



LIQUID FLUIDS FROM THERMO-CATALYTIC DEGRADATION OF WASTE LOW-DENSITY POLYETHYLENE USING SPENT FCC CATALYST

Felix Aibuedefe Aisien ^{1,*} and Eki Tina Aisien ²

¹ Department of Chemical Engineering, University of Benin, Benin City, Nigeria.

² Department of Environmental Management and Toxicology, University of Benin, Benin City, Nigeria

Article Info:

Received: 28 January 2022 Revised[.] 20 June 2022 Accepted: 20 June 2022 Available online: 30 June 2022

Keywords:

Low density polyethylene Degradation Liquid oil Temperature Spent FCC catalyst Commercial fuel

ABSTRACT

The widely-used plastics, especially low-density polyethylene (LDPE), have resulted in a considerable accumulation of plastics in the waste stream, causing a global environmental problem. Therefore, the research aims to examine the thermal and catalytic degradation of waste LDPE plastic using spent fluid catalytic cracking (FCC) catalyst and compare the properties of the produced liquid oils with commercial fuels. The potential of converting the most energy from waste plastics to valuable liquid oil, gaseous, and char was investigated. A batch reactor was used to thermally and catalytically degrade LDPE at temperatures 350 to 550°C and catalyst to plastic ratio of 0.10 to 0.25. The physical properties of the produced liquid oils, flash point, pour point, viscosity, API-gravity, carbon residue, density, etc., were determined using standard methods. We characterized the chemical properties of produced pyrolysis liquid oils with Gas chromatography-mass spectrometry (GC-MS). The liquid oil, gas, and char produced at catalyst to plastic ratio of 0.20 at 500°C were 92.7 wt.%, 6.1 wt.%, and 1.2 wt.% respectively. The thermal pyrolysis at 500°C gave 76.6 wt.%, 20.7 wt.%, and 2.7 wt.% for produced liquid oil, gas, and char, respectively. The GC-MS shows that the produced LDPE liquid oil contains many hydrocarbons from C7-C29. The major hydrocarbons common to LDPE are benzene, 1, 3 dimethyl benzene, and toluene. The produced liquid oil's properties compare favorably with that of commercial fuels.

1. INTRODUCTION

Plastic solid waste (PSW) is mainly composed of polyethylene (PE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC), and polyethylene terephthalate (PET). Polyethylene is made up of high-density polyethylene (HDPE), low-density polyethylene (LDPE), and linear low-density polyethylene (LLDPE). They account for about 40 percent of the PSW; hence it is the most common type of waste material in the waste stream (Onwudili et al., 2019). PSW causes serious environmental and waste management problems in Nigeria and other countries, including developed nations. These problems include environmental flooding, reduction in landfills space, water, and air pollution, blockage of side drains, increase in the spread of diseases, and an increase in the presence of insects and dangerous rodents (Aisien et al., 2013). However, the presence of PSW in enormous volumes in landfills, terrestrial and marine environments could be traced to its durability, less energy-efficient, inexpensive, non-biodegradable, and

good applicability nature of plastics (Aisien et al., 2013). Aisien et al. (2021) reported that one of the most effective and efficient ways of managing PSW is pyrolysis. Sosa et al. (2021) and Aisien et al. (2021) stated that pyrolysis is an environmentally friendly sustainable plastic waste management process and is the most promising resource for producing commercial fuels (gasoline, diesel, kerosene). Patni et al., (2013) reported that the pyrolysis or degradation process significantly reduces plastic waste volume, lowers decomposition temperature, low capital cost, and increases recoverable energy by producing varieties of products. Plastic degradation can either be thermal or catalytic, depending on the operating temperatures and the use of catalyst. Aisien et al., (2021) reported that catalysts had been widely used in the pyrolysis process to optimize product distribution, increase product selectivity, upgrade pyrolysis products and improve hydrocarbon distribution. Besides, catalytic pyrolysis of plastics produces liquid oil whose properties are similar to that of commercial fuels (Sharuddin et al., 2016). Some researchers have studied



thermal and catalytic pyrolysis of other waste plastics (Kunwar et al., 2018; Abbas-Abadi et al., 2013, 2014; López et al., 2017; Singh et al., 2018).

The catalytic pyrolysis of plastic waste using ZSM-5, red mud, zeolites Y, FCC, and others, produced pyrolysis oils whose properties compare favorably with commercial diesel fuel (Miandad et al., 2016; Hernandez et al., 2007). Moorthy Rajendran et al., (2020) reported catalytic pyrolysis of municipal plastic waste using HUSY, HZSM-5, HMOR, Zeolite Y, silica, and FCC catalysts produced quality fuels. The FCC catalysts are fine particles with an average size of 60 to 100 µm and a bulk density of 0.80 to 0.96 g/cm³. Also, it has large pore sizes, high temperature, steam stability, high activity, and good resistance to attrition (Chen et al., 2019). Susastriawan et al., (2020) reported that at low temperature, the smaller the zeolite size and the higher the temperature, the higher the liquid fraction yield when zeolite catalyst was used to degrade polyethylene. Similarly, Onwudili et al., (2019) studied catalytic pyrolysis of a mixture of plastics using catalysts such as FCC, ZSM-5, and zeolites Y. They stated that the yield of the liquid fraction decreased with the addition of the catalyst. The liquid fraction had properties suitable for fuel, although the number of aromatic compounds presents increased. Similarly, Santos et al., (2018) reported that zeolite USY gave a higher amount of liquid fraction, and the major components were alkylbenzenes, naphthalenes, and olefins. Also, Kyong et al., (2003) stated that liquid oil yield from PP, PE (LDPE and HDPE), and PS pyrolysis was different.

