

FUEL GASES FROM WASTE HIGH DENSITY POLYETHYLENE (HDPE) VIA LOW TEMPERATURE CATALYTIC PYROLYSIS

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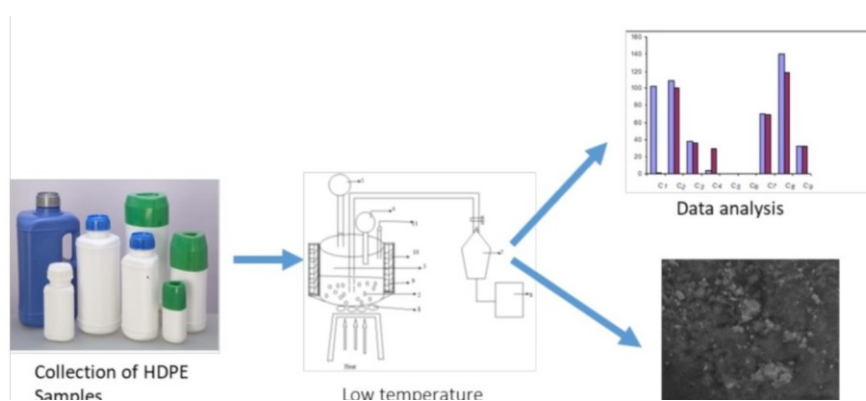
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GRAPHICAL ABSTRACT



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ABSTRACT

This study was carried out in order to obtain useful gases from waste polyethylene of high density polyethylene (HDPE) at low temperature pyrolysis. This was carried out by adapting a cylindrical pressure cooking pot of height 30.00 cm with an internal diameter 31.50 cm. The pyrolysis reaction was carried out with the influence of Fluid Catalytic Cracking (FCC) catalyst. The gases evolved during the pyrolysis reaction were collected using Tedlar bags and analysed using a BUCK 530 Gas Chromatograph. The pyrolysis reaction with fresh FCC catalyst at 150 °C and 250 °C using catalyst/sample ratio of 1:8 showed aliphatic hydrocarbons in the range of C₁-C₉ with total concentrations of 84.3969 and 526.4070 ppm respectively. The corresponding values obtained at 150 °C and 250 °C for HDPE using catalyst/sample ratio of 1:16 were obtained as 495.4315 and 385.5101 ppm respectively. The reaction with spent FCC catalyst at 150 °C and 250 °C using catalyst/sample ratio of 1:8 gave the total concentrations of 112.7276 ppm and 87.3531 ppm respectively. The corresponding values obtained at 150 °C and 250 °C using catalyst/sample ratio of 1:16 were 116.9178 and 109.4314 ppm respectively. Production of useful gases from waste polyethylene gave reasonable amounts of gaseous products which can serve as feed stock and as fuel gas.

1. Introduction

Plastics have become the material of choice in modern world and its application in the industrial field is continually increasing [1]. The amount of plastic waste is growing every year and with that comes an environmental concern regarding this problem. This increase in the amount of waste does cause some environmental problems, since plastics do not degrade quickly and can remain in the environment for a very long time [2, 3]. Their destruction by incineration and land filling poses serious environmental problems due to the release of airborne particles and carbon (iv) oxide into the atmosphere [4]. Both processes do not allow the recovery of the organic component of the waste plastic which could be part of organic life-cycle [5]. Feedstock recycling of plastic waste includes processes that transform plastic waste to their constituent monomers or basic hydrocarbon feedstock. Recycling has several meanings with regards to plastics and can be divided into primary, secondary, tertiary and quaternary forms of recycling [6].

The processing of plastic for use comparable to the original application and the processing of plastic waste into new products with lower quality level is called primary and secondary recycling respectively. Quaternary recycling involves incineration of plastic waste to recover energy. This study is concerned with tertiary recycling which deals with pyrolysis or catalytic processing of plastic waste into their hydrocarbon feedstock thereby returning the waste plastic to their constituent monomers and basic

hydrocarbon [1]. Tertiary recycling of waste can be considered not only as a solution for waste plastic disposal but also for generating an environmentally acceptable transportation fuel or feedstock for transportation of virgin plastic [6].

