

# COMPARATIVE ANALYSIS OF KEROSENE GRADE FUEL FROM PYROLYSIS OF HDPE AND LDPE WASTE PLASTICS.

## Abstract:

To curb the menace of plastic waste and energy crisis, this study investigated the conversion of high-density polyethylene (HDPE) and low-density polyethylene (LDPE) grades of plastics to kerosene. Plastics sourced from dumpsites within Port Harcourt metropolis in Rivers State, Nigeria were shredded and thermally degraded under inert condition at a temperature range of 350-400 °C. The obtained hydrocarbon liquid was further at a temperature range of 150-270°C and characterised to evaluate the physico-chemical parameters such as flash point, density, copper corrosion, and calorific value and compared against the acceptable standard. The result showed that these properties were within the permissible limit. However, the sulphur content and smoke point of HDPE and LDPE were above and below the limits, respectively. The GC-MS and GC-FID results of kerosene samples obtained from both grades of plastics indicates that the product comprised C<sub>9</sub> to C<sub>17</sub> grades.

**Keyword:** Waste management, plastics, Kerosene, Physico-chemical properties, Pyrolysis

## INTRODUCTION

The world population is approximately 7.87 billion as of July 1, 2021, and according to the medium-variant projection, the world's population will increase by 2.2 billion people between 2017 and 2050, reaching 9.8 billion people in 2050. Most of this population increase will be most evident in African countries. Nigeria's population is currently the seventh largest globally while an astronomical increase is projected in the next few years. This increase in human population is associated with a change in lifestyle, production and consumption pattern that transcends to an increase in resource consumption and waste generation (Asase *et al.*, 2009; Brunner & Rechberger, 2014).

Waste management has become a severe concern in world cities, including Nigeria (Anyanwu & Adefila, 2012; Babatunde & Uche, 2018). The generation of waste globally far exceeds the management rate (Nnaji, 2014); despite the application of the principles of waste management and the stress on adopting the 4 R's, the presence of waste has remained a significant concern (Chandler *et al.*, 1997).

Plastics are used for most of our everyday products and as such has remained inevitable. Hassanpour and Unnisa (2017) stated that over the years, the production of plastic has significantly increased; in 2009 and 2013, around 230 and 299 Mt of plastic was generated, respectively, making it a 3.9% rise from 2012. Around 280 Mt of plastics were released by 2012; 90% of these were low density polyethylene (LDPE), high density polyethylene (HDPE), polypropylene (PP), polyvinylchloride (PVC), polystyrene (PS) and polyethylene terephthalate (PET) grades of plastics. Globally, plastic resin production has risen exponentially with the increase in population; about 300 MMT of plastics have been produced annually in recent years. According to Statista, in 2015, the production volume of plastic in Nigeria reached around 411,000 metric tons, and the figure will increase to some 513,000 tons of plastic by 2020. In

2015, Nigeria's plastic consumption reached around one million tons, which will increase to some 1.5 million tons of plastic by 2020. Nodim (2022) discussed Nigeria's plastic waste and reported that the increase in plastic consumption across the country has resulted in an accelerated increase in plastic waste in Nigeria. Plastic consumption in Nigeria has increased by 116.2% within the last 15 years. Furthermore, the per capita plastic consumption has grown by five per cent (5%) annually from 4kg to 6.5 kg within this period, it is also estimated that each citizen would consume about 7.5 kg of plastic annually. On a population of about 206.1 million Nigerians, plastic consumption in Nigeria is approximately 1.545 million tonnes annually.

According to Jambeck *et al.*, (2015), Nigeria contributes 0.13–0.34 million tonnes of plastic waste to the marine environment. It is ranked ninth globally regarding marine plastic pollution. Plastic waste management can be done by applying the 4 R” of the waste management concept (reducing, reusing, recycling and recovery techniques). Peng *et al.*, (1997) reported that plastic recycling can be grouped into mechanical, energy and chemical processes. The mechanical process converts plastic to an entirely different product or item without alteration of its chemical structure. The energy process involves generating thermal and electric energy from plastic, usually leveraging processes like incineration. In contrast, the chemical process alters the chemical structure of the plastic to produce entirely new materials. The pyrolysis process is a chemical recycling process where plastics of high molecular weight thermally decomposes or crack to produce primary volatiles in the absence of oxygen or inert condition to generate products known as end products of pyrolysis that include solid residual (ash or char), non-condensable gases and condensable liquids (pyrolysis oil, pyrolytic oil, bio-oil or wax) (Aguado *et al.*, 2006; Miandad *et al.*, 2016; Wong *et al.*, 2013; Shah *et al.*, 1999).

