The influence of temperature on the formation of liquid fuel from Polypropylene plastic wastes

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Abstract. The current trend of municipal waste management in urban areas is caused by rapid changes in social, economic, political and cultural life. As a non-biodegradable polymers that have become essential materials, plastic wastes have created a very serious environmental challenge because of the huge quantities and their disposal problems. Recycling of plastics is seen as one method for reducing environmental and resource depletion. The most attractive technique of plastics recycling is pyrolysis involving the degradation of the polymeric materials by heating in the absence of oxygen. This study investigated the characteristics of pyrolysis liquid fuel (PLF) produced from polypropylene plastic wastes with temperature variations. Pyrolysis was carried out on 200 grams of polypropylene waste plastics at the operating temperature of 200°C, 250°C, 300 °C and 350 °C for 45 minutes. The liquid products were found to have carbon chain length in the range of C8-C9, similar with gasoline. The maximum density, volume and calorific value of the oil obtained were 0.8 g/cm³, 61 ml and 1307 cal/gr, respectively.

1. Introduction
During the last few decades, the production and consumption of plastics are increasing because of modern lifestyle and an urgent need for comfort. As a consequence, responsible disposal of plastic waste has created serious social and environmental problems. According to the Environment and Forestry Ministry, in 2016 Indonesia produced 64 million tons of waste with 14% being of plastic wastes [1]. Plastics degrade gradually since the molecular bonds containing carbon, hydrogen and other elements such as nitrogen, chlorine and others that make plastic very durable. The disposal of plastic by landfilling and incineration will lead to environmental pollution. Disposing of the waste to landfill is becoming undesirable due to ineffectiveness and can cause the reduction of soil nutrients. Furthermore, incineration stimulates the growing emission of harmful greenhouse gases, e.g. NOx, SOx, CO2. Therefore, recycling is seen as one method for reducing environmental and resource depletion.

Thermoplastics are general-purpose plastics used in our daily lives and usually end up as municipal solid waste with 96% of this compound being consists of polyethylene (PE), polypropylene (PP), polystyrene (PS) and polyvinylchloride (PVC) [2]. Recently, recycling of thermoplastics already occurs on wide scale. Recycling has many types of techniques including pyrolysis, gasification, hydrolysis and etc. The most attractive technique to waste minimization that has been gaining interest

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recently is pyrolysis. Pyrolysis involves the degradation of the polymeric materials by heating in the absence of oxygen [3]. The pyrolysis process begins at a temperature of about 230 °C, when thermally unstable components and volatile matters in the waste will break and evaporate along with other components [4]. The three major products that are produced during pyrolysis are condensable liquids (tar), char and non-condensable gases (52.2%, 25.2% and 22.6%, respectively) [5]. Pyrolysis was chosen by many researchers since the process able to produce high amount of liquid oil up to 80 wt% at moderate temperature around 500°C [6] that can be used as chemical feedstock or fuel. The pyrolysis process has been described as one of the environmentally acceptable treatment of waste plastics and at the same time preserving the petroleum resources [7,8].

Thermal cracking or pyrolysis operating temperature ranges between 400 and 700 °C [9]. The macromolecular structures of polymer are broken down into low molecular weight hydrocarbon oils and gases. The pyrolysis reaction consists of four progressive steps: initiation, propagation, decomposition, and termination [10].

2. Materials and methods
Plastic cup wastes (polyethylene) were collected from Bung Hatta University campus area, cleaned and dried. The dried plastic wastes were cut into small square shaped pieces (about 2 cm side). The pyrolysis setup consists of batch reactor made of stainless steel as shown in Figure 1. 200 g of plastic cup sample was loaded into the reactor in each pyrolysis reaction. The condensable liquid products were collected through the condenser and the volume was measured. After pyrolysis, the char left was weighed and the gaseous product was calculated. The pyrolysis reactions were carried out at temperature variations of 200, 250, 300, and 350°C for 45 minutes.

The calorific value of the obtained liquid fuel was performed using Bomb Calorimeter. The density of fuel produced was measured using pycnometer and calculated by using Equation 1.

\[ \rho_{\text{f}} = \frac{m_{\text{p} + s} - m_{\text{p}}}{m_{\text{p} + w} - m_{\text{p}}} \times \rho_{\text{w}} \]  

The components of the liquid product were analyzed by Gas Chromatography-Mass Spectrometry analysis (GC-MS).

3. Results and discussions

3.1 Effect of temperature on liquid fuel volume

![Figure 1. Pyrolysis setup.](image)
The effect of temperature on liquid fuel volume for the pyrolysis of plastic cup wastes is shown in Figure 2. High temperature supports the easy cleavage of bonds and thus speeds resulted in more liquid fuel produced. This shows that temperature has a significant effect on liquid fuel volume. The volume of liquid fuel produced is 23, 35, 44, and 61 ml, respectively.

![Figure 2. Effect of temperature on liquid fuel volume.](image)

3.2 Effect of temperature on product yields
The pyrolysis of plastic cup waste yielded three different products, those are, oil (liquid fuel), char and gas. The distributions of these fractions are different at various temperatures and are shown in the Figure 3.

