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Recovery of combustible gases from waste polyethylene via low temperature catalytic pyrolysis

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Abstract

Pyrolysis of three samples of waste polyethylene materials: low density polyethylene (LDPE), Polyethylene terephthalate (PET), and High density polyethylene (HDPE), were carried out by adapting a cylindrical pressure cooking pot of height 30 cm with an internal diameter of 31.5cm as the reactor. The pyrolysis reaction was carried out with the influence Naphtha Hydro-treating Unit (NHU) catalyst. The gases which evolved were collected using Tedlar and analysis was done with the aid of a BUCK 530 Gas Chromatograph. The pyrolysis reaction with fresh NHU catalyst at 150 °C and 250 °C using catalyst/sample ratio of 1: 8 showed aliphatic hydrocarbon in the range of C₁ – C₉ with total concentrations of gases (ppm) for LDPE, PET and HDPE at temperatures of 150 °C and 250 °C to be 86.3357 and 81.2315, 105.8002 and 258.2227, 97.7848 and 106.2345 respectively. The corresponding values (ppm) were obtained at 150 °C and 250 °C for LDPE, PET and HDPE using catalyst/sample ratio of 1:16 to be 54.2585 and 114.3178, 185.4353 and 91.2021, 53.1022 and 185.6128 respectively. The fuel gases revealed mainly C₁ – C₉ aliphatic hydrocarbons which can be fractionated into fuel gases, gasoline range gases and organic solvents.

Keywords: Pyrolysis, polyethylene, NHU catalyst, aliphatic hydrocarbon

Introduction

Pyrolysis, or thermolysis is an irreversible thermochemical treatment process of a complex solid or fluid chemical substance at elevated temperatures in an inert or oxygen free environment, where the rate of pyrolysis is dependent on temperature and increases with temperature. Pyrolysis is also referred to as cracking and is mostly applied to organic materials ^[1]. It can be likened to carbonization process where an organic material of higher molecular weight is decomposed or cracked to produce a solid residue with high (or higher) carbon content and some volatile products. In addition to organic materials, pyrolysis can also be applied in certain cases to inorganic materials and water as well as other aqueous solutions ^[2].

Pyrolysis reactions typically occur at temperatures between 400-800 °C. As the temperature changes, the product distribution can be altered. Lower pyrolysis temperatures usually produce more liquid and solid products, where higher temperatures usually favour the production of more gases as a result of more powerful thermal cracking reactions. The pyrolysis temperature also has significant effect on the properties of pyrolytic products. The caloric value of pyrolytic oil for example increases mostly with increasing temperature ^[3].

On the other hand, the catalyzed pyrolysis promotes the decomposition process as it improves the yield and lowers the temperature and/or reaction time. Thus the catalytic pyrolysis presents a number of advantages over thermal pyrolysis such as lower energy consumption and formation products with narrower distribution of carbon atoms, which may be directed to aromatic hydrocarbons with light and high market value ^[4,5].

A pyrolysis-based process has several advantages over other treatment processes as the technology is relatively simple and can be made compact light weight, pyrolysis can also be used for all types of solid and liquid products and can be easily adapted to changes in feedstock composition. The pyrolysis technology can be designed to produce minimal amounts of unusable by products. Furthermore, pyrolysis can be conducted as a batch lower process with minimal requirements for feedstock pre-processing ^[6].

Pyrolysis has proven to be an energetically efficient chemical technology that is used heavily in the chemical industry. Pyrolysis may be used in bio-refineries for making a wide range of products and materials on which a future sustainable society may be based including many forms of carbon, fuel gases, and other potentially valuable chemicals and chemical feed stocks.

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It is against this background that this work was designed to utilize pyrolysis reaction on waste plastic materials in order to recover valuable fuel gases.

2. Experimental

2.1 Collection and preparation of polyethylene materials

The low density polyethylene (LDPE), high density polyethylene (HDPE), and polyethylene terephthalate (PET) wastes were collected from refuse 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 [7]. The Naphtha hydrotreating unit (NHU) catalyst employed for this work was obtained from Nigerian National Cooperation (NNPC) Warri in Delta State and being a fluid catalytic cracking (FCC) catalyst, 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 15 000 x respectively. From the SEM images, it was deduced

that the catalyst particle size ranged within 5 μ m-80 μ m. In further characterizing the fresh NHU catalyst, SEM was combined with atomic absorption spectrometry (AAS) in the detection of the metal composition. The analysis indicated the presence of aluminum (7.021) and silicon (2.399) respectively.

