



Useful Products from Waste Polyethylene Terephthalate via Low Temperature Catalytic Pyrolysis

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Abstract Low temperature pyrolysis of polyethylene terephthalate (PET) was studied by adapting pressure cooking pot of height 30.00 cm with an internal diameter of 31.50 cm. The pyrolysis reaction was carried out with and without the influence of catalyst. The gases from the pyrolysis were collected in Tedlar bags and analysis was done using a Buck 530 Gas chromatogram. Results showed the total yield of gases for PET under the zeolitic effect at temperatures of 150 °C and 250 °C using catalyst/sample ratio of 1:8 to be 711.3965 ppm and 81.6068 ppm. The corresponding values obtained at 150 °C and 250 °C using catalyst/sample ratio of 1:16 were 704.8075 ppm and 699.0064 ppm. In the absence of the catalyst, aliphatic hydrocarbons within the range of 52.3644 ppm and 72.3695 ppm at 200 °C and 350 °C respectively, were obtained. The fuel gases revealed mainly C₁ – C₁₀ aliphatic hydrocarbon which can be fractionated into hydrocarbon gases (C₁-C₄), gasoline range gases(>C₇) and organic solvents (C₅-C₇).

Keywords Pyrolysis, Polyethylene terephthalate, Aliphatic hydrocarbon, zeolite

Introduction

Consumption of plastic has increased over the years and the concern with their waste generation too, because of this many studies have been done with the aim to recover or recycle the waste. Pyrolysis has been effective compared to other disposal methods, because it can reuse the energy and the raw materials contained in those waste, thereby reducing the environmental impacts caused by inadequate disposal of these plastic [1].

Thermal cracking or pyrolysis involves the degradation of polymeric materials by heating in the absence of oxygen to produce lighter hydrocarbons. The process which is usually conducted at high temperatures results in the formation of a carbonized char and a volatile fraction that may be separated into condensable hydrocarbon oil and non-condensable hydrocarbon oil. In this type of endothermic process due to the low thermal conductivity of polymers, there is a need for high temperatures which results high expenditure on energy. In order to decrease this energy, catalysts are used. Catalytic cracking of plastic wastes takes place at much lower energy consumptions and higher conversion rates [2].

The catalysts used in the catalytic degradation are solid acids such as zeolites. This type of degradation involves production of the intermediate carbenium ion by hydrogen transfer reactions and zeolites used favour these reactions due to their acid sites that help in the process of breaking the polymer macromolecules. This breaking process begins on the surface of the zeolite, because the polymer needs to be broken into smaller molecules before entering the internal pores of these solids due to the small size of their pores. Zeolites have specific molecular pores to catalytic reactive sites as well as growth of the final products within such pores is limited by its size [3].



The acidity of their active sites and its crystalline microporous structure (textural properties) favour hydrogen transfer reactions as mentioned earlier thereby making them suitable for obtaining high conversions of gas at relatively low temperatures [4,5]. The catalyst pore size and acidity as earlier mentioned are important factors in the catalytic cracking of polymers [6]. Generally, the level of cracking of polymers in polyolefin pyrolysis increases the number of acidic sites. Thus, it is known that the zeolite catalyst achieve higher conversions than non zeolitic catalysts because of these acidic sites [1].

This work was designed to carry out pyrolysis of PET with and without the effect of zeolite varying the temperature and catalyst/sample ratio in order to monitor the quantity of gases evolved.

Materials and Methods

Collection of Sample and Preparation

Polyethylene terephthalate (PET) waste was collected around refuse dumping grounds within Makurdi town, Benue State of Nigeria. The samples were thoroughly washed with detergent and properly rinsed with de ionized water to remove dirt, sandy particles and other impurities adhering to the sample. The clean PET bottles were pulverized into smaller bits to increase the surface area. The zeolite catalyst (X-23) employed for this work is a Sigma Aldrich company product and is shown by analysis to be composed of aluminium and silicon. Scanning electron microscopy (SEM) images of the zeolite catalyst were obtained at magnifications of 1000 ×, 2500 ×, 7500 ×, 10000 ×, and 15000 × respectively. From the SEM images it was deduced that the zeolite catalyst particle range within, SEM was combined with atomic absorption spectrometry (AAS) in the detection of the metal composition and analysis indicated the presence of aluminium (6.3010 ppm) and silicon (0.7220 ppm) metals.

Experimental Procedures

A pressure pot made of stainless steel of height 30 cm with an internal diameter of 31.5cm was adapted for this reaction. 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 a sand bath made of iron sheets to properly retain heat. The reactor was fitted in the sand bath heated with three Mekker burners in order to obtain the required temperatures. The reaction temperature of the batch reactor was collection by means of a thermocouple. Tedlar gas sampling bags were used for collection of evolved gases. The gases once collected were sent to a gas chromatograph for analysis of collected gaseous products.

