Comparative Study of the Chemical Compositions of Liquid Fuel from Thermal Cracking of Low and High-Density Polyethylene Plastic Waste.

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Abstract. The increase in the rate of accumulation of plastic waste (PW) has been of great concern to the world especially in the developing countries due to its non-biodegradable nature and improper waste management practices. Hence, efforts towards the conversion of this waste (PW) to resourceful materials have led us to the exploration of pyrolysis (anaerobic thermal cracking) of plastic waste under a controlled condition to produce liquid fuel. A stainless steel batch reactor was used in the cracking of the low and high-density polyethylene (LDPE and HDPE) plastic wastes into liquid fuel components at a temperature of 230°C. The liquid fuel obtained from the pyrolyzed LDPE and HDPE was analyzed using GC-MS. Fifty (50) compounds each was identified for both LDPE and HDPE which revealed the presence of mostly alkenes and aromatics in the hydrocarbon ranges of C₈ – C₂₄. This is made up of 36% of gasoline fractions range from C₆ - C₁₂, 32% of diesel fractions range C₁₃ - C₂₀, and 14% oil of residual fuel range of C₂₀ – C₂₈ and 18% of non-hydrocarbons was discovered for the HDPE while 36% of gasoline fractions range of C₆ - C₁₂, 34% of diesel fractions range C₁₃ - C₂₀, oil and 12% residual fuel range of C₂₀ – C₂₈ and 18 % of non-hydrocarbons was discovered for the LDPE. There is little or no difference in the products of pyrolysis of light and heavy polyethylene plastic waste.

Keywords: Polyethylene (PE), Thermal Cracking, Pyrolysis, GC-MS and Clean Technology.

1. Introduction

The use of plastic is of greater importance in our daily lives and its consumption has led to the drastic increase of plastic waste, PW in the twentieth century [1]. There is a higher demand for plastic, which has also increased rapidly because they are considered as solution materials to various sectors like Engineering, medicals, electronics, aerospace, etc. They are essentials for the advancement of technology due to their great physical properties such as its lightweight and flexibility compared to other materials like metals, glass, wood, and concrete [2].

According to UNEP [3], a major components of Municipal Solid Waste (MSW) is the plastic waste and it’s fast becoming the third largest MSW in developing countries. In addition, developing countries do not put into consideration the advantages of economic gain involved by utilizing some certain recycling methods but still depend solely on the conventional method of landfilling of MSW disposal. This conventional method has contributed to the major health and environmental hazards such as greenhouse gas emissions, groundwater pollution, and several other human health problems. For this reason, exploration of other methods like recycling has been a main attention for research in which PW is used as raw materials for recovery of valuable products and energy so as to solve the shortage of natural resources in the nearest future [2] [4].
PW recycling methods have been mainly grouped into four major types namely Primary recycling which involves waste scrap being processed into products with similar properties to the original products; Secondary recycling has to do with waste/scrap plastics being processed into materials that have different properties to that of the initial product; Tertiary methods deals with conversion of these wastes scrap in the production of essential fuels and chemicals or as a segregated waste and lastly Quaternary recycling involves the burning of these plastics and retrieving energy contents afterwards[5].

Each of these recycling methods is advantageous and effective for different applications. The main types of plastic used for daily commodities are thermoplastics which become soft when heat is introduced and later hardens when cooled and the other, thermosets which harden irreversibly when heat is introduced. MSW is of six main component namely, Low-Density Polyethylene (LDPE), High-Density Polyethylene (HDPE), Polyvinyl Chloride (PVC), Polystyrene (PS), Polyethylene Terephthalate PET) and Polypropylene (PP). Polyethylene plastics (both LDPE and HDPE) make up about forty percent of the MSW [2] [6].

Pyrolysis involves the cracking or breakdown of the long chain large Hydrocarbons in an anaerobic atmosphere. Gas, oil, and char are the three major products obtained during pyrolysis process and these products are of great value to production and refinery industries [7]. Compared to other MSW management practices, pyrolysis is more desirable and satisfactory environmentally because it reduces the carbon footprint of products. Pyrolysis process also lessens the amount of carbon monoxide and carbon dioxide emissions by making an effective use of inert atmosphere that is free of oxygen to avoid the formation of dioxins through product reaction with oxygen [8] [9]. This pyrolysis process is a cleaner technology, a drive towards energy security and a measure to combat fossil fuel depletion.