2.2 Experimental Procedure

A Presto pressure cooking pot made of stainless steel of height 30.00 cm with an internal diameter of 31.50 cm was converted and constructed to a fixed bed reactor and adapted for the pyrolysis reaction [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.

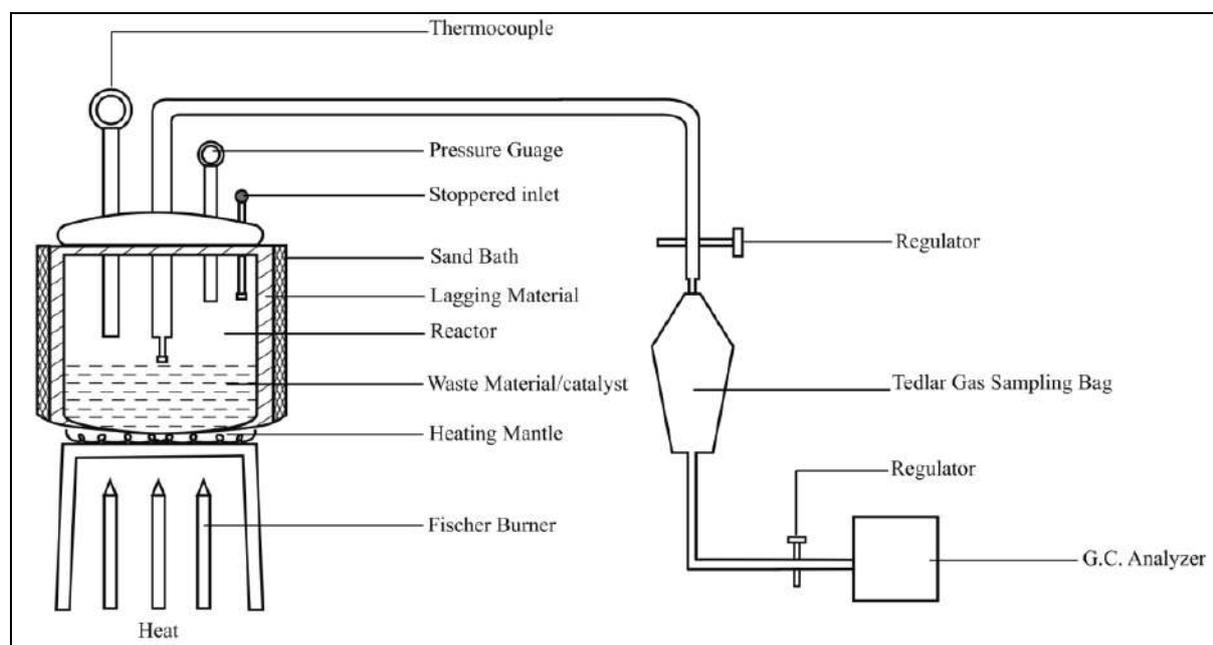


Fig 1: Layout of the pyrolysis process

2.3 Catalytic Cracking of LDPE, HDPE and PET

Two catalyst/sample ratios (1:8 and 1:16) were investigated in the catalyzed pyrolysis as described [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. The reactor was covered the heating process started. After 30 minutes into the reaction evolution of gases started slightly and this was evident as bag began to swell. After heating for about one and a half 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 LDPE, PET and HDPE with the effect fresh NHU catalyst were

characterized using a Buck 530 gas chromatography with HP-88 (10 m/0.25 mm thickness) injection volume was 10 μ L 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

3.1 Results

3.2 Discussion

Waste LDPE was pyrolysed at 150 °C and 250 °C under the effect of naphtha hydro-treating unit (NHU) catalyst first by using catalyst/sample ratio of 1:8. The result of the chromatographic analysis is presented in Table 1. From the results, the total concentration of gases obtained from the reaction at 150 °C was 86.3357 while the total concentration of gases obtained at 250 °C yielded 81.2315 ppm. This implies that the gaseous products decreased slightly with increase in temperature. This result agrees with results given

by [10, 11]. This could also be as a result of the diminishing activity of the catalyst during the reaction as a result of coke formation [12, 13]. This means that the effect of the catalyst on the yield and distribution of the product became less significant with the increasing temperature. This is in agreement with results presented by [14, 15]. Similarly, results obtained from pyrolysis of LDPE at 150 °C and 250 °C

using catalyst/sample ratio 1:16 as shown in Table 2 gave a total gas concentration of 54.2485 and 114.3178 ppm respectively. This implies that the conversion of waste LDPE to gases increased with increase in temperature resulting in enhanced aliphatic content. This agrees with results obtained [16]. Fig. 2 shows the SEM image of NHU catalyst at different resolutions.

