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

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# 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 C<sub>8</sub> – C<sub>24</sub>. This is made up of 36% of gasoline fractions range from C<sub>6</sub> - C<sub>12</sub>, 32% of diesel fractions range C<sub>13</sub> - C<sub>20</sub>, and 14% oil of residual fuel range of C<sub>20</sub> – C<sub>28</sub> and 18% of non-hydrocarbons was discovered for the HDPE while 36% of gasoline fractions range of C<sub>6</sub> - C<sub>12</sub>, 34% of diesel fractions range C<sub>13</sub> - C<sub>20</sub>, oil and 12% residual fuel range of C<sub>20</sub> – C<sub>28</sub> 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 scraps 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. Onwudili 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.

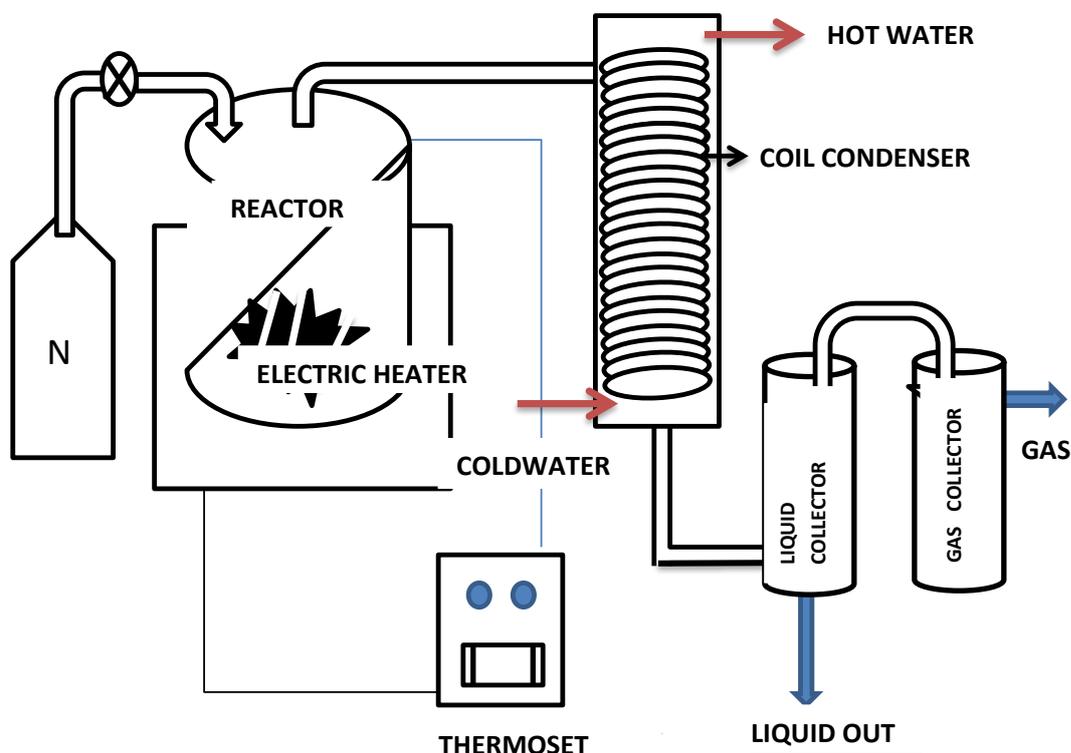
## **2. Materials and Method**

### **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	500c			
Injection Mode	Split			
Injection Temperature	1500C			
Injection Volume	1 ml			
Split Ratio	10:1			
Average Velocity	36.445cm/Sec			
Column Pressure	7.6522psi			
Column Flow	1.2211ml/Min			
Carrier Gas	Helium 99.9995% Purity			
Frequency	50Hz			
Electron Multiplier Volts	1024.9			
Column Oven Temperature Progress				
Rate (0C/min) (min)	Temperature (0C)	Hold	Time	
-	50	0		
8	300	9		
Column				

Length	30.0m
Diameter	250 $\mu$ m
Film Thickness	0.25 $\mu$ m
Total runtime	32 mins
Ms Conditions	
Source Temperature	2300C
Start mass range m/z	50
End mass range m/z	550

