



Urban Mining of Fuel Gases via Low Temperature Pyrolysis of Post-Consumer High Density Polyethylene Wastes

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ABSTRACT: Low temperature pyrolysis of high density polyethylene (HDPE) wastes was studied by adapting a cylindrical 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 catalysts. The gases evolved during the pyrolysis were collected in Tedlar bags and analysis was done using a Buck 530 Gas chromatograph. Results when the pyrolysis was without catalyst, showed aliphatic hydrocarbons in the range of C₁ – C₁₀ with a total concentration of 87.0114 ppm and 93.9733 ppm at 200 °C and 350 °C respectively. The pyrolysis was repeated under catalytic influence of zeolite using catalyst/sample ratios of 1:8 and 1:16 at 150 °C and 250 °C. Results showed that the total yield of gases for HDPE under the zeolitic effect at temperatures of 150 °C and 250 °C using catalyst/sample ratio of 1:8 to be 159.4613 ppm and 394.4499 ppm respectively. The corresponding values obtained at 150 °C and 250 °C using catalyst/sample ratio of 1:16 were 595.8016 ppm and 724.0983 ppm respectively. The hydrocarbon gases revealed C₁ – C₁₀ aliphatic hydrocarbons which can be fractionated into fuel gases (C₁ – C₄), gasoline range gases (>C₇) and organic solvents (C₅ – C₇).

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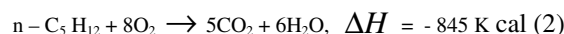
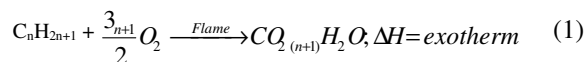
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Ethylene, with crude oil and natural gas as precursors, is one of the six major petrochemical industrial raw materials. It can be polymerized into high or low density (HDPE or LDPE) polyethylenes. These differ slightly in molecular structure depending on operating conditions, particularly pressure. Both HDPE and LDPE are thermoplastic, tough with a slightly waxy feel, and widely used for the manufacture of domestic wax, bottles, packing films and all kinds of industrial components using various methods of moulding.

Current research efforts however have tended to tilt quite heavily towards the precursor crude oil and natural gas by way of exploration Orij and Ekpeta (2016), refining Hossien and Mohammed (2017), Badmus *et al.*, (2013), fractionating Nwadinigwe *et al.*, (2016), analysis Nwadinigwe and Alumona (2017), and environmental aspects Ite and Ibok (2013) with attendant waste proliferation.

This work focuses on low temperature pyrolysis of post-consumer high density polyethylene wastes in order to recovery fuel gases from them.



The enormous energy evolved is the reason why alkanes are used as fuels.

Detailed chemical mechanism for the conversion of LDPE and HDPE to hydrocarbons is still a matter of conjecture. Loss of hydrogen atom followed by hemolytic β -fission of a C- C bond could be a possible pathway, Nwadinigwe, (2012).

MATERIALS AND METHODS

Collection and preservation of Materials: The high density polyethylene (HDPE) waste which consisted of post-consumer pharmaceutical, cosmetic, and

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yoghurt bottles, was collected from refuse dumping sites around Makurdi town, Benue State of Nigeria. The samples were washed thoroughly using detergents and rinsed properly with de-ionized water, then dried to remove moisture. The dried samples were then reduced to smaller bits to increase the surface area as described by Abdulkareem *et al.*, (2014). The zeolite catalyst employed for this work was a Sigma Aldrich Company product and is shown by analysis to be composed of aluminum and silicon. Scanning electron microscopy (SEM) images of the zeolite catalyst were obtained at magnifications of 1000 x, 2500 x, 4000 x, 7,500 x, 10000 x, and 15000 x respectively. From the SEM images it was deduced that the zeolite particle size range within 5 μ -80 μ . In further characterizing the zeolite catalyst SEM was combined with Atomic Absorption spectrometry (AAS) in the detection of the metal composition. Analysis indicated the presence of aluminum 6.301 ppm and silicon 0.722 ppm metals.

Experimental procedures: A Presto pressure cooking pot made of stainless steel (with dimensions of height 30.00 cm and an internal diameter of 31.50 cm) was converted to a fixed bed reactor and adapted for the reaction Smith (1993). 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 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. The collected gases were sent to a gas chromatograph for analysis.

Low Temperature Thermal cracking of HDPE: 1.5 Kg of the HDPE samples were crushed 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 1½ hours into the pyrolysis and this was evident as the tedlar gas sampling bags began to swell (at a temperature of about 120 °C). The gas samples were collected at 200 °C and 350 °C and after the evolution of gases, the system was allowed to cool before the reactor was opened. The residue in the reactor was collected and weighed. The gases which were collected in labeled tedlar gas sampling bags were kept for gas chromatographic analysis. This was done according to the method described by Ademiliyi and Adebayo (2007).