This research is focused on the applications of low-medium temperature (350-550°C) and moderate catalyst to plastic ratio (0.1-0.25) on the degradation of LDPE. Therefore, the optimization of LDPE pyrolysis with respect to increase liquid oil yield and quality using low-medium temperature and moderate spent FCC catalyst has not been previously considered. However, the main essence of this research is to recover energy in the form of liquid oil from LDPE waste plastics and reduce this PE waste plastic and spent FCC catalyst in the environment. Hence, the study aims to investigate the thermal and catalytic degradation of waste LDPE plastic using spent FCC catalysts and compare the properties of the produced liquid oil with commercial fuels. The objectives include comparing thermal and catalytic degradation of LDPE at different temperatures and catalyst to plastic ratio. Besides, to compare the produced liquid oil properties from LDPE with commercial fuels and evaluate the composition of the liquid oil products.

2. MATERIALS AND METHODS

2.1 Materials

We collected the waste LDPE from the Irorere Obazee landfill at Evbuozegbo-Benin, Nigeria. We got the spent FCC catalyst from Warri refinery and petrochemical company, Warri-Nigeria. The surface area, pore volume, and average pore size of the spent FCC catalyst obtained are 63.42 m²/g, 0.103 cm³/g, and 7 nm respectively. We got the pyrolysis plant with an insulated jacketed 5 kg capacity batch pyrolysis reactor from the engineering workshop, University of Benin, Benin city. We purchased analytical

grade chemicals from Sigma-Aldrich Co. Ltd. in the UK and Qualikems Fine Chemical Ltd. India.

2.2 Spent fluid catalytic cracking catalyst characterisation

The spent FCC catalyst samples were degassed at 200°C for 8hr. under vacuum to remove any contaminants. The catalyst samples' surface area, pore volume, and pore size were determined from Braunauer-Emmett-Teller (BET) technique by nitrogen adsorption and desorption isotherms from the catalyst at equilibrium vapour pressure using the static volumetric method. The nitrogen adsorption– desorption isotherms were recorded at 77 K using a Micrometrics Tristar 3000. The surface area was determined by Brunauer-Emmett-Teller (BET) model (Brunauer et al., 1938), and Barrett-Joyner-Halenda (BJH) analysis (Gregg and Sing, 1982) was used to determine the pore volume, pore diameter, and pore size distribution.

2.3 Preparation of plastic materials

The waste LDPE plastics were washed with detergent and tap water to clean them. We dried the cleaned waste plastics with sunlight. We shredded, ground, and stored the ground waste LDPE plastics in a covered plastic container.

2.4 The pyrolysis studies

The experimental pyrolysis plant shown in Figure 1 was used in this study. It was designed, fabricated, and tested as described by Aisien et al., (2021). The thermal degradation process started with charging 1 kg of prepared LDPE plastics into the heating chamber of the pyrolysis reactor after evacuating it with a vacuum pump. The reactor was heated at 15°C/min until it reached the desired temperature. The temperature was regulated by employing K-thermocouple and PID controller. The produced gaseous products were made to pass through the outlet tube connected to the two ice-cold water glass condensers. The condensable liquid products and the solid residues were collected and weighted. The experiment was each conducted in triplicates for the temperature variations (350-550°C) studied. Mabood et al., (2010) formula in equations 1 to 3 was used to evaluate the yield of the products, and the calculation of the degradation products was based on the weight/mass after weighing each product on completion of each study. Standard analysis methods and GC-MS were used to analyze and characterize the physical properties of the produced liquid oil. A similar procedure was used to carry out catalytic degradation studies. The catalyst to plastic ratio varied between 0.1 and 0.25.

2.5 Analytical methods

The standard ASTM methods were used to evaluate the physical properties of the produced liquid oil. The GC-MS and ASTM distillation was used to analyse the pyrolysis liquid oil fraction's chemical composition and properties. The calorific value was determined using the bomb calorimeter.

2.6 Statistical analysis

The Kruskai-Walli H-test (Kruskai and Walli, 1952) or





one-way analysis of variance by ranks using statistical package for social sciences (SPSS) version 20 with a significance level of p = 0.05 with n = 4 for statistical analysis of products yield data.

Liquid Yield:

$$Oil (wt.\%) = \frac{Mass of oil}{Mass of LOPE} \times 100\%$$
(1)

Residue (Char) Yield:

Char (wt.%) =
$$\frac{Mass of restaue}{Mass of LDPE} \times 100\%$$
 (2)
Gas Yield:

Gas(wt.%) = 100% - (Oil + Residue)(3)

3. RESULTS AND DISCUSSION

3.1 The effect of temperature on the degradation of LDPE plastic

The effect of temperature on the yield of pyrolysis products (liquid oil, gas, and char) at temperature range 350 to 550°C are shown in Figure 2. We observed that the yield of the produced liquid oil from LDPE gradually increased, while gaseous products decreased as the pyrolysis temperature increased from 350 to 500°C. The results show a significant difference (p<0.05) in the liquid oil and gases yields between 350 and 500°C. However, an increase in temperature to 550°C resulted in reduced liquid oil yield and an increase in gaseous product yield. The reduction in LDPE liquid oil yield at 550°C might be attributed to the fact that at 550°C, these plastics have almost wholly degraded (Chin et al., 2014; Marcilla et al., 2009; Onwudili et al., 2009). This observed trend is a function of the catalyst to plastic ratio.