2. Experimental

2.1 HDPE sample collection and preparation

The high density polyethylene waste (HDPE) were mainly collected from pharmaceutical stores as refuse and several dumping sites around Makurdi town, Benue State of Nigeria. The samples were washed thoroughly using detergent and rinsed properly with deionized water, then dried at room temperature to remove all moisture. The dried samples were reduced into smaller bits to increase the surface area. The Fluid Cracking (FCC) catalytic employed for this work was obtained from Nigerian National Cooperation (NNPC) Warri in Delta State and is shown by analysis to be composed of aluminum and silicon. Scanning Electron Microscopy (SEM) images of the fresh FCC catalyst were obtained at magnifications of 1000 x, 2500 x, 5000 x, 10000 x, and 15000 x respectively. Scanning electron microscopy (SEM) images of the spent FCC catalyst were obtained at magnification of 500 x, 1000 x, 2150 x, 5000 x, and 10000 x. From the SEM images, it was deduced that the catalyst particle size ranged within 5 μ m-80 μ m while the spent FCC catalyst gave particle sizes within the range of 8 μ m-100 μ m. In further characterizing the fresh and spent FCC catalyst, SEM was combined with atomic absorption spectrometry (AAS) in the detection of

the metal composition. The analysis indicated the presence of aluminum (5.122 and silicon 3.375 ppm) and silicon (6.480 and 5.270 ppm) respectively.

2.2 Experimental Procedure

Fig. 1 shows the layout of the pyrolysis process. A pressure pot made of stainless steel of height 30.00 cm with an internal diameter of 31.50 cm was adapted for the pyrolysis reaction [7, 8]. The cover had an outlet tube at the top for collection of the evolved gases. The reactor was effectively lagged with a fire blanket and placed in sand bath constructed with iron sheets for good heat retention. The reactor fitted in the sand bath was heated with three Mekker burners in order to attain the required temperatures which were controlled by means of a thermocouple. Tedlar bags were used for collection of the evolved gases. These gases were immediately sent for gas chromatogram for analyses.

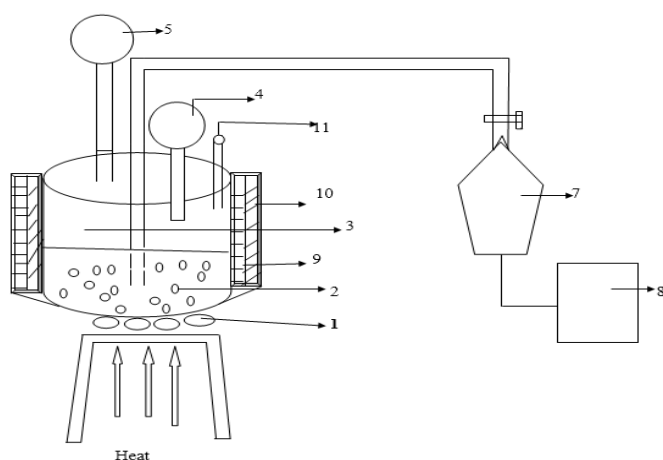


Fig. 1. Layout of the pyrolysis process, 1.Heating mantle, 2.Waste material/ catalyst, 3.Reactor, 4.Pressure, 5.Thermocouple, 6.Regulator, 7. Tedlar gas sampling long beg, 8.G.C Analyzer, 9.Lagging material, 10.Sand bath, 11.Stopered inlet

2.3 Catalytic Cracking of HDPE

Two catalyst/sample ratios (1:8 and 1:16) were investigated in the catalyzed pyrolysis [9]. The sample (polymer material 200 g) was placed at the bottom while the catalyst material was arranged in sandwich layers within the polymer sample [10]. The reactor was covered and heating commenced. After 30 minutes into the reaction, evolution of gases started slightly and this was evident as bag began to swell. After heating for about 11/2 hours at 250 °C, the system was shut down. The gases which were collected at 150 °C and 250 °C in labeled tedlar bags were analyzed. The system was shut down allowed to cool before the reactor was opened. The residue for each run was weighed.

2.4 Gas Chromatography Analysis

The gaseous products obtained from pyrolysis of HDPE with the effect of both fresh and spent FCC catalyst were characterized using a Buck 530 gas chromatography with HP-88 (10 m/0.25 mm thickness) injection volume was 10 µL with helium as the mobile phase and flame ionization detector (FID), injection and detection temperature were 250 °C and 280 °C respectively.

