the oil collector. The gas compositions were measured with a gas chromatograph equipped with a thermal conductivity detector (GC-TCD, Agilent Technologies Inc. USA).

2.2.3 Analytical Methods

The liquid product were analyzed by a gas chromatograph coupled with a mass spectrometer (GC-MS) (Agilent 6890N GC-MSD 5973N). The purpose of this analysis is to determine the carbon atom number distribution and the hydrocarbon type of the liquid products. The column was an HP5 (5% Ph-Me-Siloxane) capillary column, 30m length with 0.25mm diameter and 0.25 μm film thickness. Helium was used as the carrier gas. The temperature program used was, initial temperature of 30 ℃ for 5 minutes followed by the heating rate of 2 °C /min to 200 °C and then held at 200°C for 5 minutes followed by the heating rate of 5°C min^{-1} to 300 °C and held at 300°C for 10 minutes.

The composition of gases produced in the experiments was monitored by the GC-TCD at every 6 minutes. Gas yields were calculated from Eqs. (2.2)-(2.4) as follows (Park et al., 2010) :

$$\mathrm{F_{T,out}} = F_{N_2,in} \times \frac{C_{N_2,in}}{C_{N_2,out}} \tag{2.2}$$

$$\mathrm{F_{i,out}} = F_{T,out} \times C_{i,out} \tag{2.3}$$

$$\mathrm{Y_i} = \frac{F_{i,out}}{G} \times \frac{1}{22.4} \tag{2.4}$$

where $C_{i,\,out}$ =gas *i* concentration in the outlet gas ; $C_{N2,in}$=N_2 concentration in the carrier gas ; $C_{N2,out}$=N_2 concentration in the outlet gas; $F_{i,out}$ = gas flow rate of *i* at the outlet, Nl min^{-1}; $F_{N2,in}$ =carrier gas flow rate (at the inlet), Nl min^{-1} ; and $F_{T,out}$ = total gas flow rate at the outlet, Nl min^{-1}.

After finishing the experiments, a small amount of solid residue was remained in the reactor. The coke formation also occurred in the catalyst. The weight difference of the catalyst before and after the experiment was defined as the weight of coke. The

weight of solid residue was calculated by the difference between the total feedstock weight and liquid, gaseous and coke weights.

The proximate and ultimate analysis were conducted for solid residue samples. The higher heating value (HHV) has been calculated using a modified Dulong`s formula as a function of the carbon, hydrogen, oxygen and nitrogen contents as follows (Demirbas, 2010) :

$$HHV\ (MJ/kg) = 0.335\ C + 1.423\ H - 0.154\ O - 0.145\ N \quad (2.5)$$

where C is the carbon content (wt.%), H is the hydrogen content (wt.%), O is the oxygen content (wt.%), and N is the nitrogen content (wt.%).

2.3 Results and Discussions

The results obtained from the experimental investigation on the pyrolysis and catalytic reforming of HDPE and PS are presented and discussed in this section. The results focused on the effect of the reforming temperature and WHSV on the product yields, oil characteristics and gas composition for each feedstock.

2.3.1 Pyrolysis and Catalytic Reforming of High Density Polyethylene

2.3.1.1 Effect of the Reforming Temperature

The effect of the reforming temperature on the product yields from the pyrolysis and catalytic reforming of HDPE is shown in Fig. 2.3. It can be seen that the increase of the reforming temperature increased the yield of gaseous and coke products, whereas the yield of liquid products was decreased. The higher temperature led to the enhancement of the activity of the Y-Zeolite catalyst and then cracked some relatively large-molecular liquid products into small molecular gaseous products. The increase of the coke was mainly originated from the following reasons; on the one hand, the coking reaction was easier to occur on the surface of the Y-Zeolite at a higher reforming temperature (Neves et al., 2006). On the other hand, the Y-Zeolite catalyst has a relatively large pore size and a large supercage with its crystallite, resulting in the formation and accumulation of coke on the internal and external surfaces of the Y-Zeolite catalyst. The coke formation may not only prohibit the heat transfer and cause operating problems in the reactor, but also lower the number of active sites and the surface area of the catalyst and then lead to the increase of the operation cost (Al-Khattaf, 2002; Neves et

al., 2007). Therefore, from the viewpoint of industrial application, it is of great importance to optimize the reaction conditions and clarify the deactivation behaviors of the catalyst.

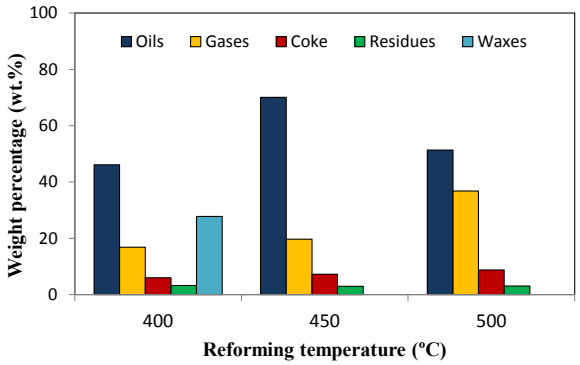

Fig. 2.3. Effect of the reforming temperature on the product yields of HDPE at the pyrolysis temperature of 450 °C and WHSV of 4 g-sample g-catalyst^{-1}h^{-1}

Furthermore, the solid wax was produced in the condenser (a kind of large molecular n-paraffin and olefin hydrocarbon mixture (C_{20}-C_{40}) and in the solid phase at the ambient temperature) at the reforming temperature of 400℃ for HDPE, which means that, at this temperature, the activity of the catalyst was not high enough and could not convert all of the pyrolysis gas into gaseous and liquid products. On the contrary, no wax formation was observed at the reforming temperature of 450 and 500°C. The thermal degradation of HDPE consists of free radical formation and hydrogen abstraction steps where wax is the main product. At the reforming temperature of 400°C, the catalyst was not active so that the product is similar to the thermal degradation process. In addition, the increase of the reforming temperature from 450 to 500°C resulted in the increase of gaseous products and the decrease of liquid products.

The liquid hydrocarbon products generated from the SPCR process were characterized by their carbon atom number distribution and hydrocarbon types which will determine their potential application as a refinery feedstock and fuel. Fig. 2.4 represents the carbon atom number distribution of the liquid products of HDPE produced by the SPCR process at the pyrolysis temperature of 450 °C, WHSV of 4 g-sample g-catalyst^{-1}h^{-1} and at different reforming temperatures from 400°C to 500 °C. The carbon atom

number distribution was classified into the gasoline fraction (C_5-C_{12}), the diesel fraction (C_{13}-C_{20}) and the heavy oil fraction (>C_{20}). It was notable that the gasoline fraction (C_5-C_{12}) was the major components of liquid products. It was due to the relatively moderate acidity and a large pore size of the Y-Zeolite catalyst as mentioned previously as well as the type and structure of polyethylene. In addition, the increase of the reforming temperature from 400 °C to 450 °C led to a marked increase in the proportion of gasoline (C_5-C_{12}), as well as an obvious reduction in the amount of heavy oil hydrocarbons (>C_{20}), which was attributed to the fact that the higher reforming temperature enhanced the activity of the Y-Zeolite catalyst and then led to intense catalytic cracking of the pyrolysis gas into smaller hydrocarbons (Aguado et al., 2007). However, when the reforming temperature increased from 450 °C to 500 °C, the change of the carbon atom number distribution of the liquid products was not significant. It could be the consequence of the coking on the catalyst surfaces at a higher temperature. The formation of coke influenced the catalyst activity by covering some of the active sites and blocking the channels which could make the inner active sites inaccessible for the reactant molecules (Miskolczi et al., 2004; Uemichi et al., 1998).

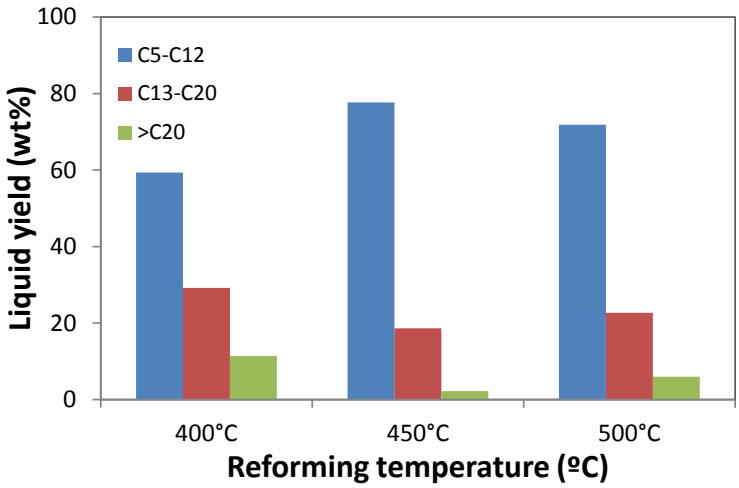

Fig. 2.4. Effect of the reforming temperature on the carbon atom number distribution of liquid products of HDPE at the pyrolysis temperature of 450 °C and WHSV of 4 g-sample g-catalyst^{-1}h^{-1}

The effect of the reforming temperature on the distribution of the hydrocarbon types of liquid products from HDPE pyrolysis can be seen in Fig. 2.5. It is well known that the thermal degradation of HDPE has been assigned to the random scission reaction which led to the formation of a large number of n-paraffin hydrocarbon species. The C-

C bond is the weakest in the HDPE structure and during the degradation process, the stabilization of the resultant radicals after the chain scission leads to the formation of carbon double bonds in the structure in addition to n-paraffin (Williams and Slaney, 2007). Consequently, the major compositions of the liquid products of HDPE thermal degradation were n-paraffin and olefins. However, in the SPCR process, because of the reforming reaction process, it was found that there was a large number of iso-paraffin, naphthene and aromatic existed in the liquid products of HDPE. The reason for this could be that most zeolites including the Y-Zeolite show an excellent catalytic effect on the cracking, the isomerization and the aromatization due to an acidic property and a micropore crystalline structure. The formation of aromatic compounds was related to both Brönsted and the Lewis sites on the catalysts, but reaction is probably more favorable on the Brönsted sites (Seo et al., 2003). In addition, during the aromatization reaction, a considerable number of hydrogen atoms are abstracted which subsequently accumulated on the catalyst surface, and then consumed in the hydrogenation of olefins. Moreover, the Y-Zeolite adsorbed polar molecules strongly, which may also lead to a possible explanation for the increase of iso-paraffins at the expense of olefins (Manos et al., 2000; Marcilla et al., 2009). Therefore, a lot of aromatics and iso-paraffins at the expense of the n-paraffins and olefins existed in the final liquid products.

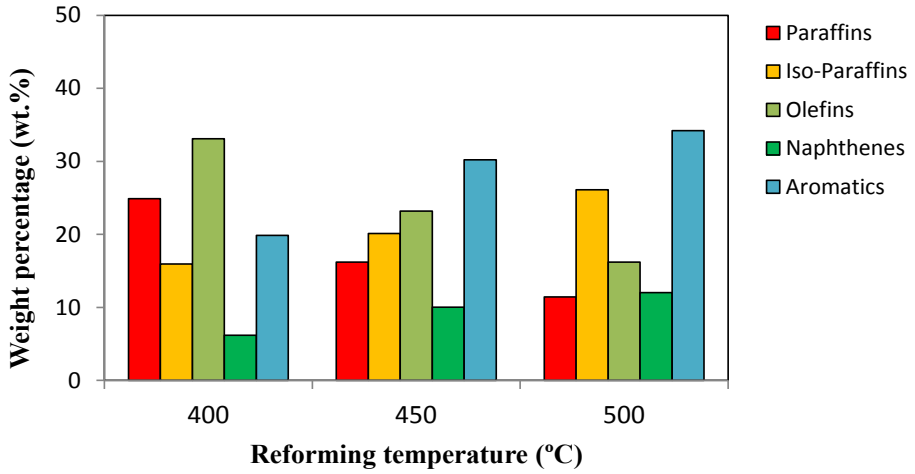

Fig. 2.5. Effect of the reforming temperature on PIONA distribution of HDPE liquid products at the pyrolysis temperature of 450℃ and WHSV of 4 g-sample g-catalyst^{-1}h^{-1}

Futhermore, Fig. 2.5 also indicated that by the increase of the reforming temperature, the proportion of aromatics, iso-paraffins and naphthenes increased while

the percentage of paraffins and olefins decreased. The reason is that, as mentioned above, the high temperature will increase the activity of the catalyst and lead to intense catalytic reforming. The reactions such as the saturation, the isomerization, the cyclization, the hydrogen transfer and the coking were at high severity (Murata et al., 2009).

The gaseous product compositions of HDPE pyrolysis as a function of the reforming temperature is shown in Fig. 2.6. The reforming temperature significantly affected the gaseous composition of the products. It was illustrated from Fig. 2.6 that with the increase of the reforming temperature, there were significant changes of the gaseous compositions of the products. As the reforming temperature increase, the mole percentage of H_2, C_1 and C_2 gases were decreased whereas C_3 and C_{4+} hydrocarbons were increased. The increase of C_3 and C_{4+} hydrocarbons were resulted from the conversion of liquid products into gaseous products. In addition, more than 80 mol% of the final gaseous products was C_2, C_3, C_{4+} hydrocarbons; which originated from the relatively moderate acidity and large pore size of the Y-Zeolite catalyst (Audisio et al., 1990; Chumbhale et al., 2005; Miskolczi et al., 2004). In large scale application, the high quality of gaseous product can be used as a fuel either for driving gas engines or for dual-fuel diesel engines. It can also be used as a heating source for the pyrolysis reactor.

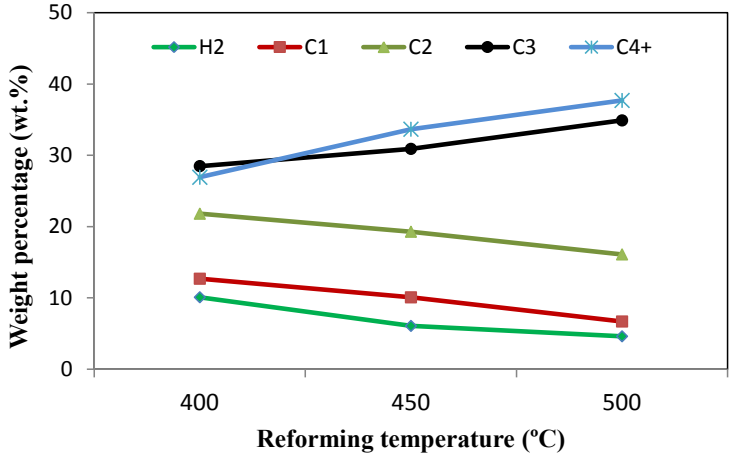

Fig. 2.6. Effect of the reforming temperature on the gaseous product composition of HDPE at the pyrolysis temperature of 450℃ and WHSV of 4 g-sample g-catalyst^{-1}h^{-1}

2.3.1.2 Effect of WHSV

In the SPCR process, another parameter affecting the products distribution is the weight hourly space velocity (WHSV). Therefore, the effect of WHSV on the products yields, as well as the composition and physicochemical properties of gaseous and liquid products of HDPE were evaluated in this section at the pyrolysis temperature of 450°C and the reforming temperature of 450°C, respectively. It can be seen from Fig. 2.7 that when both the pyrolysis temperature and the reforming temperature were fixed at 450°C, with the increase of WHSV, the fraction of gaseous products decreased whereas the liquid products increased. This is due to the fact that increasing WHSV is equal to reducing the amount of catalysts and shortening the contact time. In addition, it was found that the effect of increasing the amount of catalyst (decreasing the WHSV) on the product yields have the similar trend with that of increasing the reforming temperature.

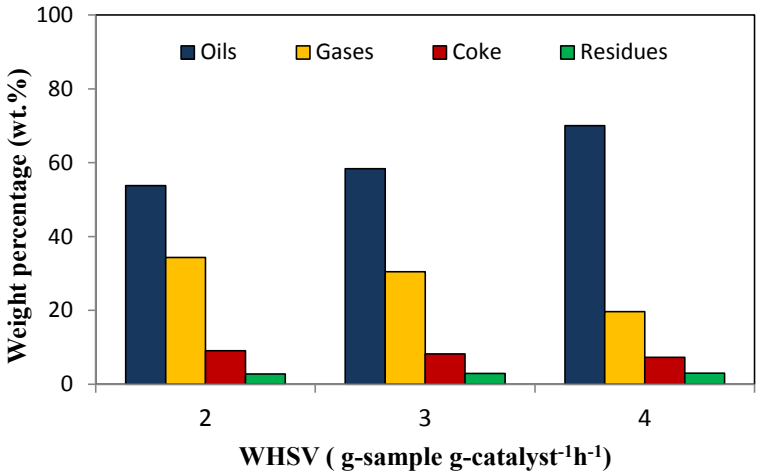

Fig. 2.7. Effect of WHSV on the product yields of HDPE at the pyrolysis temperature of 450 °C and the reforming temperature of 450 °C

The effect of WHSV on the carbon atom number distribution of HDPE liquid products was investigated at the pyrolysis temperature of 450°C and the reforming temperature of 450 °C. Fig. 2.8 indicates that the decrease of WHSV (increase of the catalyst loading) resulted in the increase of the amount of gasoline fraction. Therefore, it was found that the effect of decreasing WHSV on the product yields of HDPE has similar trend with that of increasing the reforming temperature. As mentioned above, these results were due to the increase of the catalyst loading and the contact time, which could enhance the cracking reaction of the pyrolysis gas from relatively large-molecule

hydrocarbons into small-molecule hydrocarbons. It was also observed from Fig. 2.8 that the increase of WHSV increased the amount of diesel and heavy oil fractions. However, the gasoline fraction (C_5-C_{12}) was the major component of liquid products, which is caused by the relatively moderate acidity and large pore size of the Y-Zeolite (Luo et al., 2000).

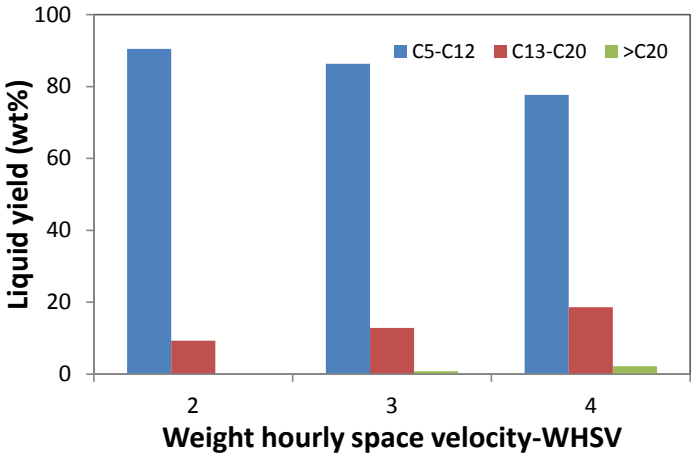

Fig. 2.8. Effect of WHSV on the carbon atom number distribution of liquid products of HDPE at the pyrolysis temperature of 450°C and the reforming temperature of 450 °C

Fig. 2.9 shows the effect of WHSV on the hydrocarbon type distribution of HDPE liquid products. The olefins, iso-paraffins and aromatics were the main type of liquid products. As discussed previously, on the one hand, the Y-Zeolite catalyst could provide a large amount of acidic sites. On the other hand, because of its special pore size, the Y-Zeolite catalyst has favorable shape selectivity for aromatic formation than non-zeolite catalyst, some intermediate carbenium ion formed by acidic zeolite would choose a pathway to aromatic formation, and some will be left over as olefin. Moreover, Fig. 2.9 also indicates that when both the pyrolysis temperature and the reforming temperature were fixed at 450 °C, the decrease of WHSV led to the increase of the percentage of iso-paraffins, naphthene and aromatic at the expense of olefins and paraffins. This is due to the fact that a lower WHSV means larger amount of catalyst and longer contact time, which could promote the overcracking and secondary reaction such as the aromatization, the isomerization, etc. It can also be seen from Fig. 2.9 that the increase of the reforming temperature and the decrease of WHSV have the similar trend on the hydrocarbon type distribution of HDPE liquid products (Luo et al., 2000).

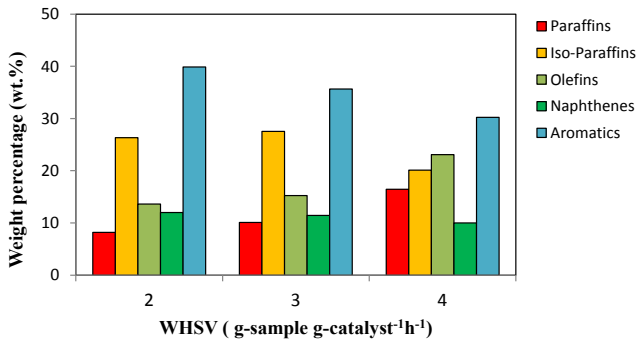

Fig. 2.9. Effect of WHSV on PIONA distribution of HDPE liquid products at the pyrolysis temperature of 450℃ and the reforming temperature of 450℃

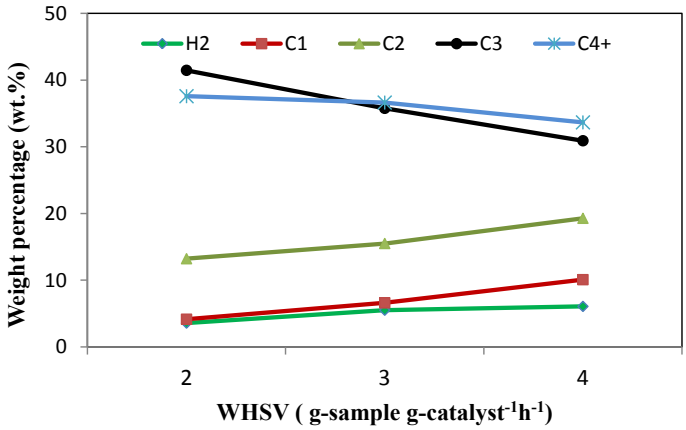

Fig. 2.10. Effect of WHSV on the gaseous product compositions of HDPE at the pyrolysis temperature of 450°C and the reforming temperature of 450 °C

The effect of WHSV on the composition of gaseous products from HDPE pyrolysis was also investigated at the pyrolysis temperature of 450°C and the reforming temperature of 450 °C. It is well known that the pore size is important for determining the size selectivity of reactants and products, which can enter and leave the active sites of the catalyst (Uemichi et al., 1998). When compared with other zeolite catalyst, such as HSZM-5, the Y-Zeolite catalyst has a relatively large pore size, which may allow a little larger molecular gaseous products to leave the Y-Zeolite catalyst. The results shown in Fig. 2.10 illustrates that with the decrease of WHSV, the proportion of H_2, C_1 and C_2 gases decreased while the percentage of C_3 and C_{4+} gases increased, which proves the fact that the Y-Zeolite catalyst has a special selectivity for C_3 and C_{4+} gases.