Moreover, for the entire temperature variation, the char yield was minimal and decreased very slightly with tem-

perature. There is no significant difference (p>0.05) in char yield with temperature. Figure 3 compares products yield with temperature for thermal and catalytic degradation of LDPE at 0.2 catalyst to plastic ratio. The T in Figure 3 represents the results of the thermal degradation of LDPE plastic. We observed that the LDPE products (liquid oil, gas, and char) yield for catalytic degradation were relatively higher than those from thermal degradation, independent of the prevailing temperature. There is a significant difference (p<0.05) in produced liquid oil and gas yields between thermal and catalytic degradation at 500°C. The maximum temperature for the optimization of liquid oil, gas, and char yields was 500°C. These observed results and trends were similar to those reported by Aisien et al., (2021), Marcilla et al., (2009), Onwudili et al., (2009), Jung et al., (2010), and Abbas-Abadi et al., (2013). However, some researchers reported reduced overall liquid oil yield and increased gas and char yields during pyrolysis of waste plastics (Abbas-Abadi et al., 2014; López et al., 2017; Demirbas, 2004).

3.2 The effect of catalyst to plastic ratio on the degradation of LDPE plastic

Figure 4 shows the effect of the catalyst to plastic ratio on the yield of LDPE pyrolysis products at different temperatures. As shown in Figure 4, we observed that at 350°C, the liquid oils yields from LDPE gradually increased, and the gas yields reduced as the catalyst to plastic ratio increased from 0.1 to 0.2. Also, a further increase of the catalyst to plastic ratio to 0.25 reversed this trend. A similar trend was observed with other temperatures, as shown in Figure 5. There is a significant difference (p<0.05) in the liquid oils and gases yields between 0 and 0.20 catalyst to plastic ratio. However, the char yield from LDPE degradation was minimal with no significant difference (p>0.05) as



FIGURE 2: Variation of the products yield with temperature at 0.1 catalyst to plastic ratio.

the catalyst to plastic ratio increased from 0.1 to 0.25. A similar trend of results was reported by Aisien et al., (2021); Abbas-Abadi et al., (2014); Kyong et al., (2003, 2002); and Sharuddin et al., (2016). They reported a similar effect of spent FCC catalysts on the yield of the pyrolysis products. Therefore, we can state that the FCC catalyst enhanced decomposition or cracking of the LDPE plastic. However, a reverse trend was reported by Kunwar et al., (2016) and Miandad et al., (2016). They stated that catalyst causes an increase in the yield of the gaseous fraction and the amount of char and reduced liquid fraction.

Moreover, Aisien et al., (2021) and Budsaereechai et al., (2019) reported that an increase in the amount of catalyst to a higher concentration did not significantly affect the yield and fuel properties of produced liquid oil. This fact is also confirmed in the degradation of LDPE using FCC catalysts in this study. Hence, it seems unnecessary to use high FCC catalyst loading. Abbas-Abadi et al., (2014) and Shraruddin et al., (2016) reported that the FCC catalyst is one of the best catalysts for the optimization of liquid oil production from plastic pyrolysis and that spent FCC cata-



FIGURE 3: Comparing products yield with temperature for thermal and catalytic pyrolysis at 0.2 catalyst to plastic ratio.

lyst still has high catalytic performance with produced liquid oil yield above 80 wt.% for all plastics.

3.3 Effect of FCC catalyst on the products yield and residence time

The effect of FCC catalyst on the products yield and residence time from the pyrolysis of LDPE plastic at 350°C is shown in Table 1. We observed that the liquid oil yield from LDPE thermal degradation was lower than catalytic degradation. Besides, the gas and char yields from thermal degradation of LDPE were higher than catalytic degradation. The residence time for the thermal degradation. There is a significant difference (p<0.05) in the reduction in residence time between thermal and catalytic degradation of LDPE plastic. This shows that the spent FCC catalyst is very effective in accelerating the LDPE degradation reaction rate. Also, the results showed no significant difference (p>0.05) in residence time of LDPE degradation with an increase in catalyst to plastic ratio.



However, the residence time of catalytic degradation



FIGURE 4: The variation pyrolysis products yield with catalyst to plastic ratio at degradation temperature of 350°C.

FIGURE 5: Comparing degradation products yield with catalyst to plastic ratio at different temperatures.

of LDPE reduced with an increased catalyst to plastic ratio. This might be due to the high surface area and acidity of the spent FCC catalyst. These results agree with other studies (Aisien et al., 2021; Abbas-Abadi et al., 2014; Kyong et al., 2003; Jung et al., 2010; Demirbas, 2004; Ahmad et al., 2014; Sakata et al., 1999; Costa et al., 2010).

3.4 The characteristics of produced liquid oil from LDPE degradation

3.4.1 Physical properties

Table 2 summarized the fuel properties (viscosity, flash point, API gravity, density, pour point, ash content, and the calorific value) of the liquid oil produced from LDPE degradation at different catalyst to plastic ratios. Table 2 also compares the LDPE produced liquid oil fuel properties with that of commercial fuels (gasoline, diesel, and kerosene). We characterized the produced liquid oil to determine its improved quality and suitability for energy generation and heating purposes. The results for the produced liquid oil from catalyst to plastic ratio of 0.1 are 2.43 cSt; 0.86 g.cm³; 32.52°C; 43°F; -6°C; 0.02%; 0.62% and 41.8 MJkg^{-I} for viscosity, density, flash point, API gravity, pour point, ash content, carbon residue, and calorific value respectively. A similar trend was observed for other catalysts to plastic ratios. Also, the results show that the fuel properties of the produced liquid oil from LDPE catalytic degradation were higher and of better quality than that from thermal degradation. Besides, the fuel properties of the produced liquid oil from LDPE catalytic degradation displayed irregular variation with an increase in catalyst to plastic ratio. Moreover, there is no significant difference (p>0.05) in the fuel properties of the produced liquid oil from LDPE with an increase in catalyst to plastic ratio. The fuel properties of the liquid oil from

LDPE compare favorably with that of commercial fuels.