3. RESULTS AND DISCUSSION

Fig. 2 and **3** shows the SEM image of fresh FCC and spent FCC catalyst at different resolutions respectively. The HDPE waste employed for this work consisted of a mixture of polyethylene ranging from pharmaceutical, cosmetic, and yoghurt waste bottles.

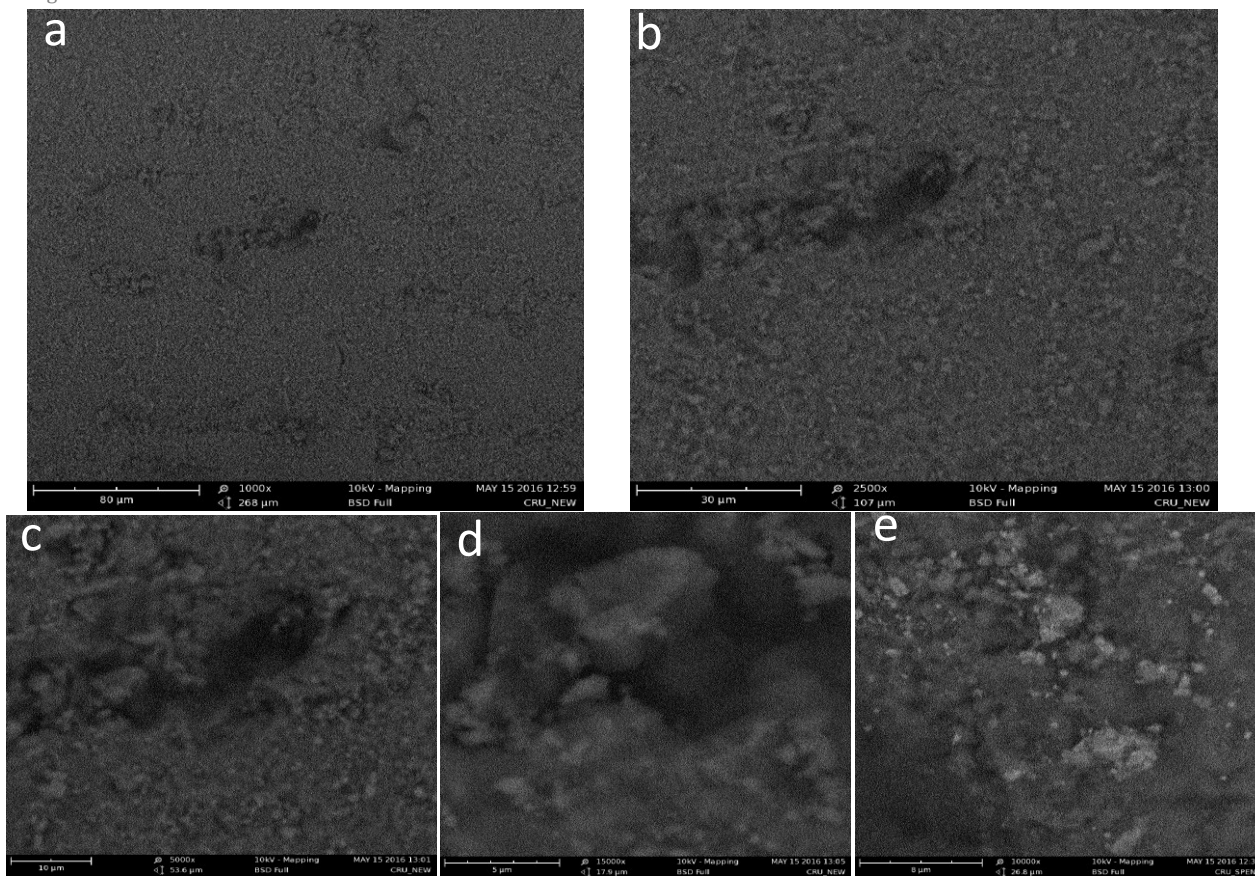


Fig. 2. SEM image of fresh FCC catalyst at: (a) 1000 X (b) 2500 X (c) 5000 X (d) 10000 X (e) 15000 X

