Pyrolysis Process of Mixed Polypropylene (PP) and High-Density Polyethylene (HDPE)
Waste with Natural Zeolite as Catalyst

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ABSTRACT

The reactor of the experiment was made from stainless steel with the diameter of 25 cm and the height of 30 cm. The liquid petroleum gas was used as a fuel in the reactor. The reactor was connected by the thermocouple that controls temperature variations at 410, 420, 430, and 450°C. Raw material contained plastic bottles and waste caps, while the natural zeolite as a catalyst was dried and cut in dimensions of 3x3 cm. A gas as the reacted product was condensed using the first condenser, then the liquid product was collected. Uncondensed gas was condensed again in the second condenser, then the liquid product was collected again. The volume of gas was calculated based on the water volume coming out of the gallon. This was repeated with varied ratios of plastics to natural zeolite (67:33; 75:25; 80:20; and 83:17 wt%). Pyrolysis was run for two hours and every 20 minutes the sample was weighed to gauge the change in mass of gas and liquid. After 120 minutes, the solid sample was examined to identify the mass of final solid. Based on the research, at the temperature of 440°C, the highest liquid yield was 68.42%. On the other hand, with the ratio of raw material to zeolite at 83:17 wt%, the largest yield of liquid was 87.31%. The liquid product in various temperature and comparisons of percentage of raw material to catalyst was found to meet diesel specifications based on The Decree of Director General of Fuels and Gas Year 200,8 Number 14,496 K/14/DJM/2,008.

Keywords: high-density polyethylene, polypropylene, pyrolysis, diesel-fuel

INTRODUCTION

Plastic has played a vital role in enhancing the living standards of human beings for more than 50 years. It is a key innovation used in many products from various sectors such as construction, healthcare, electronic, automobile, packing, and others. The demand for commodity plastics has increased due to the rapid growth of population. The global production of plastics reached about 299 million tons in 2013 and increased by 4% over 2012. The continuous rise of plastic demand leads to growing in waste accumulation per day. A statistic from 2013 reported that 33 million tons of plastic were generated in the US. In Europe, 25 million tons of plastic ended up in waste streams during the year of 2012. Statistics also established that in Europe about 38% of plastic waste went to landfills, 26% were recycled, and 36% was utilized for energy recovery. This shows that the percentage of plastic ended up in the landfills is still considerably high, thus occupying a huge space. Plastics may take up to billions of years to degrade naturally. They degrade gradually since the molecular bond containing hydrogen, carbon, and few other components such as nitrogen, chlorine, and others make plastics highly durable. The continuous disposal of plastic in landfills would definitively cause a serious environmental problem (Sharuddin, Abnisa, Daud, & Aroua, 2016).

There are four main approaches to recycling plastic wastes, which are primary, secondary, tertiary, and quaternary recycling. In primary recycling, product converted from waste plastics have a performance level comparable to that of original product made from virgin plastics. The recycling is very simple without any precaution except for the proper and clean collection of waste in the plant.

In secondary recycling, the product of plastics was conversion have less demanding performance requirement than original material. There are two main approaches to secondary recycling: One approach is to separate the plastics from their contaminant and then segregate the plastics into generic types, one or more of which are then recycled into products from virgin or primary recycled material. The other approach is to separate the plastics from their associated contaminants and re-melt them as a mixture without segregation. The treatment of plastics in a
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waste stream may include a series of material recycling methods, such as size reduction by granulators, shredder or crumbles, and separation of plastics, from other waste material and from one another.

In tertiary recycling, solid plastics are converted into smaller molecules as chemical intermediates by the use of heat and or chemical treatment. These chemical intermediates, usually liquids or gases but sometimes waxes, are suitable for the use as feedstocks for production of new petrochemicals and plastics (Kumar & Singh, 2011; Roozbehani, Motevassel, Mirdrikvand, Moqadam, & Kharaghani, 2017).

Quaternary recycling involves the recovery of the energy content of the plastic waste. The owing to the lack of other recycling possibilities, incineration (combustion) aimed at the recovery of energy is currently the most effective way to reduce the volume of organic material.

