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Surma N

Department of Chemistry,
Federal University of
Agriculture, Makurdi, Benue,
Nigeria

Ijuo GA

Department of Chemistry,
Federal University of
Agriculture, Makurdi, Benue,
Nigeria

Yusuf EY

Department of Chemistry,
Federal University of
Agriculture, Makurdi, Benue,
Nigeria

Iorhemba MA

Department of Chemistry,
Federal University of
Agriculture, Makurdi, Benue,
Nigeria

Correspondence**Surma N**

Department of Chemistry,
Federal University of
Agriculture, Makurdi, Benue,
Nigeria

Tertiary recycling of waste polyethylene to fuel gases via low temperature catalytic pyrolysis

Surma N, Ijuo GA, Yusuf EY and Iorhemba MA

Abstract

Pyrolysis of low density polyethylene (LDPE) was carried out by adapting a cylindrical pressure cooking pot of height 30.00 cm with an internal diameter of 31.50 cm as the reactor. The pyrolysis reaction was carried out with the influence of 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 spent NHU catalyst at 150 °C and 250 °C using catalyst/sample ratios of 1:8 and 1:16 for all the three samples showed aliphatic hydrocarbon in the range of C₁ – C₉. Results showed total concentrations of gases (ppm) to be 109.8282 and 53.1022 for LDPE, 96.3748 and 140.4273 for PET and 81.6393 and 49.0464 for HDPE respectively. The corresponding values (ppm) were obtained for LDPE, PET, and HDPE at 150 °C and 250 °C using catalyst/sample ratio of 1:16 to be 88.1075 and 56.1038, 81.2315 and 62.4957, 48.8769 and 53.8048 respectively. The fuel gases revealed mainly C₁ – C₉ aliphatic hydrocarbons which can be fractionated into fuel gases, gasoline range product.

Keywords: polyethylene, pyrolysis, spent NHU catalyst, fuel gases

1. Introduction

There is an increase in the manufacture and consumption of polyethylene as the day go by. All these polyethylene materials need to be disposed after being used as waste. There is therefore need to effectively manage these wastes in order to reduce the burden on the environment. This can be achieved through efficient waste plastic recycling processes which is a way of making these waste (polyethylene) become more useful. Recycling presents advantages such as reduction of environmental problems and saving both material and energy^[1, 2].

The polyethylene can be degraded in the environment by four mechanisms: photo degradation, thermo-oxidative degradation, hydrolytic degradation, and biodegradation by microorganisms^[3]. The natural degradation of polyethylene begins photo-degradation due to UV from the sun which provides activation the energy required to initiate the incorporation of oxygen atoms into the polymer, leading to thermo-oxidative degradation. In this step, the polymer becomes brittle and it's fracturing into smaller pieces until the polymer chain becomes low in molecular weight to be metabolized by microorganism. The microorganisms convert the carbon of the polymer chains to carbon-dioxide or incorporate it into bio-molecules, but this process is slow and will take at least fifty years. So, a solution to these problems will be recycling, because most commodity polymers are relatively stable, making polymer recovery poor^[4].

The current plastic reclamation technology options are generally grouped into four types: Primary recycling, secondary or mechanical recycling, feedstock or chemical recycling and quaternary or energy recycling^[5]. The most popular process is represented by the primary recycling due to their simplicity and low cost. This is the processing of polyethylene for use comparable to the original application. The disadvantage of this method is represented in the existence of a limit on the number of cycles for each material^[6]. The secondary process is represented by a physical method in which the polyethylene is shredded to granules and melted to make new products by extrusion. The processed material can be blended with virgin material to obtain superior results. The disadvantages of this method refer to the heterogeneity of the solid waste and the deterioration of product's properties in each cycles which occurs due to the low molecular weight of the recycled resin. This method is also relatively inexpensive but needs substantial initial capital investment^[4].

Feedstock or chemical recycling which is also known as tertiary recycling is defined as the process in which polymers are chemically converted to monomers or partially depolymerized to oligomers through a chemical reaction. A change occurs in the structure of the polymer. The resulting monomers can be used for new polymerizations to produce the original or related polymeric product as well as recover gasoline range fuel [7].

The chemical reactions used for decomposition of polymers into monomers are: Hydrogenation, glycolysis, hydrolysis, gasification, methanolysis, chemical depolymerisation, thermal cracking, catalytic cracking and reforming, photo degradation, ultrasound degradation, degradation in microwave reaction [8]. The chemical recycling is not fully developed and for this reason, only a few companies are working on it because this method needs a lot of investment and expert personnel. Contributing to this high cost is the fact that waste polyethylene are indeed a mixture of different materials having different processing compositions and requiring different processing conditions. Another prevalent issue with this method is the high energy input required as some waste require as high as 700 °C [9].