Therefore, the major gaseous products of the catalytic reforming of pyrolysis gas were C_3 and C_{4+} gases. When increasing the catalyst loading (lowering WHSV), the fraction of gaseous product increased and then the percentage of C_3 and C_{4+} gases increased at the expense of the H_2, C_1 and C_2 gases.

2.3.2 Pyrolysis and Catalytic Reforming of Polystyrene

2.3.2.1 Effect of the Reforming Temperature

Fig. 2.11 shows the effect of the reforming temperature on the product yields from the pyrolysis and catalytic reforming of PS. It can be seen that PS produced higher liquid products and lower gaseous products compared with HDPE. The quantity of gaseous products was very small to serve as a fuel gas either for engine or for the SPCR process. It was related to the marked differences of molecular structure of HDPE and PS. Therefore, the degradation mechanism and the thermal degradation products in the first thermal pyrolysis step are significantly different. The thermal degradation of HDPE consists of free radical formation and hydrogen abstraction steps whereas the thermal degradation of PS is a radical chain process including the initiation, the transfer and the termination steps (Kiran et al., 2000). The main composition of pyrolysis gas of HDPE flowing out from the pyrolyzer was wax while the major pyrolysis products of PS were stable aromatic components as liquid phase such as styrene, which have stable benzene ring structure and difficult to be converted into small molecular gaseous products (Liu et al., 2000; Pinto et al., 1999). Therefore, PS pyrolysis did not produce wax like in HDPE pyrolysis.

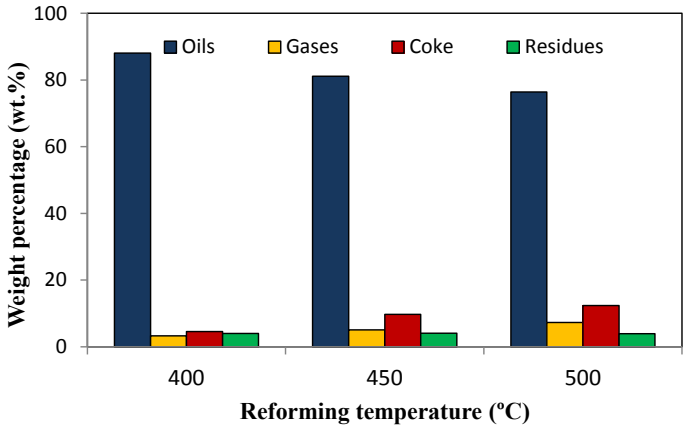

Fig. 2.11. Effect of the reforming temperature on the product yields of PS at the pyrolysis temperature of 450 °C and WHSV of 4 g-sample g-catalyst^{-1}h^{-1}

HDPE and PS also have different dissociation energy to break down the materials. Fig. 1.5 shows a direct relationship between the dissociation energy and the decomposition temperature for different plastic materials (Aguado and Serrano, 1999). PE has a higher decomposition temperature than PS due to different molecular structures of each plastic as mentioned above. Thus, PS can be decomposed at lower temperature than HDPE. However, these aromatic hydrocarbons were readily converted into coke existing on the internal and external surfaces of catalysts to make the catalyst deactivate.

The effect of the reforming temperature on the carbon atom number distribution from the pyrolysis and catalytic reforming of PS is shown in Fig. 2.12. It indicates that when the pyrolysis temperature and WHSV were fixed at 450 ℃ and 4 g-sample g-catalyst^{-1}h^{-1}, respectively, the increase of the reforming temperature significantly affected the carbon atom number distribution of the liquid products of PS derived from the SPCR process. In addition, the C_5-C_{12} was the main compositions (about 70 wt%) of liquid products derived from PS decomposition, which means the liquid products composition of PS was simpler than that of HDPE. Furthermore, as the increase of the reforming temperature from 400 °C to 450 °C, the proportion of the gasoline fraction increased while the proportion of the diesel fraction decreased. This is due to the fact that a higher temperature would enhance the activity of the Y-Zeolite and then improve the oligomerization and the hydrogen transfer reaction, which gave increase of the formation of monoaromatic hydrocarbon with a smaller molecular weight (Onwudili et al., 2009; Zhang et al., 1995). However, when the reforming temperature increased from 450 °C to 500 °C, the fraction of gasoline decreased while the fraction of diesel increased. It is due to the coking formation on the catalyst surfaces at a higher temperature. As mentioned previously, aromatic species have a greater predisposition to be involved in pathways to coke formation because of their ability to easily involve themselves in the hydrogen transfer and the cyclisation reactions. The analysis of pyrolysis oils derived from PS have been shown to be very high in aromatic compounds and the composition is dominated by the presence of styrene (Williams and Bagri, 2004). Consequently, it led to high char formation on the external and/or internal acid sites and then resulted in marked catalyst deactivations, compared with that of HDPE. Therefore, at the reforming temperature of 500 °C, the catalytic performance of the Y-Zeolite is not as efficient as at the lower reforming temperature.

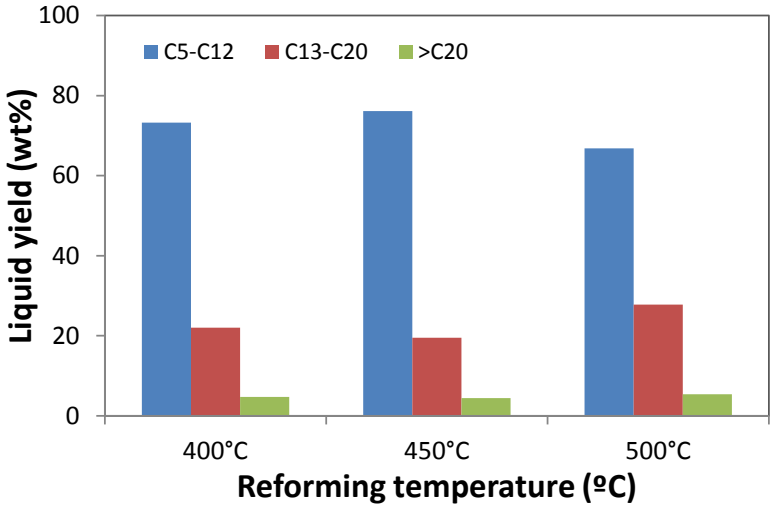

Fig. 2.12. Effect of the reforming temperature on the carbon atom number distribution of liquid products of PS at the pyrolysis temperature of 450 °C and WHSV of 4 g-sample g-catalyst^{-1}h^{-1}

Fig. 2.13 shows the effect of the reforming temperature on the hydrocarbon type distribution of liquid products from PS pyrolysis. It can be seen that when the pyrolysis temperature and WHSV were fixed at 450 °C and 4 g-sample g-catalyst^{-1}h^{-1}, respectively, with the increase of the reforming temperature, the distribution of the styrene monomer (SM), the other monocyclic aromatic hydrocarbon (OMAH) and the polycyclic aromatic hydrocabon (PAH) had an obvious change, which means that the effect of the reforming temperature on the liquid products of PS was significant.

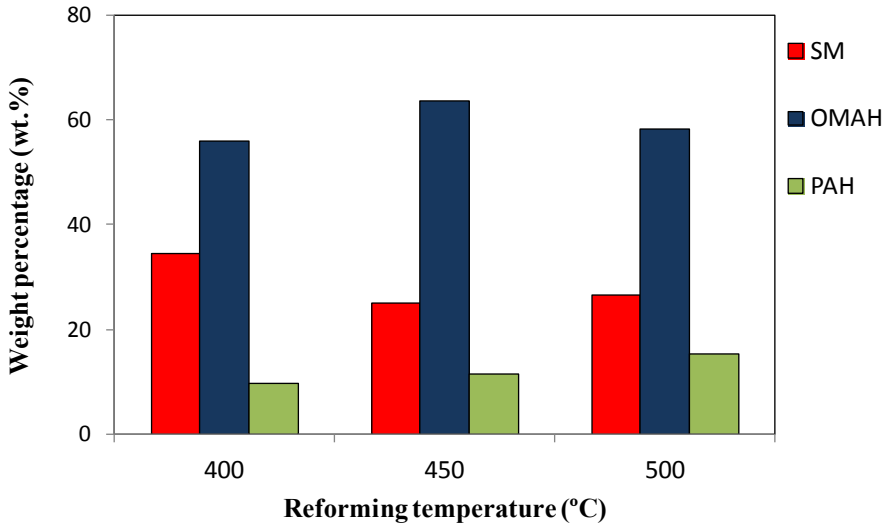

Fig. 2.13. Effect of the reforming temperature on SM, OMAH and PAH distribution of PS liquid products at the pyrolysis temperature of 450℃ and WHSV of 4 g-sample g-catalyst^{-1}h^{-1}

In contrast to HDPE, PS can be thermally depolymerized at a relatively low temperature. The thermal degradation of PS is a radical chain process including the initiation, the transfer and the termination steps in the open reaction system, which led to obtain the styrene monomer with a high selectivity. Styrene has a wide range of application in the chemical industry, e.g., in the manufacturing of plastics, synthetic rubber, resins, and insulators. Williams and Williams have reported that uncatalyzed pyrolysis of polystyrene has been shown to produce 83wt% conversion to a low viscosity oil which consisted mainly of styrene and a gas yield and char yield of less than 5wt% each (Williams and Williams, 1999)

Fig. 2.13 also indicates that there were a large number of ethylbenzene, benzene, toluene, m-xylene, methyl styrene, indan, ethyl methylbenzene and methylbenzene (monocyclic aromatic hydrocarbon), as well as naphthalene, 2-methylnaphthalene, dimethylnaphthalene, phenanthrene, methylnaphthalene and pyrene (polycyclic aromatic hydrocarbon) existed in liquid products of PS. This is mainly due to the presence of relatively moderate acid sites of the Y-Zeolites which have the potential to reduce the activation energy of the C-C bond and to hydrogenate the pyrolysis gas into all kinds of aromatic hydrocarbons. As can be seen in Fig. 2.13, considerable amounts of monocyclic aromatic hydrocarbons, such as benzene and ethylbenzene, were formed by the catalytic reforming process. These products are attributed to the further cracking and hydrogenation of styrene yielded from the pyrolyzer, which resulted in a decrease of the faction of styrene in the final oil produced. The styrene monomer and the polycyclic aromatic hydrocarbons were still main components in the final liquid products of PS, and they might be formed by β-scission of the C-C bond in the polystyrene main chain. Moreover, the increase of the amount of PAH could be related to an increase of the intramolecular hydrocarbon transfer at a higher reforming temperature (Zhang et al., 1995).

The gaseous product compositions of PS pyrolysis as a function of the reforming temperature is shown in Fig. 2.14. It can be seen that C_2 and C_3 gases (>65 mole %) were the main components of gaseous products, which originated from the relatively moderate acidity and large pore size of the Y-Zeolite catalyst (Miskolczi et al., 2004).

As the reforming temperature increase, the mole percentage of H_2, C_1 and C_{4+} gases were decreased whereas those of C_2, C_3 and hydrocarbons were increased.

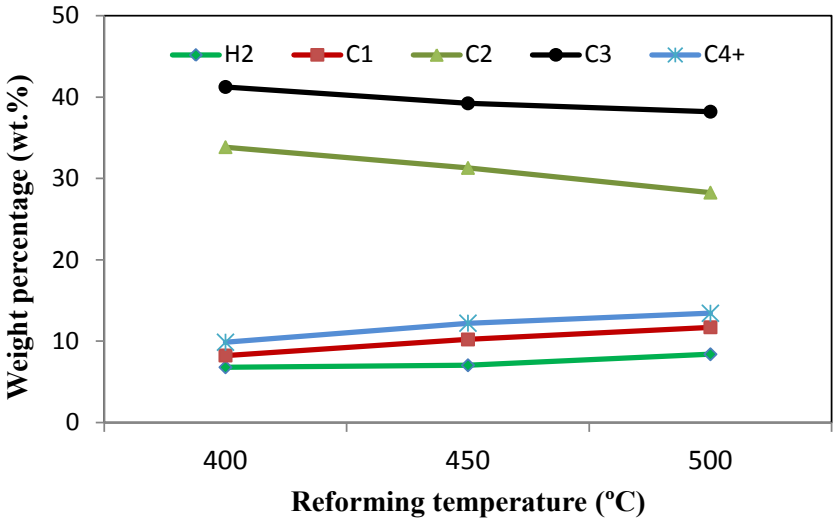

Fig. 2.14. The effect of the reforming temperature on the gaseous product composition of PS at the pyrolysis temperature of 450 °C and WHSV of 4 g-sample g-catalyst^{-1}h^{-1}

2.3.2.2 Effect of WHSV

Fig. 2.15 illustrates the effect of WHSV on the product yields of PS pyrolysis in the SPCR process. It can be seen that the faction of liquid products of PS was higher than that of HDPE while the proportion of gaseous products of PS was much lower than that of gaseous products of HDPE, which means that although increasing the amount of catalysts is equal to increasing the contact time and then improved the overcracking reactions of pyrolysates produced from the pyrolyzer, it was still difficult to reduce the activation energy to break the stable benzene ring structure of the aromatic hydrocarbons of the pyrolysis gas into samller molecular gaseous products (Murata et al., 2009). Furthermore, when compared with that of HDPE, the higher concentraion of aromatic hydrocarbons in the pyrolysis gas of PS also led to more formation of coke on the internal and external surfaces of the HY-zeolite, which led to the increase of the proportion of the solid products. It was mainly due to the fact that, as mentioned previously, the aromatic hydrocarbons especially unsaturated and polyaromatic compounds such as styrene monomer and indan and naphthalene derivatives were formed as major products in the degradation of polystyrene and then they were readily converted into coke (Uemichi et al., 1998).

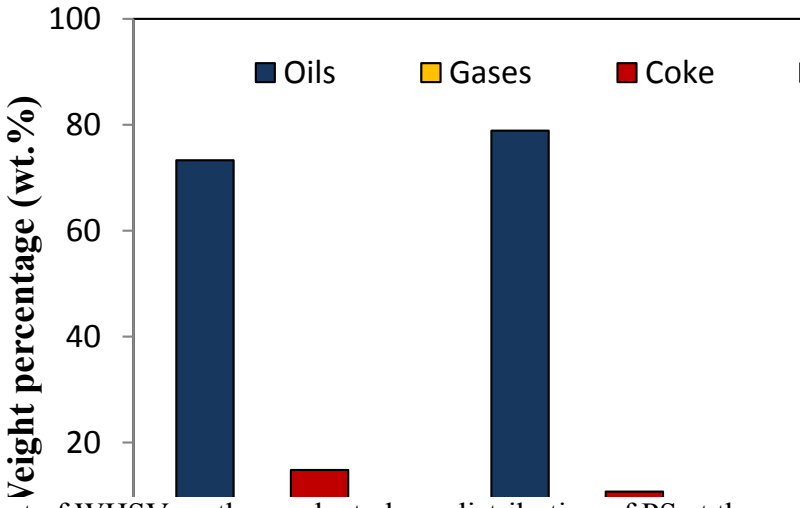

Fig. 2.15. Effect of WHSV on the product phase distribution of PS at the pyrolysis temperature of 450 °C and the reforming temperature of 450 °C

The carbon atom number distribution of PS as a function of WHSV is illustrated in Fig. 2.16. The carbon atom number distribution of PS was dominated by C_5-C_{12} with the weight fraction of more than 70%. This fraction was mainly composed of benzene, methylbenzene, ethylbenzene and styrene, which are valuable chemical feedstock and fuel used in our daily life and modern industry. In addition, there are also certain amount of C_{13}-C_{20} hydrocarbons existed in the PS oil, which were mainly consisted of some potentially harmful polycyclic aromatic hydrocarbons (Lee et al., 2002). Therefore, if the oil derived from PS would be used as combustion fuel oil, it should remove these harmful polycyclic aromatic hydrocarbons in advance. Consequently, it is preferable to recycle the PS oil as chemical crude materials rather than as fuel oil, compared with that of HDPE (Joo and Guin, 1997).

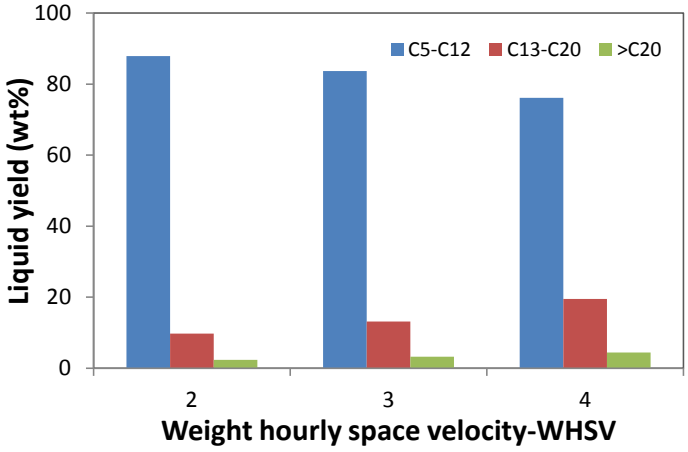

Fig. 2.16. Effect of WHSV on the carbon atom number distribution of liquid products of PS at the pyrolysis temperature of 450°C and the reforming temperature of 450 °C

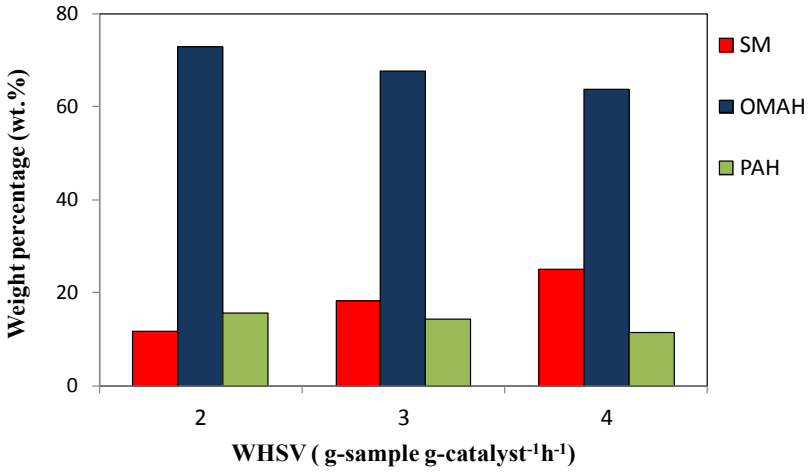

Fig. 2.17. Effect of WHSV on SM, OMAH and PAH distribution of PS liquid products at the pyrolysis temperature of 450℃ and the reforming temperature of 450℃

Fig. 2.17 shows the effect of WHSV on the hydrocarbon types of PS liquid products at both the pyrolysis temperature and the reforming temperature of 450°C. It can be observed that monocyclic aromatic hydrocarbons including the styrene monomer were the major component of liquid products of PS. As discussed above, the possible reason was that the presence of the Y-zeolite would improve the hydrogenation reaction, the oligomerization reaction and the β-scission reaction, which would convert the styrene monomer produced from the fast pyrolysis of PS in the pyrolyzer into benzene, methylbenzene and ethylbenzene (monocyclic aromatic hydrocarbon), as well as naphthalene, 2-methylnaphthalene, phenanthrene (polycyclic aromatic hydrocarbon), etc. In addition, the increase of the catalyst loading (decreasing WHSV) enhanced above conversion trend and then led to the increase of the polycyclic aromatic hydrocarbon and other monocyclic aromatic hydrocarbon at the expense of the styrene monomer. The derived PS oil could be mixed with other kinds of derived oil to improve their RON number, because of the high concentration of aromatic hydrocarbon of PS liquid products (Serrano et al., 2000).

The effect of WHSV on the composition of PS gaseous products was also investigated at the pyrolysis temperature of 450°C and the reforming temperature of 450 °C. As mentioned above, decreasing WHSV was nearly equal to increasing the amount of catalysts and increasing the contact time, which improved the overcracking of liquid products into more small molecular gaseous products. The results shown in Fig.

2.18 illustates that by the decrease of WHSV, the proportion of C_2 and C_3 of PS increased, which means that the Y-Zeolite catalyst had a special selectivity of C_2 and C_3 gases for PS. This result was consistent with some previously published reports. For instance, Puente and Sedran (de la Puente and Sedran, 1998) also reported a marked increase in C_2 and C_3 gases for the catalyzed pyrolysis of polystyrene compared to the thermal pyrolysis. Williams and Bagri (Williams and Bagri, 2004) also reported that C_2 and C_3 gases were the major composition of the gaseous products when employing the Y-Zeolite as the catalyst to recycle PS into valuable fuel and chemical feedstock in a batch system.