Table 1: Composition of gasses obtained from catalytic pyrolysis of waste LDPE at 150 °C and 250°C using fresh NHU catalyst in the ratio of 1:8 after heating for one and a half hour.

Component	Organic Compound	Reaction at 150°C concentration in ppm	Reaction at 250°C concentration in ppm
C ₁	n-Methane	Nil	4.1822
C ₂	n-Ethane	0.0387	0.0147
C ₃	n-Propane	40.3333	8.9979
C ₄	n-Butane	15.8064	Nil
C ₅	n-Pentane	Nil	46.1324
C ₆	n-Hexane	0.0074	Nil
C ₇	n-Heptane	6.2908	4.6415
C ₈	n-Octane	7.4344	9.8688
C ₉	n-Nonane	16.3357	7.3934
Total		86.3357	81.2315

Table 2: Composition of gasses obtained from catalytic pyrolysis of waste LDPE at 150 °C and 250 °C using fresh NHU catalyst in the ratio of 1:16 after heating for one and a half hour.

Component	Organic Compound	Reaction at 150 °C concentration in ppm	Reaction at 250 °C concentration in ppm
C ₁	n-Methane	Nil	2.9488
C ₂	n-Ethane	Nil	0.0054
C ₃	n-Propane	5.7065	3.5943
C ₄	n-Butane	Nil	13.7746
C ₅	n-Pentane	27.0970	82.0348
C ₆	n-Hexane	0.0018	Nil
C ₇	n-Heptane	9.2321	7.0841
C ₈	n-Octane	6.3158	Nil
C ₉	n-Nonane	Nil	4.8758
Total		54.2585	114.3178

Waste PET was also pyrolysed at 150 °C and 250 °C under the influence of NHU catalyst using catalyst/sample ratio of 1:8. Comparative composition of gases evolved from the reaction is presented in Table 3. The total concentration obtained from the pyrolysis process gave 105.8002 and

258.2227 ppm at temperature of 150 °C and 250 °C respectively. This shows that the concentration of gases increased with increasing temperature. High temperature supports cleavage of bonds and thus speeds up the reaction thereby lowering the reaction time [17, 18].

Table 3: Composition of gasses obtained from catalytic pyrolysis of waste PET at 150 °C and 250 °C using fresh NHU catalyst in the ratio of 1:8 after heating for one and a half hour.

Component	Organic Compound	Reaction at 150 °C concentration in ppm	Reaction at 250 °C concentration in ppm
C ₁	n-Methane	1.1557	14.9010
C ₂	n-Ethane	0.0185	0.0093
C ₃	n-Propane	2.4599	5.6028
C ₄	n-Butane	4.5123	Nil
C ₅	n-Pentane	39.3948	198.2999
C ₆	n-Hexane	0.0065	Nil
C ₇	n-Heptane	12.3104	4.1417
C ₈	n-Octane	8.8176	16.4454
C ₉	n-Nonane	37.1254	13.5676
Total		105.8002	258.2227

On the other, results obtained from pyrolysis of PET a 150 °C and 250 °C using catalyst/sample ratio of 1:16 gave a total concentration of 185.4353 and 91.2021 ppm respectively (Table 4). This is an indication that the total

concentration of gases decreased with increasing temperature. This could be as a result deactivation of the catalyst during the pyrolysis reaction [19].