The summary of the produced liquid oil from LDPE with temperature variation is shown in Table 3. The results of produced liquid oil from LDPE at 350°C for viscosity, density, flash point, API gravity, pour point, ash content, carbon residue and calorific value are 2.47 cSt; 0.88 g.cm⁻³; 31.8°C; 42°F; -7°C; 0.015%; 0.59% and 40.7 MJkg⁻¹ respectively. We observed a similar trend for other temperatures, and the fuel properties of the produced liquid oil from LDPE catalytic degradation show irregular variation with increased temperature. Besides, there is no significant difference (p>0.05) in the fuel properties of the produced liquid oil from LDPE with an increase in temperature. The results in Tables 2 and 3 were either close to or within the range reported for commercial fuels (Ahmad et al., 2014; Shakirullah et al., 2010) Saptoadi and Pratama, (2015). Hence, the values of the fuel properties of LDPE liquid oil determined are strongly comparable to that of commercial fuels. Shah and Jan (2014) explained that the fuel properties of the produced liquid oil compare favorably with the commercial fuels because the liquid oil contains some aromatic hydrocarbons. Santaweesuk and Janyalertadun (2017) reported that the small ash content values of the liquid oil show it is free from metal contamination and high molecular weight soot.

Therefore, we concluded that the fuel properties of the liquid oil from LDPE were independent of temperature or catalyst to plastic ratio. These results agree with some researchers' results (Bozbas, 2008; Gaurh and Pramanik 2018).

3.4.2 Chemical properties of the produced liquid oil from LDPE degradation

Figure 6 shows the comparison between the produced liquid oil from LDPE degradation at 400°C and commer-

| Catalyst to plastic ratio | Liquid oil (wt.%) | Gases (wt.%) | Char (wt.%) | Residence time (min.) |
|---------------------------|-------------------|--------------|-------------|-----------------------|
| 0 | 63.7 | 33.3 | 2 | 83 |
| 0.10 | 74.4 | 24 | 1.6 | 47 |
| 0.15 | 79.6 | 19.7 | 0.9 | 44 |
| 0.20 | 82.8 | 16.7 | 0.7 | 41 |
| 0.25 | 77.6 | 20.1 | 2.6 | 39 |

 TABLE 1: Products yield distribution and retention time for thermal and catalytic degradation of LDPE plastics at 350oC using a different catalyst to plastic ratio.

| LDPE plastic at different catalyst to plastic ratio | Viscosity @ 40°C (cSt) | Density (g/ cm³) | Flash point (°C) | API gravity @ 40°F | Pour point (°C) | Ash (wt.%) | Carbon residue (wt.%) | Calorific residue (MJ/kg) |
|--|------------------------------|---------------------|---------------------|-----------------------|--------------------|---------------|-----------------------------|---------------------------------|
| 0.00 | 1.53 | 0.89 | 27.23 | 41 | -7 | 0.01 | 0.58 | 41.4 |
| 0.10 | 2.43 | 0.86 | 32.52 | 43 | -6 | 0.02 | 0.62 | 41.8 |
| 0.15 | 2.32 | 0.88 | 32.4 | 45 | -6 | 0.01 | 0.61 | 42.5 |
| 0.20 | 2.47 | 0.87 | 31.8 | 42 | -7 | 0.015 | 0.59 | 40.7 |
| 0.25 | 2.38 | 0.83 | 30.9 | 38 | -5 | 0.03 | 0.60 | 41.3 |
| Gasoline | 0.775 -1.03 | 0.72 - 0.736 | 20.8-42 | 63.24-65.03 | 6 | 0.01 | 0.62 | 46.86 |
| Diesel | 2.0-5.3 | 0.83 - 0.85 | 55-60 | 34.97-38.98 | - | - | 0.6 | 42.51 |
| Kerosene | 0.9-2.2 | 0.78 - 0.82 | 50-55 | 41.06-49.91 | | | • | 45.46 |

TABLE 3: Comparison of the physical parameters of produced LDPE liquid oil at different temperature.

| LDPE plastic @ different temperature (°C) | Viscosity @ 40°C (cSt) | Density (g/cm³) | Flash point (°C) | API gravity @ 40°F | Pour point (°C) | Ash (wt.%) | Carbon residue (wt.%) | Calorific residue (MJ/kg) |
|--|------------------------------|--------------------|---------------------|-----------------------|--------------------|---------------|-----------------------------|---------------------------------|
| 350 | 2.47 | 0.88 | 31.8 | 42 | -7 | 0.015 | 0.59 | 40.7 |
| 400 | 2.50 | 0.89 | 32.2 | 43 | -6 | 0.01 | 0.60 | 39.8 |
| 450 | 2.48 | 0.91 | 31.3 | 41 | -7 | 0.01 | 0.61 | 39. 2 |
| 500 | 2.46 | 0.90 | 30.2 | 40 | -5 | 0.00 | 0.60 | 38.1 |
| Gasoline | 0.775 -1.03 | 0.72-0.736 | 20.8-42 | 63.24- 65.03 | - | - | | 46.86 |
| Diesel | 2.0-5.3 | 0.83-0.85 | 55-60 | 34.97-38.98 | 6 | 0.01 | | 42.51 |
| Kerosene | 0.9- 2.2 | 0.78-0.82 | 50-55 | 41.06-49.91 | - | - | | 45.46 |

cial fuels. The results show that the boiling point range for LDPE liquid oil lies between diesel and gasoline for 40-70% distillate recovery (Figure 5). This further affirms the suitability of LDPE liquid oil for energy production. These results agree with that of Graurh and Pramanik, (2018), who characterized pyrolysis liquid oil from polyethylene. They stated that the boiling point range gives information on the fuel's composition, properties, and behavior.