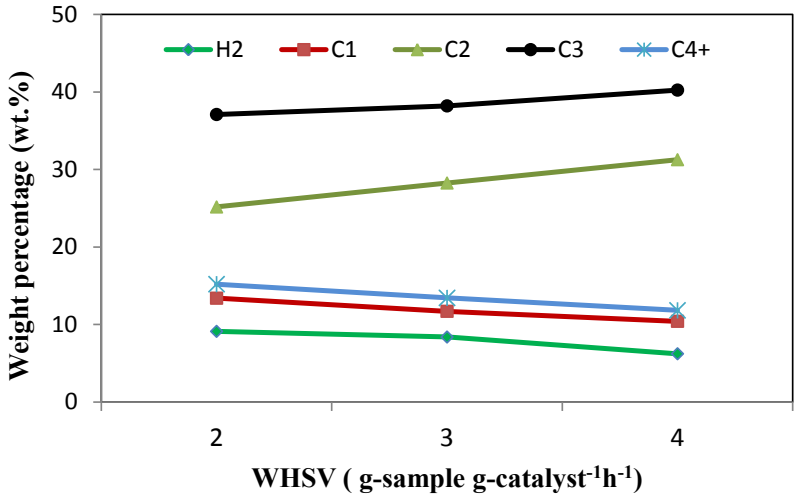

Fig. 2.18. Effect of WHSV on the gaseous product compositions of PS at the pyrolysis temperature of 450°C and the reforming temperature of 450 °C

2.3.3 Solid Residues

The proximate analysis and ultimate analysis of the solid residues produced from the pyrolysis of HDPE and PS are shown in Table 2.1. It can be seen that the solid residue from HDPE has a higher ash content than that of PS. This might be due to the different additives which normally used in plastics materials such as stabilizers, plasticizers and pigments. The moisture content of HDPE solid residue was also higher than that of PS solid residue. The higher content of ash in HDPE solid residue will absorb more moisture constituent from the atmosphere. The results also show that the solid residues produced from plastics pyrolysis have higher heating value than those of biomass. The higher heating value (HHV) of PS solid residue was higher than that of

HDPE residue due to less content of ash in PS solid residue. Therefore, they can be used as a fuel either for blending with biomass and coal or for single fuel.

Table 2.1. Proximate and ultimate analysis of solid residues (wt.%)

Solid residues	Proximate analysis			Ultimate analysis						HHV** (MJ/kg)
	Moisture	Volatile matter	Fixed carbon	Ash	C	H	N	S	O*	
HDPE	3.09	19.14	57.99	19.78	65.88	2.01	1.50	0	10.83	23.04
PS	0.91	37.44	57.28	4.37	91.14	4.09	0.09	0	0.31	36.29

* calculated by difference
** calculated using a modified Dulong`s formula

2.4 Conclusion

In this study, the sequential pyrolysis and catalytic reforming process in a continuous system has been successfully tested for the conversion of HDPE and PS into liquid and gaseous fuels using the Y-Zeolite catalyst for the catalytic reforming of pyrolysis gas generated in a pyrolyzer. The effect of the reforming temperature and WHSV on the product yields, the liquid characteristics and the gaseous composition have been investigated for both HDPE and PS samples. There were significant influences of the reforming temperature and WHSV on the products yields for both HDPE and PS. Increasing the reforming temperature and decreasing WHSV have resulted in an increase of gaseous and solid products while the liquid product decreased. The maximum oil production for HDPE (70.0wt%) and PS (88.1wt%) were obtained at the pyrolysis temperature of 450°C and 400°C respectively and at the same reforming temperature of 450°C and WHSV of 4. The gasoline fraction is the highest yield since the higher activity of Y-Zeolite catalyst.

The gaseous fraction of C_2, C_3 and C_{4+} (>75 mol %) and valuable aromatic and branched species in the gasoline range (C_5-C_{12}) (>70 wt %) were the main components of the gaseous and liquid products for HDPE, which were attributed to the molecule structure of HDPE, as well as the relatively moderate acidity and large hole size of the Y-Zeolite catalyst. In case of PS, C_2 and C_3 gases (>65 mol %) were the main components of the gaseous product. In addition, the liquid products of PS consisted of mostly monocyclic aromatic hydrocarbon, such as styrene and benzene, as well as lower con-

centrations of potentially harmful polycyclic aromatic hydrocarbons. The high quality gaseous product which is similar to liquefied petroleum gas (LPG) can be used as a fuel either for driving gas engines or for dual-fuel diesel engines. It can also be used as a heating source for the pyrolysis reactor. The residues were high calorific value solid products that can be utilized as a fuel as well.

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Chapter 3

3 Pyrolytic Oil Production from Plastic Materials Using a Modified Natural Zeolite Catalyst

Abstract

In this study, the performance of several differently treated natural zeolites in the sequential pyrolysis and catalytic reforming of polypropylene (PP) and polystyrene (PS) were investigated. The experiments were carried out in the two stage reactor using semi-batch system. The samples were degraded at 500°C in the pyrolysis reactor and then reformed at 450°C in the catalytic reformer. The results show that the mordenite-type natural zeolites could be used as efficient catalysts for the conversion of PP and PS into liquid and gaseous fuel. The treatment of natural zeolites in HCl solution showed an increase of the surface area and the Si/Al ratio while nickel impregnation increased the activity of catalyst. As a result, liquid product was reduced while gaseous product was increased. For PP, the fraction of gasoline (C_5-C_{12}) increased in the presence of catalysts. Natural zeolite with calcination process produced higher diesel fraction than other catalysts. Natural zeolite catalysts could also be used to decrease the heavy oil fraction ($>C_{20}$). The gaseous products were found that propene was dominated in all conditions. For PS, natural zeolite with the acid treatment process produced higher diesel fraction than other catalysts. Propane and propene were the main components of gases in the presence of nickel impregnated natural zeolite catalyst. Propene was dominated in pyrolysis over natural zeolite catalyst. The high quality gaseous product can be used as a fuel either for driving gas engines or for dual-fuel diesel engine.

3.1 Introduction

Economic development in the era of globalization led to an increase in plastic consumption resulting in rapid increase of waste plastic generation in the world. There are several main approaches for recycling waste plastics, i.e. material recycling, feedstock or chemical recycling and energy recovery. Though various kinds of techniques have been proposed for the conversion of waste plastics, it is generally accepted that material recycling is not a long-term solution to the present problem. Thus, feedstock recycling and energy recovery are more attractive ones (Lee et al., 2001). Waste plastics are one of the most promising resources for oil production because of its high calorific value and due to the increasing availability in local communities. Unlike paper and wood, plastics do not absorb much moisture and the water content of plastics is far lower than the water content of biomass (UNEP, 2009).

Feedstock recycling is one of the valorization strategy to recycle waste plastics via pyrolysis which involves thermochemical decomposition of organic and synthetic materials at elevated temperatures in the absence of oxygen to produce fuels. To improve the performance and quality of pyrolytic oil products, the catalytic pyrolysis has been applied by adding some catalysts in the reactor. A wide variety of commercial catalysts have been used by researchers such as zeolite, silica alumina, and FCC catalysts (Mikulec and Vrbova, 2008; Miskolczi et al., 2009; Seo et al., 2003; Wang and Wang, 2011) as well as Y-Zeolite which is used in the previous chapter. Each catalyst has different structure and composition which affect the fuel products.

Cracking reactions have also been studied for most polymers showing that the nature of the resulting products depends primarily on the polymer type. Catalytic pyrolysis of polypropylene (PP) has been studied by Ji et al. (X. Ji, 2001) using a fluidized bed reactor. The gasoline obtained in this study has Research Octane Number (RON) in the range of 84-88 while the cetane index for diesel fuel lies in the range of 40.5-45.3. Onwudili et al. (Onwudili et al., 2009) investigated the pyrolysis of polyethylene and polystyrene in a closed batch reactor to study the effect of the temperature and the residence time. The closed batch system can be effectively used to produce high grade fuel-like oils for energy production as well as chemicals.

However, a rapid deactivation of the catalyst is the main problem when applying direct catalytic pyrolysis. Therefore, placing the catalyst in separated reactor by employ-

ing the sequential pyrolysis and catalytic reforming (SPCR) system is the common solution to overcome this problem. This method has been used in the previous chapter utilizing Y-Zeolite as a catalyst. Several research works have also been done over some catalysts using this system as briefly reviewed in previous chapter. Pyrolysis of waste agricultural polyethylene film using HZSM-5 and Al-MCM-41 catalysts has been investigated resulting in heavier hydrocarbon products for Al-MCM-41 compared with HZSM-5 catalyst (San Miguel et al., 2009).

The use of commercial catalyst is somehow the main obstacle for recycling of waste plastics since it is very costly. Reducing the catalyst cost for the application in developing countries like Indonesia is very interesting challenges. Natural zeolites (NZ) which can be found in many places worldwide including Indonesia might be used as a candidate for this purpose instead of the commercial catalysts. To upgrade the catalytic properties of NZ, some preparation and modification can be applied to natural zeolites such as the calcination, the acid and alkali treatment and the metal impregnation (Cakicioglu-Ozkan and Ulku, 2005). Jeong et al. (Jeong et al., 2001) investigated the catalytic performance of alkali-treated natural zeolites from Korea in the liquid-phase catalytic degradation of high density polyethylene (HDPE). The alkali treatment of natural zeolites with moderate NaOH solution brought about the formation of mesopores and decrease in the acid site selectivity, resulting in a considerable improvement of its catalytic activity.

The similar previous work has been done by Park et al. (Park et al., 1999) with a different treatment. Natural zeolites were ion-exchanged with NH_4Cl solution to improve the catalytic performance. Another work has also been conducted by Fernandes et al. (Fernandes et al., 1999) using natural zeolite chabazite from Brazil with the ammonium exchanged treatment. The performance of the acid treated natural zeolites in the catalytic degradation of polypropylene (PP) has been studied by Hwang et al. (Hwang et al., 2002). The treatment with boric and phosphoric acid showed an increase of the surface area and the pore volume compared to those of original natural zeolites and affected the liquid products which have a narrower range of carbon numbers compared with those obtained by the thermal degradation.

The use of natural zeolites for catalytic degradation of polystyrene (PS) has been investigated by Lee et al. (Lee et al., 2001). The performance of natural zeolites after ion-exchanged with NH_4Cl solution on the degradation of PS was as effective as

HZSM-5 for the production of liquid oils with carbon numbers of C_5-C_{12} without severe deactivation. Natural zeolite catalyst produced aromatic liquid oils with over 99% of selectivity. This catalyst also showed a decrease of styrene and an increased selectivity towards ethylbenzene and propylbenzene compared to that of thermal degradation. However, the direct catalytic cracking method has been used by all researchers when utilizing natural zeolites which has several drawbacks as mentioned above. Moreover, clinoptilolite and chabazite zeolites were the natural zeolites that is the most widely used by the researchers which have different type with mordenite which is found in Indonesia. Therefore, in this study, we proposed the sequential pyrolysis and catalytic reforming system for plastics degradation using modified Indonesian natural zeolite as shown in Fig. 1.7.

3.2 Materials and Methods

3.2.1 Materials

The feedstocks used for these experiments were polypropylene (PP) and polystyrene (PS) granules manufactured by Tosoh Co. in Japan as shown in Fig. 3.1. The natural zeolite was collected from Klaten, Indonesia. The chemical composition of raw natural zeolite is shown in Table 3.1. HCl, $Ni(NO_3)_2.6H_2O$ and distilled water were obtained from Waco chemicals.

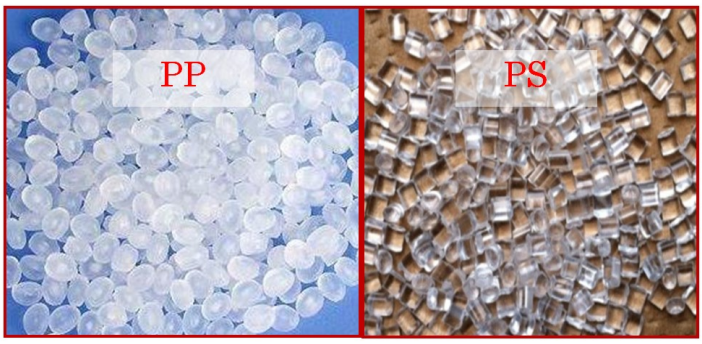

Fig. 3.1. The photographs of polypropylene and polystyrene used in this study

Table 3.1. Chemical composition of raw natural zeolite.

Compound	Percentage (wt%)	Compound	Percentage (wt%)
SiO_2	68.788	K_2O	1.083
Al_2O_3	14.399	MgO	0.485
CaO	10.674	Na_2O	0.307
Fe_2O_3	4.265		

3.2.2 Preparation of Catalysts

Three types of natural zeolites, different in the pretreatment procedure, were used to test their catalytic performance in the degradation of polypropylene (PP) and polystyrene (PS). A flowchart of the catalyst preparation can be seen in Fig. 3.2. The raw natural zeolites were ground, sieved to 100 mesh particles size and washed with distilled water at the room temperature to remove the water soluble impurities. The washed natural zeolite was dried in an oven at 120°C for 5 hours and calcined at 500°C for 3 hours. This sample was named as A-NZ and used for the first catalyst. The A-NZ sample was used to prepare the acid treated catalyst. It was prepared by treating 20 g of A-NZ with 500 ml of 1 M HCl solution under the reflux condition at the atmospheric pressure for 1 hour. After the HCl treatment, the sample was filtered and washed with distilled water until no chloride ion was detected by using $AgNO_3$ solution, after which the sample was dried at 120°C for 5 hours and calcined at 500°C for 3 hours. This sample was named as H-NZ and used for the second catalyst.

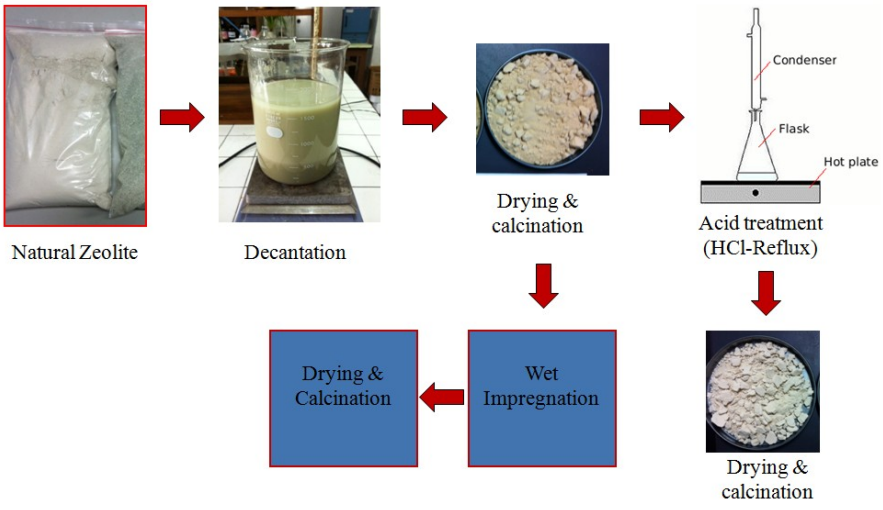

Fig. 3.2. Flowchart of catalyst preparation for natural zeolite

The third catalyst was made by mixing 20 g of A-NZ sample with 1 g of $Ni(NO_3)_2.6H_2O$ (1 wt% based on Ni metal) in distilled water at 75°C and magnetically stirred for 3 hours, after which the solvent was evaporated. After drying at 120°C for 5 hours, the nickel-containing sample was calcined at 500°C for 3 hours. This sample was named as Ni-NZ.

3.2.3 Pyrolysis and Catalytic Reforming of Plastics

Pyrolysis and catalytic reforming experiments were carried out using the semi-batch two-stage reactor. It consists of the pyrolysis reactor (pyrolyzer) and the catalytic reforming reactor (reformer). The schematic diagram of the experimental apparatus is shown in Fig. 3.3. The pyrolyzer and the reformer were made of stainless steel and covered with electric heaters. The pyrolyzer`s inner diameter and the height were 30 mm and 200 mm, respectively. The reformer`s inner diameter and the height were 10 mm and 200 mm, respectively. The reaction temperatures in both the pyrolyzer and the reformer were controlled with K-type thermocouples and heaters. A double-tube condenser was installed at the outlet of the reformer to separate gas and liquid products.

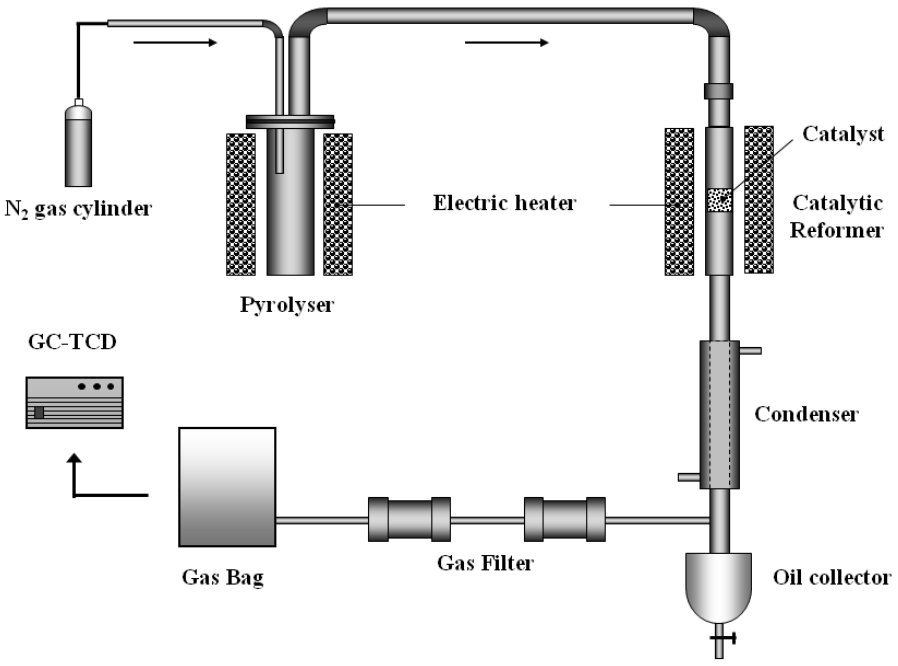

Fig. 3.3. A schematic diagram of the experimental apparatus

In these experiments, 50 g of the feedstock was fed into the pyrolizer, where the material was melted and then volatilized into the reformer. The catalyst (1 g) was loaded in the reformer, where the pyrolysis gas generated in the pyrolizer was reformed. Initially, the reformer was heated up to the preset temperature and then air in the reactors was replaced with N_2 carrier gas followed by heating the pyrolyzer to the preset temperature. The nitrogen gas flow rate was 100 ml min^{-1}. After the reforming reaction, the gas was cooled in the condenser to recover liquid products. Liquid products were then collected and weighed for the mass balance calculation. The remaining solids deposited in the pyrolyzer was defined as the residue, and the carbon left in the catalyst bed was defined as coke. Because the total amount of the residue and the coke was very small, we call the total as the solid product.

The experiments were carried out at the pyrolyzer temperature of 500°C and the reformer temperature of 450°C. The gaseous products were collected in a gas bag for 2 hours. Experiments using similar conditions but in the absence of catalyst were also conducted for comparison.

3.2.4 Characterization of Catalysts and Products

The bulk structure of natural zeolite was confirmed by the X-Ray Diffraction (XRD) analysis (Rigaku Corp., Japan) using the Copper K alpha radiation. The composition of natural zeolite was determined by the X-ray Fluorescence (XRF) analyser. Nitrogen adsorption-desorption measurements were conducted at 77 K on a Belsorp-mini II (Bel Japan). The BET specific surface area (S_{BET}) was calculated from the adsorption data in the relative pressure. The Scanning Electron Microscope (SEM: JSM-5310LV Microanalyzer, JEOL Co.) was employed to determine the surface morphology of catalysts. The fraction of liquid products were analysed by using a gas chromatography-mass spectrometry (GC-MS, QP2010S Shimadzu). The gaseous product composition was measured by a gas chromatograph equipped with a thermal conductivity detector (GC-TCD, Agilent Technologies Inc. USA).

3.3 Results and Discussions

3.3.1 Characterization of Catalysts

In order to examine the change of the pore structure in the natural zeolite and its HCl-treated sample, the XRD patterns of samples are shown in Fig. 3.4. The crystalline structures of natural zeolites vary depending on their mining sites. It can be seen that the main structure of the natural zeolite catalyst was identified to be mordenite. Most of the peaks observed at 2T (degree) = 5-35 for the natural zeolite samples can be assigned to be those of mordenite type crystalline matter as reported by Trisunaryanti et al (Trisunaryanti et al., 1996). The samples showed relatively broad base lines. This suggests that the samples contain amorphous and crystalline impurities. After the acid treatment, some impurity peaks of A-NZ disappeared which indicates that the treatment could remove a part of the impurities, while the crystalline structure was not decomposed.

The scanning electron microscope (SEM) images of natural zeolites before and after the acid treatment are shown in Fig. 3.5. It can be observed that natural zeolite has a lamellar pattern and an irregular morphology. After the HCl treatment, it can be seen that the physical destruction was appeared which means that the HCl treatment could remove some crystalline impurities as discussed previously. This is consistent with the XRD result shown in Fig. 3.4.