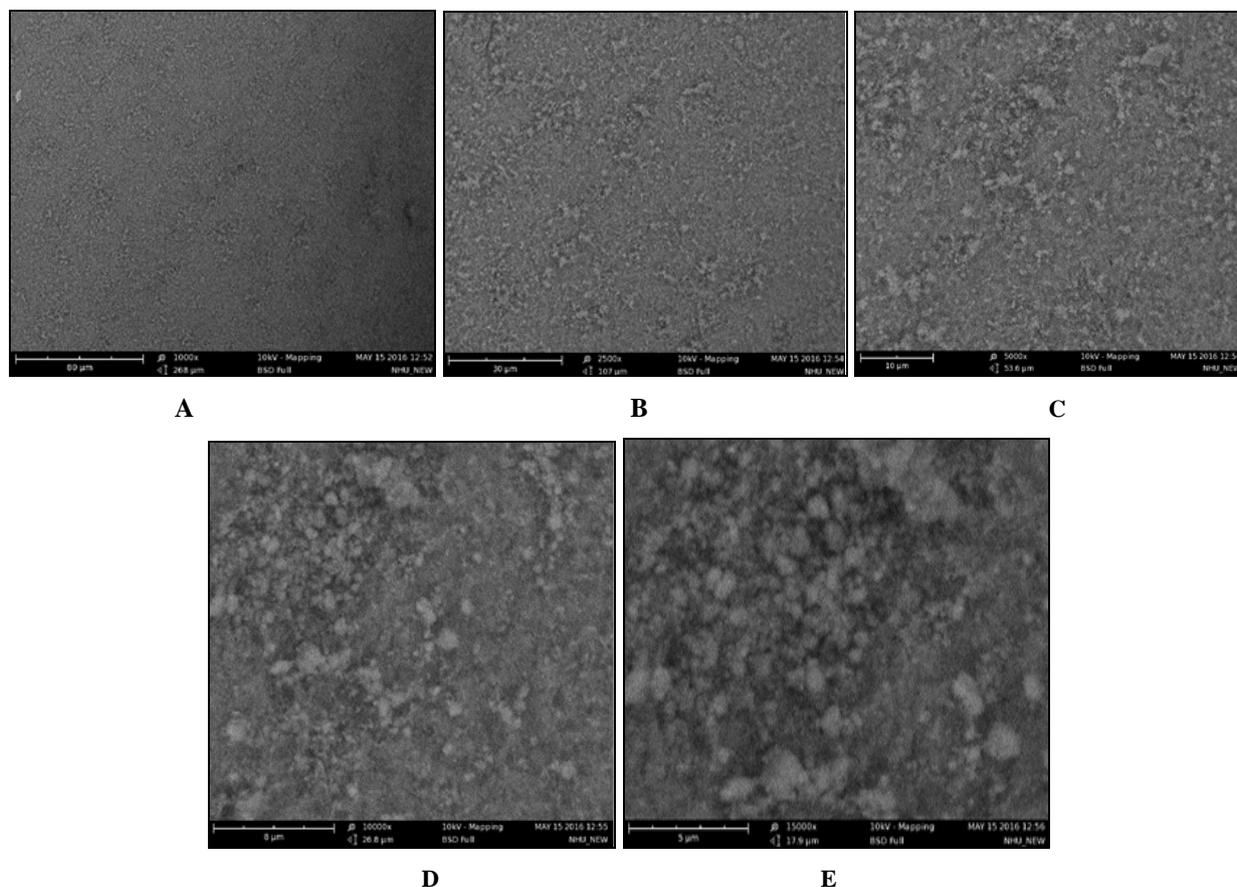


Fig 2: SEM image of NHU catalyst at: (a) 1,000 X (b) 2,500 X (c) 5000 X (d) 10000 X (e) 15000 X

Table 4: Composition of gasses obtained from catalytic pyrolysis of waste PET at 150 °C and 250 °C using fresh NHU catalyst in the ratio of 1:8 after heating for one and a half hour.

Component	Organic Compound	Reaction at 150 °C concentration in ppm	Reaction at 250 °C concentration in ppm
C ₁	n-Methane	20.6143	2.1403
C ₂	n-Ethane	0.0085	0.0108
C ₃	n-Propane	5.5560	3.2616
C ₄	n-Butane	7.1435	Nil
C ₅	n-Pentane	114.3744	55.8693
C ₆	n-Hexane	0.0076	0.0035
C ₇	n-Heptane	5.8393	4.7866
C ₈	n-Octane	17.3397	6.2508
C ₉	n-Nonane	14.5520	18.8782
Total		185.4353	91.2012

The pyrolysis of HDPE which was also done under the same conditions of temperature 150 °C and 250 °C using catalyst/sample of 1:8 gave the following results 87.7838 and 106.2345 ppm as can be seen in Table 5. Similarly, Table 6 shows that the reaction carried out using catalyst/sample ratio of 1:16 yielded results of 53.1022 and

185.6128 ppm as the total concentration of gases collected at 150 °C and 259 °C respectively. This became obvious that the concentration of gases using both catalyst/sample ratios of 1:8 and 1:16 increased with increase in temperature resulting in aliphatic content [20].

Table 5: Composition of gasses obtained from catalytic pyrolysis of waste HDPE at 150 °C and 250 °C using fresh NHU catalyst in the ratio of 1:8 after heating for one and a half hour.