3.4.3 Chemical composition of the produced liquid oil from LDPE degradation

We determined the chemical composition of the produced liquid oil by GC-MS characterization (Shimadzu. 2011). The GC-MS results are represented in Table 4 and Figures 7 and 8. The results show that the liquid oil from LDPE degradation is complex hydrocarbons with carbon atoms ranging from C₇ to C₂₉. We observed that the LDPE produced liquid oil comprise paraffin (alkanes), olefins (alkene), naphthenes (cycloalkane), and aromatics classes. As shown in Figure 7, the results are paraffin (27.5%), olefins (50%), naphthenes (12.5%), and aromatics (10%) for produced LDPE liquid oil. Also, results shown that C₇-C₁₀, (37.5%); C₁₁-C₁₅, (35.5%); C₁₆-C₂₀, (12.5%) and >C₂₀, (12.5%) were got from LDPE liquid oil. Moreover, we observed that the liquid fraction products range as gasoline range (C₄-C₁₂), diesel range (C₁₂-C₂₃), kerosene range (C₁₀-C₁₈), and motor oil range (C₂₃-C₄₀). The results obtained are gaso-

line, (60%), diesel, (45%), kerosene, (52.5%), and motor oil, (7.5%) for LDPE liquid oil. This report is in agreement with that of Jung et al., (2010). However, from the perspective of high percentage of olefins in the produced liquid oil when compared with commercial oils, the quality of the liquid oil is lower than that of commercial oils.

Figure 8 shows the GC-MS plots of LDPE produced liquid oil at optimal conditions of 500°C and 0.2 catalyst to plastic ratio. The composition of the LDPE-produced liquid oil is in Table 4. We observed that the liquid oil from LDPE degradation consists of many different hydrocarbons. The significant LDPE- produced liquid oil compounds include 1,3 dimethyl Benzene, Toluene, Naphthalene, 1-methyl, Indene 1,12-Tredecadiene, Cis-9-Tetradecadiene, 9-Tricosene, 1,19-Eicosadiene, 4-Undecene, 2-Dodecene, and Cyclododecane. These results agree with reports of some researchers (Abbas-Abadi et al., 2014; Kyong et al., 2003, 2002; Sarker and Rashid, 2013). However, they were a few variations in the primary hydrocarbon compounds from pyrolysis of LDPE, as reported by some other researchers (Sharuddin, 2016; Sarker and Rashid, 2013; Al-Salem, 2017; Mianda et al., 2019) Miandad et al., (2019) explained this difference. They report that plastic types, catalyst types and amount, temperature, and reaction time are essential determinants of the chemical composition of liquid oil from the pyrolysis of plastics.



FIGURE 6: Variation of ASTM characteristics of pyrolysis liquids and standard fuels with volume vaporised.



Hydrocarbon group types, range and liquid oil products

FIGURE 7: GC-MS analysis showing various effects of catalytic degradation on liquid oil from LDPE.



FIGURE 8: GC-MS of the pyrolysis oil from LDPE at 450°C and 0.2 catalyst to plastic ratio.

4. CONCLUSIONS

The following conclusions can be drawn:

- 1. The temperature variation and the application of spent FCC catalysts significantly impact LDPE degradation's products (liquid oil, gas, and char) yield.
- The liquid oil yield from thermal degradation of LDPE 2. was lower than that from catalytic degradation. However, the reverse is the case for gas and char yields.
- 3. The maximum temperature and catalysis to plastic ratio for optimizing LDPE were 500°C and 0.20, respectively.
- 4. The liquid oil, gas, and char produced at 500°C and catalyst to plastic ratio of 0.20 were 92.7 wt.%, 6.1 wt.%, and 1.2 wt.% respectively.
- 5. The fuel properties of the produced liquid oil from LDPE compare favorably with those of commercial fuels. The composition and quality of the produced liquid oil from LDPE were similar to gasoline and diesel.

6. The results obtained are gasoline, (60%), diesel, (45%), kerosene, (52.5%), and motor oil, (7.5%) for produced LDPE liquid oil.

FUNDING

This research did not receive any specific grant from funding agencies in public, commercial, or not-for-profit sectors.

ACKNOWLEDGMENTS

The authors wish to gratefully acknowledge Gabriel Okoduwa for his kind provision to design and fabricate a batch pyrolysis reactor.