Furthermore, HDPE and LDPE are the most commonly wasted grades of plastics Kumar and Singh (2013). These plastics are predominant in dumpsites in around Port Harcourt metropolis, hence its choice for this study. High-density polyethylene (HDPE) is a thermoplastic from the family of polyethylene and has a versatile application. It consists of a monomer called Ethylene. It has very high strength because of its high degree of crystallinity (70-95%), high molecular weight (941-965 kg/m<sup>3</sup>) Suhartono (2019), and low branching (Vijayakumar and Sebastian, 2018). Plastic is used in most industrial and domestic products due to its high strength-to-density ratio. HDPE is commonly recycled and has the number "2" as its resin identification code. On the other hand, LDPE is a thermoplastic in high-demand for commercial and other industrial products, such as parts of equipment, packaging, and greenhouses for agriculture. López *et al.*, (2011) stated that LDPE is the second largest plastic found in municipal waste in demand after polypropylene (PP). LDPE is one of the polyethylene polymers with a density between 0.915 and 0.930 g/cm<sup>3</sup>, with resin code "4."

Moreover, the ultimate and proximate analysis of HDPE and LDPE gives its volatility within the range of 99-95%, far more significant than other parameters making them suitable for pyrolysis. Abnisa *et al.*, (2014) confirmed that the higher the volatility of a polymer, the higher the oil production. Sharuddin *et al.*, (2018) stated that among the polyolefin thermoplastics, LDPE produced the highest liquid oil yield (93.1wt%), followed by HDPE (84.7wt%). Also, Seo *et al.*, (2003) reported the yield of liquid, gas and residue produced from thermal degradation of waste HDPE at 450°C to be 84.00wt%, 13.00wt%, and 3.00wt%, respectively. In addition, Kumar and Singh (2011), at a temperature of 550°C, reported the yield of plastic pyrolysis to be

liquid 79.08wt%, gas 18.42wt%, and residue 2.5wt%. Furthermore, Ahmad *et al.*, (2015) reported that the thermal cracking of HDPE was investigated over a temperature range of 250–400°C. Total liquid yield, 80.88 %w/w, gaseous, 17.24% w/w, and residue, 1.88 % w/w, was achieved at 350°C. Sharuddin. *et al.*, (2017) stated that plastic is to be pyrolyzed individually for high yield in pyrolytic oil. Unfortunately, there is limited literature on the chemical composition of kerosene from HDPE and LDPE, this study seeks to investigate this.

## MATERIALS AND METHODS

HDPE and LDPE plastics were sourced from a dumpsite in Port Harcourt metropolis, Rivers State- Nigeria, shredded and weighed. A fixed batch reactor pyrolysis plant was used separately to pyrolyze the HDPE and LDPE plastic. The plastics were loaded into the pyrolysis plant reactor, and nitrogen gas was introduced into the reactor using a determined flow rate for five minutes. A fixed batch pyrolysis plant was used to pyrolyze 7 kg of the waste plastic at a temperature range of 350- 450°C and a residence time of 2hrs. At the optimal temperature, the plastics underwent thermal decomposition to generate organic vapour; the vapour moved into the condenser and condensed, and then the condensed liquid was collected with the non-condensable gas at the central collection tank.

The high calorific value non-condensable gas was sent into the burner to aid burning for pyrolysis, while at the end of each bath, the reactor was allowed to cool and the residue removed and weighed. The volume and weight of the pyrolytic liquid and residue were determined using measuring cylinders and scales respectively. The value of the non-condensable gas was calculated using the mass balance.