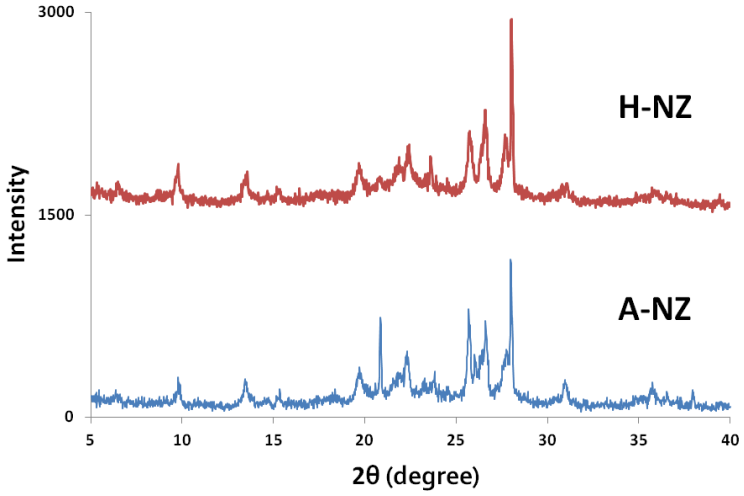

Fig. 3.4. X-Ray powder diffraction pattern of natural zeolite samples before and after the HCl treatment

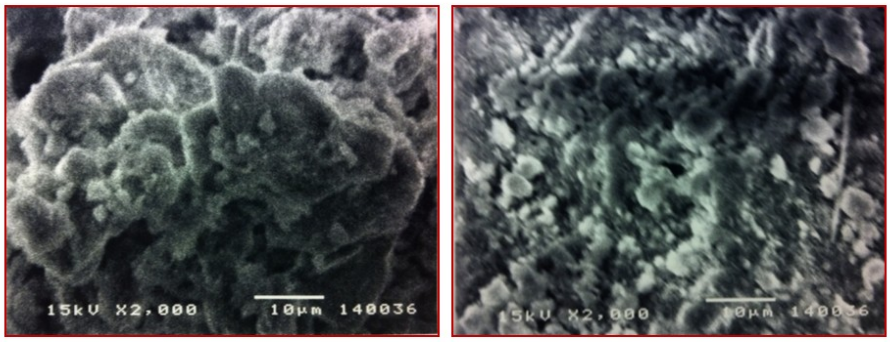

Fig. 3.5. Scanning electron microscopy (SEM) images of natural zeolite samples

The chemical composition and the BET surface area of natural zeolites before and after the HCl treatment are listed in Table 3.2. It can be seen that the acid treatment of A-NZ (Si/Al ratio=4.21) caused the dealumination, which is indicated by the increase of the Si/Al ratio. The relative ratios of alkaline and alkaline earth elements to Si were also found to have decreased by the treatment. Releasing aluminium and ferric ions indicated the partial destruction of the zeolite structure which is consistent with the SEM images. The increase of the Si/Al ratio will increase the stability of the crystal framework and reduce the coke formation during the catalytic cracking. The acid treatment has also increased the surface area which can be seen from the increase of the BET surface area. It will increase the surface area contact between the catalyst and the pyrolysis gas so that longer chain hydrocarbons can be cracked into lighter hydrocarbons.

Table 3.2. Chemical composition and BET surface area of natural zeolite before and after the HCl treatment

	Si/Al ratio	Na/Si	Mg/Si	K/Si	Ca/Si	Fe/Si	S_{BET} ($m^2.g^{-1}$)
A-NZ	4.21	0.007	0.009	0.021	0.238	0.093	91.146
H-NZ	6.75	0.002	0.008	0.010	0.050	0.036	233.94

3.3.2 Pyrolysis and Catalytic Reforming of Polypropylene

Polypropylene (PP) was degraded at 500°C in the pyrolyzer and then reformed at 450°C in the catalytic reformer. The experiments were done in the absence and presence of the catalyst. Three types of catalyst were used i.e. A-NZ, H-NZ and Ni-NZ. The liquid, gas, and solid product yields from the sequential pyrolysis and catalytic reforming of PP with and without the catalyst are shown in Fig. 3.6. Pyrolysis at 500°C in the absence of the catalyst produced 91.6% of oil. Similar result has been found by Sarker et al. (Sarker et al.) who obtained 92% of oil. In the presence of the natural zeolite catalysts, the oil yields were reduced within the range of 83.8-86.4%. The lower liquid yields have been obtained by Ji et al. (X. Ji, 2001) which produced about 50% of oils when utilizing a fluidized bed reactor. Theoretically, a fluidized bed system can enhance the heat transfer to the plastic materials which affect to the cracking reaction of long chain hydrocarbons into short chain hydrocarbons so that a part of liquid products will be converted to gaseous products.

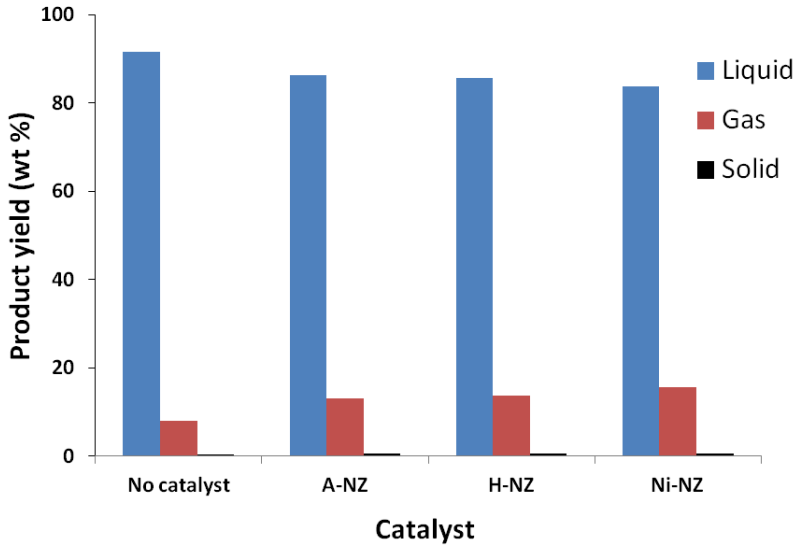

Fig. 3.6. Product yields obtained from the pyrolysis and catalytic reforming of polypropylene in the absence and the presence of catalyst

The presence of the catalyst can enhance the cracking reaction of the pyrolysis gas. This further reaction increased the gas yield for all natural zeolite catalysts. Long chain hydrocarbons have been cracked into lighter hydrocarbon gases. Fig. 3.6 indicates that H-NZ catalyst produced slightly lower liquid yield than A-NZ catalyst due to the larger surface area of H-NZ after the acid treatment which enhanced the surface contact

between the catalyst and the pyrolysis gas in the reformer. The similar result has also been found in Ni-NZ catalyst. The presence of nickel as a promoter could increase the activity of natural zeolites.

The composition of the liquid products have been changed by the presence of natural zeolite catalysts as shown in Fig. 3.7. In general, the fraction of gasoline (C_5-C_{12}) increased in the presence of the catalysts. The increase of the surface area and the presence of nickel significantly affected the selectivity of the products. The use of H-NZ catalyst increased the gasoline fraction compared to that of A-NZ catalyst. The higher surface area of H-NZ catalyst promoted the cracking reaction of heavy oil. The presence of nickel in Ni-NZ catalyst also increased the gasoline fraction. However, it was lower than that of H-NZ due to lower surface area of the catalyst. Impregnation of metal onto natural zeolite framework decreased its surface area. This phenomenon may be caused by the non homogeneous distribution of metal in the natural zeolite surface. Some of metal atoms may block the pore mouth of the zeolites (Trisunaryanti et al., 2013). The presence of the catalysts also significantly decreased the heavy oil fraction (>C_{20}). H-NZ catalyst produced the lowest heavy oil fraction. Fig. 3.7 also showed no significant difference of the diesel fuel fractions (C_{13}-C_{20}). A-NZ catalyst produced slightly higher diesel fuel than that of the reforming without catalysts while H-NZ and Ni-NZ produced lower diesel fuel yields.

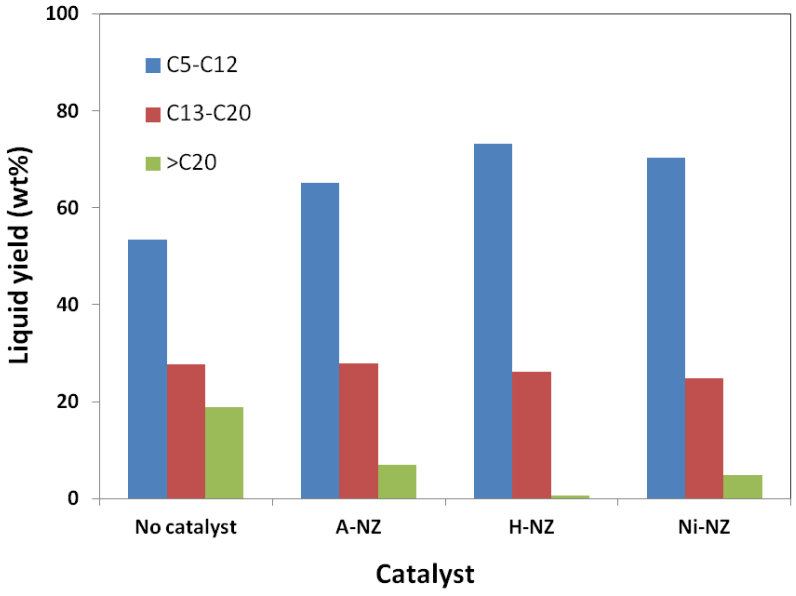

Fig. 3.7. Liquid product composition obtained from the pyrolysis and catalytic reforming of polypropylene

However, diesel yields from the total feedstock are found to be decreased when applying NZ catalyst as presented in Fig. 3.8. Ni-NZ catalyst produced the lowest diesel fraction. The presence of nickel in the catalyst surface promotes the cracking reaction which convert the diesel fraction into the gasoline fraction. The use of NZ catalyst still produced higher diesel fraction compared with Y-Zeolite with HDPE feedstock. Y-Zeolite has much higher surface area than NZ catalyst, which means that more cracking reaction has been occurred on the catalyst surface.

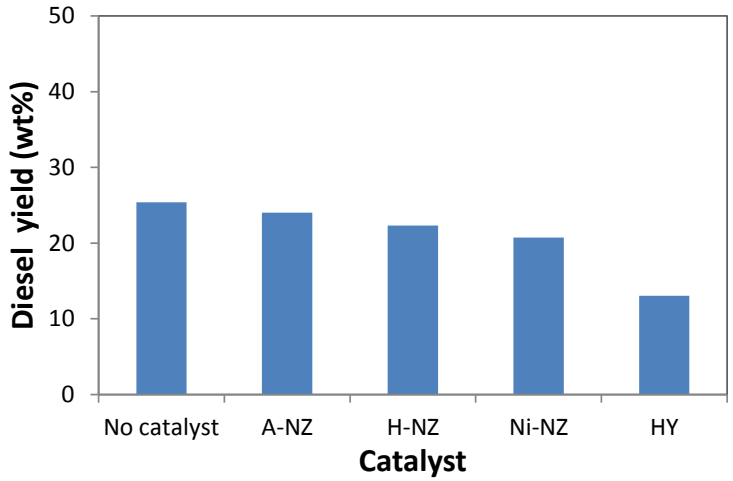

Fig. 3.8. Diesel yield obtained from the pyrolysis and catalytic reforming of plastic materials

Table 3.3 shows the effect of the catalyst on the hydrocarbon type distribution of PP liquid products. The olefins and paraffin were the main type of liquid products in the thermal cracking process. The decomposition mechanism of PP is random-chain scission. The polymer is broken up randomly into smaller molecules of varying chain lengths, producing a volatile with or without double bonds. In general terms, the initiation reactions comprise the homolytic cleavage of a carbon–carbon bond by either random or end chain scission giving rise to the appearance of two radicals. This may be followed by the intramolecular/intermolecular hydrogen chain transfer reactions forming more stable secondary radicals. Additionally, these intermediate radicals may undergo the C–C bond rupture by the β-scission to produce olefins and new radicals. Finally, termination reactions such as disproportionation towards different olefins and alkanes or bimolecular coupling between radicals might take place.

The presence of catalysts showed the increase of olefin, iso-paraffin and napthane

while paraffin reduced as shown in Table 3.3. The catalytic cracking takes place following the carbocation mechanism. Subsequently, the polymer is fragmented by the β-scission and disproportionation reactions, the former leading to olefins. Unlike the radical pathway for the thermal cracking, the skeletal isomerization occurs simultaneously with the cracking reactions giving rise to branched products. Additionally, the oligomerization, cyclization and the aromatization reactions may proceed together with the cracking.

Table 3.3. Liquid composition of the oil from PP under different catalyst (wt%)

Liquid composition	No Catalyst	A-NZ	H-NZ	Ni-NZ
Paraffin	29.22	9.57	5.43	13.36
Iso-paraffin	4.48	13.12	7.18	12.13
Olefin	59.40	64.33	69.69	65.66
Napthane	6.91	13.00	17.70	8.87

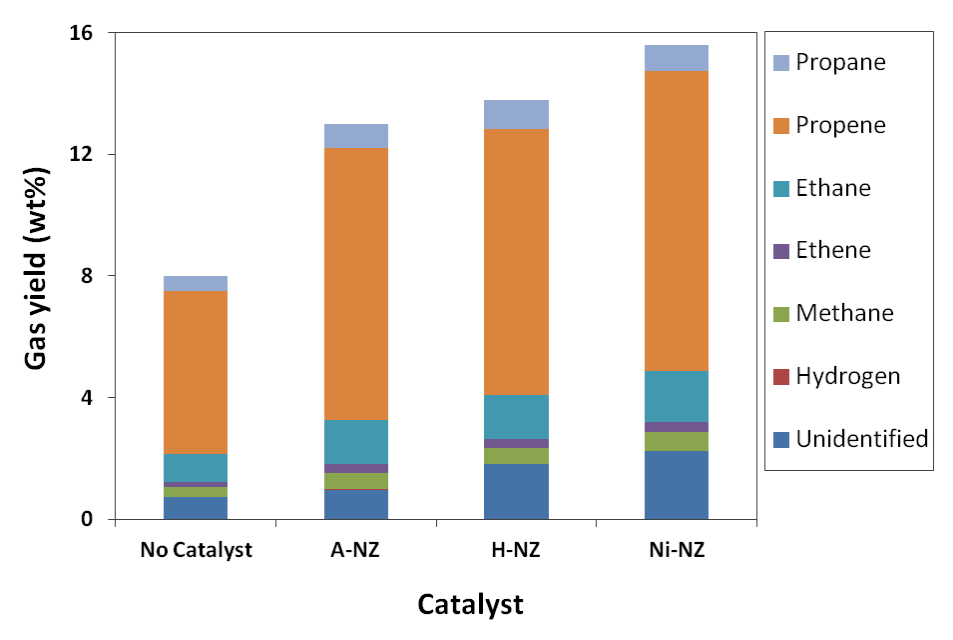

Fig. 3.9. Gaseous product composition obtained from the pyrolysis and catalytic reforming of polypropylene

Fig. 3.9 shows the gas yields obtained from the sequential pyrolysis and catalytic reforming of PP with various natural zeolite catalysts. It was found that propene was

dominated in all conditions. The unidentified gaseous products might have been gaseous hydrocarbons containing more than three carbon atoms that could not be measured by our apparatus. The presence of natural zeolite catalysts increased the yield of propene, ethane and propane. The increase of some gases have been obtained from the conversion of oil to lighter hydrocarbons after the reaction with the catalysts. Ni-NZ catalyst has higher composition for all gases by the effect of nickel presence in the catalyst. The similar results have been obtained by Ji et al. (X. Ji, 2001) which produced very high composition of propene gas. In commercial scale applications, the high quality gaseous product can be used as a fuel either for driving gas engines or for dual-fuel diesel engines. It can also be used as a heating source for the pyrolyzer.

3.3.3 Pyrolysis and Catalytic Reforming of Polystyrene

Fig. 3.10 shows the product yields obtained from the sequential pyrolysis and catalytic reforming of polystyrene (PS). PS was degraded at 500°C in the pyrolyzer and then reformed at 450°C in the catalytic reformer. The experiments were done in the same procedure and conditions with the experiments of PP. Pyrolysis of PS in the absence of the catalyst produced the liquid yield of 98%. The similar results have also been found by Williams and Bagri (Williams and Bagri, 2004) who obtained 96.6% oil. In the presence of the natural zeolite catalysts, the oil yields were reduced to about 85-95% depending on the catalysts used.

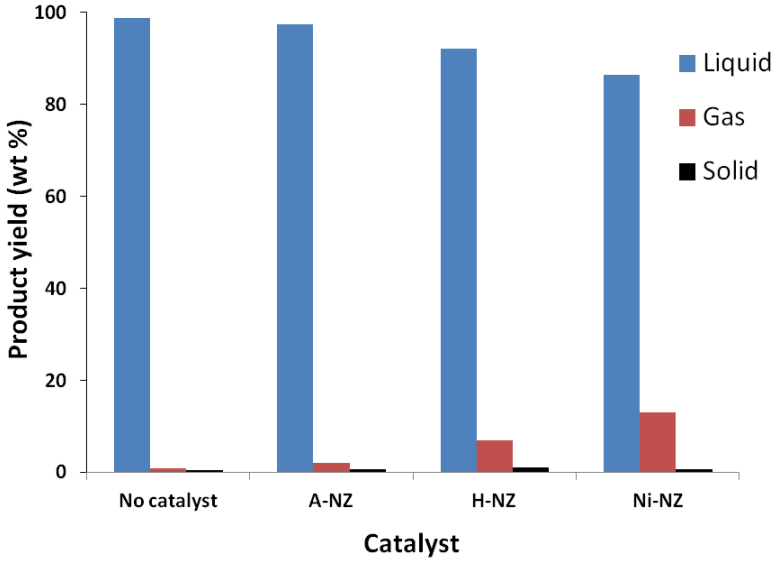

Fig. 3.10. Product yields obtained from the pyrolysis and catalytic reforming of polystyrene in the absence and the presence of catalyst

A similar trend with PP has been observed for PS. The treatments of natural zeolite catalysts have been found to decrease the oil yield and increase the gas yield as can be seen for H-NZ and Ni-NZ catalysts compared with A-NZ catalyst. The lowest liquid product has been observed by Ni-NZ catalyst. As discussed previously, the larger surface area of H-NZ and the presence of nickel in Ni-NZ catalyst are the key factors for these findings. These conditions enhanced the catalytic performance of natural zeolites. The lower liquid products have been obtained by Williams and Bagri (Williams and Bagri, 2004) which utilize commercial Y zeolite as a catalyst. This catalyst could produce oil between 69-75%.

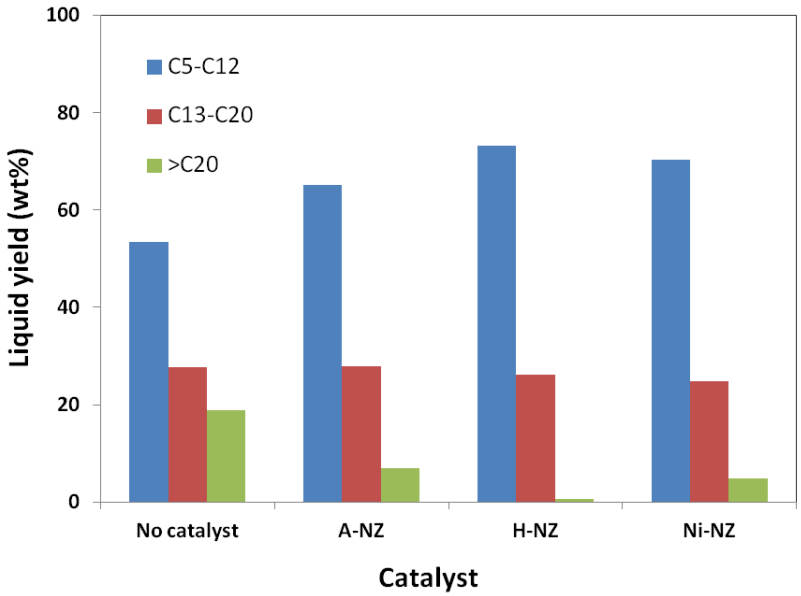

Fig. 3.11. Liquid product composition obtained from the pyrolysis and catalytic reforming of polystyrene

The composition of liquid fuels in the sequential pyrolysis and catalytic reforming of PS is shown in Fig. 3.11. The presence of the catalysts increased the yield of light oil (C_5-C_{12}) while the heavier oil (C_{13}-C_{20}) was decreased. However, H-NZ catalyst produced less light oil than others. This is due to the increase of the Si/Al ratio after the acid treatment which decreased the acidity of the catalyst. The liquid products were mainly composed of benzene, methylbenzene, ethylbenzene and styrene, which are valuable chemical feedstock and fuel used in our daily life and modern industry. In addition, there are some aromatic hydrocarbons existed in the PS oil, which were mainly consisted of some potentially harmful polycyclic aromatic hydrocarbons (Lee et

al., 2002). Therefore, if the oil derived from PS would be used as combustion fuel oil, these harmful polycyclic aromatic hydrocarbons should be removed in advance. Consequently, it is preferable to recycle the PS oil as chemical crude materials rather than as fuel oil (Joo and Guin, 1997).

Fig. 3.12 shows the diesel yield produced from the pyrolysis and catalytic reforming of polystyrene. The result showed that H-NZ catalyst produced the highest diesel fraction among other catalysts. From Fig. 3.11 we can see that H-NZ produced very low heavy oil fraction. The acid treatment for H-NZ produced higher surface area and pore size of the catalyst. This will give a chance to heavy oil which has bigger molecular size to be cracked in the catalyst so that some portion of heavy oil will be converted into the diesel fraction. H-NZ also produced higher diesel yield than the commercial Y-Zeolite catalyst.