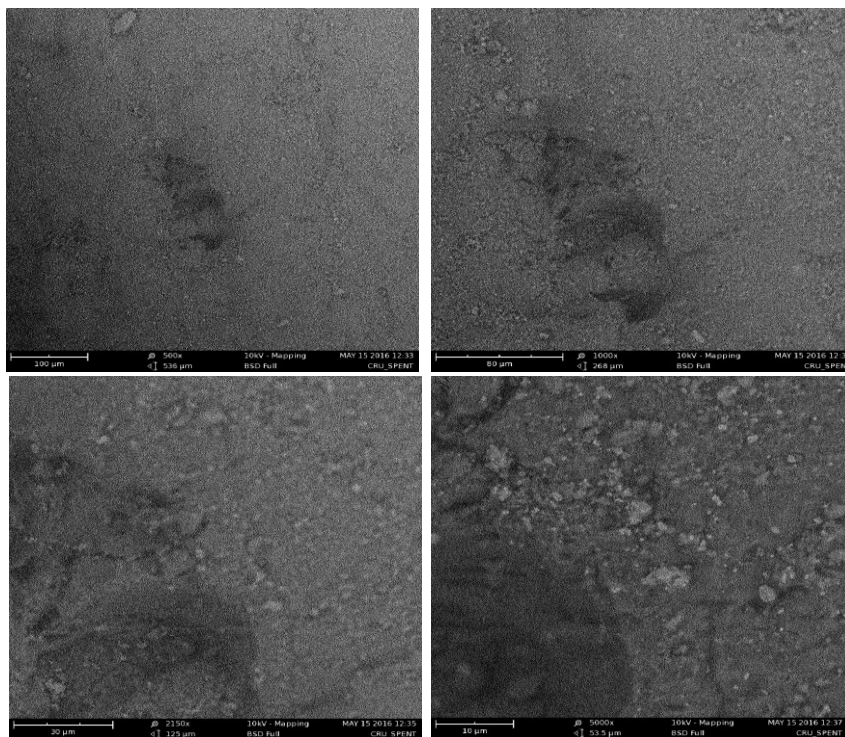


Fig. 3. SEM image of spent FCC catalyst at: (a) 500 X (b) 1000 X (c) 2150 X (d) 5000 X

At the end of the pyrolysis reaction the residue obtained weighed (120 g / 125 g) and (100 g / 120 g) were obtained for the reactions which occurred at catalyst/sample ratios of 1:8 and 1:16 respectively.

Comparative composition of the gases evolved from pyrolysis of waste HDPE at 150 °C and 250 °C using catalyst/sample ratio 1:8 is presented in **Table 1**.

Table 1: Composition of gases obtained from pyrolysis HDPE at 150 °C and 250 °C using fresh FCC catalyst with the catalyst/sample ratio of 1:8 after heating for one and a half hours

Component	Organic compound	Reaction at 150 °C		Reaction at 250 °C	
		Concentration (ppm)	(%) Concentration	Concentration (ppm)	(%) concentration
C ₁	n-Methane	2.4302	2.8794	0.3581	0.0680
C ₂	n-Ethane	17.3379	20.5430	152.9042	29.0460
C ₃	n-Propane	10.7678	12.7580	30.4614	5.7866
C ₄	n-Butane	4.9829	5.9041	33.5059	6.3650
C ₅	n-Pentane	Nil	Nil	Nil	Nil
C ₆	n-Hexane	2.7615	3.2720	8.4647	1.6080
C ₇	n-Heptane	15.3558	18.194	79.5571	15.1130
C ₈	n-Octane	16.8334	19.9450	127.8764	24.2920
C ₉	n-Nonane	13.9274	16.5020	93.2789	17.7190
Total		84.3969		526.4070	

Table 2: Composition of gases obtained from pyrolysis of HDPE at 150 °C and 250 °C using fresh FCC catalyst in the ratio of 1:16 after heating for one and a half hours

Component	Name	Reaction at 150°C	Reaction at 250°C
		Concentration (ppm)	Concentration (ppm)
C ₁	n-Methane	101.9239	0.7633
C ₂	n-Ethane	108.9239	100.2590
C ₃	n-Propane	38.3533	36.1316
C ₄	n-Butane	4.1603	28.9361
C ₅	n-Pentane	Nil	Nil
C ₆	n-Hexane	Nil	Nil
C ₇	n-Heptane	69.4687	69.1586
C ₈	n-Octane	140.6610	118.4262
C ₉	n-Nonane	32.0212	31.8353
Total		495.4315	385.5101

In **Table 1** and **Fig. 4**, the reaction occurred at a catalyst/sample ratio of 1:8 and the concentration of gases obtained at 250 °C was higher than that obtained at 150 °C. This shows that temperature affects both the reaction time and gaseous yield. At a higher temperature of 250 °C the reaction was sped up thus lowering the reaction time [11]. This becomes evident that high temperature supports easy cleavage of bonds and thus speeds up the reaction and lowers the reaction time. HDPE with a long linear polymer chain with low branching and high degree of crystallinity led to high strength properties and thus required higher temperature and more reaction time.