The recovered pyrolytic oil was further distilled at a temperature range of 150-270°C, where the kerosene fraction is recovered. The kerosene was analyzed using GC-FID and GC-MS, and their physicochemical parameters ascertained. The kerosene was compared with the regulatory standard for Household kerosene (HHK).

### Results & discussion



**Plate: 1a**



**Plate: 1b**



**Plate: 2a**



**Plate: 2b**

Plates 1a and 1b represent the shredded Low-Density Polypropylene (LDPE) before pyrolysis and generated pyrolytic oil from pyrolysis of the LDPE plastic, respectively.

Plates 2a and 2b represent the shredded High-Density Polyethylene (HDPE) before pyrolysis and generated pyrolytic oil from pyrolysis of the HDPE plastic, respectively.

### Product yield

Table 1: Percentage yield of hydrocarbon products from pyrolysis

Plastic grade	Liquid (%)	Solid (%)	Gas (%)
HDPE	82.87	9.52	7.61
LDPE	84.15	3.34	12.51

NB: Values are the average of a replicate of 3 experimental samples

The HDPE yielded a high pyrolytic liquid when compared with the LDPE (Table 1). The result agrees with the proximate and ultimate analysis of both plastics. However, both have the propensity to yield more pyrolytic liquid than other pyrolysis products although the LDPE plastic has a higher potential than HDPE plastics. The result is in agreement with the work of Sharuddin *et al.*, (2018), which reported that among the polyolefin, LDPE generates more pyrolytic liquid than HDPE.

Table 2: shows the % kerosene yield

HDPE	LDPE
33	26
26	30
19.5	29
34	31
31	3
<b>28.7</b>	<b>23.8</b>

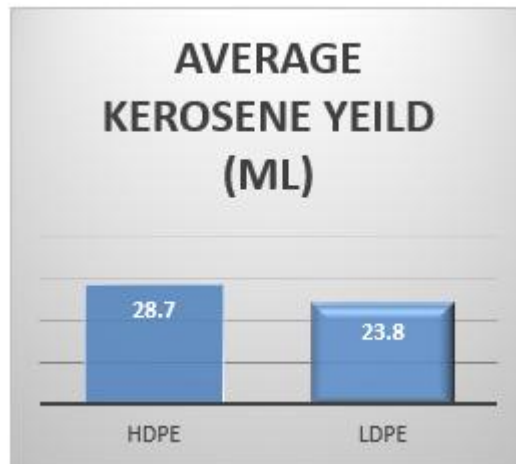


Figure1: Average % kerosene yield

Table 2: shows the kerosene yield from the distillation of 1000 ml of pyrolytic liquid each. A replicate of 5 experiments were carried out at 150-270°C. The yield was also converted to a percentage value, and from the result, HDPE yielded more kerosene than LDPE, which is also shown in Figure 1.

### Characterization

The characterization of the kerosene samples recovered from the distillation of the pyrolytic oil from both plastics was analyzed employing gas chromatography coupled with a mass spectrum (GC-MS) and Gas chromatography with flame ion detection (GC-FID) to carry out its quantification and qualification (chemical mass composition), while the physico-chemical properties analyzed utilizing the guide presented by The Nigerian Midstream and Downstream Petroleum Regulatory Authority (NMDPRA) as shown in Table 3

Table 3: Physiochemical characterization of kerosene sample from HDPE and PP plastic

S/NO	PARAMETER	UNIT	HDPE	LDPE	NMDPRA LIMIT
1	Specific gravity	-	0.76	0.77	0.830 max
2	Acid value	mgKOH/g	0.68	0.65	0.01
3	Carbon residue	% wt.	0.21	0.14	-
4	Calorific value	Mj/kg	41750	40690	45000
5	Sulphur content	-	0.10	0.01	0.015max
6	Flash point	°F	117.3	125.2	113 min
7	Smoke point	mm	23.1	20.7	22 min
8	API gravity	-	54.68	52.27	41.06 max
9	Colour	-	21.9	18.4	+18min
10	Water content	% wt.	0.10	0.18	0.05 max
11	Copper corrosion	2hr@100°C	2a	1b	1b max

