Characterisation of Fractionated oil from Pyrolysis of Low-Density Polyethylene: Comparison between Catalytic Process and Non-Catalytic Process

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Abstract:- The environmental impact of waste plastics and the need to meet the increased demand for energy, coupled with the available technology for the conversion of waste plastic to liquid fuel, triggered this research. Montmorillonite clay was used as a green catalyst for the pyrolysis of low-density polyethylene to liquid fuel. The montmorillonite was calcinated at 600°C, and mixed metal oxides were found as its chemical composition using XRF. The common elements found in CMMR are silica oxide (SiO_2, 51.34%), iron (ii) oxide (Fe_2O_3, 16.23%), potassium oxide (K_2O, 5.03%), Aluminum oxide (Al_2O_3, 19.65%) tin oxide (TiO_2, 3.00%), calcium oxide (CaO,1.47%) and oxides of chlorides (Cl, 1.46%). The gas chromatography-mass spectrometer analysis of the various distillate fractions from the crude pyrolysis liquid revealed the present various chemical differences such as alkane, alkene, alkyne, cycloalkene, cycloalkane, aromatic, alcohol, and ester. Analysis of the pyrolysis oil based on the carbon range revealed the presence of gasoline (C_5-C_{12}) (gasoline), diesel (C_{13}-C_{24}) and fuel oil ($>C_{24}$). The API, specific gravity and kinematic viscosity of some of the oil confirmed them as diesel oil. The research has demonstrated the possibility of waste reduction and the potential of producing hydrocarbon fuel from waste low-density polyethylene waste plastic using pyrolysis.

Keywords:- Low-Density Polyethylene, Pyrolysis, GC-MS, XRF, Kinematic Viscosity.

I. INTRODUCTION

The uncommon characteristics of synthetic plastics have endeared them to consumers. Synthetic plastics (SPs) are durable, hydrophobic in nature, most chemically and environmentally unreactive, reasonably climatic, thermally stable, and non-biodegradable. SPs are used in areas such as civil engineering, medical and pharmaceuticals, electronics and electricals, household utensils, automobiles, aircraft, armour suits, and packaging materials. The consequence of the general acceptance of SPs is the astonished production increment that has grown from 1.5 Mt in 1950 to 359 Mt in 2018 (Jeswani et al., 2021). SPs production will increase much more in the next 20 years because of the synergistic relationship between the production of SPs and population growth.

The production of SPs has a negative effect since huge amounts of synthetic plastic waste (SPWs) are left behind in plastic usage. According to literature, 33 Mt of SPWs were generated as far back as 2013 in the USA (US- EPA, 2014; Maafa, 2021), whereas 25 Mt was generated in Europe in 2012 (European-Plastics, 2015.; Maafa, 2021). According to Williams and Slaney (2007), landfills host more than 60% of SPWs. SPWs management has become a serious topic of concern to different environmental stakeholders because of the non-biodegradability character of the SPWs. This non-biodegradability has given rise to other challenges, such as landfill pollution, drainage and waterways blockage, the jeopardisation of terrestrial and marine organisms, and the greenhouse effect.

Reduced utilisation through the ban of some SPs has been suggested (Jeswani et al., 2021) to prevent the menace of SPWs. Unfortunately, there is no viable large-scale and economically sustainable alternative to SPs. Consequently, recycling methods such as pyrolysis, gasification, microbial degradation, and chemical recovery have been developed for the possible management of SPWs. However, the need to strengthen world fuel production has endeared the use of pyrolysis to many research because the pyrolysis oil can be upgraded to different fuel grades.

Pyrolysis, which is a thermal degradation process in an enclosure devoid of oxygen, has been used in Europe for the production of olefins and aromatic hydrocarbon because its main products are liquid oil, gas and char (Al-Salem et al., 2010; Kusenberg et al., 2022). The hydrocarbon produced from pyrolysis can be classified into fuel grades such as petrol, kerosene, diesel, jet fuel and fuel oil based on their different carbon number ranges. Researchers have utilised SPWs from low-density polyethylene, high-density polyethylene, polypropylene, and polyethylene terephthalate and polystyrene singly or in combined forms for the production of hydrocarbon fuels of different grades with the use of pyrolysis method (Kumar and Singh, 2013; Patil et al., 2017; Panda, 2018; Jaafar et al., 2022; Ghodke et al., 2023; Eze et al., 2024).

Globally, polyethylene ranked as the most demanded plastic, with over 120 Mt produced yearly and about the same amount of its waste produced (Geyer et al., 2017). Amongst the polyethene, low-density types are in the most demand because of their excellent properties' moisture and gas barrier, and lightness in weight (Rachtanapun and Rachtanapun, 2011; Driscoll and Paterson,1999). The extreme production of low-density polyethene can also be linked to its usability in commodities such as drink cartons, laundry bags, packaging items, waste bin containers, kids' play utensils and machine parts (Evode et al., 2021). Amongst the waste plastics littering the ocean, over 300 million low-density polyethylene particles have been reported to have been discovered in the Atlantic Ocean (Battsetseg et al., 2022).

Low cost, human and environmental friendliness (Rabie et al., 2018), heterogeneous character, and reusability of clay catalysts have triggered the use of clay and modified clays for thermal degradation of waste plastics to hydrocarbon fuels. To this end, calcium bentonite (Panda et al., 2018), kaolin (Hakeem et al., 2018), Fe, Ti, Zr- pillared clay (Li et al., 2017), Tungstophosphoric acid (TPA)/kaolin (Attique et al., 2020), and Fe-pillared clay (Faillace et al., 2017) have all been used during the pyrolysis of different plastics. The differences in the metallic and metallic oxide composition of various clays could have influenced the production of different hydrocarbon carbon number ranges during pyrolysis.

This investigation aims to reduce waste plastic generation by producing value-added products. It aims to produce fuel hydrocarbon ranges based on carbon number with and without the use of thermal-treated montmorillonite clay.

