Thermal Cracking of Low Temperature Conversion on Low Density Polyethylene Plastic Waste for Liquid Hydrocarbon

Heriyanti, Lenny Marlinda, Rayandra Asyhar and Sutrisno
Faculty of Science and Technology, Department of Chemistry, University of Jambi, Jambi, Indonesia

Abstract

Purpose – This work aims to study the treatment of adsorbant on the increasing liquid hydrocarbon quality produced by pyrolysis low density polyethylene (LDPE) plastic waste at low temperature. The hydrocarbon distribution, physicochemical properties and emission test were also studied due to its application in internal combustion engine. This research uses pure Calcium carbonate (CaCO₃) and pure activated carbon as adsorbant, LDPE type clear plastic samples with control variable that is solar gas station.

Design/Methodology/Approach – LDPE plastic waste of 10 kg were vaporized in the thermal cracking batch reactor using LPG 12 kg as fuel at range temperature from 100 to 300°C and condensed into liquid hydrocarbon. Furthermore, this product was treated with the mixed CaCO₃ and activated carbon as adsorbants to decrease contaminant material.

Findings – GC-MS identified the presence of carbon chain in the range of C₆–C₄₄ with 24.24% of hydrocarbon compounds in the liquid. They are similar to diesel (C₆–C₁₄). The 30% of liquid yields were found at operating temperature of 300°C. The calorific value of liquid was 46.021 MJ/Kg. This value was 5.07% higher than diesel as control.

Originality/value – Hydrocarbon compounds in liquid produced by thermal cracking at a low temperature was similar to liquid from a catalytic process.

Keywords LDPE, pyrolysis, liquid hydrocarbon, fuel

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1. Introduction

In Indonesia there are 64 million tons of waste and 9.6 million tons of them are plastic waste. According to the Ministry of Environment and Forestry in Indonesia, the rate of used plastic bags in Indonesia is more 1 million per minute in 2016. Every year, to produce plastic bags it would need about 8% of world oil production or 12 million barrels of oil and 14 million trees (Nugraha, 2016). In fact, plastic can be converted again into fuel by pyrolysis or thermal cracking. The molecular structure of the plastic was decomposed into smaller molecules by heating process at high temperature without oxygen. Therefore, plastic with a high enough caloric value can be used as an alternative energy source that equivalent to fossil fuels such as gasoline and diesel (Velma, 2015). Surono and Ismanto (2016) processed polypropylene (PP) and polyethylene (PE) plastic wastes to produce plastic oil with carbon atoms close to gasoline and kerosene. Meanwhile polyethylene-terephthalate (PET) plastic did not produce oil but powdered material. Norsujianto (2014) converted plastic waste into oil indicating the hydrocarbon component in the C4–C44 range as a new energy fuel. According to Surono (2013), the mixed PE and PP plastics were converted into fuel oil using thermal cracking at 450°C for 2 h and condensed at temperature of 21°C to produce oil having equal amount of carbon atoms, i.e., C12–C17.

Generally, the crude oil produced by the pyrolysis still contain lots of contaminants. Adsorption was one way to remove the contaminants so that the quality of oil produced is better. This product can be used as fuel and chemicals. Febriani (2015) had studied natural bentonite and activated carbon of palm shells as adsorbents. Based on XRD and SEM results, the main content in bentonite in the form of Calcium carbonate (CaCO3) succeeded in decreasing the sulfur value and increasing the caloric value.

As a consequence, the proposed work based on pyrolysis of low density polyethylene (LDPE) followed adsorption process on liquid hydrocarbon with the mixed CaCO3 and activated carbon as adsorbant has been performed in a batch reactor in a range temperature from 100 to 300°C. This work aims to investigate the treatment of adsorbant on the increasing liquid hydrocarbon quality. The hydrocarbon distribution, physicochemical properties, and emission test were also studied due to its application in internal combustion engine. This research used pure CaCO3 and activated carbon as adsorbent, the clear LDPE plastic samples and solar from gas station as control variable.

2. Experimental methods

2.1. Preparation of materials and sample

LDPE plastic waste, i.e., clear plastic for food wrapping, trash bags and plastic bags were collected from landfills around residential areas in Jambi. The plastics before used in this study were washed with soap and dried under sunshine. To increase surface area during pyrolysis process the dried plastics were crushed into a small size. According to Wahyudi (2001), the smaller size of plastic can give the greater surface area per unit weight so that liquid product was formed quickly during the pyrolysis process.