Table 3 summarizes the physico-chemical properties of the kerosene sample from HDPE and LDPE plastics. The specific gravity of the kerosene from both plastic show that they are within the permissible limit of 0.820 max value specified for cooking. The Calorific value of the plastic shows that the HDPE having high value than the LDPE; however, both have high values that can generate heat for cooking. The kerosene sample from HDPE has Sulphur above the permissible limit for cooking than the one from LDPE, which may affect its use indoors because of the danger associated with a high-value Sulphur in fuel. This elevated value for the Sulphur content for HDPE kerosene can result from the high value of Sulphur in the HDPE plastic, as reported by Dubdub& Al-Yaari (2020) in the ultimate analysis of various plastics. Both plastics have flash points above the minimum limit. Therefore, both are safe for handling and storage since the higher the flash point of the fuel, the better. The smoke point value of both plastics shows LDPE below the minimum value showing that it will likely undergo incomplete combustion. Finally, the copper content of both plastics showed HDPE above permissible limit and LDPE within the permissible limit, therefore, LDPE is mostly safe for use in metal or copper lamps since there is no corrosion problem. This result shows that the kerosene's properties from both plastics are close to that of commercial kerosene so that they can be used directly as their commercial counterpart

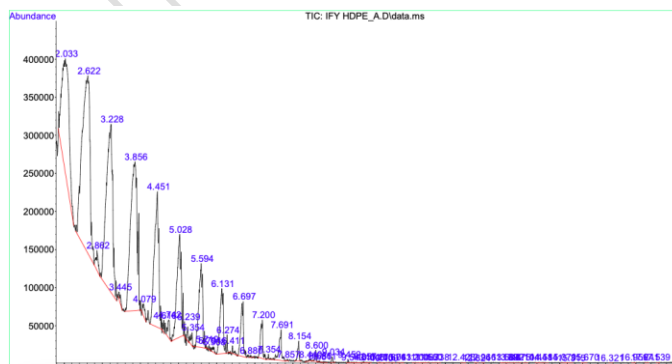


Figure 2a: GCMS result of High-Density Polyethylene (HDPE)

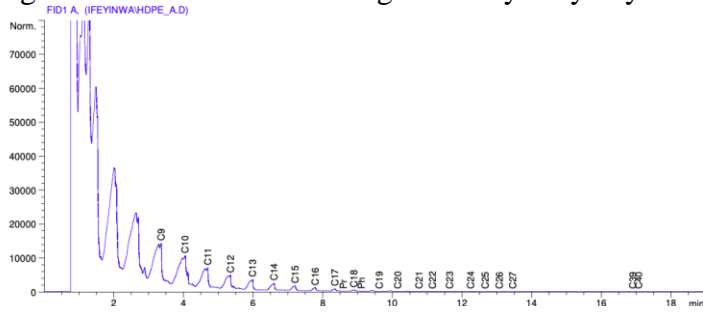
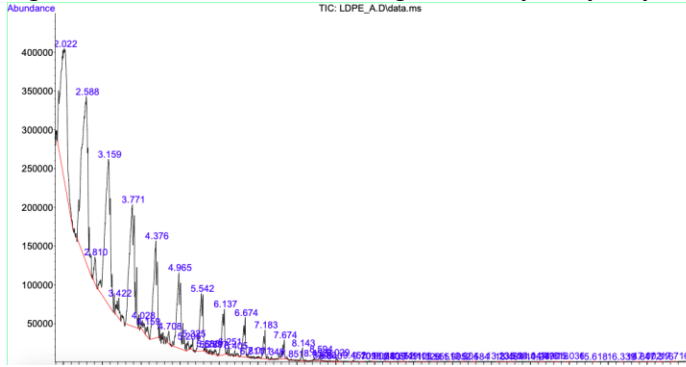


Figure 2b: GC-FID result of High-Density Polyethylene (HDPE)