II. MATERIALS AND METHODS

A. Raw Materials

Low-density polyethylene (LDP) rejected bags were collected from the water factory of the Federal University of Technology, Akure, Nigeria. The samples were sun-dried (3 weeks) for moisture reduction and then stored in an airtight container for further analysis. Montmorillonite clay (MMR) was obtained from Ado Ekiti, Nigeria.

B. Catalyst Preparation

The montmorillonite was subjected to ball milling, sieved through 125 µm and subjected to calcination (600℃, 3 h). The calcined montmorillonite (CMMR) was re-milled, sieved through 125 µm and kept in an air-tight glass container.

C. Pyrolysis Process

A fluidized bed pyrolysis reactor was employed in this study. Two different pyrolysis were carried out, one with the use of a catalyst and the second without the catalyst. LDP sample (3 kg) was fed into the reactor, and 5% catalyst was used based on the weight of the plastic. The catalyst was placed in a chamber suspended 5 cm above the plastic, and the reaction occurred at 500℃ for 3 h. The hot vapour from the reactor was condensed to liquid oil through ice-cooled water, and the oil was stored in a glass bottle. The reactor can be found in the solid waste conversion process unit, department of Chemistry, Federal University of Technology, Akure, Nigeria. Figure is the flow diagram of the experiment process of the study.

D. Fractional Distillation of Crude Pyrolysis Oil

The crude pyrolysis oil was subjected to a fractional distillation inside a round bottom flask (500 mL) equipped with a condenser-cooling system and thermometer. The set-up was a heater by the temperature-controlled heating mantle. The distillates were collected at three different temperature ranges of 0 -100℃, 101 -180 ℃, and 240 - 300℃. The distillates were coded using the plastic and catalyst names, with the upper-temperature reading. Low-density polyethylene was represented as "LDP", while "M" represents CMMR, and the upper-temperature limits chosen are 100℃, 180℃ and 300℃. Fractionated oil obtained from LDP with the catalyst at 100℃, 180℃ and 300℃ are coded respectively as LDP_{100}, LDP_{180} and LDP_{300}, while those obtained with the addition of CMMR are represented respectively as $LDPM_{100}$, $LDPM_{180}$ and $LDPM_{300}$. Flow diagram of the experiment process of the study is depicted in Figure 1.

E. Characterization

The chemical composition of the CMMR was determined using XRF, while the chemical composition of the fractionated oils was determined using gas chromatography coupled with a mass spectrum (GC-MS).

F. Physicochemical Properties of Fractionated Oil

The specific and API gravity was determined using Anton Paar (DMA 5400 density meter (80460541). The instrument measures the sample density at a specified temperature (15℃) and automatically converts the density to specific gravity (SPG) and API gravity (APIG) (ASTM D 7777). The sample viscosity was measured at 40℃ using a Stanhope seta viscometer bath (83201-2D).
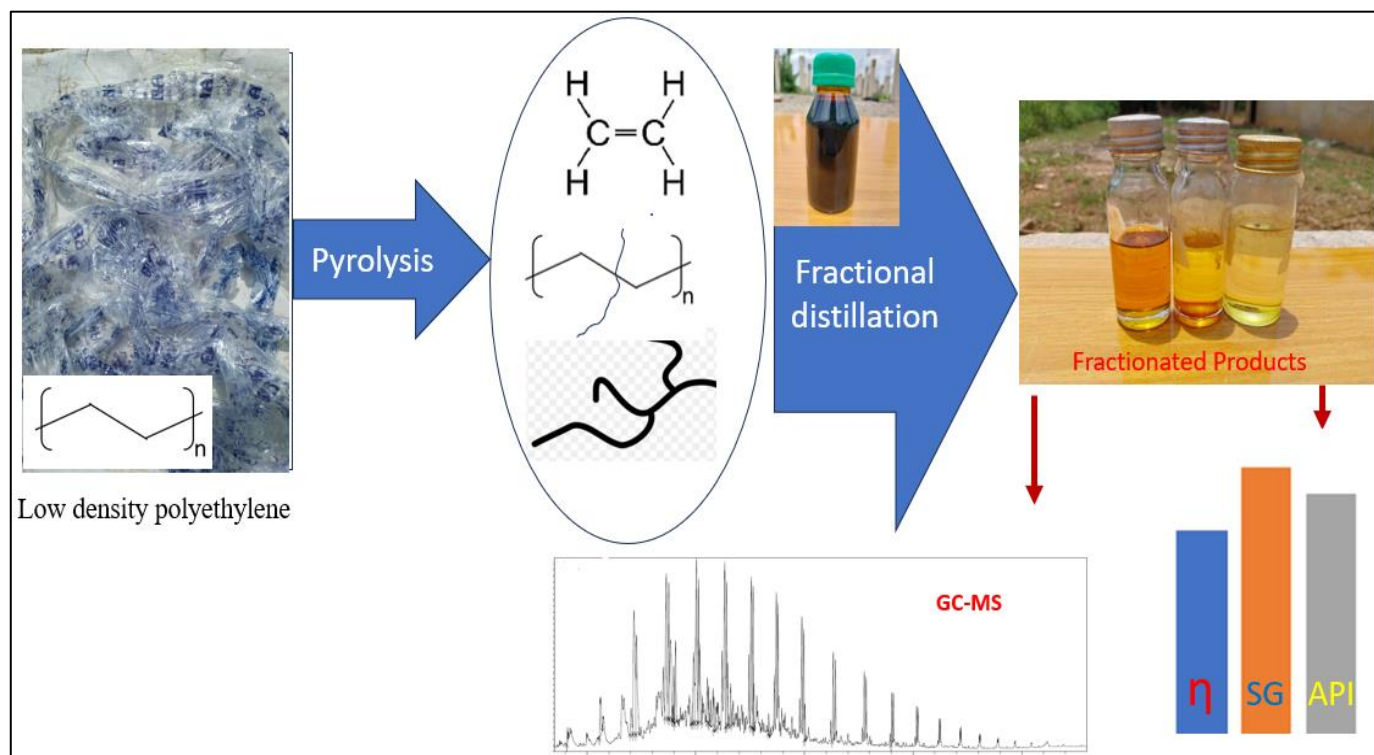
Fig 1: Flow Diagram of the Experiment Process of the Study