An alternative thermal approach for dealing with waste plastic is the so-called chemical feedstock or chemical recycling. This term has been used to describe a diversity of techniques including pyrolysis, hydrolysis, hydrogenation, methanolysis, and gasification. The most attractive technique of chemical stock is pyrolysis. Thermal cracking or pyrolysis involves the degradation of the polymeric material absence of oxygen. Unlike mechanical recycling technique in which the long polymeric chains of the plastics are preserved intact, pyrolysis produces smaller molecular weight fragments. The process is usually conducted at temperatures between 500 and 800°C and results in the formation of carbonized char and a volatile fraction that may be separated into condensable hydrocarbon oil and non-condensable high calorific value (Kumar & Singh, 2011).

Several authors have studied pyrolysis of polymers such as the mixed between polyethylene (PE) and polypropylene (PP) (Sakaki, Roozbehani, Shishesaz, & Abdollahkhani, 2014), mixed polymers containing different concentrations of low density polyethylene (LDPE), HDPE, and PP, (Roozbehani, Sakaki, Shishesaz, Abdollahkhani, & Hamedifar, 2015), polystyrene (Moqadam, Mirdrikvand, Roozbehani, Kharaghani, & Shishesaz, 2015), high density polyethylene (Levine & Broadbelt, 2009), polyolefins wastes (Mastellone & Arena, 2002), polypropylene (Gogotov & Barazov, 2014; Chen et al., 2007; Åkesson et al., 2013; Kumar & Singh, 2014), mixed between high density polyethylene and rubber seed shell (Chin et al., 2014), mixed between PE and PP (Aboulkas et al., 2010), mixed between olive residue with HDPE, (LDPE), (PP), and PS (Aboulkas et al., 2009), municipal plastic waste (MPW) consisting of a mixture of thermoplastics (HDPE, LDPE; PP; PS; and PET (Silvarrey & Phan, 2016), PE (Borusiewicz & Kowalski, 2016), coal and plastics blends (Zhou, Luo, & Huang, 2009), natural rubber (Al-hartomy et al., 2014), waste HDPE (Schwarzinger, Gabriel, Beimann, & Buchberger, 2012), binary mixtures PP and LDPE (Chowlu, Reddy, & Ghoshal, 2009), mixed between LDPE, HDPE, PP (Donaj, Kaminsky, Buzeto, & Yang, 2012).

The catalyst in the pyrolysis of plastics serves to reduce reaction time and temperature, to optimize its kinetics and to enhance the quality of the product (Moqadam et al, 2015). The catalysts utilized in upgrading plastics are generally classified into a fluid cracking catalyst, reforming catalysts, and activated carbon (Kunwar, Cheng, Chandrashekar, Sharma, 2016). Catalyst commonly used by many researchers include zeolites, cadmium, active matrix component, inactive matrix component, and binder (Roozbehani et al., 2017), silica-alumina (Moqadam et al., 2015), zeolite-based catalyst such as KBeta, HMOR, HZSM-5, HY, and KL zeolite (Levine & Broadbelt, 2009; Muenpol,Yuwapornpanit, & Jitkarnka, 2015), carbon-silica (Al-hartomy et al., 2014), zinc acetate (Siddiqui, Redhwi, & Achilias, 2012), natural zeolite without zeolite (Yuliansyah & Laksono, 2015), triethylaluminum Al (C3H5)3 (Donaj et al., 2012), commercial Y zeolite and natural zeolite (Syamsiro et al., 2014), zeolite-based catalyst such as ZSM-5, BEA, US-Y, MOR (modified nanocrystalline Y, amorphous silica-alumina (SAHA), silica-alumina and the family of mesoporous MCM material (Roozbehani et al., 2017). The aims of research are to investigate the influence of the rate of temperature and raw material to natural zeolite (wt%) on gas, liquid, and solid yields in the pyrolysis of mixed between PP and HDPE and to identify the physical properties of fuel, namely its specific gravity, API gravity, gross heating value, flash point, pour point, and kinematic viscosity.
EXPERIMENTAL SECTION