C <sub>9</sub>	3.25282e4	6138.04439
C <sub>10</sub>	2.37071e4	1.12048e4
C <sub>11</sub>	1.38058e4	2370.58398
C <sub>12</sub>	8569.04285	4213.90389
C <sub>13</sub>	5444.71725	2805.37978
C <sub>14</sub>	3516.77104	1713.05238
C <sub>15</sub>	2355.81227	675.38132
C <sub>16</sub>	932.37955	415.69955
C <sub>17</sub>	592.22209	260.83131
Pr	5.44395	4.70962
C <sub>18</sub>	346.72881	135.88375
Ph	9.79756	4.67080
C <sub>19</sub>	11.21237	4.79289
C <sub>20</sub>	3.92935	3.81636
C <sub>21</sub>	4.78862	5.00175
C <sub>22</sub>	6.11661	8.86530
C <sub>23</sub>	4.89621	5.35567
C <sub>24</sub>	13.95069	14.52678
C <sub>25</sub>	9.94804	11.61934
C <sub>26</sub>	7.41228	10.52662
C <sub>27</sub>	7.67942	9.90117
C <sub>28</sub>	-	10.20746
C <sub>29</sub>	-	10.29109
C <sub>30</sub>	-	9.02073
C <sub>31</sub>	-	-
C <sub>32</sub>	-	7.16694
C <sub>33</sub>	-	5.70927
C <sub>34</sub>	-	3.97247
C <sub>35</sub>	-	-
C <sub>36</sub>	-	-
C <sub>37</sub>	-	0.00000
C <sub>38</sub>	-	1.80159
C <sub>39</sub>	6.12610	7.10625
C <sub>40</sub>	8.47482	8.97226

Table 5: GC-MS analysis of HDPE Kerosene sample

Percentage contribution of PIONA in HDPEkerosene sample

Name of compound	Molecular formula	R. time (min)	% of total
2-Heptene, 5-methyl-	C <sub>8</sub> H <sub>16</sub>	2.033	13.062
5-Octadecene,	C <sub>18</sub> H <sub>36</sub>	2.622	21.566
Bicyclo[3.1.1]heptane, 2,6,6-trimethyl-	C <sub>10</sub> H <sub>18</sub>	2.862	0.673
Cycloheptane, methyl-	C <sub>8</sub> H <sub>16</sub>	3.228	16.611
5-Dodecene,	C <sub>12</sub> H <sub>24</sub>	3.856	15.664
3,4-Octadiene, 7-methyl-	C <sub>9</sub> H <sub>16</sub>	4.079	0.378
7-Tetradecene,	C <sub>14</sub> H <sub>28</sub>	4.451	9.023
1-Docosene	C <sub>22</sub> H <sub>44</sub>	5.028	6.882
Cyclopentane, hexyl-	C <sub>11</sub> H <sub>22</sub>	5.239	0.259
3,4-Octadiene, 7-methyl-	C <sub>9</sub> H <sub>16</sub>	5.354	0.286
1-Cyclohexylnonene	C <sub>15</sub> H <sub>28</sub>	5.719	0.021
1-Docosene	C <sub>22</sub> H <sub>44</sub>	6.131	3.301
Hexacosane	C <sub>26</sub> H <sub>54</sub>	6.697	2.292
Cyclopentane, 1-pentyl- 2-propyl-	C <sub>11</sub> H <sub>22</sub>	6.880	0.035
Heneicosane	C <sub>21</sub> H <sub>44</sub>	7.200	1.375
3-Octadecene,	C <sub>18</sub> H <sub>36</sub>	7.354	0.092
Octacosane	C <sub>28</sub> H <sub>58</sub>	7.691	1.169
Heptacosane	C <sub>27</sub> H <sub>56</sub>	8.154	0.417
Tetratetracontane	C <sub>44</sub> H <sub>90</sub>	8.600	0.214
Nonane, 4-ethyl-5- methyl-	C <sub>12</sub> H <sub>26</sub>	9.857	0.021

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Table 6: GC-MS analysis of LDPEKerosene