CaCO3 and activated carbon were proanalyzed Grade from E. Merck (Germany). A 85%:15% weight ratio of this mixed CaCO3 and activated carbon as adsorbant has been performed in a batch reactor in a range temperature from 100 to 300°C. This work aims to investigate the treatment of adsorbant on the increasing liquid hydrocarbon quality. The hydrocarbon distribution, physicochemical properties, and emission test were also studied due to its application in internal combustion engine. This research used pure CaCO3 and activated carbon as adsorbent, the clear LDPE plastic samples and solar from gas station as control variable.

2.2. Thermal cracking process

Thermal cracking process on LDPE plastic waste was done according to a previous procedure (Zainuri, 2014). Plastics of 10 kg were vaporized in the thermal cracking batch
reactor using LPG 12 kg as fuel at range temperature from 100 to 300°C and condensed into the product of liquid hydrocarbon.

Furthermore, the product was treated with the mixed CaCO₃ and activated carbon as adsorbants to decrease contaminant material. According to a previous procedure (Puspadiningrum, 2007), the adsorbant of 2.5g was loaded in flask and followed liquid product of 250 mL under stiring at temperature of 30°C for 2 h. After finishing this process, filtrate was separated from adsorbant solid. The obtained filtrate was denoted as the liquid hydrocarbon. Meanwhile, physicochemical analysis such as the calorific value and density were applied on the liquid hydrocarbon to determine its properties for application as fuel. With the same treatment on the liquid product, petroleum diesel was used as control variable.

The calorific value was obtained through a bomb calorimeter (Model: type 5E-C5500 Automatic Calorimeter AXT). Density was determined by pycnometric bottles. Beside that, diesel like hydrocarbon composition in liquid product were identified by gas chromatography-mass spectroscopy (GC-MS) with tipe QP2010 SE. The GC system was programmed at 30°C and increased to 330°C at 10°C/min for 30 min of total run time. Some compounds in liquid hydrocarbon were ionized at sources ion temperature of 260°C and a mass electron range of 40–500 were used to analysis process. The chromatograms of hydrocarbons were shown at different retention time and identified using the W9N11 MS library mass spectral library of data.

2.3. Emission test of liquid hydrocarbon
To minimize negative impact on environment the emission gas test was carried out using a motor engine and liquid hydrocarbon was used as fuel. According to a previous procedure (Norsujianto, 2014), this test was applied in a motor engine that using oil from LDPE plastic pyrolyzed before and after adsorption. Waste emission gas was identified by a gas analyzer. The emission test on motor vehicle exhaust were the process of measuring the levels of the compounds contained in motor vehicle exhaust emissions.

3. Results and discussion
When the temperature of pyrolysis increased from 100 to 130°C, plastic solids began to melt indicated by vapor and droplets of plastic oil that was still mixed with impurities. The increase of temperature to 220°C, plastic oil of 750 mL was obtained. Finally, when temperature was raised to 300°C, the process was stopped. This is due to leakage in the thermal cracking batch reactor. This occurred after a pyrolysis process lasted for 2.05 h and 3,100 mL of plastic oil was obtained. A yield of 30% was reached. It was similar to Sarker et al. (2012), plastic oil yield of 40% was obtained at 325°C. Figure 1 shows plastic oil dan residual pyrolysis solids. This liquid has characteristics, i.e yellowish brown, thick and very sharp smell. The residue color seen in brown milk. This residue has also a waxy texture as shown in Figure 1b.

When Figures 1 and 2 were compared, the difference in color between the clear LDPE plastic oil before and after adsorption was visible. This indicated that the mixed CaCO₃ and activated carbon in bleaching can bind substances causing undesirable color and odor.

3.1 Characterization of liquid hydrocarbon
Physical and chemical properties of liquid hydrocarbon. The calorific value of petroleum diesel and liquid hydrocarbon was listed in Table 1. It can be seen that the calorific value of liquid hydrocarbon increased when the value was compared with petroleum diesel. (Dewangan et al., 2016) also reported that it can be caused by the increase in H/C ratio. The
hydrocarbon content and oxygen content play a significant role in controlling the calorific value of oil. Calorific value of liquid hydrocarbon after adsorption was increased by 60.3% likewise with petroleum diesel after adsorption increased to 61.7%. This indicated that the adsorption process has a major effect on increasing the calorific value of the fuel. The adsorption by the mixed CaCO₃ adsorbent and activated carbon can decrease impurities content that can influence the calorific value.
GC-MS analysis of liquid hydrocarbon. Figure 3 shows the chromatograms of liquid product produced from pyrolyzed LDPE at 300 °C. It was detected 80 of peaks in the range of retention time. It can be also observed that the peak positions in Figure 3 were almost similar to liquid from pyrolyzed LDPE by Yang et al. (2012). It was also the same result reported by a previous study (Sarker et al., 2012), in the range of retention time less than 18 min, the carbon distribution ranging from C6 to C20 was detected. For the retention time longer than 18 min, long-chain hydrocarbon (alkenes) such as octadecene became the main compounds in the liquid hydrocarbon. It should be noted that only the peaks corresponding to the hydrocarbons in the liquid hydrocarbon derived from the pyrolysis of LDPE. The information of main peaks such as retention time and compound name are listed in Table 2.