### 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 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	C <sub>12</sub> H <sub>26</sub>	170.3348
2	3.47	2.6	3-Octyne	C <sub>8</sub> H <sub>14</sub>	110.1968
3	4.042	1.29	1,3-Dimethylbenzene	C <sub>8</sub> H <sub>10</sub>	106.165
4	4.477	1.46	Trans-2-Nonene	C <sub>9</sub> H <sub>18</sub>	126.2392
5	4.695	1.77	Cyclohexane, 2-Propenyl-	C <sub>9</sub> H <sub>16</sub>	124.2233
6	5.221	2.72	3,4-Octadiene, 7-Methyl-	C <sub>9</sub> H <sub>16</sub>	124.2233
7	6.177	1.54	E-12-Tetradecenal	C <sub>14</sub> H <sub>26</sub> O	210.3556
8	6.48	2.17	Methylcycloheptane	C <sub>8</sub> H <sub>16</sub>	112.2126
9	6.566	2.43	1-Indanone	C <sub>9</sub> H <sub>14</sub> O	138.2069
10	6.726	1.01	1-Cyclohexyl-2-Propene	C <sub>9</sub> H <sub>16</sub>	124.2233
11	6.961	1.35	Indene	C <sub>9</sub> H <sub>8</sub>	116.1598
12	7.476	1.18	Pinane	C <sub>10</sub> H <sub>18</sub>	138.2499
13	8.111	1.04	5-Undecene	C <sub>11</sub> H <sub>22</sub>	138.2499
14	8.208	1.22	5-Undecene	C <sub>11</sub> H <sub>22</sub>	138.2499
15	8.866	1.34	1-Butynylbenzene	C <sub>10</sub> H <sub>10</sub>	130.1864
16	8.693	2.29	1-Methylindene	C <sub>10</sub> H <sub>10</sub>	130.1864
17	9.078	1.3	Spiro(4,5)Decane	C <sub>10</sub> H <sub>18</sub>	138.2499
18	9.392	3.29	Cyclododecene	C <sub>12</sub> H <sub>22</sub>	166.3031
19	9.885	1.31	2-Dodecene	C <sub>12</sub> H <sub>24</sub>	168.319
20	9.892	1.6	2-Dodecene	C <sub>12</sub> H <sub>24</sub>	168.319
21	11.304	3.22	1-Tridecene	C <sub>13</sub> H <sub>26</sub>	182.3455
22	11.698	1.11	Tridecene,	C <sub>13</sub> H <sub>26</sub>	182.3455
23	11.836	1.21	2-Chloroethyl Linoleate	C <sub>20</sub> H <sub>35</sub> ClO <sub>2</sub>	342.948
24	12.042	1.1	Bicyclo[3.3.2]Decan-9-One	C <sub>10</sub> H <sub>16</sub> O	152.237
25	12.173	1.12	5-Butyl-4-Nonene	C <sub>13</sub> H <sub>26</sub>	182.3455
26	12.677	1.25	8-Dodecen-1-ol, Acetate	C <sub>14</sub> H <sub>26</sub> O <sub>2</sub>	226.355
27	12.814	4.37	1,13-Tetradecadiene	C <sub>14</sub> H <sub>26</sub>	194.3562
28	12.963	4.46	2-Tetradecene,	C <sub>14</sub> H <sub>28</sub>	196.3721
29	14.393	3.47	1,13-Tetradecadiene	C <sub>14</sub> H <sub>26</sub>	194.3562
30	15.887	4.16	E-10-Pentadecenol	C <sub>15</sub> H <sub>30</sub> O	226.404
31	17.312	3.62	1,19-Eicosadiene	C <sub>20</sub> H <sub>38</sub>	278.5157

32	17.466	3.73	3-Heptadecene,	C17H34	238.4519
33	18.668	2.54	1-Hexadecyne	C16H30	222.4094
34	19.949	2.35	1,19-Eicosadiene	C20H38	278.5157
35	21.042	4.78	Dibutyl Phthalate	C16H22O4	278.348
36	21.191	2.17	Bicyclo[10.8.0]Eicosane	C20H38	278.524
37	22.353	1.87	1,19-Eicosadiene	C20H38	278.5157
38	23.474	1.51	Bicyclo[10.8.0]Eicosane	C20H38	278.524
39	23.594	1.95	1-Docosene	C22H44	308.5848
40	24.544	1.01	1,19-Eicosadiene	C20H38	278.5157
41	24.653	2.07	9-Tricosene	C23H46	322.6113
42	25.58	0.96	1,21-Docosadiene	C22H42	306.5689
43	25.666	1.65	Cyclotetracosane	C24H48	336.6379
44	26.633	1.24	1-Docosene	C22H44	308.5848
45	27.199	2.18	Di-N-Octyl Phthalate	C24H38O4	390.5561
46	27.571	1.58	9-Tricosene	C23H46	322.6113
47	27.623	1.52	Pentadecane	C15H32	212.4146
48	28.481	1.23	Octacosyl Acetate	C30H60O2	452.7962
49	28.521	1.13	Tetracosane	C24H50	338.6538
50	30.243	1.1	Heptadecane	C24H50	240.4677