Percentage contribution of PIONA in LDPE kerosene sample

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<b>Name of compound</b>	<b>Molecular formula</b>	<b>R. time (min)</b>	<b>% of total</b>
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(Z)-5-Decene	C <sub>10</sub> H <sub>20</sub>	2.022	18.485
Cyclopropane, 1-heptyl-2-methyl	C <sub>10</sub> H <sub>20</sub>	2.588	21.916
Bicyclo[3.1.1]heptane, 2,6,6-trimethyl-	C <sub>10</sub> H <sub>18</sub>	2.810	1.047
Cyclopentane, 1-hexyl-3-methyl-	C <sub>12</sub> H <sub>24</sub>	3.159	16.301
4-Tridecene, Z	C <sub>13</sub> H <sub>26</sub>	3.771	13.483
Bicyclo[3.1.1]heptane, 2,6,6-trimethyl-, [1R-(1.alpha.,2.alpha.,5.alpha.)]-	C <sub>10</sub> H <sub>18</sub>	4.028	0.414
Bicyclo[3.1.1]heptane, 2,6,6-trimethyl-, [1R-(1.alpha.,2.alpha.,5.alpha.)]-	C <sub>10</sub> H <sub>18</sub>	4.159	0.425
4-Tridecene, (Z)-	C <sub>13</sub> H <sub>26</sub>	4.376	7.666
3,4-Octadiene, 7-methyl-	C <sub>9</sub> H <sub>16</sub>	4.708	0.365
5-Octadecene, (E)-	C <sub>18</sub> H <sub>36</sub>	4.965	6.375
3-Octadecene, (E)-	C <sub>18</sub> H <sub>36</sub>	5.205	0.297
1-Methyl-2-(4-methylpentyl)cyclopentane	C <sub>12</sub> H <sub>24</sub>	5.325	0.228
5-Octadecene, (E)-	C <sub>18</sub> H <sub>36</sub>	5.542	3.925
1-Cyclohexylnonene	C <sub>15</sub> H <sub>28</sub>	5.685	0.018
10-Methylnonadecane	C <sub>20</sub> H <sub>42</sub>	6.137	2.664
10-Methylnonadecane	C <sub>20</sub> H <sub>42</sub>	6.674	1.762
Tetratetracontane	C <sub>44</sub> H <sub>90</sub>	7.183	1.102
Heptadecane	C <sub>17</sub> H <sub>36</sub>	7.674	0.798
Hexadecane	C <sub>16</sub> H <sub>34</sub>	8.143	0.371
10-Methylnonadecane	C <sub>20</sub> H <sub>42</sub>	8.594	0.164
Undecane, 5,6-dimethyl-	C <sub>13</sub> H <sub>28</sub>	9.452	0.033

Kerosene is one of the middle distillates of petroleum containing lighter fractions of primarily saturated aliphatic hydrocarbon and low concentrations of aromatic hydrocarbons. The carbon molecules of kerosene are between C<sub>9</sub> and C<sub>16</sub>(Shepherd *et al.*, 2000). The GC-FID was used to show the concentration of each carbon atom within the kerosene sampled; the GC-FID of both samples gave their carbon concentrations. The chromatogram of both samples in Figures 2b and

3b showed a concentration of carbon molecules from C<sub>9</sub> to C<sub>40</sub>; below C<sub>8</sub> were not detected because they are the lighter fractions and very volatile, and interference can occur. The carbon concentration of both samples, as shown in Table 4, showed the peak value of carbon concentration per time at C<sub>9</sub> to C<sub>17</sub> and is within the carbon range of standard kerosene.

The GC-FID was able to determine the carbon concentration of the sample, but for the chemical composition of the sample, a GC-MS was used. From The MS, each sample was characterised correctly, and all the compounds in the samples were identified in addition to their percentage abundance. The chromatograms of both samples are shown in Figures 2a and 3a. From the chromatogram, the sample type can be identified to some extent. The chromatogram peaks of the different compounds are well-defined and show almost the same pattern as a typical kerosene chromatogram and agree with the fingerprint pattern of the GC-FID. The highest peak height and abundance percentage were recorded at 233167: 21.5666%, 220844: 16.611%, 195294: 15.664 and 178169: 9.023% for HDPE and 214034: 21.916%, 169622:18.485%, 187466:16.301%, 156433:13.483% for LDPE.