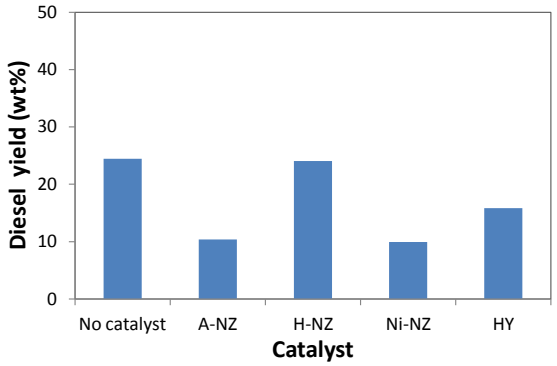

Fig. 3.12. Diesel yield obtained from the pyrolysis and catalytic reforming of polystyrene

Table 3.4 shows the effect of catalyst on the hydrocarbon type distribution of the PS liquid products. The thermal degradation of PS is a radical chain process including the initiation, the transfer and the termination steps in the open reaction system, which led to obtain the styrene monomer with a high selectivity. The other monocyclic hydrocarbons and polycyclic aromatic hydrocarbons have been found to be increase with the presence of the catalysts. The general reaction scheme can be used to represent the primary reaction pathways of PS. The initial step in the PS cracking is the protonation of polymer aromatic rings, which may result in the chain shortening, yielding a chain end cation and a saturated chain end. *Ortho*-protonation can readily lead to benzene evolution and the formation of a secondary macro cation, which may subsequently cyclize to

form an indane structure. Hydride abstraction appears to be an important reaction pathway for the chain end cations, except when the catalyst restricts the movement of polymer chains. The saturated chain ends are the likely source of alkyl benzenes, which can be formed after protonation of the chain end aromatic rings. The rearrangements and the β-scissions of macro cations can lead to the chain unsaturation, or, for the chain end cations, the formation of unsaturated volatile products such as styrene and indenes.

Table 3.4. Liquid composition of the oil from PS under different catalyst (wt%).

Liquid composition	**No Catalyst**	**A-NZ**	**H-NZ**	**Ni-NZ**
Styrene monomer	77.66	36.05	34.58	32.36
Other monocyclic aromatic hydrocarbons	21.60	52.89	52.59	55.79
Polycyclic aromatic hydrocarbons	0.16	11.06	11.75	10.26

The gas yields produced from the sequential pyrolysis and catalytic reforming process of PS is shown in Fig. 3.13. Propane and propene were the main components of the gas product in the presence of Ni-NZ catalyst. The presence of nickel increased the selectivity of the products. Reforming over H-NZ catalyst produced almost the similar proportion for all gases except for hydrogen. Propene was dominated in the reforming over A-NZ catalyst. The presence of the catalysts have significantly increased the gas yield compared with those of PP as shown in Fig. 3.9. Williams and Bagri (Williams and Bagri, 2004) reported slightly different results when utilizing ZSM-5 and Y zeolite catalysts. The main gases produced from the catalytic pyrolysis of PS were alkane and alkene gases from C_1 to C_4. Ethene and propene and lower concentrations of methane, ethane and propane were the main gases produced with the zeolite ZSM-5 catalyst, whereas equal concentrations of ethane, propene, methane, ethane and propane were produced with the Y-Zeolite catalyst.

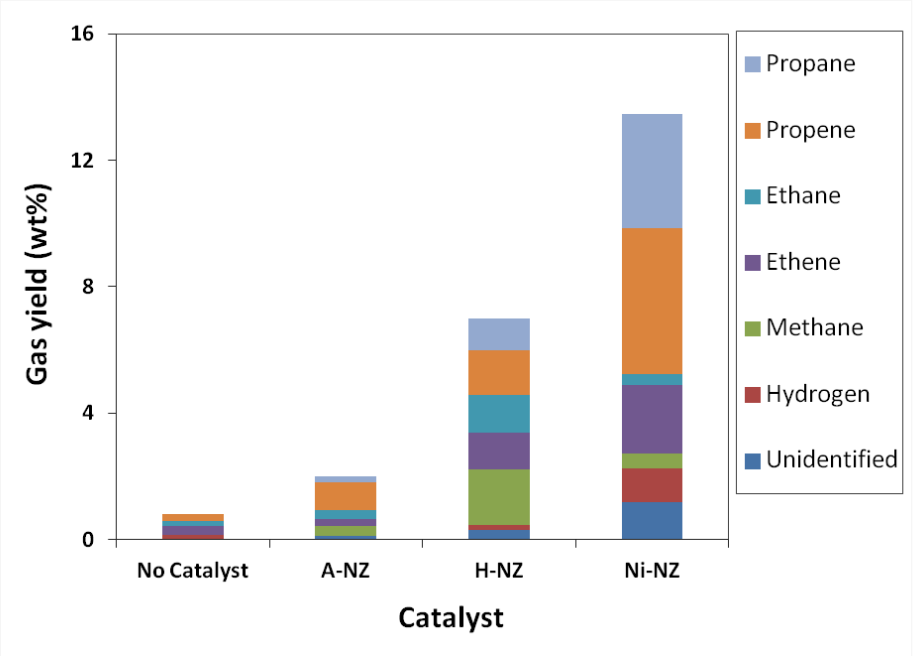

Fig. 3.13. Gaseous product composition obtained from the pyrolysis and catalytic reforming of polystyrene

3.4 Conclusion

The mordenite-type natural zeolites, either with the calcinations treatment (A-NZ) or the HCl treatment (H-NZ) or the nickel impregnation (Ni-NZ) could be used as efficient catalysts for the conversion of PP and PS into liquid and gaseous fuels by the sequential pyrolysis and catalytic reforming process. Natural zeolites after the HCl treatment (H-NZ) showed an increase of the surface area and the Si/Al ratio compared with that of A-NZ catalyst. The presence of nickel in Ni-NZ increased the activity of the catalyst which enhanced the cracking reaction of pyrolysis gas. As a result, liquid product was reduced while gaseous product was increased.

For polypropylene, the fraction of gasoline (C_5-C_{12}) increased in the presence of the catalysts. The use of H-NZ catalyst increased the gasoline fraction compared with A-NZ catalyst. The presence of nickel in Ni-NZ catalyst also increased the gasoline fraction. However, it was lower than H-NZ catalyst due to a lower surface area of the catalyst. A-NZ catalyst produced higher diesel fraction than other catalysts. Natural zeolite catalysts could also be used to decrease the heavy oil fraction (>C_{20}). It was found that the gaseous products was dominated by propene in all conditions. The presence of natural zeolite catalysts increased the yield of propene, ethane and propane.

Pyrolysis of polystyrene in the absence of the catalyst produced a liquid yield of 98%. In the presence of the natural zeolite catalysts, the oil yields were reduced to about 85-95% depending on the catalysts used. The treatments of natural zeolite catalysts have been found to decrease the oil yield and increase the gas yield as can be seen for H-NZ and Ni-NZ catalysts compared with A-NZ catalyst. The presence of catalysts increased the yield of light oil (C_5-C_{12}) while the heavier oil (C_{13}-C_{20}) was decreased. H-NZ catalyst produced higher diesel fraction than other catalysts. Propane and propene were the main components of gases in the presence of Ni-NZ catalyst. Reforming over H-NZ catalyst produced almost the similar proportion for all gases except for hydrogen. Propene was dominated in the reforming over A-NZ catalyst. The high quality gaseous product can be used as a fuel either for driving gas engines or for dual-fuel diesel engines.

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Chapter 4

4 Pyrolytic Oil Production from Municipal Plastic Wastes in a Pilot Scale Reactor

Abstract

Fuel oil production from municipal plastic wastes by the sequential pyrolysis and catalytic reforming process have been studied in this paper. Three kinds of municipal plastic wastes were collected from final disposal sites and a small recycling company in Yogyakarta city, Indonesia. Commercial Y-Zeolite and natural zeolite catalysts were used in this study. The batch-type pilot scale reactor with the capacity of 1.6-2.6 kg feedstock/batch was used and 100 g of the catalyst was loaded in the reforming reactor. The experiments were carried out at the pyrolyzer temperature of 450°C and the reforming temperature of 450°C. The results show that the feedstock types strongly affect the product yields and the quality of liquid and solid products. HDPE waste produced the highest liquid fraction. The highest diesel fraction has been produced in PE bag 2 (with crushing and washing) while PE bag 1 (without crushing and washing) produced the highest gasoline fraction. The catalyst presence reduced the liquid fraction and increased the gaseous fraction. Pyrolysis with natural zeolite catalyst produced higher liquid product compared with Y-Zeolite catalyst. Furthermore, pyrolysis of municipal plastic wastes produced higher heating value solid products than those of biomass and low rank coal, so that they still can be used for blending with biomass and coal.

4.1 Introduction

The growth of the plastic consumption has been occurring rapidly in the last six decades due to their excellent properties which can be used to replace the use of some other materials including wood and metals. In Indonesia, like many developing nations, plastic consumption has also increased due to economic development and rapid urbanization. In 2011, Indonesia has consumed 10 kg plastics per capita per year. However, the great number of consumptions would increase the product of waste plastics which led to the environmental problems. The role of scavengers for collecting waste plastics was very important in developing countries since there was no separation process of the municipal solid waste before coming to the final disposal site. Nevertheless, there was only few part of the waste plastics that can be collected by scavengers because of the economic value reason. Therefore, alternative process such as pyrolysis which can process most types of waste plastics is an emerging solution for Indonesia.

Pyrolysis of plastic materials have been investigated by many researchers. There are four types of mechanisms of plastics pyrolysis (Buekens and Huang, 1998) i.e. the end-chain scission or the depolymerization, the random-chain scission, the chain stripping and the cross-linking. The thermal degradation behaviour of plastics has been investigated by Aboulkas et al. (Aboulkas et al., 2010). The activation energy and the reaction model of the pyrolysis of polyethylene (PE) and polypropylene (PP) have been estimated for non-isothermal kinetic results. The pyrolysis reaction models of polyethylene can be described by the "contracting sphere" model, whereas that of polypropylene can be described by the "contracting cylinder" model.

The low thermal conductivity and high viscosity of plastics are the major challenges for designing the cracking reactor. The design of the pyrolysis reactor should take into account the heat transfer and the contact mode. Several reactor systems have been developed and used such as batch/semi batch (Miskolczi and Nagy, 2012), fixed bed, fluidized bed, spouted bed, microwave (Hussain et al., 2012) and screw kiln (Serrano et al., 2001). Batch or semi-batch reactors have been used by many researchers because of its simple design and easy operation. The fixed bed reactor is the most classical reactor which is acceptable for waste plastics that do not need to be shredded and crushed.

A large number of papers have been published describing the pyrolysis of plastics. There are only few papers utilizing real waste plastics as feedstock. Waste plastics can be classified as industrial and municipal plastic wastes according to their origins (Buekens and Huang, 1998). These groups have different qualities and properties. Industrial plastic wastes (IPW) are those arising from the plastics manufacturing and processing industry. Municipal plastic wastes (MPW) normally remain a part of municipal solid wastes as they are discarded and collected as household wastes. In Yogyakarta city, Indonesia, waste plastics contributed 9.96% to the municipal solid wastes (BPPT, 2005). Detailed composition of solid wastes collected from Piyungan landfill site is shown in Fig. 4.1.

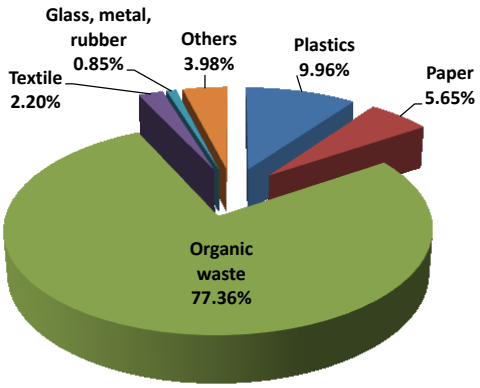

Fig. 4.1. Composition of municipal solid waste from Piyungan landfill site in Yogyakarta city, Indonesia (BPPT, 2005)

Pyrolysis and catalytic reforming of MPW which comprise PE, PP and PS have been studied by Wang and Wang (2011) over nickel-loaded silica alumina catalysts. Bhaskar et al. (2003) have compared the thermal degradation products from MPW and model mixed plastics. The presence of polyethylene therephthalate (PET) in model mixed plastics and MPW increased the formation of new chlorinated hydrocarbons in liquid products and also drastically decreased the formation of inorganic chlorine content. The role of impurities in MPW was also significant. The impurities were toxic for acidic catalysts and led to easy deactivation of catalysts in the case of conversion of MPW (Wang and Wang, 2011).

Upgrading of pyrolytic oil produced from MPW has also been investigated using FCC catalyst as a cracking catalyst (Lee, 2009). The addition of FCC catalyst in the degradation process showed the improvement of liquid and gas yields and also high fraction of heavy hydrocarbons in the oil product due to more cracking residue. Non-catalytic pyrolysis process has also been studied using waste PE, PP and PS (Demirbas, 2004). The results showed that waste PS produced higher liquid while waste PE and PP produced higher gaseous products.

The quality of the product is the main consideration in developing a recycling technology converting waste plastics into fuels. Therefore, determination of practical properties of fuel is very important such as the cetane number, the density, the viscosity, the pour point, etc. The properties of fuels are expected to be similar to conventional fuels. However, there are few references in respect to these properties since the measurement of practical properties needs a large quantity of products, not produced in most experimental works. In general, the presence of catalysts may reduce the density, the viscosity, the pour point and increase the cetane number (Miskolczi, 2006). The cetane number of oil produced from polyethylene should be high due to its composition of exclusively linear chain hydrocarbons. However, the pour point and the cloud point will be low because of the high concentration of wax (Blazso, 2006).

In this chapter, the study of the sequential pyrolysis and catalytic reforming system of municipal plastic wastes obtained from a final disposal site in Yogyakarta city, Indonesia over commercial and Indonesian natural zeolite catalysts has been conducted. The system used in this study was similar to the previous chapter study as shown in Fig. 1.7 while the size of the reactor was larger than that of the previous study. The liquid products can be used either for fueling a diesel engine by blending with commercial diesel fuel or for partial substitute of kerosene in a pressurized cooking stove (Saptoadi and Pratama, 2014). Finally, the solid products can be used as a fuel by briquetting it to produce a high quality solid fuel (Sutoyo, 2014).

4.2 Materials and Methods

4.2.1 Materials

The feedstock used for these experiments were three kinds of municipal plastic wastes, i.e. polyethylene bag with (PE bag 2) and without (PE bag 1) crushing and washing, and high density polyethylene (HDPE) waste after crushing and washing. PE

bag 1 was obtained from Piyungan disposal site while PE bag 2 and HDPE waste were obtained from a small plastic recycling company in Yogyakarta city, Indonesia. The appearance of the feedstock are shown in Fig. 4.2. The recycling process flowchart of waste plastics in the company can be seen in Fig. 4.3. They used a simple process i.e. sorting, crushing, washing and drying. The catalysts used for these works were commercial Y-Zeolite and natural zeolite.

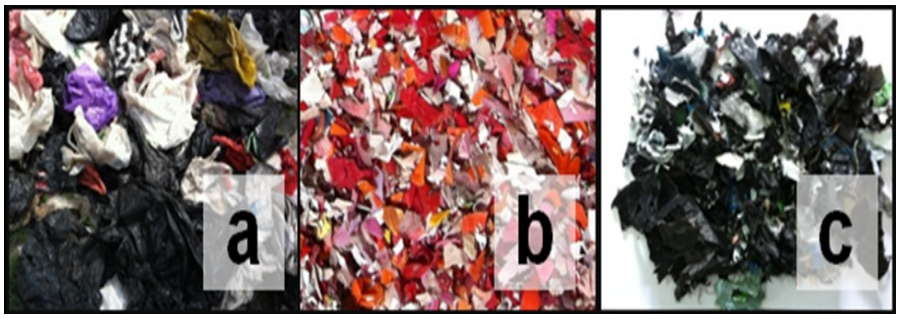

Fig. 4.2. The feedstock used in the experiments : a) PE bag 1, b) HDPE waste dan c) PE bag 2

The Y-Zeolite (CBV 780 CY) was obtained from Zeolyst International. It has SiO_2/Al_2O_3 with the mole ratio of 80, the unit cell size of 24.24 Å and the surface area of 780 m^2/g in the powder form. The diameter of the pellet was 1.6 mm which contains 20% of aluminum oxide as a binder. Natural zeolite was collected from Klaten, Indonesia. The natural zeolite was calcined at 500^oC for 3 hours to remove some volatile substances.

Fig. 4.3. Flowchart of recycling of waste plastics in Yogyakarta city, Indonesia

Table 4.1. Chemical composition and BET surface area of natural zeolite (NZ)

	Si/Al ratio	Na/Si	Mg/Si	K/Si	Ca/Si	Fe/Si	S_{BET} ($m^2.g^{-1}$)
NZ	4.21	0.007	0.009	0.021	0.238	0.093	91.146

The chemical properties and the BET surface area of natural zeolite is shown in Table 4.1. In order to examine the crystalline structure in the natural zeolite, the XRD patterns of sample is shown in Fig. 4.4. It varied depending on their mining sites. It can be seen that the main structure of the natural zeolite catalyst was identified to be mordenite. Fig. 4.3 shows five main peaks in the 2θ region i.e. 9.66, 22.36, 25.72, 26.56 and 27.68. Most of the peaks observed at 2θ (degree) for the natural zeolite samples can be assigned to be those of mordenite type crystalline matter as reported by Trisunaryanti et al (1996). The samples showed relatively broad base lines. This suggests that the samples contain amorphous and crystalline impurities.

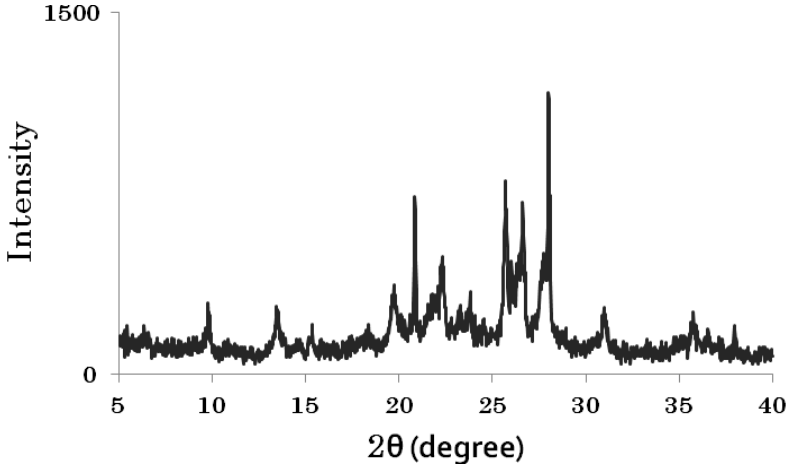

Fig. 4.4. X-Ray powder diffraction pattern of natural zeolite sample

4.2.2 Pyrolysis and Catalytic Reforming Experiments

Pyrolysis and catalytic reforming experiments were carried out in a pilot scale two stage reactor using batch system. It consists of the pyrolysis reactor and the catalytic reforming reactor. The snapshot of the experimental apparatus is shown in Fig. 4.5. The pyrolysis reactor and the reformer were made of stainless steel and covered with electric

heaters. The pyrolyzer`s inner diameter and height are 200 mm and 400 mm, respectively. The reformer`s inner diameter and height are 100 mm and 400 mm, respectively. A shell and tube type condenser was installed at the outlet of the reformer to separate gas and liquid products. An oil collector was installed at the bottom of the apparatus.

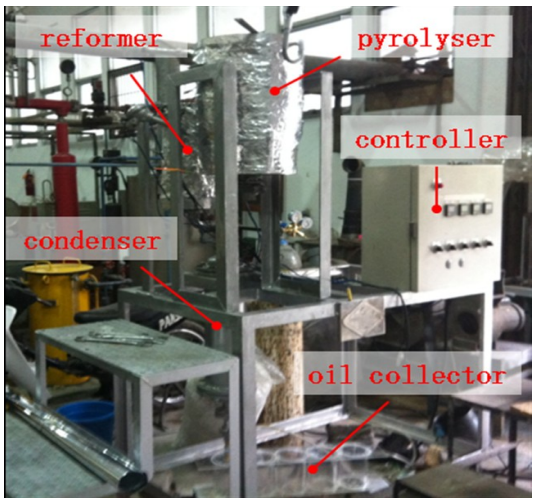

Fig. 4.5. The snapshot of experimental apparatus

In these experiments, 1.6-2.6 kg of the feedstock was fed into the pyrolysis reactor. The pyrolyzer and the reformer were then heated up to the preset temperatures. The catalyst (100 g) was loaded in the catalytic reforming reactor, where the pyrolysis gas generated in the first reactor was reformed. After having the reforming reaction, the gas was condensed into liquid products in the condenser. Liquid products were then collected and weighed for the mass balance calculation.

The experiments were carried out at the pyrolyzer temperature of 450°C and the reforming temperature of 450°C. The gaseous products were burned off to prevent emissions from hydrocarbon gases.

4.2.3 Liquid Product Analysis

The fraction of liquid products were analysed by using a gas chromatography-mass spectrometry (GC-MS, QP2010S Shimadzu). The column was DB-1 (Crossbond R 100% dimethylpolysiloxane) capillary column, 30m length with 0.25 mm diameter and 0.2 μm film thickness. Helium was used as the carrier gas. The temperature program used was; the initial temperature of 80°C for 5 min followed by the heating rate of

8 °C /min to 305 °C and then held at 305°C for 17 min. The other properties were analyzed based on the ASTM methods as shown in Table 4.2.