The quaternary or energy recycling method refers to recovery of plastic's energy content. The most effective way to reduce the volume of organic materials which involves the recovery of energy is represented by incineration. This method is a good method because it generates considerable energy from polymers, but it's not ecologically acceptable because of health risk from airborne toxic substances. In this study, low temperature catalytic pyrolysis was carried out in order to recover 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 [10]. The spent Naphtha hydro treating 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 5µm-80 µm. In further characterizing the spent 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

Figure 1 shows the layout of the pyrolysis process. 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 [11]. 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.

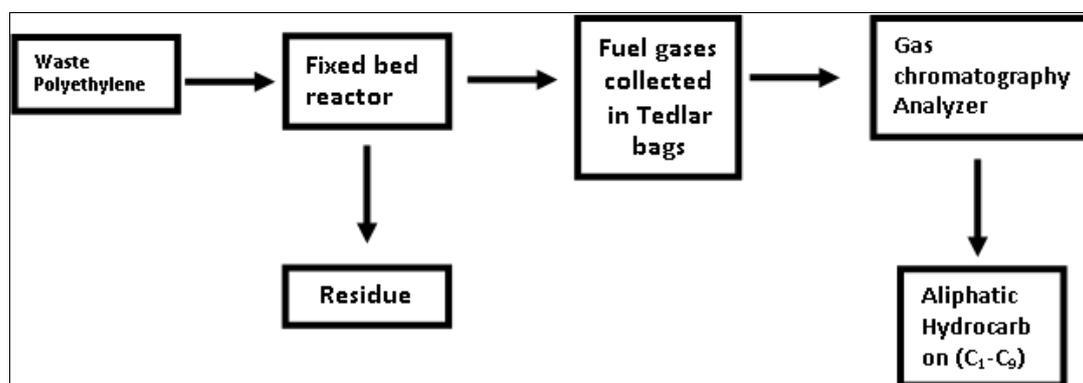


Fig 1: Layout of the pyrolysis process

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 by Borsodi and his colleagues [12] with slight modifications. The sample (polymer material 200 g) was placed at the bottom while the catalyst material was arranged in sandwich layers within the polymer sample as described by Nguamo and colleagues [13]. 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 spent NHU 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

The pyrolysis of waste LDPE was done at 150 °C and 250 °C under the effect of spent naphtha hydro heating unit (NHU) catalyst first with catalyst/sample ration of 1.8. The result obtained from the chromatographic analysis is presented in Table 1. From the results, the total concentration of gases obtained when the gases were collected at 150 °C was 109.8282 while the total concentration of gases obtained at 250 °C yielded 53.1022

ppm. This implies that the total concentration of gases decreased with increase in temperature. The catalyst was seen to be more active at the beginning of the reaction but then probably became deactivated towards the end of the reaction. This indicates that the effect of the catalyst on the yield and distribution of the product became less significant with increasing temperature. This is in agreement with results presented by Aguado *et al.* [14].

Table 1: Composition of gasses obtained from catalytic pyrolysis of waste LDPE at 150 °C and 250 °C using spent 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	0.6859	0.2925
C ₂	n-Ethane	0.0188	0.0057
C ₃	n-Propane	2.7688	2.4227
C ₄	n-Butane	5.3753	Nil
C ₅	n-Pentane	42.2676	43.5146
C ₆	n-Hexane	0.0068	0.0005
C ₇	n-Heptane	12.5493	Nil
C ₈	n-Octane	8.9557	0.0299
C ₉	n-Nonane	37.2053	6.8364
Total		109.8282	53.1022

Similarly, results obtained from pyrolysis of LDPE at 150 °C and 250 °C using spent catalyst/sample ratio of 1:16 gave a total concentration of 88.1075 and 56.1038 ppm respectively (Table 2). This indicates that the gases recovered from pyrolysis of waste LDPE under the

influence of spent NHU catalyst decreased with increasing in temperature. It became obvious that at the start of the reaction, the effect of the catalyst was more potent but then dropped towards the end giving lower concentrations at 250 °C [15, 16].

Table 2: Composition of gasses obtained from catalytic pyrolysis of waste LDPE at 150 °C and 250 °C using spent 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	0.3080	0.4000
C ₂	n-Ethane	0.0332	0.0052
C ₃	n-Propane	40.8841	2.3643
C ₄	n-Butane	15.0008	Nil
C ₅	n-Pentane	Nil	38.4605
C ₆	n-Hexane	0.0075	0.0025
C ₇	n-Heptane	5.9649	Nil
C ₈	n-Octane	7.8634	2.5574
C ₉	n-Nonane	18.0457	12.3140
Total		88.1075	56.1038

Generally, the catalytic pyrolysis with waste LDPE, total higher concentrations were obtained at 150 °C with the reaction which took place using catalyst/sample ratio of 1.8. It became obvious that the effect of the product was more pronounced at lower temperatures. This is an indication that the spent NHU catalyst though regenerated, lead to faster cracking reactions leading to smaller residence time, [17]. 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 C₅ 42.2676; C₉ 37.2053 ppm and C₅ 43.5146; C₉ 6.8364 ppm respectively.