III. RESULT AND DISCUSSION

A. XRF Characterisation of the Catalyst

The element composition of the CMMR is presented in Table 1. Silica oxide (SiO_2, 51.34%), iron (ii) oxide (Fe_2O_3, 16.23%), potassium oxide (K_2O, 5.03%), Aluminum oxide (Al_2O_3, 19.65%), tin oxide (TiO_2, 3.00%), calcium oxide (CaO, 1.47%) and oxides of chlorides (Cl, 1.46%) are the significant oxide present. Various authors have reported all the metal oxides detected in this study. For example, 54.00, 17.00, 5.20, 1.50, 2.50, 0.40, and 1. 50, respectively have been reported for SiO_2, Fe_2O_3, CaO, MgO, NaO and K_2O (Egirani et al., 2019), SiO_2(64.76%), Fe_2O_3 (0.90%), K_2O (0.24%), Al_2O_3 (14.95%), TiO_2(0.16%), CaO, (1.59%), Na_2O (0.10%) MgO (1.87%) and MnO (0.01%) (Castellini et al., 2017), and SiO_2(54.17%), Fe_2O_3 (3.13%), K_2O (1.82%), Al_2O_3 (20.92%), TiO_2(0.37%), PbO, (0.16%), SiO (0.10%), CaO (1.14%), and ZrO_2 (0.05%) (Siahpoosh and Soleimani, 2017). The different sources of the clay and soil types could have influenced the differences in the chemical composition and the percentage weight of the metallic oxide various reported MMR by the different authors. The metal oxides discovered in the CMMR have been documented as suitable catalysts for various industrial applications such as pyrolysis, biodiesel production and synthesis (Panda et al., 2018; Hakeem et al., 2018; Attique et al., 2020).

Table 1: Matetallic Oxide in the CMMR

Metal Oxides	Weight (%)
SiO_2	51.34
V_2O_5	0.15
Cr_2O_3	0.04
MnO	0.17
Fe_2O_3	16.23
Co_3O_4	0.07
CuO	0.05
Nb_2O_3	0.02
SO_3	0.50
CaO	1.47
K_2O	5.03
BaO	0.16
Al_2O_3	19.65
Ta_2O_5	0.03
TiO_2	3.00
ZnO	0.01
Ag_2O	0.02
Cl	1.46
ZrO_2	0.59

B. Physicochemical Properties of the Fractionated Oils

The physicochemical properties of pyrolysis oil are very important in revealing its nature and the proper way to use it. This study determined the physicochemical properties of the fractionated oil, including kinematic viscosity, API gravity, and specific gravity.

The influence of the distillation temperature is visible in the results of the specific gravity of the fractionated oils (Figure 2). The SPG of the oils increased with an increase in the distillation temperature. Oil distillates obtained at 100℃ upper temperatures have SPG of 0.74 (LDP_{100}) and 0.77 ($LDPM_{100}$), the lowest of all the various distillates. The distillates at an upper temperature of 180℃ had lower values of 0.78 (LDP_{180}) and 0.82 ($LDPM_{180}$) compared to 0.79 (LDP_{300}) and 0.85 ($LDPM_{300}$) of those oils with an upper-temperature limit of 280℃ and 300℃. The SP obtained in this research compared well with 0.79-0.85 recorded for

liquid fuel from polyethylene wax (Chaiya et al., 2020). Another experiment reported SPG of 0.8125, 0.866, 0.868 and 0.8719 for oil from mixed plastic pyrolysis against 0.8445 of diesel fuel (Pratama and Saptoadi 2014). SPG of 0.7932 was reported for polypropylene pyrolysis oil and 0.80 for petroleum (Anbarasu and Sivakumar, 2012; Hudec et al., 2009). From the literature (Pratama and Saptoadi, 2014 Anbarasu and Sivakumar, 2012; Hudec et al., 2009), $LDPM_{300}$ could probably be a diesel, while the rest might be petrol.

The importance of APIG value in the fuel business is enormous; APIG dictates the bench amount of any fuel. APIG can be used to detect adulteration and the quality of fuel. For example, a high APIG of diesel indicates a high percentage of light cuts in the diesel. At the same time, a lower value signifies a higher percentage of heavy cuts, which is undesirable and consequently attracts lower market value (Aboul-Fotouh et al., 2019). The oil with the lowest SPG has the highest APIG, which is expected because of the inverse proportionality between the SPG and APIG. An APIG of 46.67 was reported for oil from waste plastic pyrolysis, and it was affirmed that light fuel has an APIG equals or greater than 40° (Anbarasu and Sivakumar, 2012) Thus, the API of 59.72, 49.91, 47.61, 52.27 and 41.06 respectively for LDP_{100}, LDP_{180}, LDP_{300}, $LDPM_{100}$, and $LDPM_{180}$ oils can be classified as light oil, while APIG of 34.97 for $LDPM_{300}$ could go for heavy oil (Figure 2). The SPG results of the oils have established that the oil produced is either petrol or diesel. Thus, the APIG result has collaborated with the SPG outcome.

Kinematic viscosity is vital in atomising fuel, engine performance, pollutant emission, and fuel pump (Sharma et al., 2020). Amongst all the oils (Figure 2), only two with 300℃ upper temperatures have kinematic viscosity (2.25-LDP_{300}; 2.54 -$LDPM_{300}$) that met the acceptable value of 2 - 4.5 cSt for diesel fuel (Januszewicz et al., 2023), while only LDP_{180} (1.12) met the 1.20 standard for kerosene (Cahyono et al., 2020). The rest of the oil might be light fractions, maybe naphtha. The low viscosity observed could be an advantage in preventing engine blockage (due to the thickening of the oil, most especially at low temperatures), flow resistance, ignition delay and economic loss because of the use of extra heating to prevent congealability of the oil. Some other researchers have also reported low kinematic viscosities in their plastic pyrolysis oil study. Januszewicz et al. (2023) have reported kinematic viscosity of 1.69 and 1.22 for polypropylene and polystyrene pyrolysis oils, which are lower than the recommended value for diesel oil.