Thermal Cracking of PET

1.5 kg of PET samples were shredded and stuffed in the reactor and heated for about 3 hours until the temperature reached 350 °C. The reaction temperature was monitored and controlled by means of a thermocouple. The gases started evolving after 1_{1/2} hours into the reaction and this was evident as the tedlar gas sampling bags began to swell (at a temperature of about 120 °C), the gases which were collected in labeled tedlar bags were kept for analysis.

Catalytic Cracking of PET

200 g of the sample was taken and heated with the effect of the catalyst. The catalyst was in the ratio of 1:8 and 1:16. In the catalytic reaction, the sample (polymer material) was placed at the bottom while the catalyst material was arranged in sandwich layers within the polymer sample [7]. The reactor was covered and then heating commenced, after 30 minutes into the reaction (at 120 °C) evolution of gases started slightly after 1_{1/2} hours at about 250 °C the system was shut down. The gases which were collected at 150 °C and 250 °C in labeled tedlar gas sampling bags were then analyzed. The system was allowed to cool down before the reactor opened. The residue after each run was collected and weighed.

Gas chromatographic Analysis

The gaseous products obtained from pyrolysis of HDPE with and without the effect of catalysts were characterized using a BUCK 530 gas chromatograph and HP-88 column (10 m/0.25 mm thickness). Injection volume was 10 µL with helium as mobile phase and flame ionization detector (FID), injection and detection temperatures were 250 °C and 280 °C respectively.



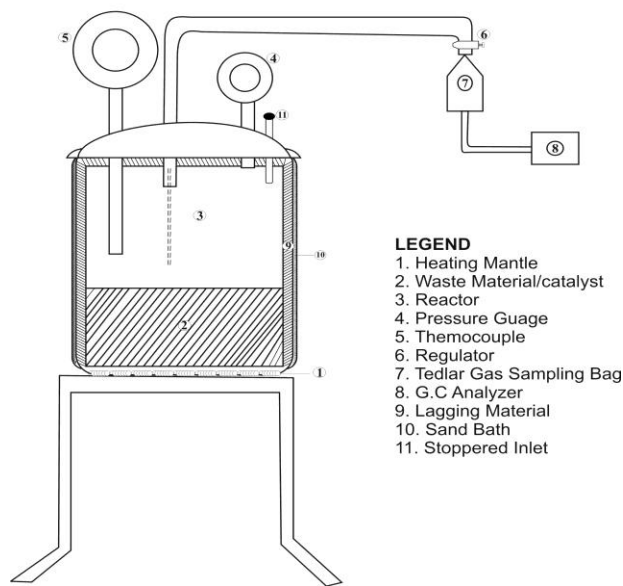


Figure 1: Layout of the process

Gas chromatographic Analysis

The gases obtained from pyrolysis of PET with and without the effect of catalyst were characterized using a buck 530 Gas chromatograph. Analyses which produced peaks were identified as aliphatic hydrocarbons were within the carbon number range of C₁-C₁₀.

3. Results and Discussions

Polyethylene terephthalate waste used for this reaction were bottles used in packaging drinking water and the pyrolysis was carried out without the effect of catalyst. Comparative composition of the gases evolved from pyrolysis of waste PET at 200 °C and 350 °C, the results are presented in Table 1 and Fig 2.

Table 1: Composition of gases obtained from pyrolysis of PET at 200 °C and 350 °C after heating for 3 hours.

Component	Organic Compound	Reaction at 200 °C Concentration (ppm)	Reaction at 350 °C Concentration (ppm)
C ₁	n- Methane	3.6671	4.2408
C ₂	n- Ethane	5.4876	8.4525
C ₃	n- Propane	11.2146	16.5000
C ₄	n- Butane	3.6394	5.4494
C ₅	n- pentane	5.8271	5.7924
C ₆	n- Hexane	4.3205	10.4111
C ₇	n- Heptane	0.9436	1.8864
C ₈	n-Octane	12.2607	13.1740
C ₉	n- Nonane	5.0937	6.4632
Total		52.3644	72.3695