On the other hand, as can be seen in Table 2 above, the most dominant components observed at 150 °C and 250 °C using catalyst/sample ratio of 1.16 gave the most dominant components in C₃ 40.8841; C₉ 18.0457 ppm and C₅ 38.4605; C₉ 12.3140 ppm respectively.

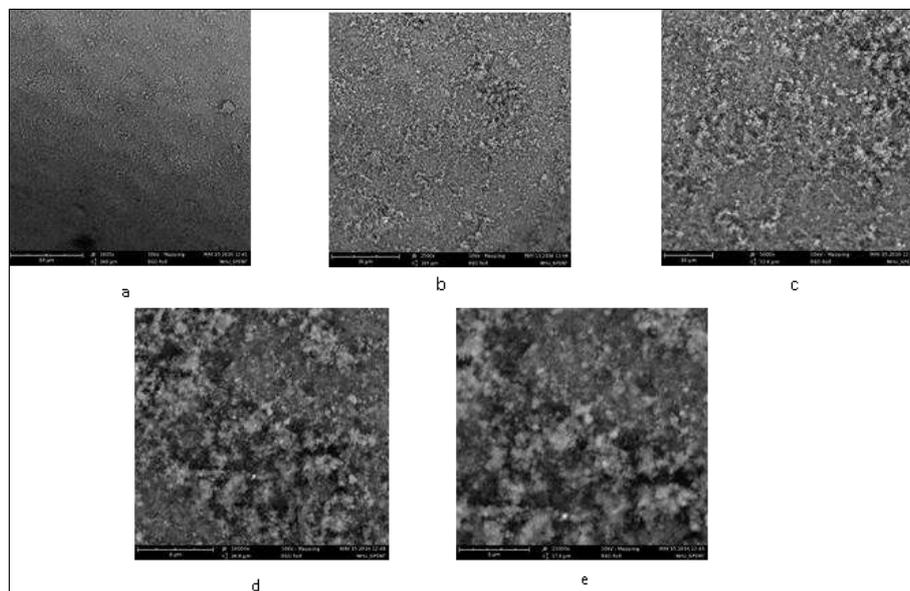


Fig 2: SEM image of Spent NHU catalyst at: (a) 1,000 x (b) 2,500 x (c) 5,000 x (d) 10,000 x (e) 15,000 x

The catalyst pyrolysis of PET using catalyst/sample ratio of 1.8 given in Table 3 below gave the most dominant components in C₅ 64.9952; C₄ 14.1152 ppm and C₁ 7.8996; C₅ 29.4627 ppm for the gases collected at 150 °C

respectively. Generally, with the catalytic pyrolysis of waste PET the total higher concentration was observed in the reaction which occurred using catalyst/sample ratio of 1.8 at 250 °C.

Table 3: Composition of gasses obtained from catalytic pyrolysis of waste PET at 150 °C and 250 °C using spent 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	1.4292	75.8996
C ₂	n-Ethane	0.0088	0.0121
C ₃	n-Propane	3.8626	14.9056
C ₄	n-Butane	14.1152	Nil
C ₅	n-Pentane	64.9952	29.4627
C ₆	n-Hexane	Nil	0.0009
C ₇	n-Heptane	7.0970	5.3086
C ₈	n-Octane	Nil	6.7426
C ₉	n-Nonane	4.8668	Nil
Total		96.3748	140.4273

Pyrolysis of high density polyethylene HDPE was also done under the same conditions of temperature (150 °C and 250 °C) using catalyst /sample ratio of 1.8, Table 4. The total concentration of 81.6393 and 49.0464 ppm were obtained at 150 °C and 250 °C respectively. Thus implies that the concentration of gases decreased with increasing

temperature. This means that the effect of the catalyst on the yield and distribution of the product became less significant with increasing temperature. This agrees with results presented by [18] when they carried out pyrolysis reaction of the HDPE using zeolite catalyst.