REFERENCES

Abbas-Abadi, M.S, Haghighi, M.N., Yeganeh, H. 2013. Evaluation of pyrolysis product of virgin high density polyethylene degradation using different process parameters in a stirred reactor. Fuel Process Technol. 109, 90-95. https://doi.org/10.1016/j. fuproc.2012.09.042

| TABLE 4: GC-MS composition | ition of produced oil f | from LDPE degradation. |
|----------------------------|-------------------------|------------------------|
|----------------------------|-------------------------|------------------------|

| S/N | Retention time (min) | Area (%) | Compound | Molecular Formula | Molecular weight |
|-----|----------------------|----------|--|--|------------------|
| 1 | 3.523 | 2.11 | Toluene | C ₇ H ₈ | 92.140 |
| 2 | 3.512 | 1.20 | Bicyclo [4.2.0]octa-1,3,5-triene- methyl | C ₈ H ₈ | 104.149 |
| 3 | 3.670 | 1.20 | Benzene, 1,3-dimethyl- | C ₈ H ₁₀ | 106.165 |
| 4 | 3.905 | 1.04 | 1-(2-propenyl) cyclopentene | C ₈ H ₁₂ | 108.181 |
| 5 | 4.245 | 1.12 | 1,2-dimethyl-1-cyclohexene | C ₈ H ₁₄ | 110.200 |
| 6 | 4.526 | 3.14 | Indene | C ₉ H ₈ | 116.160 |
| 7 | 5.435 | 1.32 | Indane | C ₉ H ₁₀ | 118.176 |
| 8 | 5.563 | 1.08 | Benzene, 1-ethyl-4-methyl- | C ₉ H ₁₂ | 120.192 |
| 9 | 5.927 | 1.20 | Naphthalene | C ₁₁ H ₈ | 126.171 |
| 10 | 5.956 | 1.03 | 4-Nonene | C ₉ H ₁₈ | 126.239 |
| 11 | 6.051 | 2.85 | 2-Methylindene | C ₁₀ H ₁₀ | 130.186 |
| 12 | 6.567 | 2.34 | 9-Methylbicyclo [3.3.1] nonane | C ₁₀ H ₁₈ | 138.254 |
| 13 | 6.870 | 1.06 | 2-methylpropyl cyclohexene | C ₁₀ H ₁₈ | 138.254 |
| 14 | 6.985 | 2.72 | 1-Decene | C ₁₀ H ₂₀ | 140.266 |
| 15 | 7.020 | 1.43 | Trans-3-Decene | C ₁₀ H ₂₀ | 140.266 |
| 16 | 8.123 | 2.30 | Naphthalene, 1-methyl | C ₁₁ H ₁₀ | 142.197 |
| 17 | 8.742 | 1.26 | 4-Undecene | C ₁₁ H ₂₂ | 154.292 |
| 18 | 9.347 | 2.12 | Naphthalene, 1.6 dimethyl- | C ₁₂ H ₁₂ | 156.224 |
| 19 | 10.231 | 1.45 | 1,6-Dimethyl decahydronaphthalene | C ₁₂ H ₂₂ | 166.303 |
| 20 | 10.542 | 1.50 | 2-Dodecene | C ₁₂ H ₂₄ | 168.319 |
| 21 | 10.748 | 1.10 | Cyclododecane | C ₁₂ H ₂₄ | 168.319 |
| 22 | 10.984 | 2.30 | Naphthalene, 2-methyl | C ₁₁ H ₁₀ | 142.197 |
| 23 | 11.307 | 3.34 | 1-Tridecene | C ₁₃ H ₂₆ | 182.346 |
| 24 | 11.543 | 2.51 | Tridecane | C ₁₃ H ₂₈ | 184.360 |
| 25 | 11.674 | 1.57 | Naphthalene, 2-methyl | C ₁₁ H ₁₀ | 142.197 |
| 26 | 11.924 | 3.85 | 2-Tetradecene | C ₁₄ H ₂₈ | 196.372 |
| 27 | 12.316 | 1.57 | 1-Pentadecene | C ₁₅ H ₃₀ | 210.400 |
| 28 | 12.945 | 2.21 | Cis-9-Tetradecadiene | C ₁₄ H ₂₈ O | 212.352 |
| 28 | 13.130 | 3.52 | Pentadecane | C ₁₅ H ₃₂ | 212.410 |
| 30 | 14.643 | 1.89 | 3-Heptadecene | C ₁₇ H ₃₄ | 238.452 |
| 31 | 17.401 | 1.63 | 1-Octadecene | C ₁₈ H ₃₆ | 252.487 |
| 32 | 18.257 | 2.23 | Octadecane | C ₁₈ H ₃₈ | 254.494 |
| 33 | 18.722 | 2.87 | 1-Nonadecene | C ₁₉ H ₃₈ | 266.512 |
| 34 | 22.435 | 2.16 | 1,19-Eicosadiene | C ₂₀ H ₄₂ | 282.550 |
| 35 | 24.541 | 1.78 | 1-Docosene | C ₂₂ H ₄₄ | 308.585 |
| 36 | 25.467 | 1.54 | 9-Tricosene | C ₂₃ H ₄₆ | 322.621 |
| 37 | 26.038 | 2.46 | Cyclotetracosane | C ₂₄ H ₄₈ | 336.638 |
| 38 | 26.542 | 2.89 | Tetracosane | C ₂₄ H ₅₀ | 338.654 |
| 39 | 29.123 | 1.64 | Nonacosane | $C_{29}H_{60}$ | 408.787 |
| 40 | 30.156 | 1.35 | Cyclohexasiloxane, dodecamethyl- | C ₁₂ H ₃₆ O ₆ S _{i6} | 444.924 |

Abbas-Abadi, M.S., Haghighi, M.N., Yeganeh, H., McDonald, A.G. 2014. Evaluation of pyrolysis process parameters on polypropylene degradation products. J Anal Appl Pyrolysis. 109, 272-277. https://doi. org/10.1016/j.jaap.2014.05.023

Ahmad, I., Khan, M.I., Khan, H., Ishaq, M., Tariq, R., Gul, K. et al., 2014. Pyrolysis study of polypropylene and polyethylene into premium oil products, Int. J. Green Energy 12, 663-671. https://doi.org/10.1080 /15435075.2014.880146 Aisien, F.A., Amenaghawon, A.N., Adeboyejo, A.R. 2013. Application of recycled rubber from scrap tire in the removal of phenol from aqueous solution. Pacific Journal of Science and Technology. 14 (2), 330-341. https://doi.org/10.4314/jasem.v17i3.10