There have been a number of published articles on the pyrolysis of polyethylene plastics (for LDPE and HDPE). For example, Chanashetty and Pau I [10] undertook pyrolysis of LDPE and PP experiment using temperature ranges from 100 OC to 400 OC and obtained a 50-65% conversion to fuel oil. Onwuadi et al [6] also investigated the pyrolysis of LDPE, PS and their mixtures between temperatures of 300 OC to 500 OC, LDPE was thermally degraded at 425OC. This work seeks to evaluate the cracking of Low Density Polyethylene (LDPE) Plastic Waste. The success of this work will enhance the effectiveness of plastic waste processing to useful products in Nigeria and Africa in general in an economically affordable manner and hence reduce the environmental hazard posed by their indiscriminate dumping.

2. Materials and Method

Materials

Two different types of polyethylene plastic wastes (PPW), High-Density Polyethylene (HDPE) and Low-Density Polyethylene (LDPE) were used in this experiment. The PPW was obtained from waste bins and garbage from Ota, South-West Nigeria. They were then sorted, cleaned to remove dirt and then shredded into smaller particle sizes.

Experimental Procedures

LDPE and HDPE Plastic wastes were each collected and prepared by cutting into smaller particle sizes of 3 to 4 mm and charged into a semi-batch pyrolysis reactor. From Fig 1, the continuous batch reactor of capacity 300 ml is a lagged cylindrically shaped stainless steel container with a mild steel cover. The reactor was electrically heated with a 2 kW heating element equipped with an automatic temperature controller and connected to it was a coil condenser, liquid and gas collectors. 20g of PPW sample was used in each experiment and fed into the reactor, tightly closed and purged with nitrogen gas at the start of each experiment. The heating element was turned on at the specified temperature to heat the PPW pyrolyzed and cracked it until oil fractions begin to evolve, condensed and collected.
Fig. 1  Schematic Representation of the Pyrolysis Set Up

Analytical Methods

Analysis of the pyrolysed oil was done using Gas Chromatography - Mass Spectrophotometry (GC-MS) to determine the chemical compositions of the hydrocarbon products. The GC-MS and column oven temperature conditions used are stated in the table below.

Table 1: GC/MS condition

| GC-MS Agilent 433UI HP-5ms Ultra Inert |
|----------------------------------------|
| Column Oven Temperature | 500°C |
| Injection Mode            | Split |
| Injection Temperature     | 1500°C |
| Injection Volume          | 1 ml  |
| Split Ratio               | 10:1  |
| Average Velocity          | 36.445 cm/Sec |
| Column Pressure           | 7.6522 psi |
| Column Flow               | 1.2211 ml/Min |
| Carrier Gas               | Helium 99.9995% Purity |
| Frequency                 | 50 Hz |
| Electron Multiplier Volts | 1024.9 |

| Column Oven Temperature Progress |
|----------------------------------|
| Rate (0°C/min) | Temperature (0°C) | Hold Time |
| (min)          |                   |           |
| 8              | 300               | 9         |
| 0              | 50                | 0         |
**Table 2:** Chemical Compositions of the Liquid Fuel Products from Pyrolysis of HDPE