![Figure 3. Effect of temperature on product yields.](image)

The oil and gas constituted major product as compared to the char fractions. The recovery of condensable fraction (liquid fuel) increased with gradual increase of temperature. A maximum of 21.7% of the liquid fuel has been obtained at temperature of 350°C. The maximum yield of char 5.2% was obtained at the temperature of 250°C. The yield of char was increased with increasing pyrolysis
temperature up to 250°C and then decreases. The highest yield of gas 87.3% was obtained at a pyrolysis temperature of 200°C. With the increasing of temperature, the gas yield is decreased. From low to moderate temperature, the liquid fuel yield increases resulting in a decrease of char yield. As a result, the pyrolysis process showed an inverse ratio between solid yields (char) and liquid products (oil). It is due to the fact that the higher the pyrolysis temperature, the components in the plastic cup wastes would be decomposed sharply. As more components were decomposed, the char production is lessened and the oil produced is rising.

3.3 Effect of temperature on calorific value
For each pyrolysis temperatures, the liquid fuel calorific value was tested using a bomb calorimeter. The calorific values for oil produced is shown in Figure 4. The calorific value of oil produced declined up to a temperature of 250°C, after that, it would increase significantly. The highest calorific value of 1307 cal/gr was achieved using pyrolysis reaction temperature of 350°C.

![Figure 4. Effect of temperature on calorific value.](image)

3.4 Effect of temperature on liquid fuel density

![Figure 5. Effect of temperature on liquid fuel density.](image)
In liquid fuel yield, as illustrated in Figure 5, the density inclined up to temperature of 250°C, and then it would decrease. However, the density of liquid fuel produced was in the range of 0.71-0.8 gr/cm³, which is close to the density of gasoline. According to Director General of Oil and Gas Decree No.3674 K/26/DJM/2006, the standard gasoline has a density of 0.715-0.770 gr/cm³ (15°C) [11].

3.5 GC-MS of liquid fuel produced
Assessment of chemical composition features of oil the oil sample obtained from plastic cup wastes can be illustrated by qualitative examination of their GC traces. The hydrocarbon oil can have dramatically varied compositions in C₅ to C₄₀ carbon range. Light oils are typically products in the C₃ to C₁₂ carbon range. They include aviation gas, naphta, and automotive gasoline. Mid-range products are typically in a relative broad carbon range (C₆ to C₂₆) and include kerosene, jet fuel, and diesel products. Classic heavy oils include fuel No. 6 and lube type oil [12].

The GC-MS analysis were carried out to verify the exact composition of the liquid fuel obtained at 350°C (Figure 7) and summarized in the Table 1.

![Figure 6. GC-MS chromatograms of liquid fuel obtained at 350°C.](image)

Using GC-MS, 6 components were detected from the liquid fuel obtained at 350°C. The highest peak areas of total ion chromatogram (TIC) of the compounds displayed by Cyclohexene, 1,3,5-Trimethyl- (CAS) 1,3,5- trimethylcyclohexane at retention time of 2.034. The components present in plastic cup waste pyrolytic oil are mostly derivatives of alkenes, aromatic and aliphatic hydrocarbons with carbon number of C₈-C₁₃.

### Table 1. GC-MS composition of liquid fuel obtained at 350°C.

| No | Retention Time | % Height | Compound | Formulas | Relative Molecules |
|----|----------------|----------|----------|----------|-------------------|
| 1  | 2.034          | 0.61     | Cyclohexene, 1,3,5- trimethyl- (CAS) 1,3,5- trimethylcyclohexane | C₉H₁₈ | 126.24 |
| 2  | 3.122          | 0.17     | Undecane, 2,8- dimethyl- (CAS) | C₁₁H₂₄ | 156.18 |
| 3  | 4.663          | 0.15     | 1-nonen-4,6,8- trimethyl- (CAS) 4,6,8 trimethyleneone-1 | C₁₀H₁₈ | 154 |
| 4  | 8.750          | 0.19     | 1- tridecanol (CAS) n-tridecanol | C₁₃H₂₈O | 200.36 |
| 5  | 10.614         | 0.08     | Octadecane,3- ethyl- 5,2 ethylbutyl (CAS) | C₁₆H₃₆ | 112.10 |
| 6  | 10.910         | 0.06     | Dodecane, 2,6, 11- trimethyl- (CAS) 2,6, 11 trimethyldecane | C₁₀H₂₂ | 142.29 |
4. Conclusion
Thermal pyrolysis of plastic cup wastes were performed in a batch reactor at a temperature variation of 200, 250, 300 and 350°C for 45 minutes. The maximum liquid fuel yield was 21.7% at temperature of 350°C. The pyrolysis process showed an inverse ratio between solid yields (char) and liquid products (oil). The functional groups present in the pyrolytic oil are mostly derivatives of alkenes, aromatic and aliphatic hydrocarbons. It was found that the pyrolytic oil contains compounds having carbon chain length in the range of C₈-C₁₃. The density of liquid fuel produced was in the range of 0.71-0.8 gr/cm³, which is close to the density of gasoline. A simple batch pyrolysis method can convert plastic cup waste to liquid hydrocarbons with yields which varies with temperature.

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