Though pyrolysis is a complex chemical reaction, the influence of the catalyst was obvious in that all the oils obtained with the aid of the catalyst had higher gravity than their counterparts produced without the catalyst. Multiple interrelated, interaction, and interconvertible processes, such as cracking, dehydrogenation, protonation, and catenation, could have influenced the characteristics of the CMMR-obtained pyrolysis oil.
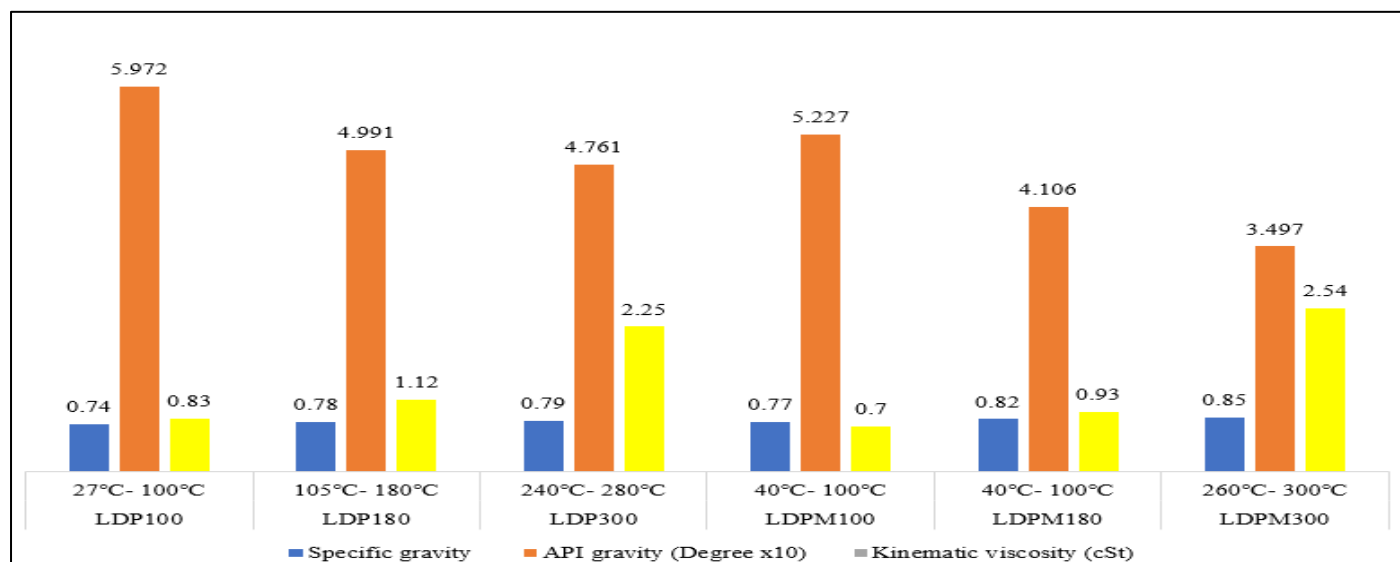

Fig 2: Specific Gravity, API Gravity and Kinematic Viscosity of Samples

C. GC-MS

Tables 2-7, present the various chemical composition detected in the fractionated oil based on temperature difference. Alkane, alkene, alkyne, cycloalkene, cycloalkane, aromatic, alcohol, and ester. The basis on distillation temperature, 47 (40 - 100℃, Table 2), 18 (100 -1 80℃, Table 3), and 25 (240 - 280℃, Table 4) chemical compounds were identified for non-catalytic pyrolysis, while 18 (40 - 100℃, Table 5), 30 (100 - 180℃, Table 6), and 30 (240 - 280℃, Table 7) respectively were found in catalytic pyrolysis oil. The catalytic effect was evident in the types of products obtained; while fractionated oil without a catalyst was made up of many alkenes, those from catalytic pyrolysis had less alkene. There could have been some chemical rearranged leading to the utilisation of the carbon double bonds due to the presence of the catalyst. The most prominent compounds (using percentage area value of equal or greater than 4) in LDP_{100} are o-Xylene (aromatic), 1-nonanol (fatty alcohol),

heptane, 4-ethyl- (alkane), tridecane (alkane), 1-dodecene (alkene), tridecane (alkane), 1-dodecanol (fatty alcohol), dodecane (alkane), 1-pentadecene (alkene) and tetradecane (alkane). Inversely, cyclo-compounds such as dicyclopentadiene (cycloalkene), bicyclo[2.2.2]oct-2-ene (cycloalkene), bicyclo[2.2.2]oct-5-en-2-one (cyclo-hydroxy compound), bicyclo[2.2.1]hept-2-ene, 2,3-dimethyl- (cyclo-alkene) and 4,7-methanoisobenzofuran-1,3-dione (dicarboxylic acid) were obtained with the aid of catalysis at the same distillation temperature. Using a simulated reaction mechanism has established the possibility of cyclic hydrocarbon formation during pyrolysis (Wijayanti et al., 2022). The prominent compounds in LDP_{180} are 1-decene (alkene), undecane (alkane), 1-dodecene (alkene), and tridecane (alkane), while $LDPM_{180}$ has nonadecane (alkane), naphthalene, 2-methyl- (alkane), 1 tetradecanol (fatty alcohol), octadecane (alkane), 1-hexadecanol (fatty alcohol) and heneicosane (alkane). However, 1-tridecene (alkene), dodecane (alkane), 1-pentadecene and tetradecane