| Peak | Retention Time (min) | Area % | m/z | Chemical Formula | Compound | m/z |
|------|----------------------|--------|-----|------------------|----------|-----|
| 52   | 19,508               | 4,33   | 266 | C_{18}H_{38}     | n-Octadecana | 254 |
|      |                      |        |     | C_{15}H_{32}     | h-Pentadecana | 212 |
|      |                      |        |     | C_{14}H_{30}     | n-tetradecana | 198 |
|      |                      |        |     | C_{20}H_{42}     | n-Eicosane   | 282 |
|      |                      |        |     | C_{21}H_{14}FEN_{2}O_{3} | [N-(phenyl-2-pyridinyl)methylene] benzamime-N,N] | 398 |
| 57   | 20,603               | 4,37   | 276 | C_{19}H_{40}     | n-Nonadecana | 268 |
|      |                      |        |     | C_{21}H_{14}FEN_{2}O_{3} | [N-(Phenyl-2-2pyridinyl)methylene] benzamime-N,N] | 398 |
|      |                      |        |     | C_{20}H_{42}     | n-Eicosane   | 282 |
|      |                      |        |     | C_{18}H_{38}     | n-Octadecana | 254 |

Figure 3.
The Chromatographic Peaks of Liquid Hydrocarbon from LDPE Pyrolyzed at Range Temperature of (a) 100–300°C in this Work, (b) 100–400°C, reported by Sarker et al. (2012)
indicating that liquid hydrocarbon composition (C14-C21) was similar with petroleum diesel (C15-C18).

3.2 Characterization of adsorbant
In this research, characterization of the mixed CaCO3 and activated carbon before and after adsorption was done. This was done to see the changes that occur in the adsorbant after the adsorption process. Figure 4 shows that the diffraction peak characteristic of calcite was clearly observed at $2\theta = 29.23^\circ$ dan $29.39^\circ$, corresponding to JCPDS 47-1743. It indicated that the adsorption did not change crystal structure of calcite significantly.

3.3 Emission test of liquid hydrocarbon
Figure 5 shows the highest emission gas produced by liquid hydrocarbon is CxHy gas. This was due to incomplete combustion so that CxHy gas produced was higher than CO, NO, NO2.
NO\textsubscript{x}, and SO\textsubscript{x}. However, it can be seen that the gas concentration produced by liquid hydrocarbon after adsorption had been decreased. It can be concluded that the adsorption can give a good effect on reducing of the concentration of emission gas produced by motor engine. In this gas exhaust emission test, SO\textsubscript{2} produced was 0 ppm. It was possibly because the plastic raw material used was clear LDPE plastic. In addition, the SO\textsubscript{2} gas produced was still in small concentration so it cannot be detected by the exhaust gas gauge. Similarly, NO\textsubscript{2} gas produced was 0 ppm. Furthermore, CH\textsubscript{4} and CO\textsubscript{2} gas emissions are listed in Figure 6.

Figure 6 shows the emission of CH\textsubscript{4} gas produced on liquid hydrocarbon after adsorption was decreased when compared with before adsorption. It indicated that the adsorption can decrease methane concentration from while the CO\textsubscript{2} gas produced increased. It can be said that the combustion happened was already good. According to Guntur et al. (2011), the CO\textsubscript{2} concentration indicated a completely burning conditions at the burning room. The higher the CO\textsubscript{2} concentration, the better the combustion process.
4. Conclusions
According to the results of GC-MS, liquid hydrocarbon from pyrolyzed LDPE had a C6-C14 range hydrocarbon. Liquid hydrocarbon before adsorption was more wasteful than liquid hydrocarbon after adsorption. Adsorption using a mixture of 85% CaCO3 and 15% activated carbon can reduce exhaust gas emissions.

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Corresponding author
Sutrisno can be contacted at herasutrisno@unja.ac.id