The GS-MS results of both samples showed that the samples contain several different compounds. Since the investigation was on kerosene, the compounds that were of interest were selected out of the many compounds and are listed in Tables 5 and 6. The selection of the compound was based on if the compound falls within the already established groups of compounds in kerosene. Standard kerosene is made up of *n*-Paraffin, Iso-Paraffin, Naphthene and Aromatics. The measured compounds from the samples contain hetero-containing compounds of nitrogen, halogen, oxygen and sulphur. However, the emphasis was on the PIONA groups, so therefore the several compounds of interest were grouped into the paraffin (*n*-alkanes), Iso-paraffin (isoalkanes), Olefins (alkene), Naphthene (Cycloalkanes) and Aromatics hydrocarbons.

The Tables showed the concentrations of the PIONA available in both samples; from the tables, the HDPE comprises 1, Paraffin within the concentration range of 0.214% to 2.295%; this figure comprises straight chain alkanes of high carbon range. 2. Iso-Paraffin of 0.021%, this figure was from Nonane, 4-ethyl-5-methyl-. 3. Olefin, which includes different forms of alkene groups, both the mono-alkene and di-alkenes, has the highest concentration abundance in the range of 0.092% to 21.560%. 4, The Naphthene comprising of the cycloalkanes was also present in the sample at the range of 0.035 % to 16.611%; there was also a cycloalkene with a concentration of 0.021% observed. The LDPE kerosene also showed several compounds as listed in Table 6, and these compounds were also grouped based on PIONA hydrocarbons and their concentrations also listed: 1. Paraffins comprises of the concentration range of 0.371% to 1.102%, and the figure contains alkanes of high carbon atoms range. 2. Iso Paraffin in the sample are Iso-alkanes in the range of 0.033% to 2.644%. 3. Olefins in the LDPE kerosene are also the highest, with a concentration range from 0.297% to 18.485%, comprising mono alkenes and di-alkenes. 4. Naphthene present in the sample was only the cycloalkanes, and of the range 0.018% to 21.916%, the highest value was registered by Cyclopropane, 1-heptyl-2-methyl.

Table 7: Composition of distilled products

Samples	Paraffin (%)	Iso Paraffin (%)	Olefin (%)	Naphthene (%)	Aromatics (%)
HDPE Sample	5.467	0.021	70.254	17.599	-
LDPE Sample	2.279	4.623	50.596	40.349	-
Kerosene	55.2	-	-	40.9	3.9

In general, as shown in Table 7, the chemical composition of the samples from the HDPE and LDPE plastics was grouped and compared with that of the standards for kerosene. From the results, the HDPE kerosene sample contains Paraffin (5.467 %), Iso-paraffin (0.021%), Olefin (70.254%), Naphthene (17.599%) and no aromatic hydrocarbon. The LDPE sample contains Paraffin (2.279 %), So-paraffin (4.623%), Olefin (50.596%), Naphthene (40.349%) and also no aromatic hydrocarbon. The olefins were the highest in abundance in both samples though not in the standard kerosene. The Naphthene of the LDPE (40.349%) sample was higher than the HDPE (17.599%) and the same as the standard limit (40.9%). The paraffin of both samples is less than the standard limits of 55.2%, and aromatics were absent.

## CONCLUSION

This study has shown the feasibility of the production of HHK from HDPE and LDPE. The study also showed that HDPE plastic produces more kerosene than LDPE plastic. Both types of plastic meet the Household kerosene (HHK) standards set by the NMDPRA, except for some minor differences in sulphur content and smoke point. The GC-FID analysis showed that both plastics have the highest abundance of carbon molecules in C<sub>9</sub> to C<sub>16</sub>. Additionally, GC-MS analysis showed that both plastics have a chemical composition similar to standard kerosene, with the absence of aromatic compounds and the presence of olefin compounds, which can be attributed to their polymerization. Overall, the resulting kerosene has similar properties to commercial kerosene and can be a suitable alternative for domestic use.

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