(alkane) are present in both oils. The catalyst effect could have caused the differences in the chemical compositions of the two oils. LDP_{300} has 1-dodecene (alkene), tridecane (alkane), 1-tridecene (alkane), Dodecane (alkane), Hexadecane (alkane), tetradecane (alkane), 1-tetradecanol (fatty alcohol), heneicosane (alkane) and 1-hexadecanol (fatty alcohol), conversely, $LDPM_{300}$ 1-tridecene (alkane), dodecane (alkane), 1-pentadecene (alkane), nonadecane (alkane), Naphthalene, 2-methyl- (aromatic), 1-tetradecanol (fatty alcohol), tetradecane (alkane), octadecane (alkane) and heneicosane (alkane). Although there are overlap of the same compounds in both the LDP_{300} and $LDPM_{300}$ oil, the production of aromatic in $LDPM_{300}$ may be linked to the catalyst effect. Other authors have reported the pyrolysis oils identified in this study during the study of thermal degradation of plastics (Kumar and Singh, 2013; Patil et al., 2017; Panda, 2018; Jaafar et al., 2022; Ghodke et al., 2023; Eze et al., 2024)

Table 2: GC-MS of LDP_{100}

	R.Time	Area%	Chemical name	Chemical formular
1	3.587	0.85	Cyclopentene, 1-(1-acetic acid	$C_7H_{10}O_2$
2	3.678	1.72	Cyclohexene, 1-ethyl-	C_8H_{14}
3	3.76	0.42	1-Cyclohexene-1-carboxylic acid	$C_7H_{10}O_2$
4	3.808	2.21	Octane, 1-chloro-	$C_8H_{17}Cl$
5	3.94	4.35	o-Xylene	C_8H_{10}
6	4.03	0.71	1-(2-Propenyl) cyclopentene	C_8H_{12}
7	4.085	2.2	1,8-Nonadiene	C_9H_{16}
8	4.145	2.01	Cyclopentane, 1,2,3-trimethyl-	C_8H_{16}
9	4.265	7.81	1-Nonanol	$C_9H_{20}O$
10	4.398	6.45	Heptane, 4-ethyl-	C_9H_{20}
11	4.455	2.45	2-Nonene, (E)-	C_9H_{18}
12	4.57	2.2	Cyclohexane, (2-methylpropyl)-	$C_{10}H_{20}$
13	4.66	0.82	Cyclododecene, (E)-	$C_{12}H_{22}$
14	4.756	0.42	Cyclohexane, 2-propenyl-	C_9H_{16}
15	4.8	0.24	3-Octyne, 2-methyl-	C_9H_{16}
16	5.118	0.64	Cyclopentene, 1-butyl-	C_9H_{16}
17	5.17	0.72	Cyclohexene, 3-(2-methylpropy	$C_{10}H_{18}$
18	5.245	0.39	Benzene, propyl-	C9H12
19	5.363	0.74	Benzene, 1-ethyl-2-methyl-	C_9H_{12}
20	5.503	0.55	Octane, 2,6-dimethyl-	$C_{10}H_{22}$
21	5.693	0.7	1,9-Decadiene	$C_{10}H_{18}$
22	5.874	7.56	1-Nonanol	$C_9H_{20}O$
23	5.935	1.38	Mesitylene	C_9H_{12}
24	6.009	4.68	Tridecane	$C_{13}H_{28}$
25	6.071	1.11	trans-3-Decene	$C_{10}H_{20}$
26	7.335	1.27	1,10-Undecadiene	$C_{11}H_{20}$
27	7.503	5.91	1-Dodecene	$C_{12}H_{24}$
28	7.636	4.5	Tridecane	$C_{13}H_{28}$
29	7.693	0.55	4-Undecene, (E)-	$C_{11}H_{22}$
30	7.735	0.45	Bicyclo[2.2.2]oct-5-en-2-one	$C_8H_{10}O$
31	8.723	1.19	Bicyclo[2.2.2]oct-2-ene	C_8H_{12}
32	8.85	0.58	Bicyclo[2.2.1]hept-2-ene, 2,3-di	C_9H_{14}
33	9.069	5.26	1-Dodecanol	$C_{12}H_{26}O$
34	9.194	4.31	Dodecane	$C_{12}H_{26}$
35	9.247	0.47	6-Dodecene, (E)-	$C_{12}H_{24}$
36	10.408	1.49	1,11-Dodecadiene	$C_{12}H_{22}$
37	10.541	4.72	1-Pentadecene	$C_{15}H_{30}$

38	10.657	4.16	Tetradecane	$C_{14}H_{30}$
39	10.704	0.84	Cyclododecane	$C_{12}H_{24}$
40	12.067	0.31	Cyclotetradecane	$C_{14}H_{28}$
41	13.108	0.67	1,19-Eicosadiene	$C_{20}H_{38}$
42	13.312	2.91	Pentadecane	$C_{15}H_{32}$
43	14.438	2.37	1-Tetradecanol	$C_{14}H_{30}O$
44	14.526	2.08	Heptadecane	$C_{17}H_{36}$
45	15.596	1.69	1-Nonadecene	$C_{19}H_{38}$
46	18.278	0.95	Heneicosane	$C_{21}H_{44}$

Table 3: GC-MS of LDP_{180}

	R. Time	Area%	Chemical name	Chemical formular
1	3.745	0.39	Benzene, 1-ethyl-4-methyl-	C_9H_{12}
2	4.119	5.59	1-Decene	$C_{10}H_{20}$
3	4.295	6.71	Undecane	$C_{11}H_{24}$
4	5.616	14.03	1-Dodecene	$C_{12}H_{24}$
5	5.769	10.43	Tridecane	$C_{13}H_{28}$
6	7.159	15.46	1-Tridecene	$C_{13}H_{26}$
7	7.282	10.14	Dodecane	$C_{12}H_{26}$
8	7.345	1.30	E-11-Tetradecen-1-ol trifluoroacetate	$C_{16}H_{27}F_3O_2$
9	8.497	2.83	1,11-Dodecadiene	$C_{12}H_{22}$
10	8.623	11.03	1-Pentadecene	$C_{15}H_{30}$
11	8.739	7.68	Tetradecane	$C_{14}H_{30}$
12	8.823	3.34	Naphthalene, 2-methyl-	$C_{11}H_{10}$
13	9.887	1.85	1,13-Tetradecadiene	$C_{14}H_{26}$
14	12.434	0.77	1,19-Eicosadiene	$C_{20}H_{38}$
15	12.527	3.89	1-Heptadecene	$C_{17}H_{34}$
16	14.95	1.88	Heptadecane	$C_{17}H_{36}$
17	16.31	1.23	1-Nonadecene	$C_{19}H_{38}$
18	16.412	1.45	Heneicosane	$C_{21}H_{44}$