Table 4.2. ASTM methods used for liquid analysis

Properties	**ASTM method**
Density	ASTM D1298
Kinematic viscosity	ASTM D 445
Flash point	ASTM D 93
Pour point	ASTM D 97
Water content	ASTM D95
Heating value	ASTM D240

4.3 Results and Discussions

4.3.1 Effect of Different Types of Feedstock

The product yields as the effect of different types of the feedstock can be seen in Fig. 4.6. Commercial Y-Zeolite was used in these experiments. PE bag 1 obtained from the final disposal site still produced water and the highest portion of solid residue because of uncrushed and unwashed sample. It means that very high impurities were exist in the sample. The water might be obtained from organic material impurities which normally have high moisture content. These impurities have also led to a high percentage of gaseous product. The organic materials such as biomass produced a high gaseous fraction up to 50% during the pyrolysis process (Encinar et al., 2009; Williams and Horne, 1995). All samples produced higher solid residues compared with those of pure plastics as reported by others which produce less then 5% of residues (Park et al., 1999; Seo et al., 2003). It means that the impurities were dominated in the solid residues. HDPE waste produced the highest liquid fraction and the lowest gaseous fraction. The strong structure of HDPE made it more difficult to crack the hydrocarbon chains into lighter hydrocarbons.

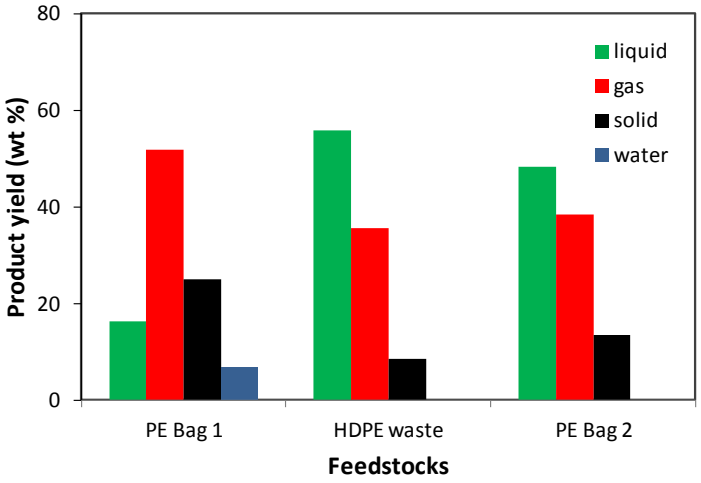

Fig. 4.6. Effect of different types of feedstock on the product yields of MPW pyrolysis

The impurities of the MPW can be seen from elemental analysis which is found elsewhere. The elemental analysis of the waste plastics is shown in Table 4.3. The waste plastics contain mainly carbon which shares around 80% by weight. From the table we can see that the presence of impurities contributed to the increase of hydrogen, oxygen and nitrogen contents of the feedstock. Thus, the carbon content has been reduced by the impurities. The main possible impurities which is found in MPW is organic materials such as from food wastes.

Table 4.3. Elemental analysis of waste plastics (Cho et al., 2009; Kumar et al., 2013)

Elements (wt%)	Virgin HDPE	Waste HDPE	Mixed plastics
C	85.58	80.58	79.9
H	13.67	13.98	12.6
O	-	5.19	5.10
N	0.11	0.60	-
S	-	0.080	-
Cl	-	-	1.13

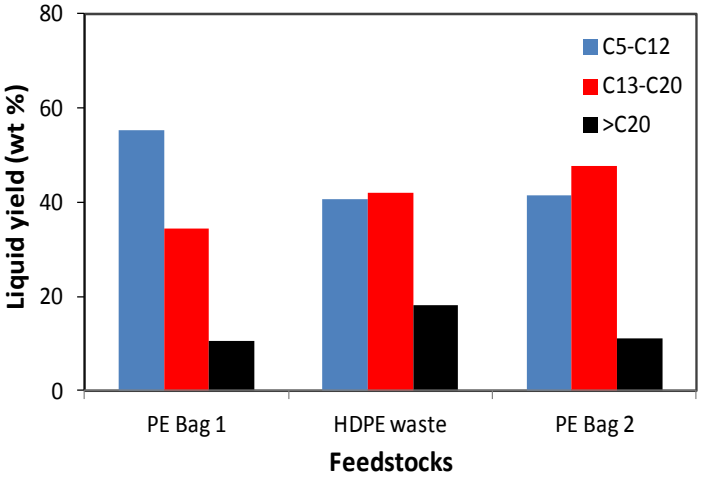

Fig. 4.7. Effect of different types of feedstock on the liquid fraction composition of MPW pyrolysis

However, the heavy oil fraction was still high in the oil from HDPE waste as shown in Fig. 4.7 indicating the low quality of the oil. The liquid products have been classified into three groups i.e. the gasoline fraction (C_5-C_{12}), the diesel fuel fraction (C_{13}-C_{20}) and the heavy oil (>C_{20}). As can be seen in Fig. 4.7, PE bag 2 produced the highest diesel fraction while PE bag 1 produced the highest gasoline fraction. As mentioned previously, the organic materials presence in PE bag 1 contributed to the high fraction of gasoline as reported by Lei et al. (2011) for biofuel production. It was found that C_6-C_{14} chemical compounds were up to 95% of bio-oils. HDPE waste yielded lower diesel fuel fraction than that of PE bag 2. This is due to the different materials in PE bag 2 which consist mostly of low density polyethylene.

The properties of the liquid products from the pyrolysis and catalytic reforming of MPW are shown in Table 4.4. The properties of commercial diesel fuels in Indonesia are also shown in Table 4.5 for comparison. Indonesia produced two kinds of diesel fuels viz. Diesel 48 (solar) and Diesel 51 (Pertamina Dex). Diesel 48 was commonly used for transportation vehicle since the government subsidizes this kind of fuel. As can be seen in Tables 4.4 and 4.5, the density of waste plastics oils (WPO) is acceptable for substituting commercial diesel fuels. As mentioned previously, the presence of catalysts and increasing temperature may reduce the density of fuels. The increase of the density will increase the volumetric energy density of the fuel and advance the dynamic injection timing which finally affects the engine combustion and emission.

Table 4.4. Properties of liquid products for various feedstock

Properties	Units	PE Bag 1	HDPE waste	PE Bag 2
Density @ 15°C	g/cm3	0.8544	0.7991	0.824
Kinematic viscosity @ 40°C	cSt	1.739	2.319	1.838
Flash point	°C	<10	<10	<10
Pour point	°C	24	27	24
Water content	%vol	0.1	0.5	trace
Heating value	MJ/kg	41.45	42.82	46.67

However, the kinematic viscosity of WPO was lower than those of commercial diesel fuels for PE bag 1 and PE bag 2. The higher fraction of gasoline and the lower fraction of heavy oil contributed to the lower kinematic viscosity. The viscosity plays a significant role in the lubrication of fuel injection systems, particularly those incorporating rotary distributor injection pumps that rely fully on the fuel for lubrication within the high pressure pumping mechanism (Hansen et al., 2005). Lower fuel viscosity lead to greater pump and injector leakage reducing the maximum fuel delivery and ultimately power output. The flash points were lower than those of diesel fuels. The flash point is an important parameter in relation to fuel storage. Higher flash point will be safer for storing and transporting the fuels.

WPO produced higher pour point than those of diesel fuels since the presence of heavy oil which normally has a high pour point. This property becomes very important when running a diesel engine under very low temperature condition especially in subtropical countries. The oil produced from polyethylene has very high linear paraffins. The tendency of paraffin crystals to aggregate up at a low temperature to form sheet can result in fuel-filter blockages (Scheirs, 2006). The water content presence in WPO was high. The presence of water will reduce the energy content in the fuel and finally affect to the performance of diesel engine. Water also cause sparking, spitting and flashback of the flame, which result in loss of heat as a result of improper combustion (Lee, 2006).

Table 4.5. Properties of commercial diesel fuels according to Indonesian Government regulation (DEMRI, 2006)

Properties	**Units**	**Diesel 48 (Solar)**	**Diesel 51 (Pertamina Dex)**
Cetane number		48	51
Density @ 15°C	g/cm3	0.815-0.870	0.820-0.860
Kinematic viscosity @ 40°C	cSt	2.0-5.0	2.0-4.5
Flash point	°C	min 60	min 55
Pour point	°C	max 18	max 18
Water content	mg/kg	max 500	max 500
Sulfur content	%wt	max 0.35	max 0.05
Ash content	%wt	max 0.01	max 0.01

Chemical compounds in the pyrolytic oil will boil at a certain temperature defining the distillation range of the oil. Distillation range is the difference in degrees between the initial boiling point (IBP) and the end point. Thus distillation range will vary according to the type of oil. Fig. 4.8 shows the distillation curve of the pyrolytic oil and commercial diesel fuel. The figure shows that the distillation temperature of the pyrolytic oil was lower than that of diesel fuel. The presence of gasoline fraction in the pyrolytic oil reduced the distillation temperature of the oil.

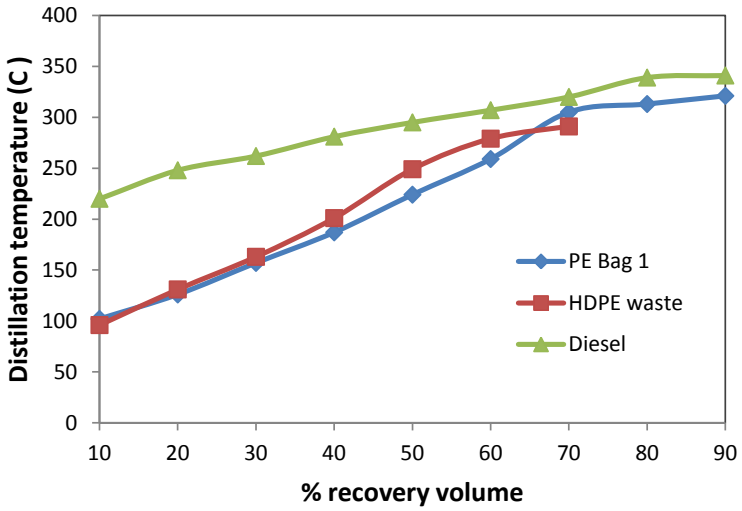

Fig. 4.8. Distillation curve of the pyrolytic oil and commercial diesel fuel

The cetane index of the pyrolytic oil can be calculated based on the data from the distillation curve in Fig. 4.8. The cetane index is used as a substitute for the cetane number of diesel fuel. It is calculated based on the fuel density and the distillation range. The calculation method follows the ASTM method. There are two ASTM method for the cetane index calculation namely ASTM D976 and ASTM D4737. The formula for these methods are as follows :

ASTM D976

Cetane Index = $454.74 - 1641.416\,D + 774.74\,D^2 - 0.554\,T50 + 97.803[\log10(T50)]^2$

where D = fuel density and

T50 = the temperature corresponding to the 50% point on the distillation curve in degrees C

ASTM D4737

Cetane Index = $45.2 + 0.0892(T10N) + 0.131(T50N) + 0.0523(T90N) + 0.901B(T50N) - 0.420B(T90N) + 4.9x10\text{-}4(T10N)^2 - 4.9x10\text{-}4(T90N)^2 + 107B + 60\,B^2$

where T10N = T10 - 215

T50N = T50 – 260 : T90N = T90 - 310

when T10, T50, and T90 are temperatures at 10%, 50%, and 90% volume distilled in degrees C and

B = [exp(-3.5DN)] - 1 when DN = density - 0.85

The cetane indexes of the pyrolytic oil and diesel fuel are shown in Table 4.6. The result shows that PE bag 1 produced a lower cetane index than that of diesel fuel while HDPE waste produced a higher cetane index. The cetane index or the cetane number is a measure of the fuel ignition and combustion quality characteristics. Fuels with a low cetane number will cause hard starting, rough operation, noise and increase the smoke opacity. A lower cetane number also means longer ignition delays, allowing more time for fuel to vaporize before combustion starts. A higher cetane index of the oil produced from HDPE waste is because of the linear paraffin in HDPE which is dominant in the final product.

Table 4.6. Cetane index of the pyrolytic oil and diesel fuel

	Method	PE Bag 1	HDPE waste	Diesel
Calculated Cetane Index (CCI)	ASTM D976	34	61	54
	ASTM D4737	25	-	51

4.3.2 Effect of Catalysts

Fig. 4.9 shows the product yields obtained from the sequential pyrolysis and catalytic reforming of municipal plastic wastes as the effect of catalysts. PE bag 2 has been used as a feedstock in these experiments. It can be seen that the thermal pyrolysis (without catalyst) produced the highest liquid fraction. The presence of catalyst reduced the liquid fraction and increased the gaseous fraction. Theoretically, the catalyst can enhance the cracking reaction of the pyrolysis gas. Long chain hydrocarbons have been cracked into lighter hydrocarbon gases. Pyrolysis over natural zeolite catalyst produced larger amount of liquid products compared with Y-Zeolite catalyst. This is due to different activity between natural zeolite and Y-Zeolite. The NZ and Y zeolite catalysts have different properties so that they will produce different composition of the products. As can be seen from the data in Chapters 2 and 3, Y zeolite has the surface area of 780 m^2/g which is much larger than NZ catalyst whose surface area is only 91.146 m^2/g. The larger surface area of Y zeolite gives more contact between the catalyst and the pyrolysis gas so that more cracking reaction will be occured. Therefore, Y zeolite produces higher gaseous product and lower liquid product since the longer chain hydrocarbon will be cracked into shorter chain hydrocarbons. The liquid composition also has a similar trend. The heavy oil and the diesel fraction of Y zeolite were found to be lower than those of NZ catalyst since some heavy oil and diesel fraction have been cracked into the gasoline fraction.

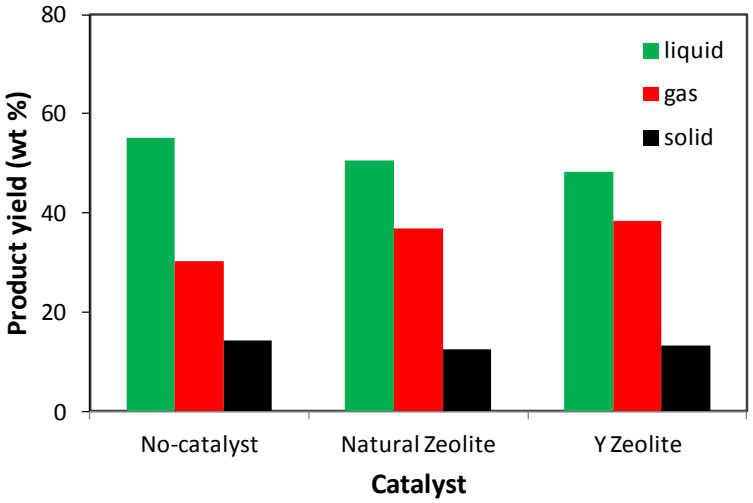

Fig. 4.9. Effect of catalysts on the product yields of MPW pyrolysis

However, the presence of catalysts have slight effect on the product yields. This might be due to the presence of impurities as mentioned previously. The impurities which contains some toxic materials will deactivate the catalysts. Thus, the catalysts will have the activity at the beginning of the reforming process and deactivate in the end of the process.

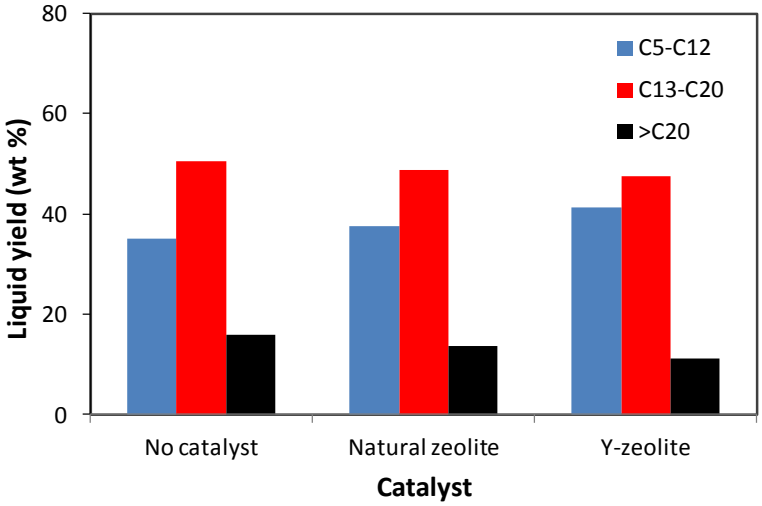

Fig. 4.10. Effect of catalysts on the liquid fraction composition of MPW pyrolysis

Fig. 4.10 shows the carbon atom number distribution of WPO over different catalysts. The heavy oil fraction (>C_{20}) could be slightly reduced which affected to the quality of the oils. On the other hand, the gasoline fractions (C_5-C_{12}) were increased because of the cracking of longer chain hydrocarbons into lighter chain hydrocarbons. The

diesel fraction was almost the similar in all conditions. This is because the balance between the addition of the diesel fraction from the heavy oil cracking and the reduction of the diesel fraction cracked into the gasoline fraction.

Table 4.7 shows the properties of liquid products over different catalysts. Similar results have been obtained for all properties. The presence of the catalysts slightly decreased the pour point. However, the values were still higher than those of commercial diesel fuels. This condition will make WPO become solid in a low temperature condition. The problems with a high pour point of WPO can be overcome by using additional heater before injecting the fuel to ensure fluidity and keep the viscosity of the fuels. The heating value of WPO were similar to the common commercial fuels due to the same origin of plastics and commercial fuels which are produced from petroleum oil.

Table 4.7. Properties of liquid products for different catalysts

Properties	**Units**	**No catalyst**	**Y-Zeolite**	**Natural Zeolite**
Density @ 15°C	g/cm3	0.8719	0.824	0.868
Kinematic viscosity @ 40°C	cSt	1.999	1.838	2.191
Flash point	°C	<10	<10	<10
Pour point	°C	27	24	24
Water content	%vol	0.5	trace	trace
Heating value	MJ/kg	46.74	46.67	45.58

4.3.3 Solid Residues

The proximate analysis and the heating value of the solid residue produced are shown in Table 4.8. The results show a higher ash content of solid residues produced from MPW compared with raw plastics as reported in previous chapter. PE bag 1 produced higher ash content of the solid product than others due to the high impurities which reduce the heating value of the product. PE bag 2 has the lowest ash content and the highest heating value. In waste plastics, fixed carbon and volatile matter contributed to the high heating value of solid products. Unlike biomass, volatile matters in waste plastics contain mostly hydrocarbon gases which have high energy content. Therefore,

plastic pyrolysis produced higher heating value solid products than those of biomass and low rank coal as reported by others (Demirbas, 2007; Sheng and Azevedo, 2005). They can be used either for blending with biomass and coal or for single fuel.

Fig. 4.11. The photographs of solid residues produced from pyrolysis of MPW

Table 4.8. Proximate analysis of solid residues

	Composition (wt.%)		
	PE Bag 1	**HDPE waste**	**PE Bag 2**
Moisture	1.12	1.74	2.32
Volatile matter	35.29	58.56	44.47
Fixed carbon	14.13	8.59	25.88
Ash	49.47	31.11	27.33
Heating value (MJ/kg)	19.80	26.35	31.53

4.4 Conclusion

The sequential pyrolysis and catalytic reforming of Indonesian municipal plastic wastes have been done over Y-Zeolite and natural zeolite catalysts. The results show that the feedstock types strongly affect the product yields and the quality of liquid and solid products. HDPE waste produced the highest liquid fraction. However, the heavy oil fraction was still high in the oil from HDPE waste. The highest diesel fraction has been produced in PE bag 2 while PE bag 1 produced the highest gasoline fraction. The catalyst presence reduced the liquid fraction and increased the gaseous fraction. Pyroly-

sis with natural zeolite catalyst produced higher liquid products compared with Y-Zeolite catalyst. However, the presence of catalysts have slight effect on the product yields. This might be due to the presence of impurities in MPW. The quality of WPO was still lower than those of commercial diesel fuels according to the oil properties. Blending of WPO and diesel fuels will obtain better quality of oil. MPW pyrolysis produced higher heating value solid products than those of biomass and low rank coal, so that they still can be used for blending with biomass and coal.

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Chapter 5

5 Performance and Emission Analysis of Blends of Waste Plastic Oil and Diesel Fuel in a Diesel Engine

Abstract

In this chapter, the performance and emission of a diesel engine have been studied using blends of waste plastics oil with diesel fuel under different loads condition. The waste plastics oil (WPO) used in this study was produced from the sequential pyrolysis and catalytic reforming of polyethylene bag after crushing and washing (PE bag 2) using natural zeolite (NZ) catalyst. Engine tests were conducted using a four cylinder, four strokes, and water cooled diesel engine. The engine type was Nissan Diesel SD22 Series with the compression ratio of 22. The experiments were conducted at the rated engine speed of 1800 rpm. The results show that the brake thermal efficiencies are slightly higher as compared to that of diesel. However, the difference was not significant since the calorific value of WPO is found to be similar with that of diesel. Furthermore, the brake specific fuel consumption (BSFC) is slightly reduced when blending diesel fuel with WPO. Reduction of BSFC means the increase of the thermal efficiency of the engine as mentioned above. Moreover, the blends of WPO with diesel fuel at various engine loads are also found to have influences on the emissions of NO_x, HC, CO and the smoke opacity. The NO_x emission is found to be lowered by blending diesel with WPO. The decreased NO_x emission is due to the decrease of the in-cylinder temperature by the effect of the non-homogeneity of WPO. The emissions of HC and CO of WPO-diesel blends are higher than that of diesel. The increased CO emission is due to incomplete combustion by the effect of the decrease of the in-cylinder temperature, poor mixture preparation and local rich regions. Finally, the smoke opacity for WPO blends are slightly higher at higher loads. Higher smoke opacity may be due to poor atomization of WPO fuel.

