Catalytic Pyrolysis of Waste Plastic Mixture

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Abstract. Inorganic waste especially plastics still become a major problem in many places. Low biodegradability of this materials causes the effort in recycling become very difficult. Most of the municipal solid waste (MSW) recycling facilities in developing country only use composting method to recover the organic fraction of the waste, while the inorganic fraction is still untreated. By pyrolysis, plastic waste can be treated to produce liquid fuels, flammable gas and chars. Reduction in volume and utilization of the liquid and gas as fuel are the major benefits of the process. By heat integration actually this process can become a self-sufficient system in terms of energy demand. However, the drawback of this process is usually due to the diverse type of plastic in the MSW creating low grade of liquid fuel and harmful gases. In this study, the mixture of plastics i.e. polypropylene (PP) and polyethylene terephthalate (PET) is treated using pyrolysis with catalyst in several operating temperature. PET is problematic to be treated using pyrolysis due to wax-like byproduct in liquid which may cause pipe clogging. The catalyst is the mixture of natural zeolite and bentonite which is able to handle PP and PET mixture feed to produce high grade liquid fuels in terms of calorific value and other fuel properties.

Keywords: Catalytic pyrolysis; Natural zeolite; Waste plastics.

1. Introduction
Plastic fraction inside the municipal solid waste (MSW) is difficult to be decomposed, and its quantity is increasing continuously by the time. The increasing demand of plastics materials in all sectors is due to its characteristics of relatively low manufacturing cost, durable, lighter and flexible. Therefore, plastic consumption around the world is increasing by 4 percent every year [1]. In general, waste plastic have the composition of 46% high and low density of polyethylene (HDPE and LDPE), 16% polypropylene (PP), 16% polystyrene (PS), 7% polyvinyl chloride (PVC), 5% polyethylene terephthalate (PET), 5% acrylonitrile-butadiene-styrene (ABS), and 5 percent other polymers [2]. This intensive usage of plastics in daily life will eventually end up in waste disposal problem. Plastic waste is a non-biodegradable material, so it has a negative impact on the environment. Based on data in 2011, the total number of plastic waste produced worldwide reached 280 million tons [3].

By the advancement of technology, plastic waste can be turned into alternative fuels using a heat treatment process called pyrolysis. Most of the research was conducted to characterize the fuel from...
pyrolysis using LDPE, HDPE, PP, and PS as the feedstock. Pyrolysis can be described as a chemical reaction of decomposition process by thermal and chemical of organic matter into carbon rich solid and vapor. Pyrolysis end products possess half of the carbon content from the feedstock organic matter, while, some part of the vapor phase can be condensate into liquid product and the rest is uncondensable [4].

The benefit of pyrolysis is producing high energy content products which are char, tar and gas from a low energy content of solid waste. In this process, the conversion ratio of the three products dependent on some operating conditions which are the heating rate, the maximum temperature, the processing time at the maximum temperature, the pressure, and the catalysts. One of the low cost catalyst that widely used for this application is natural zeolite.

The zeolite structure consists of tetrahedral unit of AIO₄ and SiO₄ which are interconnected through oxygen atoms. According to Smart and Moore [5], the role and activity of zeolite in catalyst is determined by the amount of acid sites located on the surface. The acid sites behave as Bronsted and Lewis acid. The Bronsted acid is the donor of H⁺ while Lewis acid is able to bind with free electron pair. Prior to be used as a catalyst, natural zeolite should be activated in order to eliminate the impurities in the zeolite. Zeolite activation process also aims to modify the properties of the zeolites in terms of surface area and acidity. Increasing surface area and acidity will increase the catalytic activity of the natural zeolite. One of the advantages of natural zeolite is the ease of modification of the surface area and the acidity [6].

According to Xingzhong [7], there are three common methods for pyrolysis, namely thermal cracking, catalytic cracking, and cracking-catalytic reforming. The selected type of pyrolysis in this research was cracking-catalytic reforming using fixed bed reactor. On reforming cracking-catalytic or known as the two steps processes, plastics is decomposed at high temperatures first and then undergo catalytic reforming.

In terms of heating rate, there are two main types of pyrolysis i.e. fast pyrolysis and slow pyrolysis. Slow pyrolysis requires slower heating rate, and lower temperatures than the fast pyrolysis. In general, the slow pyrolysis is designed to get more of solid products or char even the other product phases is still exist [4]. The pyrolysis reaction with Q as the heat required is represented by eq.1 [8].

\[ C_6H_2O_6 + Q \rightarrow \text{Char} + \text{Liquid} + \text{Gas} + H_2O \]  

(1)

2. Materials and Methods

2.1. Material

The raw material in this study was using plastic wastes of polypropylene (PP) and polyethylene terephthalate (PET) from used water bottles obtained from waste disposal facility in Jogjakarta City Indonesia. One kilogram of the raw material used for every processing time, either single type or mixture of them. Before used, PET and PP bottles are crushed into 2-3 cm long plastic flakes. The catalyst used in this research was a mixture of nature zeolite and bentonite obtained from Klaten, Central Java, Indonesia. The ratio between natural zeolite and bentonite was 70%:30%. A catalyst formed into pellet with 5 mm in diameter and 10 mm in length. The catalyst/plastic waste ratio was 10% in each process. The maximum temperature was set at 400°C, 450°C and 500°C.