| Peak | Retention Time | Area % | Compound Name | Molecular Formula | Molecular Weight |
|------|----------------|--------|----------------|-------------------|------------------|
| 1    | 3.224          | 1.43   | 4-Ethyl-5-Methyl-Nonane | C12H26          | 170.3348         |
| 2    | 3.47           | 2.6    | 3-Octyne | C8H14            | 110.1968         |
| 3    | 4.042          | 1.29   | 1,3-Dimethylbenzene | C8H10           | 106.165          |
| 4    | 4.477          | 1.46   | Trans-2-Nonene | C9H18            | 126.2392         |
| 5    | 4.695          | 1.77   | Cyclohexane, 2-Propenyl- | C9H16           | 124.2233         |
| 6    | 5.221          | 2.72   | 3,4-Octadiene, 7-Methyl- | C9H16           | 124.2233         |
| 7    | 6.177          | 1.54   | E-12-Tetradecenal | C14H26O         | 210.3556         |
| 8    | 6.48           | 2.17   | Methylcycloheptane | C8H16           | 112.2126         |
| 9    | 6.566          | 2.43   | 1-Indanone | C9H14O          | 138.2069         |
| 10   | 6.726          | 1.01   | 1-Cyclohexyl-2-Propene | C9H16           | 124.2233         |
| 11   | 6.961          | 1.35   | Indene                   | C9H8            | 116.1598         |
| 12   | 7.476          | 1.18   | Pinane                   | C10H18          | 138.2499         |
| 13   | 8.111          | 1.04   | 5-Undecene | C11H22          | 138.2499         |
| 14   | 8.208          | 1.22   | 5-Undecene | C11H22          | 138.2499         |
| 15   | 8.866          | 1.34   | 1-Butylbenzene | C10H10          | 130.1864         |
| 16   | 8.693          | 2.29   | 1-Methylindene | C10H10          | 130.1864         |
| 17   | 9.078          | 1.3    | Spiro(4,5)Decane | C10H18          | 138.2499         |
| 18   | 9.392          | 3.29   | Cyclodecene | C12H22          | 166.3031         |
| 19   | 9.885          | 1.31   | 2-Dodecene | C12H24          | 168.319          |
| 20   | 9.892          | 1.6    | 2-Dodecene | C12H24          | 168.319          |
| 21   | 11.304         | 3.22   | 1-Tridecane | C13H26          | 182.3455         |
| 22   | 11.698         | 1.11   | Tridecane | C13H26          | 182.3455         |
| 23   | 11.836         | 1.21   | 2-Chloroethyl Linoleate | C20H35ClO2 | 342.948         |
| 24   | 12.042         | 1.1    | Bicyclo[3.3.2]Decan-9-One | C10H16O | 152.237         |
| 25   | 12.173         | 1.12   | 5-Butyl-4-Nonene | C13H26          | 182.3455         |
| 26   | 12.677         | 1.25   | 8-Dodec-1-OL, Acetate | C14H26O2 | 226.355         |
| 27   | 12.814         | 4.37   | 1,13-Tetradecadiene | C14H26          | 194.3562         |
| 28   | 12.963         | 4.46   | 2-Tetradecene, | C14H28          | 196.3721         |
| 29   | 14.393         | 3.47   | 1,13-Tetradecadiene | C14H26          | 194.3562         |
| 30   | 15.887         | 4.16   | E-10-Pentadecenol | C15H30O         | 226.404          |
| 31   | 17.312         | 3.62   | 1,19-Eicosadiene | C20H38          | 278.5157         |

3. Identification of Components:

The mass spectra database of National Institute Standard and Technology (NIST) library was used for the interpretation of the GC-MS. The spectrum of component unknown was compared with the spectrum of components known. The names of the materials tested and their molecular weight were confirmed.
Table 3: Chemical compositions of the liquid fuel products from pyrolysis of LDPE