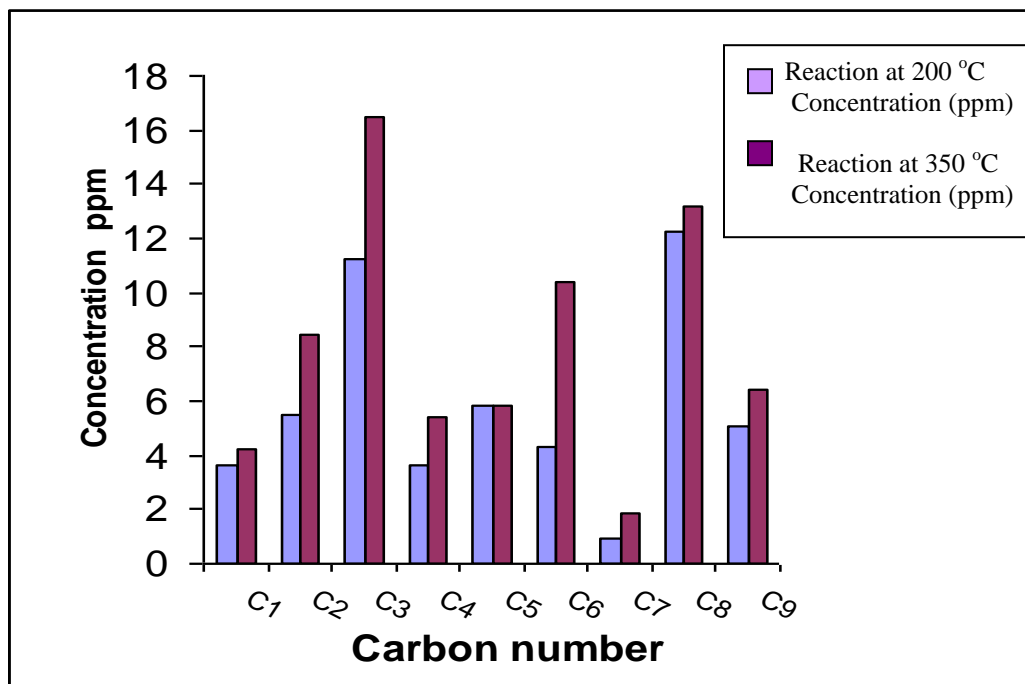


Figure 2: Composition of gases obtained from pyrolysis of PET at 200 °C and 350 °C after heating for 3 hours

From these results, it can be seen that the total concentrations of gases obtained at 350 °C were higher than the gases obtained at 200 °C. This increase in gas yield could probably be due to the rate of main chain sigma bond cleavage reactions in more thermally energetic high temperature environments. Also, the growing yield of gas could be caused by the difference in stability of polymer chains, therefore at 350 °C, the carbon-carbon bonds of the PET cracks more rapidly than at lower temperatures thus resulting to high yields. This result agrees with results obtained by Ammar and Sawson, 2009 [8] who worked on pyrolysis of plastic materials for the production of fuel like liquid hydrocarbons.

The pyrolysis reaction which was conducted at 200 °C gave the highest compositions in C₂ 5.4876 ppm; C₃ 11.2146 ppm; and C₈ 13.1740 ppm. At 350 °C the highest compositions were observed in C₂ 8.4245 ppm; C₃ 16.5000 ppm; C₆ 10.4111 ppm and C₈ 13.1740 ppm. It is observed that the C₂ carbon atom is one of the dominant gases obtained from gases obtained the structure and degradation pattern of polyethylene since it is built up of C₂ monomers [9].

PET waste was pyrolysed at 150 °C and 250 °C under the effect of zeolite first at a ratio of 1:8.

The result of the gas chromatographic analysis represented in Table 2 and Fig 3.

Table 2: Composition of gases obtained from catalytic pyrolysis of waste PET using zeolite catalyst with catalyst / sample ratio of 1: 8 after heating for one and half hours.

Component	Organic Compound	Reaction at 150 °C Concentration (ppm)	Reaction at 250 °C Concentration (ppm)
C ₁	n- Methane	2.0733	2.3317
C ₂	n- Ethane	233.2564	17.2026
C ₃	n- Propane	43.2333	10.7892
C ₄	n- Butane	5.2896	5.0935
C ₅	n- pentane	40.3589	2.3057
C ₆	n- Hexane	13.4428	13.5524
C ₇	n- Heptane	87.2049	16.2553
C ₈	n-Octane	186.7902	14.0762