2.2. Pyrolysis Methods

The pyrolysis process is done in the reactor chamber with the diameter of 23 cm and the height of 35 cm. At the top of the heating chamber, there is a smaller chamber to store the catalyst which is connected with a condenser and a phase separator. The reactor was made from stainless steel material equipped with a programmable electric heater. By using a constant heating rate, 1 kg of the plastic feedstock (PP only of PP and PET mixture) was heated to the maximum desired temperature from room temperature. The pyrolysis temperatures used for PP were 400°C, 450°C and 500°C. And for PP-PET mixture was used 400°C. During the process, the pressure inside the reactor was maintained
constant at 1 atm. The plastic vapour produced from the heating chamber flew into the catalyst bed then to the condenser and finally to the separator. The maximum temperature was maintained until pyrolysis process finished that indicated by no liquid and gas product was collected from the separator. The amount of both products was collected and measured every 10 minutes consecutively up to 120 minutes. The pyrolysis liquid product (oil) was characterized by analytical Gas Chromatography coupled with Mass Spectrophotometry QP2010S from SHIMADZU, while for analyzing the oil high heating value a bomb calorimeter was used (Galenkamp).

3. Results and Discussion

The pyrolysis product yields of PP with and without catalyst in three different temperatures is shown in Table 1. It is shown by non-catalytic process that the temperature has a significant effect on the product proportion among liquid, char and gas. For the non-catalytic processes, the increase of the processing temperature from 400 to 500 °C will increase the liquid product yield while reducing the solid yield. Similar results obtained by Abadi et al. [9] and Jung et al. [10], who observed that the increase of pyrolysis temperature will decrease char production in pyrolysis without catalyst. Higher temperature of the process can decompose better the volatile compound fraction of the feedstock to become condensable product.

However, the result become completely different for catalytic reactor, the higher pyrolysis temperature will reduce the liquid product. This effect is due to the cracking mechanism of the condensable gases entering the catalyst bed to become shorter carbon chain of non-condensable compounds, thus, the gas yield is increase. The effect is getting intense at the higher temperature since the catalytic effect will increase at higher temperature. Generally, a catalyst with high surface area can change the nature of the pyrolysis and affect on the pyrolysis results even in low catalyst contents [11-12].

| Pyrolysis product | Non-catalyst product yield (g) | Catalytic product yield (g) |
|-------------------|-------------------------------|----------------------------|
|                   | 400°C | 450°C | 500°C | 400°C | 450°C | 500°C |
| Liquid            | 782.67 | 796.09 | 810.21 | 784.19 | 755.83 | 532.06 |
| Char              | 11.33  | 10.64  | 10.45  | 9.87   | 8.17   | 9.12   |
| Gas               | 206    | 193.27 | 179.34 | 205.94 | 236    | 458.82 |

During the experiment using feedstock mixture of PP and PET, wax-like material was produced and accumulated inside the piping system and also in the bottom of liquid product. The wax was collected and weight separately. All the pyrolysis product weight using plastic mixture in various ratio is represented in Table 2. Higher PET fraction in raw material will produce lower liquid product but higher wax and solid content. Miandad et al. [1] has reported the similar finding that PET content in the pyrolysis feedstock will increase the char product and gas significantly and decrease the liquid oil product.

| Pyrolysis product | Ratio of raw material |
|-------------------|-----------------------|
|                   | PP:PET=9:1 product (g) | PP:PET=7.5:2.5 product (g) | PP:PET=6.5:3.5 product (g) |
| Liquid            | 723.82                | 515.39                | 390.3                |
| Char              | 22.51                 | 58.8                  | 465.74               |
| Gas               | 247.22                | 394.43                | 84.75                |
| Wax               | 6.45                  | 31.38                 | 59.21                |

In terms of heating value (Table 3), the pyrolysis oil of PP without catalyst has slightly lower caloric content than the oil from catalytic cracking. The catalyst breakdown the long chain compound
into shorter chain with higher heating value. Seo, et al [13] also reported the same results that the catalyst will decrease liquid oils product volume, but increase C3-C10 compound in liquid oils significantly while decrease C11-C18 compound and eliminate >C19 compound. For the feedstock mixture, PET addition tend to reduce the calorific value of the oil. This may be due to wax product existence.

![Figure 1. GC-MS result of selected liquid products at 400°C](image)

**Table 3. Heating Value result of liquid oils product (high value)**

| Catalyst      | Raw material                  | Temperature | Average HHV (cal/g) |
|---------------|-------------------------------|-------------|---------------------|
| Without catalyst | 100% polypropylene     | 400°C       | 10,711               |
| Without catalyst | 100% polypropylene     | 450°C       | 10,829               |
| Without catalyst | 100% polypropylene     | 500°C       | 10,991               |
| Using catalyst  | 100% polypropylene     | 400°C       | 10,942               |
| Using catalyst  | 100% polypropylene     | 450°C       | 11,067               |
| Using catalyst  | 100% polypropylene     | 500°C       | 11,190               |
| Using catalyst  | 90% PP and 10% PET         | 400°C       | 11,048               |
| Using catalyst  | 75% PP and 25% PET         | 400°C       | 10,805               |
| Using catalyst  | 65% PP and 35% PET         | 400°C       | 10,599               |

Similar with the heating value measurement data, GCMS results in Fig. 1 show that by adding catalyst, the lower carbon chain compound percentage is getting higher. The catalyst was successful in cracking the long chain of hydrocarbon vapor entering the catalyst bed before condensation. Meanwhile, PET tends to reduce the total heating value of the pyrolytic oil. It indicated that the catalyst require higher temperature to be able to treat feedstock with PET content.

4. **Conclusion**

The processing temperature, catalyst and raw material content affect significantly in the pyrolysis. In this study, the best temperature to produce the highest quantity liquid oils without catalyst is the highest temperature (500°C), while using catalyst is the opposite. By using the catalyst, the amount of C3-C10 compound is increase which leads to the increasing of oil calorific value. PET is the type of plastic that is unsuitable to be treated with pyrolysis, but by mixing PET with PP as raw materials and using proper catalyst the problem can be minimized. Based on this study the lowest content of PET (10%) can give optimum results in terms of oil production and the heating value.
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