| Peak | Retention Time | Area % | Compound Name | Molecular Formula | Molecular Weight |
|------|----------------|--------|----------------|-------------------|------------------|
| 1    | 3.264          | 1.17   | 1,2-dimethyl cyclohexane | C8H16 | 112.2126 |
| 2    | 4.506          | 1.09   | Cyclooctanone        | C8H14O | 126.1962 |
| 3    | 4.643          | 1.02   | 4-Nonene            | C9H18 | 126.2392 |
| 4    | 5.004          | 1.02   | 2-methylpropyl Cyclohexane | C10H20 | 140.2658 |
| 5    | 5.244          | 2.82   | 7-methyl-3,4-Octadiene, | C9H16 | 124.2233 |
| 6    | 6.171          | 1.37   | trans-4-Decene      | C10H20 | 140.2658 |
| 7    | 6.491          | 1.65   | methylCycloheptane  | C8H16 | 112.2126 |
| 8    | 6.577          | 1.94   | 9-Methylbicyclo[3,3,1]nonane | C10H18 | 138.254 |
| 9    | 7.024          | 1.16   | 9-Methylbicyclo[3,3,1]nonane | C10H18 | 138.254 |
| 10   | 7.51           | 1.26   | 2,5,5-Trimethyl-1,6-heptadiene | C10H18 | 138.2499 |
| 11   | 8.185          | 1.22   | 5-Undecene          | C11H22 | 154.2924 |
| 12   | 8.815          | 0.99   | 4,8-dimethyl-1,7-Nonadiene | C11H20 | 152.277 |
| 13   | 9.072          | 1.06   | 2-Pentanylcyclopentane | C10H20 | 140.2658 |
| 14   | 9.398          | 3.4    | 14-methyl-(Z)-8-hexadecen-1-ol | C17H34O | 254.4513 |
| 15   | 9.839          | 1.23   | 2-Dodecene          | C12H24 | 168.319 |
| 16   | 10.365         | 1      | Cyclodecane         | C12H24 | 168.319 |
| 17   | 10.754         | 1.1    | 1,5-Dimethyldecaphalene | C12H22 | 166.3031 |
| 18   | 10.863         | 1.2    | Octacosyl heptadecfluorobutyrate | C32H57F7O2 | 606.7826 |
| 19   | 11.132         | 3.23   | 1-Octadeyne         | C18H34 | 250.4626 |
| 20   | 11.286         | 3.68   | 1-Tridecene         | C13H26 | 182.3455 |
| 21   | 11.59          | 2.81   | 2,3,4-Trimethylhexan | C9H20 | 128.2551 |
| 22   | 11.681         | 2.2    | 5-Butyl-4-Nonene    | C13H26 | 182.3455 |
| 23   | 11.819         | 2.06   | 1,1-Dimethyl-2-propylcyclohexane | C11H22 | 154.297 |
| 24   | 12.671         | 1.79   | trans-Pinane        | C10H18 | 138.2499 |
| 25   | 12.797         | 3.31   | 14-methyl-(Z)-8-hexadecen-1-ol | C17H34O | 254.4513 |
| 26   | 12.963         | 4.52   | 2-Tetradecene       | C14H28 | 196.3721 |
| 27   | 14.376         | 2.67   | 1,12-Tridecadiene   | C13H24 | 180.3297 |
The liquid fuel extracts was gasoline as identified compounds, DPE - IOP and LDPE contains same pyrolyzed HDPE and LDPE, it can hydrocarbons in the C areas of more than 3% for liquid fuel for both shows similar compositions. From the GC MS analysis has established the identity of the compounds present in the liquid fuel of the plastics revealed the presence of hydrocarbons in the C8 – C24 range. By comparing the compounds present in the liquid fuel of the pyrolyzed HDPE and LDPE, it can be deduced from Fig. 4 that the carbon number distribution of HDPE and LDPE contains same fractions but slightly different percentage composition. For HDPE, gasoline

| No. | Retention Time (min) | Name                                      | Molecular Formula | Mass (amu) |
|-----|----------------------|-------------------------------------------|-------------------|------------|
| 28  | 14.537               | 1-Pentadecene                             | C15H30            | 210.3987   |
| 29  | 15.876               | 7-Dodeceno-1-ol, acetate                  | C14H26O2          | 226.355    |
| 30  | 17.306               | trans-2-Dodeceno-1-ol, trifluoroacetate   | C14H23F3O2        | 280.3264   |
| 31  | 17.461               | cis-3-Heptadecene                         | C17H34            | 238.4519   |
| 32  | 18.656               | 1,19-Eicosadiene                          | C20H38            | 278.5157   |
| 33  | 18.811               | 1-Octadecene                              | C18H36            | 252.4784   |
| 34  | 19.068               | trans-9-Octadecene                        | C18H36            | 252.4784   |
| 35  | 19.938               | Pentadecanal                              | C15H30O           | 226.3981   |
| 36  | 21.081               | Z-5-Nonadecene                            | C19H38            | 266.513    |
| 37  | 21.161               | Octadecane                                | C18H38            | 254.4943   |
| 38  | 21.014               | Dibutyl Phthalate                         | C16H22O4          | 278.348    |
| 39  | 21.186               | Bicyclo[10.8.0]Eicosane                   | C20H38            | 278.524    |
| 40  | 22.3                 | Cyclooctacosane                           | C20H40            | 280.5316   |
| 41  | 22.341               | Bicyclo[10.8.0]Eicosane                   | C20H38            | 278.524    |
| 42  | 22.444               | Z-5-Nonadecane                            | C19H38            | 266.513    |
| 43  | 23.524               | 1-Heneicosane                             | C21H44            | 296.5741   |
| 44  | 23.543               | 1-Docosene                                | C22H44            | 308.5848   |
| 45  | 23.617               | 8-Heptapentadecane                        | C22H46            | 310.6006   |
| 46  | 24.596               | 9-Tricosene                               | C23H46            | 322.6113   |
| 47  | 25.659               | 1-Pentadecane                             | C15H32            | 212.4146   |
| 48  | 25.614               | Cyclotetracosane                          | C24H48            | 336.6379   |
| 49  | 25.672               | Tetracosane                               | C24H50            | 338.6538   |
| 50  | 27.182               | 1-n-octyl phthalate                       | C24H50O4          | 390.5561   |