Plastic bottles considered as polypropylene (PP) and waste caps considered as high-density polyethylene (HDPE) were used in the research. Raw materials were bought from waste collectors at the Tirtonadi Bus Station, Surakarta, Central Java, Indonesia. Natural zeolite as a catalyst was bought from Bratachem. The pyrolysis equipment consisted of a reactor with a capacity of two kilograms, diameter of 25 cm and height of 40 cm, a condenser, two thermocouples, two liquid storages, a manometer, and three gas storages. Liquid petroleum gas was used for the combustion process. Two thermocouples were installed to monitor the process, one in the pyrolytic chamber (reactor) and the other at the exit line of the condenser. The raw material was cleaned and then cut into approximately uniform sizes of 3x3 cm. Approximately 800 grams of plastic bottles and 200 grams of cap waste were put into the reactor which was connected to a thermocouple to control the temperature operation. The pipe at the top of the reactor was connected to the cyclone which separates gas from solid. Gas produced by the reaction was condensed using the first condenser, resulting in a liquid product that was then collected. Part of the produced gas which was not condensed was condensed again in the second condenser and the yield was then stored in three gallons. The gas volume was calculated based on the volume of water flowing from the gallon. The operation was repeated with various ratios of plastics to natural zeolite, 67:33 wt%; 75:25 wt%; 80:20 wt%; and 83:17 wt%. Pyrolysis was performed for two hours, and every 20 minutes a sample was weighed to measure the mass changes of the gas and liquid. After 120 minutes, a solid sample was examined to determine the mass of the final solid. The other properties were analyzed with the ASTM method (Syamsiro et al., 2014) as shown in Table 1. The liquid product was analyzed in Petroleum, Gas, and Coal Laboratory, Chemical Engineering Department, Universitas Gadjah Mada, Yogyakarta, Indonesia. The caps as sources of HDPE waste and plastic bottles as a source of PP are presented in Figure 1(a) and Figure 1(b).

Table 1. Analysis of Liquid with Variations in Temperature and Weight Percentage of Raw Material to Natural Zeolite

<table>
<thead>
<tr>
<th>No.</th>
<th>Characteristics</th>
<th>Unity</th>
<th>Indonesian National Standard</th>
<th>Temperature Variation</th>
<th>Zeolite Composition Variation</th>
<th>(Syamsiro et al., 2014)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Specific Gravity at 60/60 F</td>
<td>-</td>
<td>0.742</td>
<td>0.7752</td>
<td>0.7765</td>
<td>0.77</td>
</tr>
<tr>
<td>2.</td>
<td>API Gravity</td>
<td>-</td>
<td>-</td>
<td>51.0</td>
<td>50.7</td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>Gross Heating Value</td>
<td>MJ/kg</td>
<td>≥41.87</td>
<td>46.59</td>
<td>46.403</td>
<td>20.091</td>
</tr>
<tr>
<td>4.</td>
<td>Flash Point PM c.c</td>
<td>°C</td>
<td>min 60</td>
<td>&lt;20</td>
<td>&lt;20</td>
<td>10</td>
</tr>
<tr>
<td>5.</td>
<td>Pour Point</td>
<td>°C</td>
<td>Maks 18</td>
<td>-12</td>
<td>-6</td>
<td></td>
</tr>
<tr>
<td>6.</td>
<td>Kinematic Viscosity at 40 °C</td>
<td>mm²/s</td>
<td>2.0-5.0</td>
<td>1.426</td>
<td>1.410</td>
<td>1.4</td>
</tr>
</tbody>
</table>

Figure 1. Caps as the source of HDPE waste (a) and plastic bottles as source of PP waste (b)
RESULTS AND DISCUSSION

As shown in Figure 3, the graph gives information about the relationship between liquid mass and temperature variation. At temperature 410 °C from beginning the starting condition to the first twenty minutes, the mass degraded very slowly. After twenty minutes, degradation rapidly increased. It is interesting to note that after two hours the total liquid mass was relatively stable at approximately 500 grams. On the other hand, in varied catalyst rates there was no liquid from the initial condition until the first twenty minutes, but after one hour the decomposition of liquid advanced much faster.

The changes in gas volume over time and the percentage of raw material and catalyst are shown in Figure 4(a) and (b). The production of gas started after a third of an hour. The total volume of gas at three temperatures variants (410, 420 and 430 °C) was twice higher than at 440°C. Meanwhile, from the four variations of rates of plastics to natural zeolite catalyst (66: 33 wt%; 75: 25 wt%; 80: 20 wt%, and 83: 17 wt%) as in Figure 3(b). the volume of gas in the weight percentage ratio of plastic waste to the catalyst at 83:17 was the lowest.