From the result in **Table 2** and **Fig. 5**, the reaction occurred at a catalyst of 1:16 and the concentration of gases obtained at 150 °C were slightly higher than the gases collected at 250 °C. This is an indication that the total products decreased slightly with increase in temperature [12].

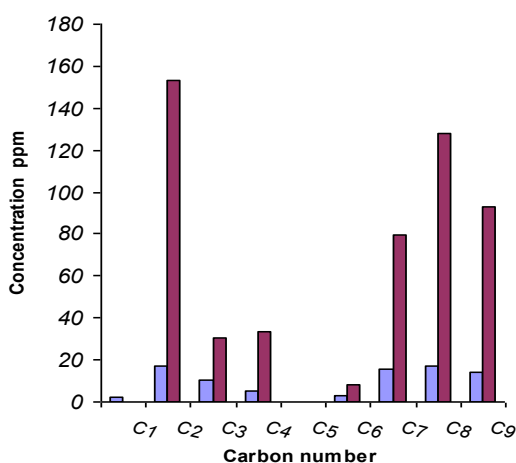


Fig. 4. Composition of gases obtained from pyrolysis of HDPE at 150 °C and 250 °C using fresh FCC catalyst with the catalyst/sample ratio of 1:8

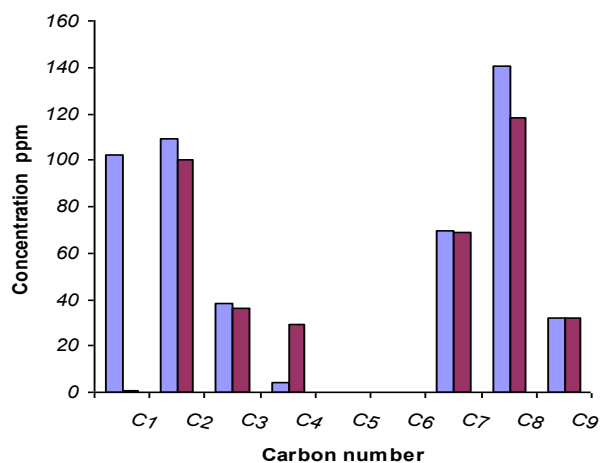


Fig. 5. Composition of gases obtained from pyrolysis of HDPE at 150 °C and 250 °C using fresh FCC catalyst with the catalyst/sample ratio of 1:16

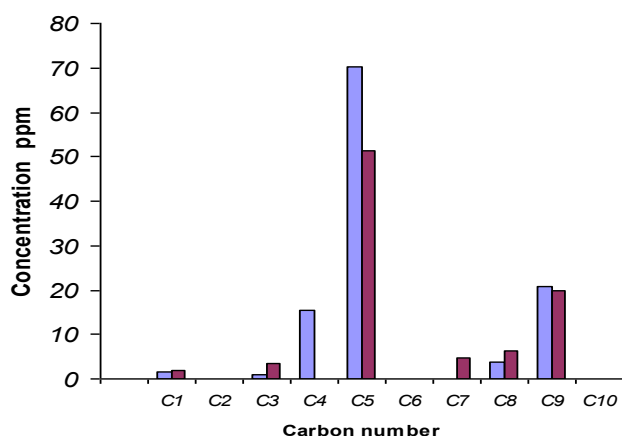
With the FCC catalyst in pyrolysis reaction, the activity of the catalyst is expected to drop with increasing coke yield this could have been the reason in the drop of the total of the gaseous products in the reaction at 250 °C.

The composition of gas was analyzed as given from the result in **Tables 1 and 2** as well as Figures 2 and 3 respectively. These show that the dominant components could be observed in {C₂ (17.3379 ppm), C₃ (10.7678 ppm), C₆ (15.3558 ppm), C₈ (16.8334 ppm)} and {C₂ (152.9045), C₃ (30.4014 ppm), C₄ (33.5009 ppm), C₇ (79.5571 ppm), C₈ (127.8764 ppm) and C₉ (93.2789 ppm)} respectively. In every case one of the dominant components could be observed in C₂. This could be explained relating with the structure and degradation pattern of polyethylene because it is built up from C₂ monomers [13].