**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	Cyclododecane	C12H24	168.319
17	10.754	1.1	1,5-Dimethyldecahydronaphthalene	C12H22	166.3031
18	10.863	1.2	Octacosyl heptafluorobutyrate	C32H57F7O2	606.7826
19	11.132	3.23	1-Octadecyne	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

28	14.537	3.58	1-Pentadecene	C15H30	210.3987
29	15.876	3.15	7-Dodecen-1-ol, acetate	C14H26O2	226.355
30	17.306	2.6	trans-2-Dodecen-1-ol, trifluoroacetate	C14H23F3O 2	280.3264
31	17.461	3.91	cis-3-Heptadecene	C17H34	238.4519
32	18.656	1.93	1,19-Eicosadiene	C20H38	278.5157
33	18.811	2.82	1-Octadecene	C18H36	252.4784
34	19.068	1.13	trans-9-Octadecene	C18H36	252.4784
35	19.938	1.88	Pentadecanal	C15H30O	226.3981
36	21.081	2.86	Z-5-Nonadecene	C19H38	266.513
37	21.161	1.03	Octadecane	C18H38	254.4943
38	21.014	4.36	Dibutyl Phthalate	C16H22O4	278.348
39	21.186	1.26	Bicyclo[10.8.0]Eicosane	C20H38	278.524
40	22.3	2.31	Cycloeicosane	C20H40	280.5316
41	22.341	1.16	Bicyclo[10.8.0]Eicosane	C20H38	278.524
42	22.444	2.22	Z-5-Nonadecene	C19H38	266.513
43	23.524	1.01	Heneicosane	C21H44	296.5741
44	23.543	2.23	1-Docosene	C22H44	308.5848
45	23.617	1.475	8-Heptylpentadecane	C22H46	310.6006
46	24.596	1.4	9-Tricosene	C23H46	322.6113
47	25.659	1.01	Pentadecane	C15H32	212.4146
48	25.614	1.06	Cyclotetracosane	C24H48	336.6379
49	25.672	1.56	Tetracosane	C24H50	338.6538
50	27.182	1.83	Di-n-octyl phthalate	C24H50O4	390.5561

#### 4. RESULTS AND DISCUSSION

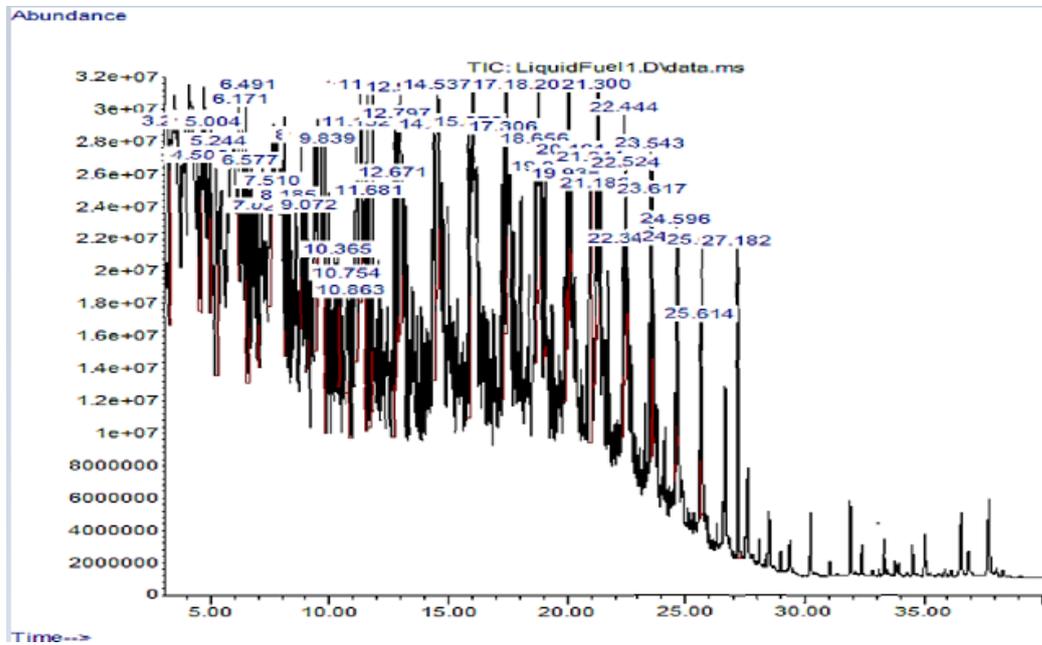
The results appropriated to the GC-MS analysis has established the identity of the number of compounds or fractions of the liquid fuel obtained from the pyrolysed PPW. Identification of compounds was also done through the mass spectrophotometry attached with the GC. The liquid fuel extracts was dark 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-Tridecene (3.22%), Cyclododecene (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-Dodecen-1-ol acetate (3.15%), 14-methyl-(Z)-8-hexadecen-1-ol (3.31% & 3.40%), 1-Pentadecene (3.58%), 1-Tridecene (3.68%), cis-3-Heptadecene (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].