Catalytic Cracking of HDPE: Two catalyst/sample ratios (1:8 and 1:16) were investigated in the catalyzed pyrolysis as described by Osueke and Ofondu (2011)

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 Abdulkareem *et al.*, (2014). The reactor was covered and heating commenced. After 30 minutes into the reaction (at 120 °C) evolution of gases started slightly and after 1½ 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 allowed to cool down before the reactor was opened. The residue after each run was collected and weighed.

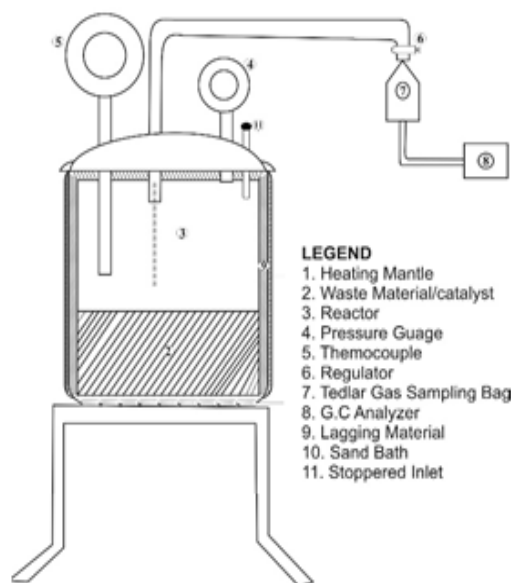


Fig. 1 layout of the process

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 thin thickness). Injection volume was 10 μ L with helium as the mobile phase and flame ionization detector (FID), injection and detection temperatures were 250 °C and 280 °C respectively Gary (1979).

RESULTS AND DISCUSSION

The high density waste polyethylene employed for this work consisted of a mixture of polyethylene pharmaceutical, cosmetic, and yoghurt waste bottles. The weight obtained at the end of the pyrolysis reaction was 900 g while 110 g and 120 g were obtained at the end of the catalytic pyrolysis at catalyst/sample ratios of 1:8 and 1:16 respectively.

Comparative composition of the gases evolved from pyrolysis of waste HDPE at 200 °C and 350 °C is represented in Fig 2. Detailed chemical mechanism for the conversion of HDPE to low molecular weight

hydrocarbons is still a matter of conjecture. Loss of a hydrogen atom followed by the homolytic β -fission of a C – C bond could be a plausible pathway Nwadinigwe (2012).

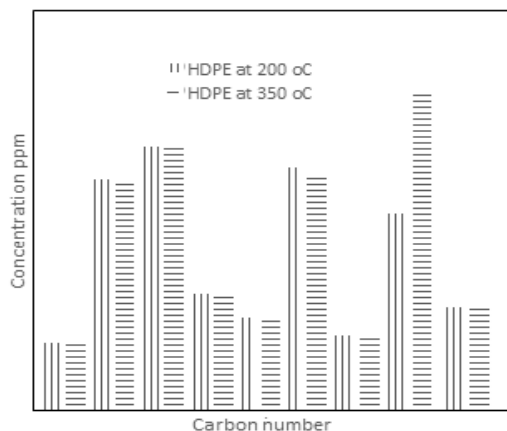


Fig 2: Composition of gas obtained from pyrolysis of waste HDPE at 200°C and 350°C

It is observed from the results that the total yield of gases obtained at 350 °C is higher than the total yield obtained at 200 °C. This shows that the temperature affects both the reaction time and yield of liquid, as well gaseous products. High temperature thus speeds up the reaction and lowers the reaction time Sacchin and Singh (2011).

From the pyrolysis reaction carried out at 200 °C, the prominent percentage composition of carbon atoms were observed in C₂ 14.4367 ppm; C₃ 16.5059 ppm; C₄ 7.2777 ppm; C₆ 15.1965 ppm and C₈ 12.3268 ppm. On the other hand results of pyrolysis reaction performed at 350 °C gave the prominent composition in C₂ 14.3430 ppm; C₃ 16.4367 ppm; C₆ 14.8305 ppm and C₈ 19.9588 ppm. This result shows that useful gases were obtained via pyrolysis of HDPE at temperatures of 200 °C and 350 °C. The yields of the gases however increased with higher temperature. C₂ carbon atom is one of the dominant components observed. This could be explained with the structure and degradation pattern of polyethylene because it is built up from C₂ monomer Borsidi *et al.*, (2011). In figure 3 is presented the gaseous composition when the catalyst/sample ratio is 1:8. The yield of gases was higher at 250 °C compared with the gases collected at 150 °C. From the results presented in fig 4, the reaction also occurred at 150 °C and 250 °C at catalyst/sample ratio of 1:16, here too the gas yield was higher at 250 °C than what was obtained at 150 °C. It became clear that the effect of the zeolite catalyst on the pyrolysis of HDPE on the yields and distribution of the products were less significant with the increasing temperature,

this is in agreement with results obtained by Miskolczi, (2004).