Table 3: Composition of gases obtained from pyrolysis of HDPE at 150 °C and 250 °C with spent FCC catalyst using catalyst/sample ratio of 1:8 after heating for one and a half hours.

Component	Organic Compound	Reaction at 150 °C		Reaction at 250 °C	
		Concentration	(%)	Concentration	(%)
		ppm	Concentration	ppm	Concentration
C ₁	n-Methane	1.6735	1.4845	1.7855	2.0440
C ₂	n-Ethane	0.0051	0.0045	0.0109	0.0124
C ₃	n-Propane	0.9277	0.8229	3.3977	3.8890
C ₄	n-Butane	15.4172	13.6760	Nil	Nil
C ₅	n-Pentane	70.3596	62.4150	51.2582	58.6790
C ₆	n-Hexane	0.0041	0.0036	0.0035	0.0040
C ₇	n-Heptane	Nil	Nil	4.7962	5.4900
C ₈	n-Octane	3.6629	3.2493	6.2605	7.1668
C ₉	n-Nonane	20.6775	18.3420	19.8404	22.7120
C ₁₀	n-Decane	Nil	Nil	Nil	Nil
Total		112.7276		87.3531	

From the results in **Table 3**, the total concentration of gaseous products obtained at 150°C was 112.7276 ppm while that obtained at 250°C gave 87.3531 ppm. This means that the effect of the catalyst on the yield and distribution of the product became less significant with increasing temperature [14, 15].

**Figure 6:** composition of gases obtained 150°C and 250 °C using spent FCC catalyst at ratio 1:16

The dominant components in the reaction as shown in Fig 6 were observed in C₄ (15.4172 ppm), C₅ (70.3596 ppm) and C₉ (20.6775 ppm).

Again this result revealed that the dominant gases were within the gasoline range which is typical of FCC catalysts. The total concentration of gases obtained at 250 °C with fresh FCC catalyst using the same sample at the same catalyst/sample ratio yielded higher concentration of gases. This could be as a result of coke formation which diminishes the action of FCC catalyst [16]. The yield of gases obtained were however greater than those obtained through thermal pyrolysis.

In **Table 4**, the pyrolysis data from HDPE which occurred at 150 and 250 °C using catalyst/sample ratio of 1:16 are being presented. From the results the total concentration of gaseous products collected

at 150 °C and 250 °C were obtained to be (116.9178 ppm) and (109.4314 ppm) respectively. The dominant components were observed in C₅ (78.0995 ppm) and C₉ (18.2544 ppm) for gases collected at 150 °C. On the other hand C₅ (42.0682 ppm) C₇ (12.4087 ppm), C₈ (8.8217 ppm) and C₉ (37.4087 ppm) were the dominant components observed in the gases collected at 250 °C. The gas yield was higher at 250 °C which became evident that the effect of the catalyst on the pyrolysis of HDPE on the yields and distribution of the products were significant with increasing temperature.

Generally, the spent FCC catalyst has high activity for hydrocarbon cracking reactions and selectivity to non-aromatic C₅ – C₁₁ hydrocarbons which are evident in all the results from the samples see [Table 4](#). Olefins which were also revealed as part of results obtained by using spent FCC catalyst [[17](#)].

Generally the spent catalysts are expected to show diminishing activity but then, there were still significantly effective in the pyrolysis reaction as the spent FCC catalyst was able to show high cracking activity, yielding better gasoline range products than in purely thermal cracking [[18](#)]. This result agrees with the result presented on the catalytic pyrolysis of polystyrene over ZSM-5 Mordenite, sulphur promoted zirconia and E-cat [[19](#)]. Lee *et al.*, [[20](#)] also observed that at 430 °C in a semi batch reaction the pyrolysis of HDPE using E-cat showed high cracking activity and yielding better liquid gasoline products than in purely thermal cracking.

The values of the gas concentrations however showed that there was a decrease in the concentration of gases which could be attributed to the formation of coke entrapped in the pore of the catalyst thereby diminishing its activity with time [[15](#)].