Table 4: GC-MS of LDP_{300}

S/N	R.Time	Area%	Chemical name	Chemical Formular
1	4.016	0.62	1-Decene	$C_{10}H_{20}$
2	5.566	5.33	1-Dodecene	$C_{12}H_{24}$
3	5.696	5.01	Tridecane	$C_{13}H_{28}$
4	7.105	11.29	1-Tridecene	$C_{13}H_{26}$
5	7.231	10.61	Dodecane	$C_{12}H_{26}$
6	8.437	3.99	1,11-Dodecadiene	$C_{12}H_{22}$
7	8.699	8.38	Hexadecane	$C_{16}H_{34}$
8	8.735	2.73	4-Nonene, 5-butyl-	$C_{13}H_{26}$
9	8.913	1.69	1-Octadecyne	$C_{18}H_{36}$
10	9.833	3.61	1,13-Tetradecadiene	$C_{14}H_{26}$
11	10.073	6.65	Tetradecane	$C_{14}H_{30}$
12	10.106	0.77	Cyclotetradecane	$C_{14}H_{28}$
13	10.956	0.77	Dodecane, 2,6,10-trimethyl-	$C_{15}H_{32}$
14	11.141	2.61	1,12-Dodecanediol	$C_{12}H_{26}O_2$
15	11.264	8.68	1-Tetradecanol	$C_{14}H_{30}O$
16	11.36	6.05	Heneicosane	$C_{21}H_{44}$
17	11.393	0.79	Cyclododecane	$C_{12}H_{24}$
18	11.522	0.51	1-Pentadecene	$C_{15}H_{30}$
19	12.376	2.23	1,19-Eicosadiene	$C_{20}H_{38}$
20	12.485	6.63	1-Hexadecanol	$C_{16}H_{34}O$
21	12.61	0.6	1-Dodecanol	$C_{12}H_{26}O$
22	13.543	1.6	9-Octadecen-1-ol, (Z)-	$C_{18}H_{36}O$
23	14.89	3.51	Octadecane	$C_{18}H_{38}$
24	16.232	3.55	1-Nonadecene	$C_{19}H_{38}$
25	18.944	1.79	Behenic alcohol	$C_{22}H_{46}O$

Table 5: GC-MS of $LDPM_{100}$

S/N	R.Time	Area%	Chemical name	Chemical formular
1	3.644	0.55	Benzene, propyl-	C_9H_{12}
2	3.738	0.84	Benzene, 1-ethyl-4-methyl-	C_9H_{12}
3	4.148	2.97	1-Decene	$C_{10}H_{20}$
4	4.775	11.05	Dicyclopentadiene	$C_{10}H_{12}$
5	5.625	27.5	Bicyclo[2.2.2]oct-2-ene	C_8H_{12}
6	5.737	18.39	4,7-Methanoisobenzofuran-1,3-dione	$C_9H_4O_3$
7	6.844	15.8	Bicyclo[2.2.2]oct-5-en-2-one	$C_8H_{10}O$
8	6.964	5.3	Bicyclo[2.2.1]hept-2-ene, 2,3-dimethyl-	C_9H_{14}
9	7.039	3.69	1,4-Cyclohexadiene, 1-methyl-	C_7H_{10}
10	7.13	2.66	1-Dodecene	$C_{12}H_{24}$
11	7.42	2.01	1,4-Cyclohexadiene, 1-methyl-	C_7H_{10}
12	8.066	1.85	1,3-Cycloheptadiene	C_7H_{10}
13	8.255	0.87	Dimethyl sulfone	$C_2H_6O_2S$
14	8.593	1.64	1-Tridecene	$C_{13}H_{26}$
15	9.978	1.62	1-Pentadecene	$C_{15}H_{30}$
16	10.084	1.51	Tetradecane	$C_{14}H_{30}$
17	12.51	1.09	1-Heptadecene	$C_{17}H_{34}$
18	12.599	0.67	Heptadecane	$C_{17}H_{36}$

Table 6: GC-MS of $LDPM_{180}$

S/N	R.Time	Area%	Chemical name	Chemical formular
1	4.103	0.28	1-Decene	$C_{10}H_{20}$
2	5.627	2.4	1-Dodecene	$C_{12}H_{24}$
3	7.02	1.53	1,11-Dodecadiene	$C_{12}H_{22}$
4	7.161	10.16	1-Tridecene	$C_{13}H_{26}$
5	7.279	6.41	Dodecane	$C_{12}H_{26}$
6	8.506	2.22	cis-9-Tetradecen-1-ol	$C_{14}H_{28}O$
7	8.645	7.99	1-Pentadecene	$C_{15}H_{30}$
8	8.758	5.47	Nonadecane	$C_{19}H_{40}.$
9	8.84	5.7	Naphthalene, 2-methyl-	$C_{11}H_{10}$
10	8.94	0.34	Cyclododecane	$C_{12}H_{24}$
11	8.985	1.31	1-Docosene	$C_{22}H_{44}$
12	9.075	3.48	Naphthalene, 2-methyl-	$C_{11}H_{10}$
13	9.83	0.62	9-Octadecen-1-ol, (Z)-	$C_{18}H_{36}O$
14	9.903	3.56	1,13-Tetradecadiene	$C_{14}H_{26}$
15	10.035	9.5	1-Tetradecanol	$C_{14}H_{30}O$
16	10.135	5.19	Tetradecane	$C_{14}H_{30}$
17	10.306	0.43	1-Pentadecene	$C_{15}H_{30}$
18	10.535	1.86	Naphthalene, 1,3-dimethyl-	$C_{12}H_{12}$
19	10.592	1.1	Naphthalene, 2,6-dimethyl-	$C_{12}H12$
20	10.689	1.13	cis-11-Tetradecen-1-ol	$C_{14}H_{28}O$
21	10.837	1.32	1-Decanol, 2-hexyl-	$C_{16}H_{34}O$
22	11.03	0.73	1-Pentadecyne	$C_{15}H_{30}$
23	11.426	6.21	Octadecane	$C_{18}H_{38}$
24	11.463	1.47	Cyclotetradecane	$C_{14}H_{28}$
25	11.723	0.99	17-Pentatriacontene	$C_{35}H_{70}$
26	11.944	0.58	Acetic acid, chloro-, hexadecyl ester	$C_{18}H_{35}ClO_2$
27	12.555	6.13	1-Hexadecanol	$C_{16}H_{34}O$
28	12.64	4.76	Heneicosane	$C_{21}H_{44}$
29	12.675	0.84	1-Dodecanol	$C_{12}H_{26}O$
30	13.356	0.59	Cyclohexane, 1-(1-tetradecylpen	$C_{35}H_{70}$