C ₉	n- Nonane	89.2231	Nil
	n- Decane	10.5270	Nil
Total		711.3965	81.6068

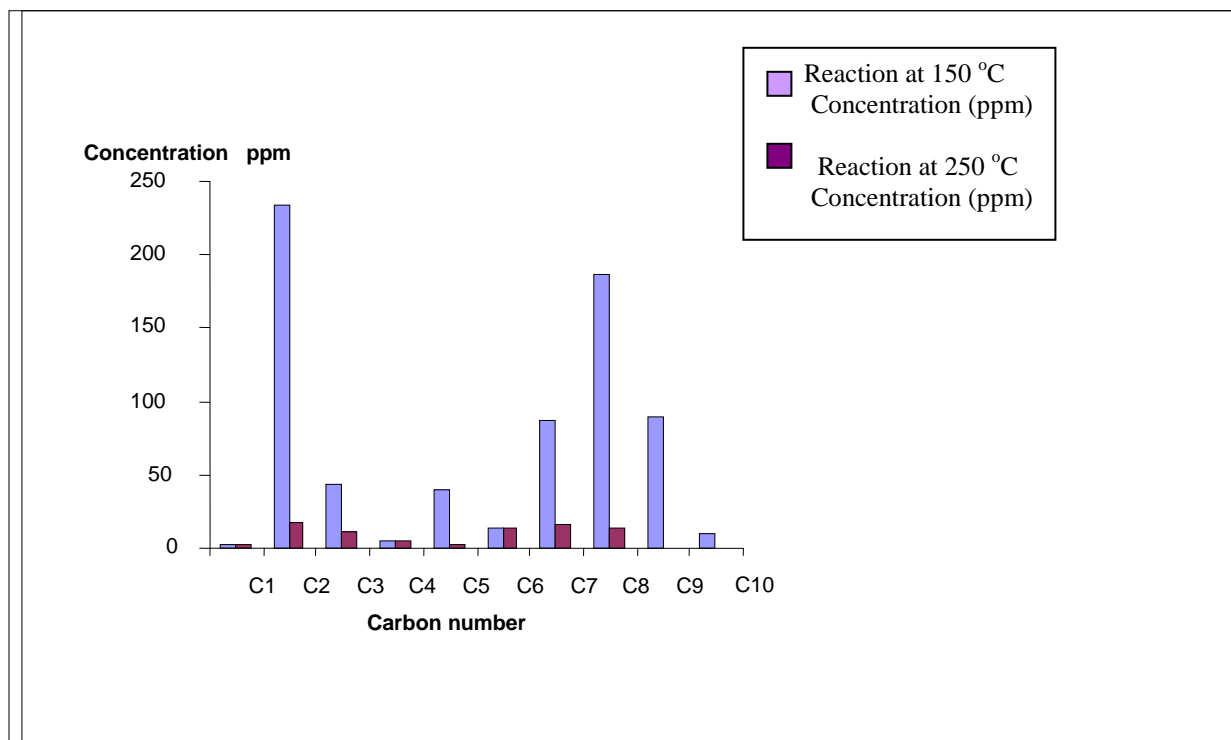


Figure 3: Composition of gases obtained from catalytic pyrolysis of waste PET using Zeolite catalyst with catalyst to sample ratio of 1:8 after heating for 1 $\frac{1}{2}$ hours

From the result it is observed that the total concentration of gases obtained from the reaction at 150 °C and 250 °C was 711.3965 ppm and 81.6068 ppm respectively. The highest components from the results were observed in C₂ 233.2564 ppm; C₃ 43.2333 ppm; C₅ 40.3559 ppm, C₇ 87.2049 ppm; C₈ 16.2555 ppm; C₉ 14.0792 ppm; for all the gases collected at 250 °C. It can be deduced from these results that conversion increased catalyst loading as the effect of higher temperatures did not increase the concentration of the gases.

Table 3: Composition of gases obtained from catalytic pyrolysis of waste PET using zeolite catalyst at 150 °C and 250 C° with catalyst / sample ratio of 1: 16 after heating for 1 $\frac{1}{2}$ hours.

Component	Organic Compound	Reaction at 150 °C Concentration (ppm)	Reaction at 250 °C Concentration (ppm)
C ₁	n- Methane	2.7567	3.1589
C ₂	n- Ethane	299.6780	230.3373
C ₃	n- Propane	42.7923	39.3339
C ₄	n- Butane	5.1978	4.5789
C ₅	n- pentane	40.1683	38.1841
C ₆	n- Hexane	13.3889	13.0448
C ₇	n- Heptane	85.9695	85.6750
C ₈	n-Octane	184.0711	184.4313
C ₉	n- Nonane	89.1631	89.0616
C ₁₀	n- Decane	111.6218	11.0616
Total		704.8075	699.0064