Component	Organic Compound	Reaction at 150 °C concentration in ppm	Reaction at 250 °C concentration in ppm
C ₁	n-Methane	Nil	1.5622
C ₂	n-Ethane	0.0332	0.0192
C ₃	n-Propane	40.8594	2.7493
C ₄	n-Butane	15.0016	5.0461
C ₅	n-Pentane	Nil	39.7946
C ₆	n-Hexane	0.0075	12.3882
C ₇	n-Heptane	5.9627	8.8338
C ₈	n-Octane	7.8658	36.2403
C ₉	n-Nonane	18.0543	Nil
Total		87.7848	106.2345

Table 6: Composition of gasses obtained from catalytic pyrolysis of waste HDPE at 150 °C and 250 °C using fresh NHU catalyst in the ratio of 1:16 after heating for one and a half hour.

Component	Organic Compound	Reaction at 150 °C concentration in ppm	Reaction at 250 °C concentration in ppm
C ₁	n-Methane	0.2925	20.8683
C ₂	n-Ethane	0.0057	0.0083
C ₃	n-Propane	2.4227	5.3375
C ₄	n-Butane	Nil	6.8005
C ₅	n-Pentane	43.5146	115.1097
C ₆	n-Hexane	0.0005	0.0075
C ₇	n-Heptane	Nil	5.7499
C ₈	n-Octane	0.0299	14.5246
C ₉	n-Nonane	6.8364	Nil
Total		53.1022	185.6128

The pyrolysis reaction of LDPE at 150 °C and 250 °C using catalyst/sample ratio of 1:8 (Table 1) gave the most dominant components in C₃ 40.3333 ppm, C₉ 16.3353 ppm and C₅ 46.1324 ppm, C₈ 9.8688 ppm for gases collected at 150 °C and 250 °C respectively. The catalytic cracking of PET using catalyst/sample ratio of 1:8 gave the most dominant components in C₅ 64.9952, C₄ 14.1152 ppm and C₅ 39.3948, C₉ 37.1254 ppm at 150 and 250 °C respectively. In another cracking reaction, the pyrolysis reaction of PET which took place using catalyst/sample ratio of 1:16 gave the most dominant components in C₅ 114.3744, C₁ 20.6143 ppm and C₅ 55.8693, C₉ 14.5020 ppm for the gases collected at 150 °C and 250 °C respectively. High density polyethylene HDPE was also pyrolysed under the conditions of temperature (150 °C and 250 °C) using sample/catalyst ratio of 1:8. The most dominant components were observed in C₃ 40.8594, C₉ 18.0543 ppm and C₅ 39.7949, C₈ 36.2403 ppm for reactions which occurred at 150 °C and 250 °C respectively. For the reaction took place using catalyst/sample ratio of 1:16, the most prominent components were C₅ 43.5146 and C₅ 115.1097, C₁ 20.8623 were collected at 150 °C and 250 °C respectively.

It is generally observed that FCC catalyst results in more gasoline range products. This is attributed to the bimodal pore size distribution and mild properties of the NHU catalyst^[21]. This is evident in the results as most of the C-atoms within the range of C₅-C₉ were higher in concentrations in all the three samples (LDPE, PET, and HDPE) with NHU catalyst. It was also observed that one of the most dominant C-atom in for all the three samples was seen to be C₅^[22], the hydro treating nature of the catalyst could have encouraged deoxidation which resulted to addition of hydrogen. Also the NHU catalyst has shown high activity for hydrocarbon cracking reactions with selectivity of non-aromatics C₅-C₁₁ hydrocarbons which is evident in all the samples. The fresh NHU catalyst was expected to show diminishing activity during the pyrolysis reaction because coke formation is a common problem with the most catalysts in petroleum and polyolefin pyrolysis research^[23]. From these results higher concentrations were however obtained with increase in temperature meaning that the fresh NHU pellets were not easily deactivated. Diminishing activity was only shown in the pyrolysis reaction involving LDPE and PET using catalyst/sample ratio of 1:8 and 1:16 respectively.

Conclusion

Combustible gases were recovered from the catalytic cracking of LDPE, PET, and HDPE using fresh NHU catalyst. The catalyst has shown high activity for

hydrocarbon cracking reactions with selectivity for aliphatic hydrocarbon within the range of C₁-C₉ as this was evident in all the three samples. The highest total concentration was observed in PET for the reactions which took place using catalyst/sample ratio of 1:8, 258.2227 ppm at 250 °C. The total concentrations as observed from the catalytic pyrolysis process gave results for the three samples in the following increasing order: PET > HDPE > LDPE. The gas yield however increased with increasing temperature and the component C₅ was observed as one of the highest component in all the three samples. This study has shown that combustible gases were obtained from NHU catalyst thereby making it an effective method in producing useful gases. The quantity of polyethylene waste which would have served as a menace to the environment can also be reduced by this method therefore, resources will be conserved and the burden on the environment will be reduced.

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