4. RESULTS AND DISCUSSION

The results appropiated to the GC-MS analysis has established the identity of the number of compounds or fractions of the liquid fuel obtained from the pyrolysed PPW. Identification of compounds was also done through the mass spectrophotometry attached with the GC. The liquid fuel extracts was dark yellow in colour. Fifty compounds were detected for the pyrolysis of both the LDPE and HDPE. It is interesting to know that liquid fuel for both shows similar compositions. The eight major compounds confirmed for HDPE were 1-Tridecane (3.22%), Cyclododecane (3.29%), 1,19-Eicosadiene (3.62%), 3-Heptadecene (3.73%), E-10-Pentadecenol (4.16%), 1,13-Tetradecadiene (4.37%), 2-Tetradecene (4.46%), Dibutyl Phthalate (4.78%) with the retention time of 11.304, 9.392, 17.312, 17.466, 15.887, 12.814, 12.963 and 21.042 minutes respectively. The nine major compounds also confirmed for the LDPE were 1-Octadecyne (3.23%), 7-Dodeceno-1-ol acetate (3.15%), 14-methyl-(Z)-8-hexadecen-1-ol (3.31% & 3.40%), 1-Pentadecane (3.58%), 1-Tridecane (3.68%), cis-3-Heptadecane (3.91%), Dibutyl Phthalate (4.36%), 2-Tetradecene (4.46%) with the retention time 11.132, 15.876, 12.797, 9.398, 14.537, 11.286, 17.461, 21.014 and 12.963 minutes respectively. This conforms to the findings of Shah et al.[11]. It was observed that at a particular retention time, 12.963, the same compound namely 2-Tetradecene was confirmed for both the HDPE and LDPE. Also Bicyclo[10.8.0]Eicosane was confirmed. The compound obtained here is similar to the compound obtained by Patil, Varma, Gajendra, & Mondal [12].

Characterization of Liquid Products

From the GC-MS analysis results, Fig. 2 and Fig. 3 represent the total ion chromatography graph of the liquid fuel products, which showed the peak areas of all the identified compounds, particularly peak areas of more than 3% for the major compounds detected. Both plastics revealed the presence of hydrocarbons in the C8 – C24 range. By comparing the compounds present in the liquid fuel of the pyrolyzed HDPE and LDPE, it can be deduced from Fig. 4 that the carbon number distribution of HDPE and LDPE contains same fractions but slightly different percentage composition. For HDPE, gasoline
(C6 – C12) fraction had 36%, diesel (C13 – C20) fraction had 32%, C21- C28 fraction 14% and the none hydrocarbon fraction range gave 18% while for LDPE, gasoline (C6 – C12) fraction had 36%, diesel (C13 – C20) fraction had 34%, C21- C28 fraction 12% and the none hydrocarbon fraction range also gave 18% [13].

Fig. 2: Total Ion Chromatography of the pyrolyzed LDPE

Fig. 3: Total Ion Chromatography of the pyrolyzed HDPE
5. CONCLUSION

In spite of all environmental problems caused by plastic wastes, it is still a valuable raw material for petrochemical and refinery industries. The thermal cracking of LDPE and HDPE operated using a semi-batch reactor has been used to obtain useful hydrocarbon fractions at a temperature of 230oC. GC-MS showed the compositional analysis of the liquid fuel obtained containing mainly aliphatic and aromatic compounds within the carbon range of C8 to C24. The liquid products obtained have similar products to fossil fuels which can be used as alternative fuels for a more sustainable and cleaner environment when necessary blending is done for upgrading.

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