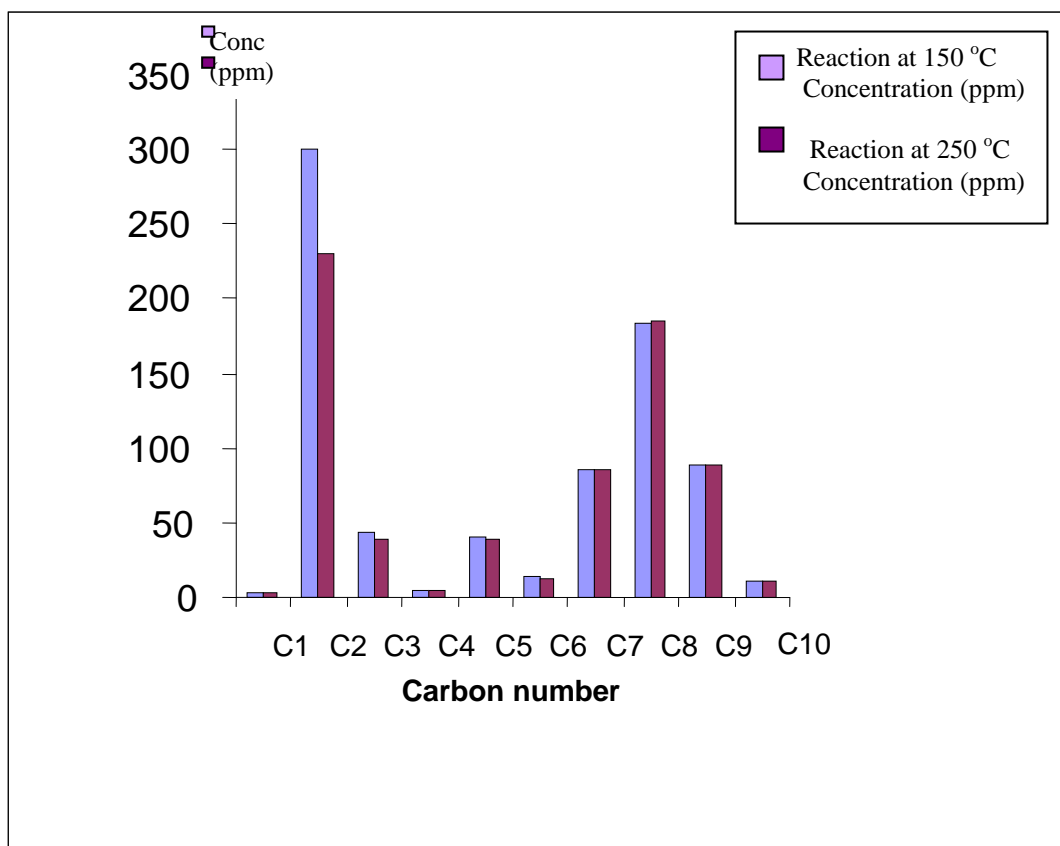


Figure 4: Composition of gases obtained from catalytic pyrolysis of waste PET using zeolite catalyst at 150 °C and 250 °C with catalyst to sample ratio of 1:16 after heating for 1½ hours

Result obtained from pyrolysis PET at 150 °C and 250 °C using catalyst/sample ratio of 1:16 gave a total concentration of 704.8075 ppm and 699.0064 ppm respectively. The result is presented in Table 3 and Fig 4. This is an indication that the total gas yields decreased slightly with increase in temperature. The result of the gas sample analysis obtained at 150 °C revealed that the dominant components were observed in C₂ 229.6780 ppm; C₃ 42.7923 ppm; C₅ 40.1683 ppm; C₈ 184.0711 ppm and C₉ 89.1631ppm. At 250 °C, the dominant compounds were C₂ 230.3373 ppm; C₃ 39.3339 ppm; C₅ 38.1841 ppm; C₇ 85.6750ppm and C₈ 89.0616ppm.

Generally, catalytic reactions under the influence of zeolite using PET yielded high concentration of hydrocarbon gases. This is clear indication that the zeolite catalyst has shown to be effective in improving the quantity of product obtained from pyrolysis of polyethylene. The acidity of the active sites and the crystalline microporous structure of the zeolites catalyst favoured hydrogen transfer reactions thereby making them suitable for obtaining higher conversion at relatively lower temperature [10,11].

Conclusion

Gaseous fuels were produced from thermal and catalytic cracking using zeolite catalyst had lower degradation temperature and faster gaseous product generation rate than thermal cracking. The gas chromatographic analysis result showed the compositions of gaseous products of thermal cracking to contain only aliphatic hydrocarbons in the range of C₁ – C₉ while the catalytic cracking revealed hydrocarbon within the range of C₁ – C₁₀. This study demonstrated that thermal catalytic cracking are effective methods that could be used to achieve reasonable



conversion of waste plastics to useful fuel products. It will help in controlling environmental and resources problems posed by plastic waste disposal and the burden on the environment will be reduced.

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