5.1 Introduction

Many steps are being taken around the world to alternate petroleum based fuel due to the impact of the increase in the oil price and the reality of petroleum depletion. The urgent need for alternative fuel is essential to replace the conventional fuels. In addition, due to the rapid growth of automotive vehicles in the transportation sector, the consumption of oil keeps increasing. Waste plastics oil (WPO), which is produced from pyrolysis of waste plastics, can be a candidate for substituting petroleum based fuel due to the abundant sources of waste plastics.

Diesel engines as one of internal combustion engines which are widely used either in automotive vehicle or in power plant have a high potential for employing WPO as a fuel. Diesel engines have the highest thermal efficiency among any regular internal or external combustion engines due to their high compression ratio. Diesel engines are the most preferred power generators due to its excellent driveability and a higher thermal efficiency. Despite their advantages, they emit high levels of NO_x and smoke which will have an effect on human health. Hence, the strict emission regulation and the depletion of petroleum fuels have necessitated the search for alternative fuels for diesel engines (Kumar et al., 2013; Mani et al., 2011; Mani et al., 2009).

The root causes for these emissions are non-stoichiometric combustion, dissociation of nitrogen and impurities in the fuel and air. Reducing the major exhaust emissions of HC, CO, NO_x, solid particles and increasing the performance can also be done by adding the suitable additives to the fuel reduced with the present technology (Kumar et al., 2012). They are chemicals, which are added in small quantities either to enhance the fuel performance, or to correct deficiencies as desired by the current legislation.

Use of efficient diesel engines need encouragement in the future since they consume less fuel and significantly reduce the green house gas emissions like carbon dioxide. The efforts to achieve the reduction of the engine emissions and the fuel consumption while keeping the engine performance can be performed based on the injection characteristics. The most important injection characteristics are the injection pressure, the injection duration and the injection timing. The injection process influences the harmful NO_x and smoke emissions.

Diesel engines induct only air during the intake process. Late in the compression process, fuel is injected directly into the combustion chamber and mixes with air that

has been compressed to a relatively high temperature. The high temperature of the air serves to ignite the fuel. The power output of the diesel is controlled by controlling the fuel flow rate while the volumetric efficiency is approximately constant (Matthews, 2006). Although the fuel-air ratio is variable, diesel engines are always operated with overall fuel-lean.

Unlike the combustion process in the spark ignition engine, which occurs at almost the constant volume, the combustion process in the diesel engine is relatively slow, and the fuel-air mixture continues to burn during a significant portion of the expansion stroke (fuel continues to be injected during this portion of the expansion stroke) and the high pressure that would normally result from combustion is relieved as the piston recedes. After the combustion process is completed, the expansion process continues until the piston reaches BDC. Diesel engines may complete the five general engine processes with either a 2-stroke cycle or a 4-stroke cycle. Furthermore, diesel engines may be subclassified into either an indirect injection diesel engine or a direct injection diesel engine.

Utilization of WPO for fueling diesel engines is currently getting more attention. However, very little has been done to test this fuel in diesel engines. The performance and emission of WPO have been investigated in a direct injection diesel engine (Mani et al., 2009). Ignition delay was longer by about 2.5 ^{o}CA in the case of WPO compared to diesel. The thermal efficiency was found to be higher up to 75% of the rated power. Blending of WPO with diesel fuel have also been studied by some researchers (Kumar et al., 2013; Mani et al., 2011). The performance and emission of WPO in a diesel engine strongly depend on the chemical composition and the physical properties of WPO.

Mani and Nagarajan studied the effect of the injection timing on the performance and the emission characteristics of a direct injection diesel engine running on WPO. The result showed that by retarding injection timing, the brake thermal efficiency of the engine was found to be higher. On the other hand, the emissions of NO_x, CO and unburned hydrocarbons were found to be decrease. Retardation of the injection timing leads to fast start of combustion and combustion continues in the power stroke (Mani and Nagarajan, 2009). The exhaust gas recirculation (EGR) has been introduced to reduce the NO_x emission from diesel engines (Mani et al., 2010). The NO_x emission was found to be reduced due to the presence of higher heat capacity gases that reduces the peak combustion temperature.

However, most of the study discussed above have been done at the compression ratio of 17.5. Utilization of WPO at a higher compression ratio of diesel engines have not yet been studied. The compression ratio is the key parameter during combustion of the fuel in a compression ignition engine. A higher compression ratio gives faster laminar flame speed and consequently reduce the ignition delay period (Hirkude and Padalkar, 2014). In this chapter, we studied the performance and emission of a diesel engine by blending waste plastics oil (WPO) with diesel fuel at a higher compression ratio of the diesel engine. WPO used in this study was obtained by the experimental work conducted in the previous chapter.

5.2 Materials and Methods

5.2.1 Materials

The waste plastics oil (WPO) used in this experiments produced from the sequential pyrolysis and catalytic reforming of polyethylene bag after crushing and washing (PE bag 2) using natural zeolite (NZ) catalyst with the calcination treatment. In these experiments, about 2 kg of the feedstock was fed into the pyrolysis reactor. The experiments were carried out at the pyrolyzer temperature of 450°C and the reforming temperature of 450°C. The physical properties of waste plastics oil and diesel fuel is summarized in Table 5.1. WPO-diesel blends of 10% and 20% were used to test the engine. These blends are denoted as 10% WPO and 20% WPO. The appearance of WPO-diesel blends is shown in Fig. 5.1.

Table 5.1. Physical properties of waste plastics oil and commercial diesel fuel

Properties	**Units**	**Waste plastics oil**	**Diesel**
Density	g/cm^3	0.868	0.845
Kinematic viscosity	mm^2/s	2.191	4.012
Flash point	°C	<10	66.5
Pour point	°C	24	6
Water content	% vol	trace	trace
Heating value	MJ/kg	45.58	45.79

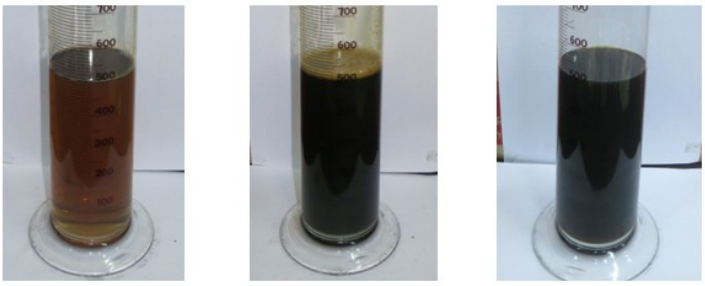

Fig. 5.1. Diesel fuel and WPO-diesel blends used in the experiments

Because of the limitation of the equipment, we did not measure elemental analysis of WPO. However, from the reference, some elemental analysis of WPO can be obtained. The elemental analysis of WPO is shown in Table 5.2. The chemical composition of WPO strongly depends on the waste plastics used as a feedstock. The carbon content of WPO ranges around 70-80% of the total components in WPO.

Table 5.2. Elemental analysis of waste plastic oil (Hariram and Vishnu, 2015; Islam et al., 2004)

Elements (wt%)	Waste plastic oil (HDPE, LDPE,PVC, PP)	Waste plastic oil (Bangladeshi MPW)
C	81.58	72.20
H	12.31	14.04
O	5.43	0.01
N	0.17	ND
S	0.41	ND
Ash	0.1	0.30

5.2.2 Experimental Set up of Diesel Engine

Engine tests were conducted on a four cylinder, four strokes, and water cooled diesel engine. The engine type was Nissan Diesel SD22 Series with the compression ratio of 22. The instrument panel and the snapshot of the diesel engine test bed can be seen in Fig. 5.2 and Fig. 5.3. The technical specifications of the test engine are given in

Table 5.3. The engine was coupled to an edy current dynamometer to provide the engine load. The air consumption of the engine was measured by using an U-tube manometer. The fuel flow rate was measured on volumetric basis using a burrete and a stopwatch. A thermocouple in conjunction with a digital temperature indicator was used to measure the exhaust gas temperature. The exhaust emissions were measured by using Star Gas and Optima 7 analysers. The experiments were conducted at the rated engine speed of 1800 rpm.

Table 5.3. Technical specifications of the test engine

Engine parameter	**Specification**
Make of model	Nissan SD22 Series
Injection system	Direct injection
Displacement	2164 cc
Cylinder number	4
Bore	83 mm
Stroke	100 mm
Compression ratio	22 : 1
Cooling system	water

The calculation of some parameters need to be done based on the data from experiments such as the torque, the power, the brake thermal efficiency and the brake specific fuel consumption. The formulas of each parameter are as follows :

Torque (T)

$$T = m \; x \; g \; x \; l \; (Nm) \tag{5.1}$$

where: g = gravitational acceleration (9.81 m/s^2)

l = length of torque arm (m)

m = mass measured in dynamometer (kg)

Brake Power (P)

$$P = \frac{2\pi.n.T}{60000} \; (kW) \tag{5.2}$$

where: n = rotational speed (rpm)

Brake Specific Fuel Consumption (BSFC)

$$BSFC = \frac{m_f}{P} \ (kg/kW.h) \tag{5.3}$$

$$m_f = \frac{b}{t} \cdot \frac{3600}{1000} \cdot \rho_f \ (kg/h) \tag{5.4}$$

where: m_f = fuel consumption (kg/h)

b = volume of burrete (50 cc)

t = time required for 50 cc fuel consumption (s)

ρ_f = density of fuel (kg/l)

Brake Thermal Efficiency (BTE)

$$BTE = \frac{P.K}{Q_f} \ x \ 100 \ (\%) \tag{5.5}$$

$$K = \frac{749}{p_a - \varphi . p_s} \sqrt{\frac{273+\theta_a}{293}} \tag{5.6}$$

where: K = correction factor for the torque and the power to standard condition

(p= 760 mmHg、 T= 20^{o}C, humidity = 65%)

p_a = atmospheric pressure (mmHg)

p_s = saturation vapour pressure (mmHg)

θ_a = room air temperature (^{o}C)

φ = relative humidity

$$Q_f = H \ x \ m_f \ x \ 4.184 \ / \ 3600 \ (kW) \tag{5.7}$$

where: H = calorific value of fuel (kcal/kg)

Fig. 5.2 The instrument panel of the diesel engine test bed

Fig. 5.3 Engine test bed used in the experiments

5.3 Results and Discussions

5.3.1 Brake Thermal Efficiency

Fig. 5.4 shows the variation of the brake thermal efficiency with respect to the load for diesel fuel and WPO-diesel blends. When the increase of the load and the brake power, the cylinder peak pressure will also increase as reported by Mani and Nagarajan (Mani and Nagarajan, 2009) and this is shown in Fig. 5.5. The increase of the cylinder peak pressure will affect to the increase of the ignition temperature. The higher combustion temperature then will increase the brake thermal efficiency of the engine.

It can also be observed from the figure that, WPO-diesel blends show slightly higher brake thermal efficiencies at 57-86% load compared to that of diesel fuel. As can be seen from the properties of WPO as shown in Table 5.1, the kinematic viscosity of WPO was lower than that of diesel fuel. The lower viscosity will make the fuel easily to be injected into the combustion chamber and will be sprayed into the combustion chamber more uniform. The second reason is that WPO contains some heavy oil hydrocarbon. The heavy oil will be injected deeper due to the higher ignition temperature of heavy oil so that there is enough time for heavy oil to penetrate in the combustion chamber. However, the difference was not significant as also reported by Gungor et al. (Güngör et al.,

2015). At the full load condition, blending diesel with WPO did not change the thermal efficiency of the diesel engine. The maximum increase of the brake thermal efficiency by about 6.77% could be obtained at 71% load when blending with 20% WPO. Blending with 10% WPO gave 3.09% increase of the brake thermal efficiency at the same load. Nevertheless, the difference of the brake thermal efficiency was not as high as another result (Kumar et al., 2013). This may be due to the calorific value of WPO which is found to be similar to that of diesel as can be seen in Table 5.1. The thermal efficiency of the diesel engine strongly depends on the energy content of the fuel.

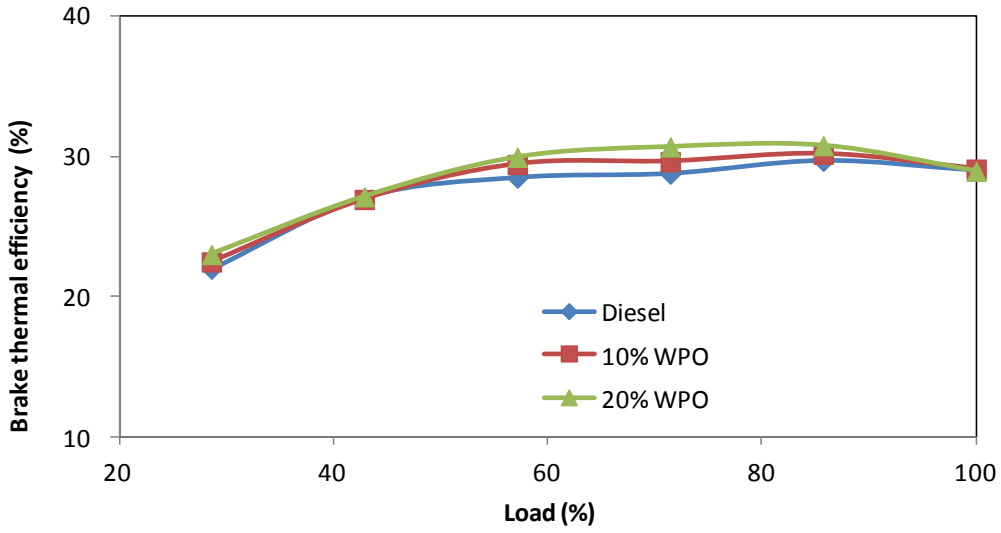

Fig. 5.4. Variation of brake thermal efficiency with load

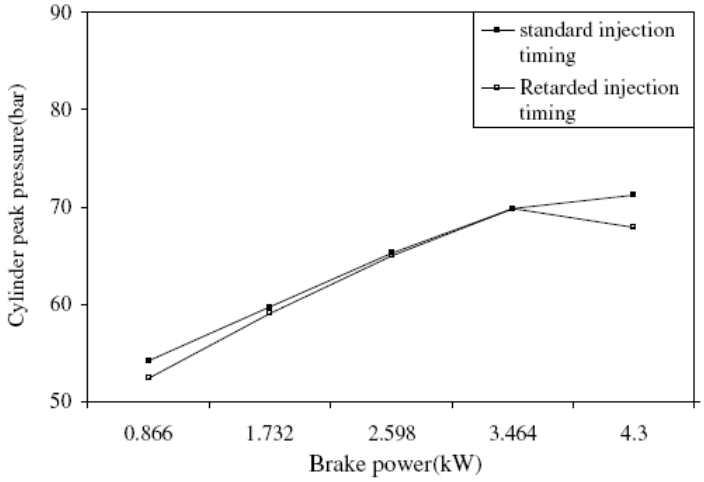

Fig. 5.5. Variation of cylinder peak pressure with brake power (Mani and Nagarajan, 2009)

In contrast to the above results, the brake thermal efficiency of WPO-diesel blends was found to be lower than that of diesel fuel. Reduction in the brake thermal efficiency by 1.9% was noticed at the full load for 100% WPO when compared with diesel fuel (Mani et al., 2011). Much lower reduction has been found by Kumar et al. which has 23.12% of the brake thermal efficiency at the full condition for diesel fuel compared with 19.13% of the brake thermal efficiency for 20% WPO, which mean there was about 17% of reduction in the brake thermal efficiency. The reason for this result is the fact that the calorific value of WPO used in their experiments was much lower than that of diesel fuel. Another reason is the higher compression ratio which is used in this study compared with the other studies which used 17.5 of the compression ratio. The higher compression ratio may increase the engine efficiency (Hirkude and Padalkar, 2014).

5.3.2 Brake Specific Fuel Consumption

The changes of the brake specific fuel consumption (BSFC) with the load for diesel and WPO-diesel blends are presented in Fig. 5.6. BSFC measures how efficiently an engine is using the fuel supplied to produce work. BSFC varies from 369.6 g/kW.h at a low load to 286.9 g/kW.h at the full load for diesel fuel and it varies from 366.0 g/kW.h to 282.8 g/kW.h for 10% WPO, 355.8 g/kW.h to 279.9 g/kW.h for 205 WPO. It can be seen that as the load increases the BSFC decreases for all fuels as expected. In the actual condition, the increase of the load will increase the fuel consumption since more energy required to balance the load. However, as mentioned in Eq. 5.3, the BSFC is the ratio of the fuel consumption and the output power. Based on the experimental data, we can see that the increase of the power produced from the engine was higher than the increase of the fuel consumption. As a result, the BSFC will decrease. As discussed previously, the larger increase of the power is due to the increase of the in-cylinder pressure and the temperature which affected to the increase of the thermal efficiency. At the same time, it can also be seen that BSFC is slightly reduced when blending diesel fuel with WPO. Reducing BSFC means the increase of the thermal efficiency of the engine. As mentioned previously, the reason is that the lower kinematic viscosity of WPO and the heavy oil presence in WPO which affected to the better combustion reaction in the combustion chamber. However, the result also shows the similar BSFC at several loads due to the similar calorific value of WPO as previously discussed.

The different results have been found by the others (Kumar et al., 2013). The brake specific energy consumption became higher with the increase in the concentration of WPO in the blends. This is due to a low calorific value of WPO used in their experiments. In order to reduce BSFC and increase the thermal efficiency of the engine, some modification of the operating parameters can be done such as the injection timing and the injection pressure (Mani and Nagarajan, 2009). When the injection timing is retarded from 23^{o} bTDC to 14^{o} bTDC, the BSFC was found to be lower while the thermal efficiency was found to be higher. Retardation of the injection timing leads to fast start of combustion which increases the effective pressure to do work.

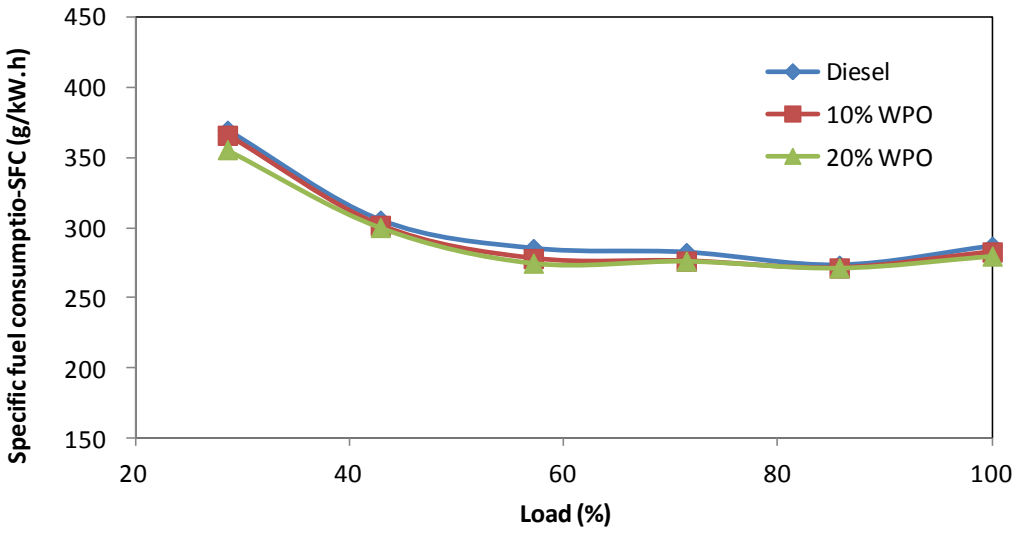

Fig. 5.6. Variation of brake specific fuel consumption with load

5.3.3 Exhaust Gas Temperature

The variation of the exhaust gas temperature with the load is shown in Fig. 5.7. The exhaust gas temperature varies from 240 ^{o}C at a low load to 540 ^{o}C at the full load for diesel whereas in the case of WPO-diesel blends it varies from 240 ^{o}C to 520 ^{o}C for 10% WPO and from 230 ^{o}C to 510 ^{o}C for 20% WPO. The results show that the exhaust gas temperature increased by increasing the load. The reason is that from the simple fact that more amount of fuel was required by the engine to generate the extra power for additional loading (Kumar et al., 2013). It can also be seen that the exhaust gas temperature was found to be slightly lower at a higher load when blending diesel with WPO fuel. WPO is a mixture of hydrocarbons which have both low and heavy fraction

of hydrocarbon chains. The presence of low fraction of hydrocarbon has lower energy content which may reduce the exhaust gas temperature.

Similar result has been found by Hamzah et al. and Sudrajad et al. when running WPO under various engine speeds. The higher exhaust gas temperature of diesel fuel may be caused by the higher boiling point for diesel fuel thus causing a higher exhaust gas temperature compared to WPO (Hamzah et al., 2014). Another reason for a lower exhaust gas temperature for WPO is due to a lower viscosity resulting in a lesser penetration of the fuel into the combustion chamber and the lesser amount of heat developed (Sudrajad et al., 2011). The exhaust gas temperature is affected by the combustion temperature, in-complete and retarded combustion. A lower exhaust gas temperature has also been found in a diesel engine when using fuel produced from pyrolysis of waste vehicle tires (İlkılıç and Aydın, 2011). The lower calorific value of this fuel is the main reason for the lower exhaust gas temperature.