Gas chromatographic analysis generally revealed that the components of gases were in the range of C₁-C₉, [[21](#), [22](#)]. The gases are very useful for example C₁ – C₄ gases can be used in diverse ways. Methane also known as marsh gas is the main component in natural gas; it is a colourless odourless and flammable gas. Ethane is also a colourless and odourless gas and the second most abundant component in natural gas. Ethane is also used to produce ethylene which is a raw material for the production of plastic material. Another use is as a refrigerant. Propane is also a flammable hydrocarbon in the alkane series, which is also present in natural gas and used as bottled gas. It finds other uses in fuel engine, oxy-gas torches and portable stores [[23](#), [24](#)]. Butane undergoes free radical chlorination to form chlorobenzene and chlorobutane as well as other derivations. Butane is also used as a feed stock for production of ethylene. It is used in refineries to enhance octane number of motor gasoline when blended with propane and other hydrocarbon may be referred commercially LPG. It is also used as a fuel in lighter and propellants in aerosol sprays.

The other gases obtained were within the range of C₅- C₉. The gases are also very useful for example, pentane which is a colourless gas with the odour of

petroleum similarly n-hexane is also a colourless gas with petroleum like odour. Hexane however, is also used to extract vegetable oil from crops such as Soyabean etc. It is also used in cleaning textile, and printing and cleaning furniture. Some glue used in roofing and shoe leather container hexane. Quick drying glues also contain n-hexane it is also contained in gasoline. N-heptane and n-octane has

the odour of gasoline and are considered as a component of gasoline. Nonane a colourless flammable liquid occurs primarily in the component of petroleum distilled fraction commonly called kerosene which is used in fueling tractors or as jet fuel. It is also used as a fuel additive and as a fuel additive and as a component in biodegradable detergent.

Table 4: Pyrolysis data from HDPE which occurred at 150 and 250 °C using spent catalyst/sample ratio of 1:16

Component	Organic compound	Reaction at 150 °C		Reaction at 250 °C	
		Concentration ppm	(%) Concentration	Concentration ppm	(%) Concentration
C ₁	n-Methane	1.0875	0.0093	0.9115	0.8329
C ₂	n-Ethane	0.0066	0.0056	0.0185	0.0169
C ₃	n-Propane	1.4538	1.2434	2.7350	2.4990
C ₄	n-Butane	14.1784	12.1260	5.2807	4.8250
C ₅	n-Pentane	78.0995	66.7980	42.0682	38.4420
C ₆	n-Hexane	0.0041	0.0035	0.0068	0.0060
C ₇	n-Heptane	Nil	Nil	12.4087	11.3390
C ₈	n-Octane	3.6335	3.1077	8.8217	8.0613
C ₉	n-Nonane	18.2544	15.6130	37.1803	33.9750
C ₁₀	n-Decane	Nil	Nil	Nil	Nil
Total		116.9178		109.4314	

4. Conclusion

In this work, thermo-catalytic pyrolysis of contaminated high density polyethylene (HDPE) was studied using fresh and spent FCC catalyst. It was observed that the pyrolysis reaction gave aliphatic hydrocarbon within the range of (C₁-C₄; C₅-C₉) and (C₁-C₄; C₇-C₉) for the reactions which occurred using catalyst/sample ratios of 1:8 and 1:16 respectively. The corresponding carbon number obtained using spent FCC catalyst (C₁-C₄;

C₇-C₉) using catalyst/sample ratio of 1:8 and 1:16 respectively. From these results, it became obvious that the FCC catalyst resulted in more gasoline range products as higher values were obtained within the range of C₇-C₉. The FCC catalyst used also gave high activity for hydrocarbon cracking reactions and selectivity of C₇-C₉. High values of C₂ carbon atoms were also obtained from the reactions using both fresh and spent FCC catalysts.

The pyrolysis of HDPE has not only reduced the solid waste by 50%; 62.5% and 55% ; 60% by volume for the fresh and spent FCC catalyst for the reactions which occurred using catalyst/sample ratios of 1:8 and 1:16 respectively, useful gases which can be fractionated into fuel gases, gasoline range gases and organic solvents were also obtained. The result obtained showed that temperature affects both the reaction time and gaseous yield. High temperature supports easy cleavage of bonds

resulting in increased reaction rate thereby lowering the reaction time. Also, the effect of the catalyst on the yield and distribution of the product became less significant with increasing temperature. Fresh FCC catalyst unsurprisingly gave higher gaseous yield than the spent.

Declaration of interest: There are no conflict of interest, as such, this summary statement will be ultimately published if the article is accepted.

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