Figure 5a and 5b illustrate changes of solid residue over time based on temperature and percentage of raw material. The graphs in Figure 5a describe mass changing of solid residue at different temperatures. Liquid, gas, and solid yields in different temperatures and the weight percentage of raw material to catalyst is shown in Figure 6 and Figure 7.
Figure 4. Change of gas volume profile (mL) over time (minutes) with variation in (a) temperature, and (b) percentage ratio raw material to catalyst

Figure 5. Mass change of solid residue (grams) over time (minutes) with variation in (a) temperature and (b) weight percentage of raw material to the catalyst

The vertical bar chart describes the relationship between the yields of liquid, gas, and solid and temperature variations. There are four temperature variations namely 410, 420, 430 and 440 °C. The most distinguishing feature is at 440 °C where the liquid yield was highest at 68.42%. On the other hand, the proportions of liquid yield in temperature variations of 410, 420 and 430°C were 54.86%, 62.12%, and 56.38% respectively. These results corroborate those of other research (Aboulkas et al., 2010; Moqadam et al., 2015) in which thermal and catalytic degradation polystyrene mainly produces liquid.

According to a study on mixed plastic waste composed of 75% of polyolefins and 25% PS (Kaminsky, Schlesselmann, & Simon, 1996) the product comprised 46.6 wt% liquid, 35 wt% gas, and 2.2 wt% solid. Another study (Paradela, Pinto, Gulyurtlu, Cabrita, & Lapa, 2009), used a mixture of HDPE, LDPE, PP, PS, PVC, PET with the concentration of liquid, solid, gas, wax, were 40, 30, 15, 10, 3 and 2 wt% respectively. Its results showed that the liquid obtained was higher at the lower temperature of 650°C which was around the 48 wt%. However, the oil fraction consisted of 52% heavy fraction such as heavy oil, wax, and carbon black. In contrast, it is was up.

It is interesting to note that in the temperature variation of 410 and 430°C the gas yield was relatively the same at approximately 40%. Meanwhile, at 440°C yield gas was less than at the other three variations. The gases resulting from pyrolysis of mixed (PP) and (LDPE) are C_6, C_6-C_{10}, C_{11}-C_{13}, and >C_{13}. The highest gas yield with the variation of PP (80%)+LDPE (20%) at 11.17% was lower than the yield of mixed PP and HDPE. The vertical bar chart illustrates the relationship of the composition of zeolite and raw material with liquid, gas, and solid yields. There are four variations given in the comparison of raw material to natural zeolite (66:33 wt%; 75:25 wt%, 80:20 wt%, and 83:17 wt%)
The most striking feature is that the higher the rate of zeolite to raw material, the greater liquid yield. It can be seen that at a rate of raw material to the natural zeolite of 80:20 wt% the gas yield was two times that at 75:25 wt%. It is also noticeable that gas yield at 66:33 wt% variation was half that at 83:17 wt%. On the other hand, according to variations in the ratio of raw material to zeolite, the largest liquid yield was 87.31%. The percentages of liquid yield at the other three variants were 86.83, 75.41, and 73.31% in that order. In contrast, in the pyrolysis of polystyrene, when the mass of catalyst has increased the yield of liquid is reduced (Al-Salem & Lettieri, 2010). It is interesting to note that in these variations there was no solid residue resulting from this process.

Liquid product from various temperatures and natural zeolite compositions were analyzed in Petroleum, Gas, and Coal Laboratory, Chemical Engineering Department, Universitas Gadjah Mada, Indonesia. The liquid analysis result can be seen in Table 1. Table 1 shows that according to data analysis the liquid product is suitable solar (diesel) fuel based on Decree of The Director General of Oil and Gas Year for 2,008 Number 14,496 K/14/DJM/2,008, Ministry of Energy and Mineral Resources of the Republic Indonesia, concerning the Standards and Quality (Specifications) of Oil Fuels of the Combustible Oil Variety Traded in Indonesia. Likewise, the research found that the proportion of liquid plastic produced by pyrolysis of 100% plastic provided a GHV of 44.7 MJ/kg (Paradela et al., 2009). The liquid products were found to be similarities to diesel fuel in the value of, specific gravity, gross heating value, pour point, and kinematic viscosity.
CONCLUSIONS

From the research, the followings can be concluded.

1. The temperature of 440ºC produced the highest liquid yield at 68.42% and highest gas yield was 45.14% at 410ºC, while there was no solid residue at any temperature variation.
2. The ratio of plastics raw material to the catalyst of 66:33 wt% provided the highest liquid and solid yields at 87.13% and 26.69% respectively.
3. The liquid product was found to be suitable as a diesel fuel base on Decree of the Director General of Oil and Gas Year 2008.

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