Table 4: Composition of gasses obtained from catalytic pyrolysis of waste PET at 150 °C and 250 °C using spent 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	4.1822	0.4509
C ₂	n-Ethane	0.0147	0.0056
C ₃	n-Propane	8.9977	2.4416
C ₄	n-Butane	Nil	Nil
C ₅	n-Pentane	46.1324	43.4364
C ₆	n-Hexane	0.0006	0.00
C ₇	n-Heptane	4.6415	Nil
C ₈	n-Octane	9.8688	3.5933
C ₉	n-Nonane	7.3934	12.5673
Total		81.2315	62.4957

Waste PET samples were also pyrolysis at 150 °C and 250 °C under the influence of spent NHU catalyst. Comparative composition of the gases evolved as analyzed using a gas

chromatogram gave a total concentration of 96.3748 and 140.4273 ppm respectively. With the reaction which occurred using catalyst/sample ratio of 1.8 and results are

presented in Table 3. This shows that the gas concentration increased slightly with increase in temperature. High temperature supports cleavage of bond and thus speed up the reaction thereby lowering the reaction time [19,20]. On the other hand, results obtained from pyrolysis of PET at 150 °C and 250 °C using catalyst/sample ratio of 1.16 gave a total concentration of 81.2315 and 62.4957 ppm respectively and results are presented in Table 4. This implies that the total concentration of gases decreased with increasing temperature. This could be as a result of deactivation of the catalyst during the pyrolysis reaction because, the spent NHU catalyst is expected to show diminishing activity since

coke formation is a common problem with most catalyst [21]. Generally, the catalyst pyrolysis with HDPE, total higher concentration was obtained at 150 °C with the reaction which took place using catalyst/sample ratio of 1.8 (Table 5). The pyrolysis reaction of HDPE at 150 °C and 250 °C using catalyst/sample ratio of 1.8 gave the most dominant components in C₅ 47.1888; C₉ 19.2311 ppm and C₅ 30.9888 ppm respectively. On the other hand, the most dominant components from the reaction which took place at 150 °C and 250 °C using catalyst/sample ratio of 1.16 were observed in C₃ 11.1071, C₁ 10.0579 and C₅ 30.2583; C₉ 14.0388 ppm respectively.

Table 5: Composition of gasses obtained from catalytic pyrolysis of waste HDPE at 150 °C and 250 °C using spent 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	0.8096	0.7014
C ₂	n-Ethane	0.0102	0.0049
C ₃	n-Propane	3.1515	1.7377
C ₄	n-Butane	Nil	Nil
C ₅	n-Pentane	47.1888	30.2987
C ₆	n-Hexane	0.0033	0.0022
C ₇	n-Heptane	5.0052	Nil
C ₈	n-Octane	6.2397	2.3127
C ₉	n-Nonane	19.2311	13.9888
Total		81.6393	49.0464

Similarly, the reaction which took place using catalyst/sample ratio of 1.16 as shown in Table 6 yielded results of 48.8789 and 53.8048 ppm as the total concentration of gases collected at 150 °C and 250 °C

respectively. This became obvious that the total concentration of gases increased slightly with increasing temperature.

Table 6: Composition of gasses obtained from catalytic pyrolysis of waste HDPE at 150 °C and 250 °C using spent 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	10.0579	5.4017
C ₂	n-Ethane	3.3649	0.0050
C ₃	n-Propane	11.1071	1.7660
C ₄	n-Butane	6.5796	Nil
C ₅	n-Pentane	5.8765	30.2583
C ₆	n-Hexane	4.6244	0.0023
C ₇	n-Heptane	0.1591	Nil
C ₈	n-Octane	6.9844	2.3327
C ₉	n-Nonane	0.1230	14.0388
Total		48.8769	53.8048

Generally, the spent NHU catalyst has high activity for hydrocarbon cracking reactions and selectivity to non-aromatic hydrocarbons which evident in all the results from the samples [22]. The carbon atoms obtained from the analysis of gases are aliphatic in nature which is in agreement with the expectation that the bimodal pure size distribution and mild properties of the NHU catalyst would allow the formation of more [23]. The spent NHU catalyst was expected to show diminishing activities since coke formation is a common problem with most catalysts. This could have been the reason for the drop in the total concentration of the gases in the reactions which took place at 250 °C.

Conclusions

Useful fuel gases were obtained from catalytic cracking of LDPE, PET and HDPE with the effect of spent NHU catalyst. The highest total concentration of 140.4273 ppm was observed in PET for the reaction which occurred at 250

°C using catalyst/sample ratio of 1.8. The total yields as obtained from the catalytic pyrolysis process gave results in the increasing order: PET>LDPE>HDPE. The gas yield increased generally with increase in temperature and in every reaction, the component C₅ was observed to be one of the highest in all the three samples. The catalyst has shown high activity for hydrocarbon cracking reactions with selectivity for hydrations within the range of C₁ – C₉ and this is seen in all the three samples. The pyrolysis of these waste polyethylene materials has shown that instead of constituting a menace to the society, it could serve as an energy source.

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