(c), 334 https://doi.org/10.4314/jaseth.v1/318 rolysis of waste polypropylene plastic using spent FCC catalyst, Envion. Technol. Inno. 22, 101455. https://doi.org/10.1016/j. eti.2021.101455

- Al-Salem, S.M., Antelava, A., Constantinou, A., Manos, G., Dutta, A. 2017. A review on thermal and catalytic pyrolysis of plastic solid waste (PSW). Journal of Environ. Manage. 197, 177-198. https:// doi.org /10.1016/j.jenvman.2017.03.084.
- Bozbas, K. 2008. Biodiesel as an alternative motor fuel: production and policies in the European union. Renew Sustain Energy Rev., 12, 542-552. . https://doi.org/10.1016/j.rser.2005.06.001
- Brunauer, S., Emmett, P.H., Teller, E.1938. Adsorption of gases in multimolecular layers, J. Am.Chem. Soc, 60, 309-319.
- Budsaereechai, S., Andrew J.H., Ngernyen, H. 2019. Catalytic pyrolysis of plastic waste for the reduction of liquid fuels for engines. Royal Society Chem. Adv. 9, 5844-5857. https://doi.org/10.1039/ c8ra10058f
- Chen, X., Ren, L., Yaseen, M., Wang, L., Liang, J., Linang, R., Chen, X., Guo, H., 2019. RSC Adv., 9, 6515-6525. https://doi.org/10.1039/ c8ra07943a
- Chin, B.L.F., Yusup, S., Al Shoaibi, A., Kannan, P., Srinivasakannan, C., Sulaiman, S.A. 2014. Kinetic studies of co-pyrolysis of rubber seed shell with high density polyethylene. Energy Convers Manage 87, 746-753. https://doi.org/10.1016/j.enconman.2014.07.043
- Costa, P., Pinto, F., Ramos, A.M., Gulyurtlu, I., Cabrita, I., Bernardo, M.S. 2010. Study of the pyrolysis kinetics of a mixture of polyethylene, polypropylene, and polystyrene. Energy & Fuels, 24(12): 6239-6247. https://doi.org/10.1021/ef101010n
- Demirbas, A. 2004. Pyrolysis of municipal plastic wastes for recovery of gasoline-range hydrocarbons. J Anal Appl Pyrolysis. 72, 97-102. https://doi.org/10.1016/j.jaap.2004.03.001.
- Gaurh, P., Pramanik, H. 2018. Production and characterization of pyrolysis oil using waste polyethylene in a semi-batch reactor. Indian J. of Chem. Techn. 25, 336-344.
- Gregg, S., Sing, K. 1982. Adsorption, surface area and porosity. Academic Press, London, Adsorption, surface area and porosity. 2nd ed. Academic Press, London.
- Hernandez, M. R., Gomez, A., García, A. N., Agullo, J., Marcilla, A. 2007. Effect of the temperature in the nature and extension of the primary and secondary reactions in the thermal and HZSM-5 catalytic pyrolysis of HDPE, Appl. Catal. A: General, 317, 183. https://doi. org/10.1016/j.apcata.2006.10.017
- Jung, S.H., Cho, M.H., Kang, B. S., Kim, J.S. 2010. Pyrolysis of a fraction of waste polypropylene and polyethylene for the recovery of BTX aromatics using a fluidized bed reactor. Fuel Process. Technol. 91, 277-284. https://doi.org/10.1016/j.fuproc.2009.10.009
- Kruskai, W.H., Wallis, W.A. 1952. Use of ranks in one-crition variance analysis J. Am. Stat. Assoc. 47: 260, 583-621. https://doi.org/10.1 080/01621459.1952.10483441
- Kunwar, B., Cheng, H.N., Chandrashekaran, S.R., Sharma, B.K. 2016. Plastics to fuel: A review. Renew. Sustain. Energy Rev. 54, 421-428. https://doi.org/10.1016/j.rser.2015.10.015
- Kyong, H.L., Nam, S.N., Dae, H.S., Seo, Y. 2002. Comparison of plastic types for catalytic degradation of waste plastics into liquid product with spent FCC catalyst. Polym. Degrad. Stab. 78:539-544.
- Kyong, H.L., Sang, G.J., Kwang, H.K., Nam, S.N., Dae, H.S., Park, J. et al., 2003. Thermal and catalytic degradation of waste high-density polyethylene (HDPE) using spent FCC catalyst. Korean J. Chem. Eng. 20: 693-697.
- López, G., Artetxe, M., Amutio, M., Bilbao, J., Olazar, M. 2017. Thermochemical routes for the valorization of waste
- polyolefinic plastics to produce fuels and chemicals. A review. Renew. Sustain. Energy Rev. 73, 346-368. https://doi.org/10.1016/j. rser.2017.01.142
- Mabood, F., Jan, M.R., Shah, J., Jabeen, F., Hussain, Z. 2010. Catalytic conversion of waste low-density polyethylene into fuel oil. J. Iran. Chem. Res. 3, 121-131.
- Marcilla, A., Beltrán, M. I., Navarro, R.A. 2009. Thermal and catalytic pyrolysis of polyethylene over HZSM5 and HUSY zeolites in a batch reactor under dynamic conditions, Appl. Catal. B: Environ. 86, 78-86. http://dx.doi.org/10.1016/j.apcatb.2008.07.026.
- Miandad, R., Barakat, M.A., Aburiazaiza, A.S., Rehan, M., Nizami, A.S. 2016. Catalytic pyrolysis of plastic waste: A review. Process. Saf. Environ. Prot. 102, 822-838. https://doi.org/10.1016/j. psep.2016.06.022