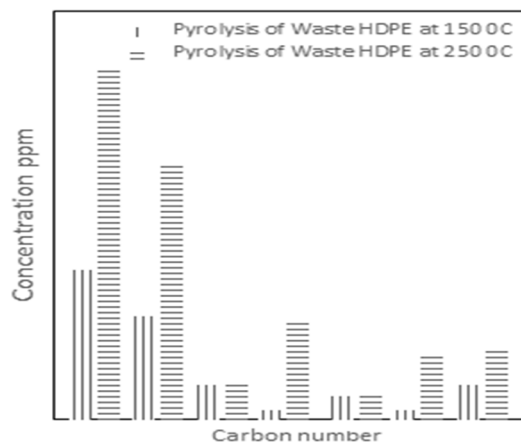


Fig 3: Composition of Gases Obtained From Catalytic Pyrolysis of Waste HDPE at 150 °C and 250 °C Using Catalyst/Sample Ratio 1:8 (Reaction with zeolite catalyst)

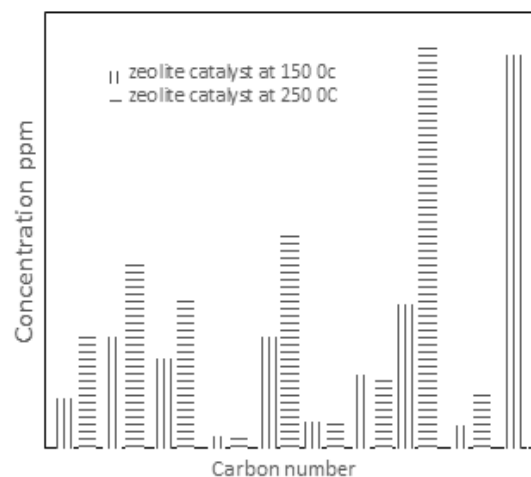


Fig 4: Composition of gases obtained from catalytic pyrolysis of waste HDPE Using zeolite catalyst at 150°C and 250°C with catalyst/sample ratio of 1:16

The composition of gas was analysed by the gas chromatograph and the results are already presented in fig 3 and in fig 4. The dominant components were in C₁ 66.1801 ppm; C₃ 45.2271 ppm; C₄ 15.0015 ppm while in fig 4, the dominant components were observed in C₁ 29.1893 ppm; C₂ 63.6581 ppm; C₃ 51.7032 ppm; C₅ 64.0931 ppm; C₇ 42.4603 ppm; C₈ 82.7655 ppm and C₁₀ 226.0256 ppm. In every case one of the dominant components that was observed is C₂. Its occurrence has already been explained in terms of the structure and degradation pattern of polyethylene because it is built up from C₂ monomers Borsidi *et al.*, (2011). This result shows that lighter hydrocarbon increased in concentrations over what was obtained thermally which is in accordance with the expectation that the catalyst should promote breaking down of

polymer feed to lighter fractions as compared with the pyrolysis reaction without the influence of the catalyst.

From the result it is observed generally that the zeolite catalyst favoured production of gaseous products. This agrees with results obtained by Lin and Yang, (2005) who conducted catalytic reactions of post-consumer polymer waste over fluidized cracking catalyst for production of hydrocarbons. In their result they obtained C₁ – C₃ and C₅ – C₉ hydrocarbons. It can be seen from the results that the total concentration of gases obtained at 150 °C was lower than the total concentration of gases obtained at 250 °C when the results in Fig 3 and Fig. 4 are compared.

This could be explained thus the effect of temperature on the reaction time for pyrolysis of HDPE increases with increase in temperature because high temperature supports the easier cleavage of bonds and thus speeds up reaction. However, HDPE is a long linear polymer chain with low branching and high crystallinity led to high strength properties and thus required time for decomposition. Sacchin and Singh (2011). Also, comparing the total components of gases in Fig 3 and Fig 4, it is obvious that higher yields were obtained in figure 4.

Conclusion: This study demonstrates that low temperature pyrolysis of high density polyethylene whether catalyzed or uncatalyzed is effective method that could allow reasonable conversion of waste polyethylene to useful fuel gases and at the same time reduces the bulk size of the waste. The fuel gases contained mainly aliphatic hydrocarbons which can be fractionated into gaseous fuels, gasoline range products and other organic solvents. The use of low temperature pyrolysis reduced cost by lowering energy input and still generated useful hydrocarbon gases.

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