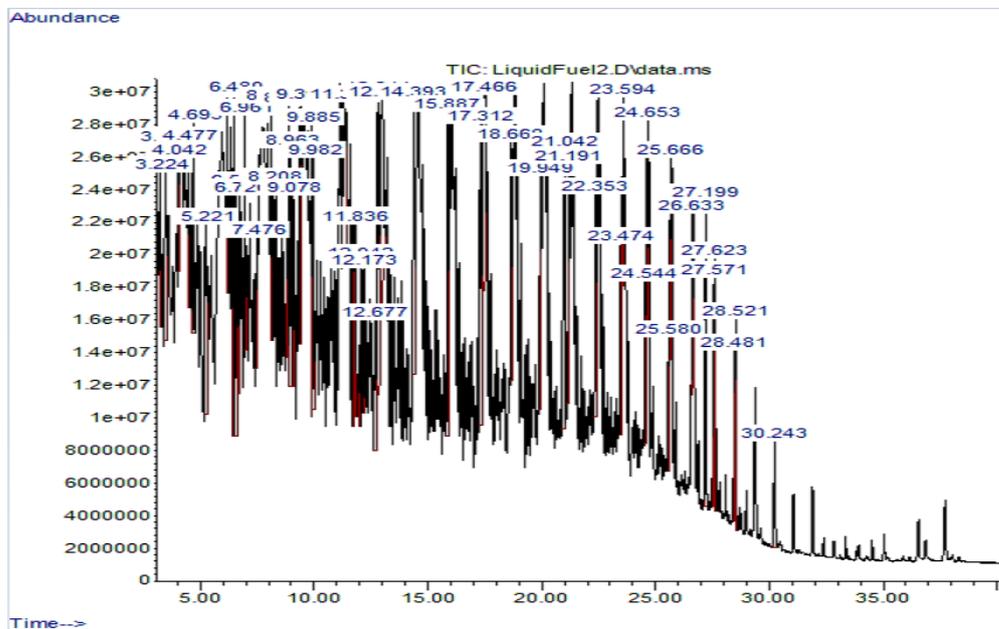
#### Characterization of Liquid Products

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

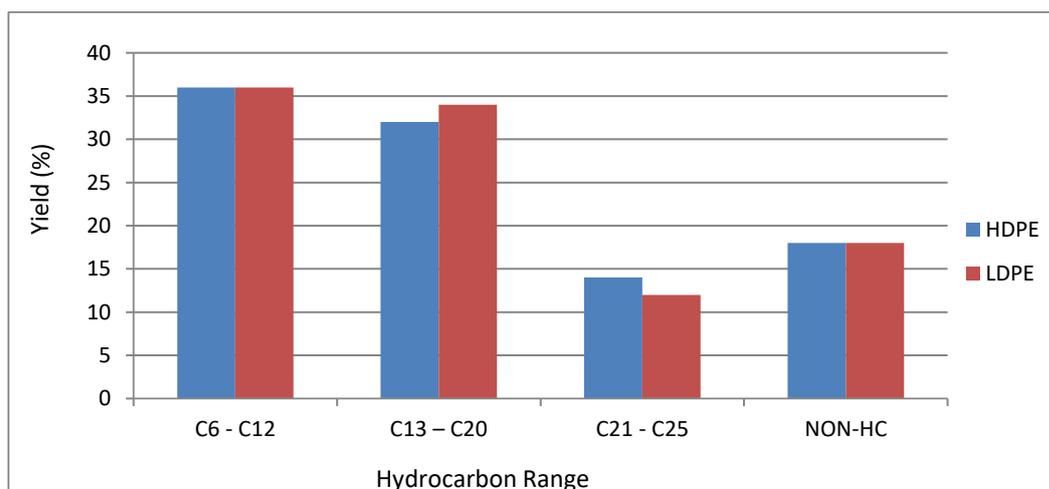
(C6 - C12) fraction had 36%, diesel (C13 – C20) fraction had 32%, C21- C28 fraction 14% and the none hydrocarbon fraction range gave 18% while for LDPE, gasoline (C6 - C12) fraction had 36%, diesel (C13 – C20) fraction had 34%, C21- C28 fraction 12% and the none hydrocarbon fraction range also gave 18% [13].



**Fig. 2:** Total Ion Chromatography of the pyrolyzed LDPE



**Fig. 3:** Total Ion Chromatography of the pyrolyzed HDPE



**Fig. 4:** Comparison of Hydrocarbon Ranges

## 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 230°C. 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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