Table 7: GC-MS of LDPM$_{300}$

S/N	R.Time	Area%	Chemical name	Chemical formular
1	4.103	0.29	1-Decene	$C_{10}H_{20}$
2	5.627	2.47	1-Dodecene	$C_{12}H_{24}$
3	7.02	1.57	1,11-Dodecadiene	$C_{12}H_{22}$
4	7.161	10.46	1-Tridecene	$C_{13}H_{26}$
5	7.279	6.59	Dodecane	$C_{12}H_{26}$
6	8.645	8.22	1-Pentadecene	$C_{15}H_{30}$
7	8.758	5.62	Nonadecane	$C_{19}H_{40}$.
8	8.84	5.87	Naphthalene, 2-methyl-	$C_{11}H_{10}$
9	8.94	0.35	Cyclododecane	$C_{12}H_{24}$
10	8.985	1.35	1-Docosene	$C_{22}H_{44}$
11	9.075	3.58	Naphthalene, 2-methyl-	$C_{11}H_{10}$
12	9.83	0.64	9-Octadecen-1-ol, (Z)-	$C_{18}H_{36}O$
13	9.903	3.66	1,13-Tetradecadiene	$C_{14}H_{26}$
14	10.035	9.77	1-Tetradecanol	$C_{14}H_{30}O$
15	10.135	5.34	Tetradecane	$C_{14}H_{30}$
16	10.306	0.44	1-Pentadecene	$C_{15}H_{30}$
17	10.535	1.91	Naphthalene, 1,3-dimethyl-	$C_{12}H_{12}$
18	10.592	1.13	Naphthalene, 2,6-dimethyl-	$C_{12}H_{12}$
19	10.689	1.17	cis-11-Tetradecen-1-ol	$C_{14}H_{28}O$
20	10.837	1.36	1-Decanol, 2-hexyl-	$C_{16}H_{34}O$
21	11.03	0.75	1-Pentadecyne	$C_{15}H_{30}$
22	11.426	6.39	Octadecane	$C_{18}H_{38}$
23	11.463	1.52	Cyclotetradecane	$C_{14}H_{28}$
24	11.723	1.02	17-Pentatriacontene	$C_{35}H_{70}$
25	12.555	6.31	1-Hexadecanol	$C_{16}H_{34}O$
26	12.64	4.9	Heneicosane	$C_{21}H_{44}$
27	12.675	0.86	1-Dodecanol	$C_{12}H_{26}O$
28	13.356	0.61	Cyclohexane, 1-(1-tetradecylpen	$C_{35}H_{70}$
29	15.017	1.26	Anthracene	$C_{14}H_{10}$
30	16.328	3.17	1-Nonadecene	$C_{19}H_{38}$