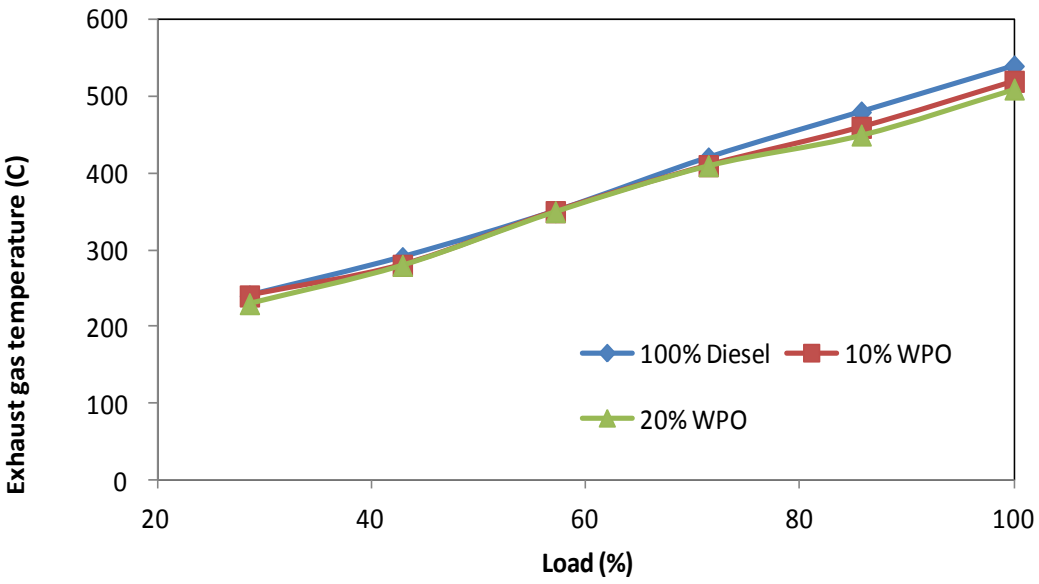

Fig. 5.7. Variation of exhaust gas temperature with load

5.3.4 Nitrogen Oxides

The nitrogen oxides (NO_x) is formed as a result of the oxidation of nitrogen in the air during burning of the air-fuel mixture in the combustion chamber. The formation of NO_x is highly dependent on the in-cylinder temperature, the oxygen concentration and the residence time for the reaction to take place (Mani et al., 2009). The variation of ni-

trogen oxides with the load is shown in Fig. 5.8. It was observed that the NO_x emission increases with the increase of the load from 208 ppm at a low load to 331 ppm at the full load condition for diesel fuel and from 166 ppm at a low load to 287 ppm at the full load for 20% WPO. The increase of the NOx emission with the increase of the load is due to the increase of the in-cylinder temperature which can be seen by the increase of the exhaust gas temperature as shown in Fig 5.7. The increase of the in-cylinder temperature is caused by the increase of the peak pressure as the effect of the load increase.

The formation of NO_x from the diesel engine is determined by the interaction of the chemical and physical processes occurring within the combustion chamber. There are three primary sources of NO_x i.e. the thermal NOx, the fuel NO_x and the prompt NO_x. The thermal NO_x results from the oxidation of atmospheric nitrogen under high temperature, in the post-flame region of the combustion system. The major factors that influence the thermal NO_x formation are the temperature, the concentration of oxygen and nitrogen, and the residence time. The fuel NOx comes from the conversion of fuel bound nitrogen to NO_x during combustion. During combustion, the nitrogen bound in the fuel is released as a free radical and ultimately forms free N_2 or NO. The prompt NO_x is the third source attributed to the reaction of the atmospheric nitrogen, N_2, with free radicals such as C, CH and CH_2 fragments derived from fuel.

The virgin plastic matrials such as PE, PP and PS have very low nitrogen contents in their composition. However, some waste plastics have higher nitrogen contents due to the impurities in the waste plastics. Table 4.3 and 5.2 show the elemental analysis of the waste plastics and waste plastics oil. Waste HDPE contains 0.6% of nitrogen while mixed plastics contain no nitrogen. The most important thing to reduce NOx formation in a diesel engine is by controlling the combustion condition itself such as temperature, fuel mixing, residence time, and injection timing.

The figure also shows that the NO_x emission was found to be lower by blending diesel with WPO. The decreased NO_x emission is due to the decrease of the in-cylinder temperature as the effect of non-homogeneity of WPO. Similar result has been reported by Sudrajad et al. at various engine speeds (Sudrajad et al., 2011). There are some different methods widely used to reduce NO_x from diesel engine i.e. the exhaust gas recirculation, the retarded injection timing, the fuel denitrogenation, the stage injection of fuel, the water injection, etc. The exhaust gas recirculation (EGR) is one of the most

effective techniques being adopted for reducing the NO_x emission. The reduction in the NOx emission with the increase of EGR percentage is due to the presence of inert gas (CO_2 and H_2O) in EGR. These gases absorb energy released by combustion, which reduces the peak combustion temperature in the combustion chamber (Mani et al., 2010). The retarded injection timing also reduced the NO_x emission for WPO (Mani and Nagarajan, 2009).

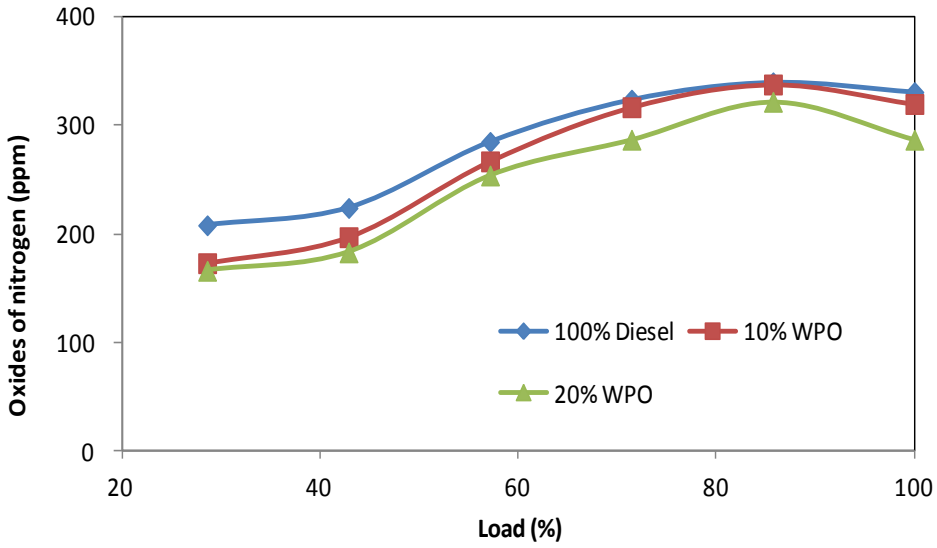

Fig. 5.8. Variation of nitrogen oxides with load

5.3.5 Unburned Hydrocarbon

The unburned hydrocarbon (HC) is a useful measure of combustion inefficiency which consists of fuel that is incompletely burned. The variation of unburned hydrocarbon with the load for tested fuels is shown in Fig. 5.9. The HC emission varies from 17 ppm at a low load to 3 ppm at the full load conditions for diesel and from 23 ppm at a low load to 5 ppm at the full load conditions for 20% WPO. It can be noticed that the concentration of the hydrocarbon of WPO is higher than that of diesel. The higher HC emission in WPO-diesel blends compared to diesel may be attributed to the reason that the fuel spray did not propagate deeper into the combustion chamber. When the WPO blend fuel injected and mixed with air, because of non-homogeneity of fuel-air mixture, some local spots in the combustion chamber will have mixture that will be too lean to combust properly, and some fuel spots may be too rich with unsufficient oxygen to burn all the fuel (Mani et al., 2011).

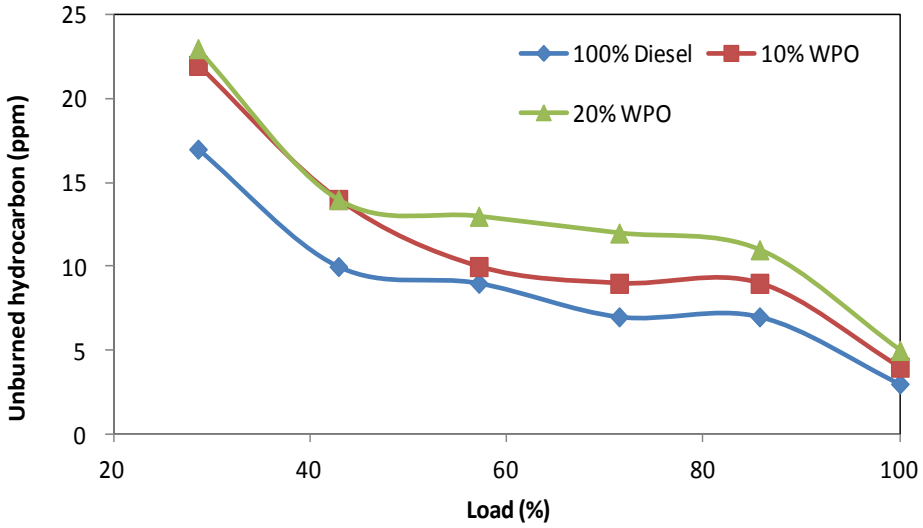

Fig. 5.9. Variation of unburned hydrocarbon with load

Unburned hydrocarbon emissions are also related to the fuel volatility and the viscosity. High viscosities lead to larger droplet sizes and reduce the vapour pressure (Kumar et al., 2013). At a lower load, large amounts of excess air and a low exhaust gas temperature and lean fuel air mixture regions may survive to escape into the exhaust. The HC emission was decreasing with the increase of the load. At a light load, a high fuel supply also lead to higher hydrocarbon. The retarded injection timing may be applied for WPO to reduce the HC emission in diesel engines (Mani and Nagarajan, 2009). On the other hand, EGR may increase the HC emission since the reduction of oxygen in the inlet charge. Lack of oxygen is responsible for the reduced oxidation rate which leads to incomplete combustion, hence higher HC emissions (Mani et al., 2010).

5.3.6 Carbon Monoxide

Fig. 5.10 shows the variation of the CO emission with the load. The CO emission is mainly due to the lack of oxygen, poor air entrainment, mixture preparation and incomplete combustion during the combustion process (Mani et al., 2011). In general, diesel engine operates with lean mixtures and hence the CO emission would be low. CO is an intermediate product in the combustion of hydrocarbon fuels. Hence, the CO emission is greatly dependent on the air fuel ratio relative to the stochiometric proportions.

The concentration of CO ranged from 269 ppm at a low load to 85 ppm at the full load conditions for diesel, whereas for WPO-diesel blends it varied from 281 ppm at a low load to 91 ppm at the full load for 10% WPO and from 295 ppm at a low load to 106 ppm at the full load for 20% WPO. The increased the CO emission is due to incomplete combustion as the effect of reducing the in-cylinder temperature, the poor mixture preparation and local fuel rich regions.

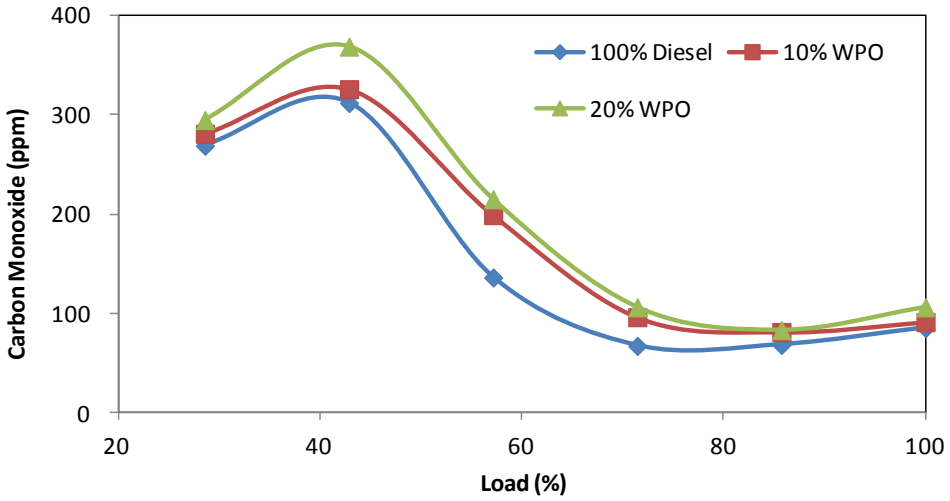

Fig. 5.10. Variation of carbon monoxide with load

The figure also shows the reduced CO emissions at a higher load. The reason is that at a higher load, the in-cylinder peak pressure increased which increased the in-cylinder temperature. A higher combustion temperature will enhance the oxidation rate converting hydrocarbon fuel into carbon dioxides (CO_2). Hence, the CO emission will be significantly reduced. However, at a lower load, the CO emission was also reduced. The reason is that at a lower load, the air fuel ratio was high, which means there was more excess air that could be reacted with CO to produce CO_2. The retarded injection timing and EGR could also be used to reduce the CO emission for WPO (Mani and Nagarajan, 2009; Mani et al., 2010). The retarded injection timing resulted in a higher heat release leading to complete combustion, whereas EGR raised the intake air temperature that could lead to a reduction of the CO emission.

5.3.7 Smoke Opacity

Smoke is solid soot particles suspended in exhaust gas. The smoke opacity is important because it gives an indication of the concentration of pollutant leaving a smoke stack. Fig 5.11 shows the variation of the smoke opacity with the load for diesel and WPO-diesel blends. The smoke opacity ranges from 1.1% at a low load to 4.3% at the full load for diesel and from 1.1% at a low load to 5.5% at the full load for 20% WPO. It can be observed that the smoke opacity was almost similar at lower loads. However, the smoke opacity for WPO blends were higher at higher loads. A higher smoke opacity may be due to poor atomization of WPO fuel. Bigger size of fuel molecules contained in WPO is considered to result in poor atomization. Non-homogenity of WPO fuel will also affect to the higher smoke of WPO fuel. A lower combustion temperature, reduced duration of combustion and rapid flame propagation may also be the reasons for a higher smoke opacity.

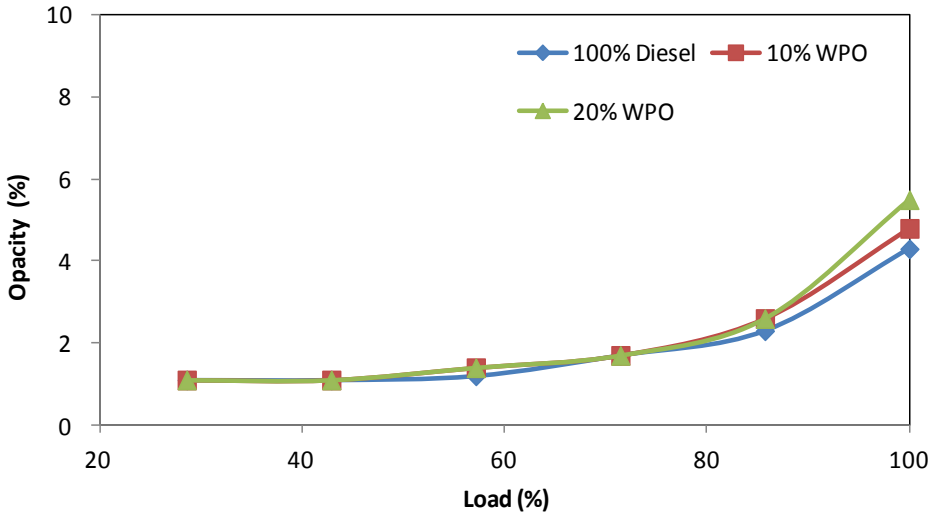

Fig. 5.11. Variation of smoke opacity with load

Nevertheless, EGR and the retarded injection timing could not be used to reduce the smoke opacity for WPO. The smoke opacity increased with the increase of the EGR percentage (Mani et al., 2010). The reason is due to partial replacement of air by exhaust gases, which results in combustion instability. The retarded injection timing also increased the smoke opacity of WPO. Higher smoke values may be due to unburned and partially reacted hydrocarbons. Similar trend was also found when running diesel engines with waste tyre pyrolysis oil (İlkılıç and Aydın, 2011; Murugan et al., 2008).

5.4 Conclusion

In this study, diesel engine tests have been done using blends of WPO with diesel fuel under different loads to investigate the impact of WPO on the performance and emission characteristics of the engine. Brake thermal efficiencies are slightly higher as compared to that of diesel. However, the difference was not significant since the calorific value of WPO which is found to be similar than that of diesel. BSFC is slightly reduced when blending diesel fuel with WPO. Reduction of BSFC means the increase of the thermal efficiency of the engine as mentioned above. The exhaust gas temperatures are found to be slightly lower at a higher load when blending diesel with WPO fuel. The presence of low fraction of hydrocarbon has lower energy content which may reduce the exhaust gas temperature.

The blends of WPO with diesel fuel at various engine loads are found to have influences on the emissions of NO_x, HC, CO and smoke opacity. The NO_x emission is found to be lower by blending diesel with WPO. The decreased NO_x emission is due to the decrease of the in-cylinder temperature as the effect of non-homogeneity of WPO. The concentration of HC of WPO blends is higher than that of diesel. The higher HC emission in WPO-diesel blends compared to diesel may be attributed to the reason that the fuel spray does not propagate deeper into the combustion chamber. The increased CO emission is due to incomplete combustion as the effect of reducing the in-cylinder temperature, poor mixture preparation and local rich regions. Finally, the smoke opacity is almost similar at lower loads. However, the smoke opacity for WPO blends are higher at a higher load. A higher smoke opacity may be due to poor atomization of WPO fuel. Bigger size of fuel molecules contained in WPO is considered to result in poor atomization.

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Chapter 6

6 Conclusions and Recommendations

6.1 Conclusions

In this study, the sequential pyrolysis and catalytic reforming of plastic materials has been investigated experimentally in lab-scale and pilot-scale reactors for utilizing the waste plastics oil in a diesel engine. Commercial Y-Zeolite catalyst and natural zeolite with some treatments have been used for catalytic cracking of the pyrolysis gases. The investigation on the performance and emission of waste plastics oil-diesel blends have been conducted using a four cylinder, four strokes and water cooled diesel engine with the compression ratio of 22.

Based on the findings and investigations of this study, some conclusions can be summarized as follows :

- When utilizing Y-Zeolite catalyst, the maximum oil production for HDPE (70.0wt%) and PS (88.1wt%) were obtained at the pyrolysis temperature of 450°C and 400°C respectively and at the same reforming temperature of 450°C and WHSV of 4. At these conditions, the diesel yield which can be obtained for HDPE and PS is 18.61% and 21.99%, respectively. The gasoline fraction is the highest yield since the higher activity of Y-Zeolite catalyst.
- The gaseous fraction of C_2, C_3 and C_{4+} (>75 mol %) are the main components of the gaseous products for HDPE, while C_2 and C_3 gases (>65 mol %) are the main components of the gaseous products of PS. The high quality gaseous product which is similar to liquefied petroleum gas (LPG) can be used as a fuel either for driving gas engines or for dual-fuel diesel engines. It can also be used as a heating source for the pyrolysis reactor.
- The residues produced in the pyrolysis reactor also produced solid products with high calorific values which can be utilized as a fuel as well.
- When utilizing natural zeolite catalyst, the maximum oil production for PP and PS are 86.4% and 97.4% respectively after the calcination treatment (A-NZ). The maximum diesel yield can be obtained utilizing A-NZ catalyst for PP and natural zeolite catalyst after calcinations and acid treatment (H-NZ) for PS. Natural zeolite cata-

lysts produced higher diesel fraction due to the lower activity of natural zeolite than Y-Zeolite catalyst.

- The gaseous product is dominated by propene (C_3) for PP and by propane and propene (C_3) for PS. These gases can also be used as a fuel to replace LPG.
- The experiments using real waste plastics (MPW) have also been done utilizing Y-Zeolite and A-NZ catalysts. HDPE waste produced the highest liquid product. However, the heavy oil fraction is still high. The highest diesel fraction has been produced from polyethylene bag after after crushing and washing (PE bag 2). The reforming over A-NZ catalyst produced higher liquid fraction compared with Y-Zeolite catalyst. However, the presence of catalysts have slightly affect to the product yields. This might be due to the presence of impurities in MPW. The quality of WPO was still lower than those of commercial diesel fuels in regards to the oil properties.
- The diesel engine tests have also been done using blends of WPO with diesel fuel under different loads to investigate the impact of WPO on the performance and emission characteristics of the engine. The brake thermal efficiencies are slightly higher as compared to that of diesel. However, the difference was not significant since the calorific value of WPO is found to be similar with that of diesel. The blends of WPO with diesel fuel are found to have influences on the emissions of NO_x, HC, CO and the smoke opacity. The NO_x emission is found to be lower by blending diesel with WPO. The emissions of HC, CO and the smoke opacity of WPO-diesel blends are higher than those of diesel.

6.2 Recommendations

In order to commercialise the sequential pyrolysis and catalytic reforming (SPCR) technology for recycling of waste plastics and to better understand the SPCR process, the following works are recommended for further studies :

- The interaction among different plastic materials is still unknown and need to be investigated since real waste plastics normally consist of some different plastic materials. By knowing this characteristics, the separation process do not need to be done in handling waste plastics.

- The preparation and modification of natural zeolite catalyst using different methods should be investigated to compare the catalytic effect. The impregnation with other materials such as Cr, Cu and Pd can also be investigated.
- The effect of the contamination in real waste plastics should be investigated in more detail. Virgin and real waste plastics should be investigated in bigger scale. The melting process before the pyrolysis process can also be investigated to remove some impurities before coming to the pyrolyzer.
- The distillation process to separate the diesel fraction should also be investigated to obtain the fuel that have similar properties with commercial diesel fuel. The other treatments to reduce some properties such as the water content, the ash content, and the pour point can also be studied.
- After obtaining the fuel which has similar properties with diesel fuel, the engine tests using 100% WPO should be investigated to understand the performance and emission of diesel engine running with WPO.