- Miandad, R., Rehan, M., Barakat, M.A., Aburiazaiza, A.S., Khan, H., Ismail, I.M.I., Dhavamani, J., Gardy, J., Hassanpour, A., Nizami, A.S. 2019. Catalytic pyrolysis of plastic waste: Moving toward pyrolysis-based biorefineries. Front. Energy Res. 7:27. https://doi. org/10.3389/fenrg.2019.00027
- Moorthy Rajendran, K., Chintala, V., Sharma, A., Pal, S., Pandey, J.K., Ghodke, P. 2020. Review of catalyst materials in achieving the liquid hydrocarbon fuels from municipal mixed plastic waste (MMPW). Mater Today Commun. 24, 100982. https://doi.org/10.1016/j.mtcomm.2020.100982
- Onwudili, J.A., Insura, N., Williams, P.T. 2009. Composition of products from the pyrolysis of polyethylene and polystyrene in a closed batch reactor: effects of temperature and residence time. J. Anal. Appl. Pyrol. 86, 293-303. https://doi.org/10.1016/j.jaap.2009.07.008
- Onwudili, J.A., Muhammad, C., Williams, P.T. 2019. Influence of catalyst bed temperature and properties of zeolite catalysts on pyrolysis-catalysis of a simulated mixed plastics sample for the production of upgraded fuels and chemicals. J. Energy Inst. 92, 1337-1347. https://doi.org/10.1016/J.JOEI.2018.10.001
- Patni, N., Shah, P., Agarwal, S., Singhal, P. 2013. Alternate Strategies for Conversion of Waste Plastic to Fuels. ISRN Renewable Energy. 2013, 1-7. https://doi.org/10.1155/5917
- Sakata, Y., Uddin, M.A., Muto, A. 1999. Degradation of polyethylene and polypropylene into fuel oil by using solid acid and non-solid acid catalysts. J Anal Appl Pyrolysis. 51, 135-155. https://doi. org/10.1016/S0165-2370(99)00013-3
- Santaweesuk, C., Janyalertadun, A. 2017. The Production of Fuel Oil by Conventional Slow Pyrolysis Using Plastic Waste from a Municipal Landfill International Journal of Environ. Sci. Dev., Vol. 8, No. 3,168-173. https://doi.org/10.18178/IJESD.2017.8.3.941
- Santos, B.P.S., Almeida, D., Marques, M.F.V., Henriques, C.A. 2018. Petrochemical feedstock from pyrolysis of waste polyethylene and polypropylene using different catalysts. Fuel 215, 515-521. https:// doi.org/10.1016/j.fuel.2017.11.104
- Saptoadi, H., Pratama, N.N., 2015. Utilization of plastics wastes oil as a partial substitute for kerosene in pressurized cookstoves. Int. J. Environ. Sci. Dev. 6, 363-371. https://doi.org/10.7763/IJESD.2015. V6
- Shah, J., Jan, M.R. 2014. Conversion of waste polystyrene through catalytic degradation into valuable products. Korean J. Chem. Eng. 31, 1389-1398. https://doi.org/10.1007/s11814-014-0016-4
- Sarker, M., Rashid, M.M. 2013. A waste plastic mixture of polystyrene and polypropylene into light grade fuel using
 - Fe₂O₃ catalyst. Intern. J. Renewable Energy Tech. Res. 2(1), 17-28.
- Shakirullah, M., Ahmad, I., Ahmad, W., Ishaq, M. 2010. Oxidative desulphurization study of gasoline and kerosene: Role of some organic and inorganic oxidants. Fuel Proc.Technol., 91(11): 1736-1741. https://doi.org/10.1016/j.fuproc.2010.07.014
- Sharuddin, S.D.A., Abnisa, F., Daud, W.M.A.W., Aroua, M.K. 2016. A review on pyrolysis of plastic wastes. Energy Convers. Manage, 115, 308-326. http://dx.doi.org/10.1016/j.enconman.2016.02.037
 Shimadzu. 2011. Analysis of gasoline using GC/MS. 21, 20-21.
- Singh, M.V., Kumar, S., Sarkerb, M. 2018. Waste HD-PE plastic, deformation into liquid hydrocarbon fuel using pyrolysis-catalytic cracking with a CuCO₃ catalyst Sustainable Energy Fuels. 2, 1057-1068. https://doi.org/10.1039/C8SE00040A
- Sosa, O., Valin, S., Thiery, S., Salvador, S. 2021. Pyrolysis of solid waste and its components in a lab scale induction-heating reactor. Detritus 15, 107-112. https://doi.org/10.31025/2611-4135/2021.15094
- Susastriawan, A.A.P., Purnomo, Sandria, A. 2020. Experimental study of the influence of zeolite size on low-temperature pyrolysis of low-density polyethylene plastic waste. Therm. Sci. Eng. Prog.17, 100497. https://doi.org/10.1016/j.tsep.2020.100497
- Syamsiro, M., Cheng, S., Hu,W., Saptoadi, H., Pratama, N.N., Trisunaryanti, W., et al., 2014. Liquid and gaseous fuel from waste plastics by sequential pyrolysis and catalytic reforming processes over Indonesian natural zeolite catalysts. Waste Technol. 2, 44-51. https://doi.org/10.12777/wastech.2.2.44-51