From the analysis of the pyrolysis oil based on the carbon range, C_5-C_{12} (gasoline), C_{13}-C_{24} (diesel) and >C_{24} (fuel oil) (Yang et al., 2016). LDP$_{100}$ has the highest number of hydrocarbons (37) in the range of C_5-C_{12} (Figures 3 and 4). Thus, having the highest gasoline content (86.43%) amongst the fractionated oil. This was followed by LDPM$_{100}$, with 12 of its compounds within the range of C_5 -C_{12}, and recorded 72.22% gasoline. The highest diesel content (72%) was recorded for LDP$_{300}$, followed closely was LDPM$_{300}$ (60%). On a careful assessment based on the total number of hydrocarbons detected in each of the fractionated oils, LDPM$_{300}$ has the highest diesel. This is because it has 30 detected compounds against 25 detected in LDP$_{180}$. Amongst all the oils, only LDPM$_{180}$ has fuel oil, probably due to the catalyst effect. It was also discovered that all the oil produced with the aid of a catalyst recorded the presence of organic chlorine compounds. These compounds could have come from the ink used for the name and logo tag on the nylon. The analysis results from Figure 4 also imply that most of the pyrolysis oil could be utilised as jet fuel. According to Alhikami and Wang (2021), hydrocarbon ranges from 9 to 15 can be used for powering jet engines.
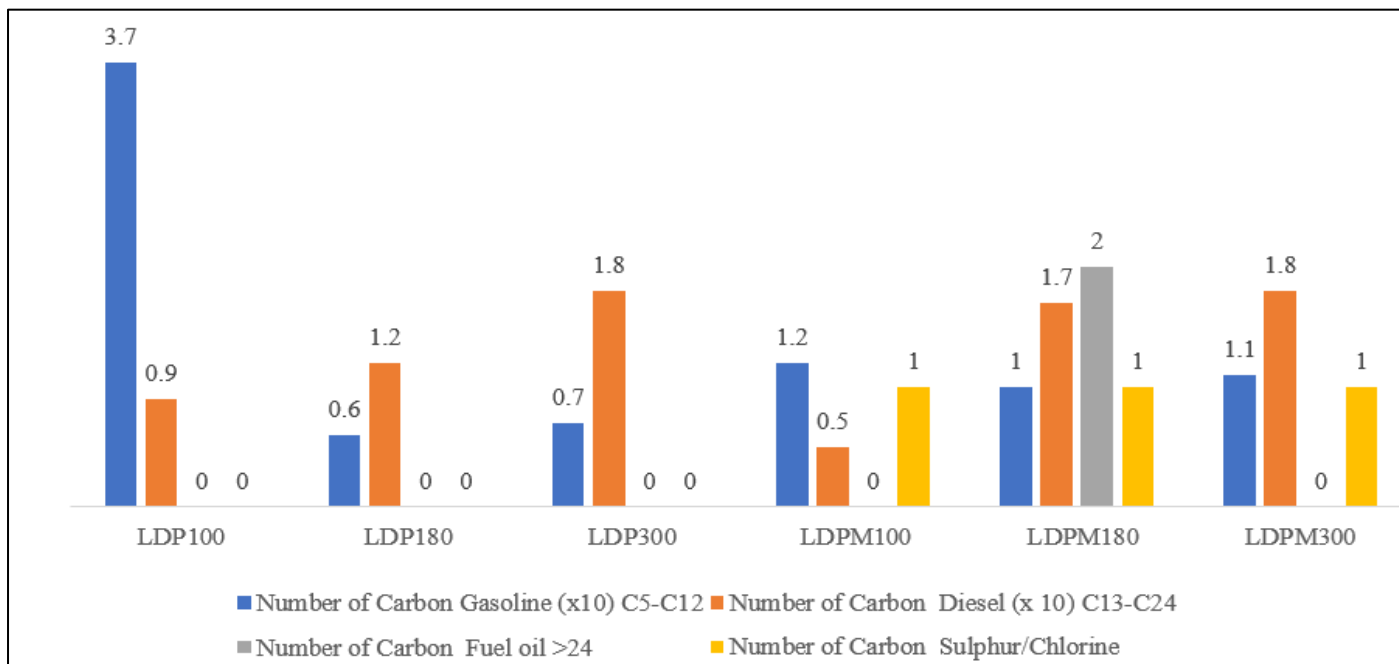
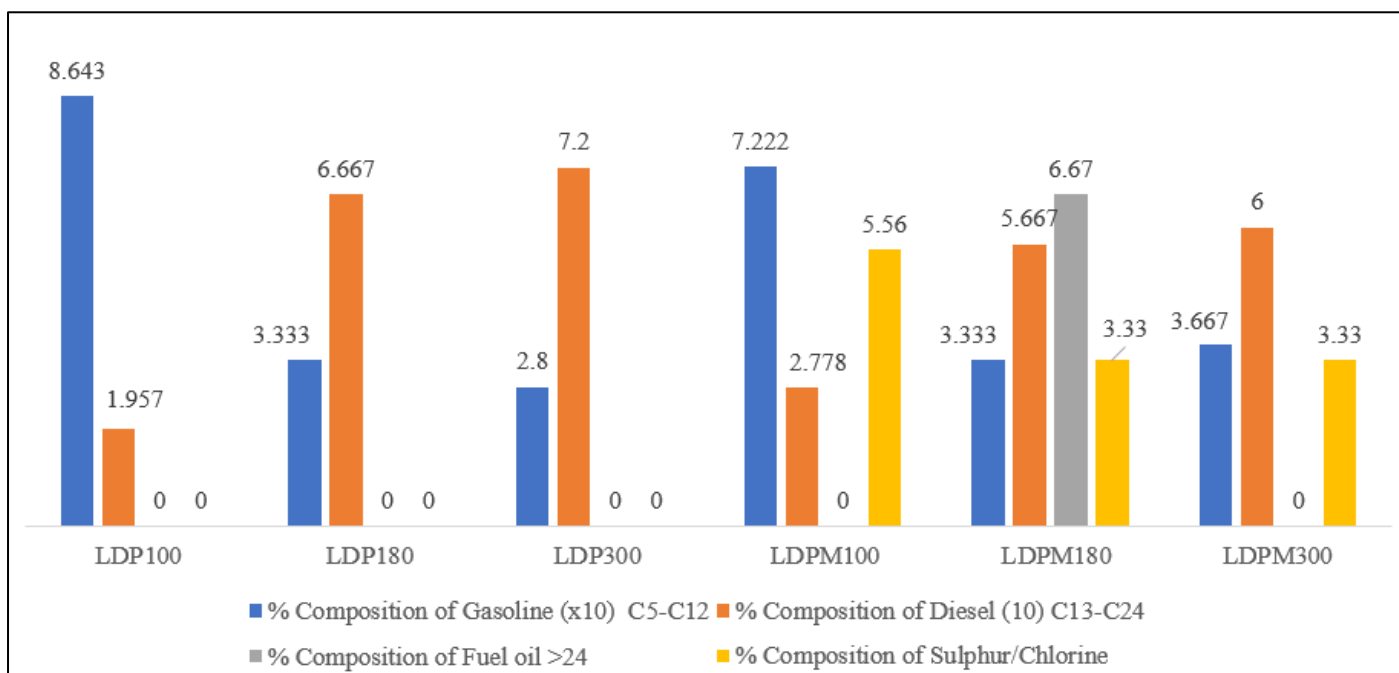Fig 3: Number of Hydrocarbons based on Carbon Number Range

Fig 4: Percentage Composition Hydrocarbons based of Carbon Number Range

IV. CONCLUSION

The research has shown that the threat of waste plastics can be reduced in a useful manner for the production of value-added products such as fuel oils. The green catalyst from montmorillonite affected the chemical composition of the produced oils. The physicochemical properties of the oils revealed that some of the others are in the diesel oil category. The fractionated oils from the catalysed pyrolysed are noticed to have higher cyclo-compounds. The catalytic-aided pyrolysis oils have more diesel content than the uncatalysed oil. They are signifying the possibility of catalytic conversion to higher hydrocarbons. The research has provided gasoline, diesel and fuel oil from waste low density polyethylene.

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