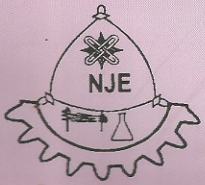
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THERMAL AND CATALYTIC DEGRADATION OF POLYETHYLENE BASED WASTE MATERIALS.

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ABSTRACT

This study investigated the destructive distillation of polyethylene based waste material and to investigate improvements using catalysts. The main procedure employed was to set up a destructive distillation reactor in which Liquefied petroleum gas was used for heating, and the improvements in yield and quality when "Magnasiev 370" used in the fluid catalytic cracking (FCC) unit of the Kaduna Refining and Petrochemical Company (KRPC) and lead sulfide Catalyst on the distillation products. It was discovered that the thermal degradation without catalyst was faster at 450°C than catalytic degradation at 420°C using the FCC Catalyst. The liquid products at the different operating conditions had similar characteristics, in that they all contained products with boiling ranges of gasoline, kerosene and gas oils. It was concluded that catalyst and temperature have prominent role to play in the enhancement of the degradation of polyethylene materials.

Keywords: Destructive Distillation, Polyethylene, Waste Materials, Catalysts.

INTRODUCTION

Used plastics are accumulating in our environment at an alarming rate. They are everywhere strewn along road ways, stuck in trees, and piled up beneath our kitchen sinks. In the rural areas, these bags decrease the productivity of the arable land because they do not rot or turn into compost (Vincent, 2004). Also, despite the common belief that plastic bags decompose and disappear, they actually slowly break down into toxic bits that pollute our oceans, rivers, lakes and soil (Larry 1977). In addition, countless animals, most notably marine mammals, choke to death after mistaking plastic bags for food (Edwards, 2000).

Destructive distillation relates to a process of transformation of a compound or material into one or more substances by heat alone (without oxidation) (Lewis 2005). Many researchers have been looking into how waste can be converted to energy potentials effectively. Catalytic pyrolysis using Y-zeolite and ZSM-5 on polyethylene had been studied (Bagri and Willaims, 2002)

This project is aimed at generating energy potentials from waste polyethylene so as to discourage its combustion as means of disposal, encouraging conservation of non renewable energy resources, in an environmentally acceptable manner. It has been established that fuels from residual substances and biologically regenerating raw materials represent the future of energy development.

This research studied the effects of other cracking catalysts such as Magnasiev 370 (FCC Catalyst) and lead sulfide catalysts, and operating temperatures of 420°C and 450°C on the liquid product yield and quality. Waste pure water sachets were used as the source of waste polyethylene.

MATERIALS AND METHODS

Sample Collection
For the purpose of this research, polyethylene pure water sachets were collected and used as feed.
Sample Preparation
Sorting: Pure water sachets were sorted out manually from other polymer products.
Washing and Drying: The sorted waste sachets were washed with detergent to remove dirt then dried.
Size Reduction and Loading: The plastics were then size reduced before being charged into the reactor.
Destructive Distillation: After the waste polyethylene feed was charged into the reactor, the reactor was then tightened with the clamps, and then connected to the glass condenser, the cooling water was then connected to the condenser for effective condensation of the product before finally putting on the Gas heater (Ademiluyi, 2004)

Temperature, time and product was monitored and recorded throughout the reaction (until there is no more observable product formed).

REACTOR UNIT SET-UP

The reactor unit setup consisted of the following:
1. The Reactor interior was made up of a cylindrical stainless steel material

2.The Reactor Exterior (lag casing) was made of

Galvanized steel.
3. Glass wool was used as the lagging material.
4. Mild steel bars were used as clamps
5. Screws were attached to the clamps
6. Thermometer (,)
7. Thermocouple (,)
8. Thermowell
9. Condenser
10. Cooling water source

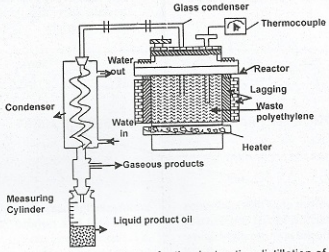


Figure 1: Experimental setup for the destructive distillation of polyethylene

PRODUCT'S PROPERTY DETERMINATION

The following properties were determined:

i) density ()
ii) specific gravity (S.G)
iii) API Gravity
iv) Colour

v) Density Conversions

$$\rho_4^{t} = \rho_4^{20} - \alpha(t-20)$$

$$\rho_5^{15} = \rho_4^{20} + \frac{0.0035}{\rho_4^{20}}$$

where;
ρ_t = Relative density/ specific gravity
α = Thermal expansion coefficient
t = Temperature °C

vi) pH
A pH meter was used to determine the pH of the product.

vii) Conductivity
Using the dip of a conductivity meter, the meter sensor dip was first cleaned and the reading set to zero before it was then interchanged with the sample and the new reading taken in mS (Perry 1984).

vii) Flash and Fire Point
The sample was poured into the sample cup of Pensky-Martens apparatus to the mark of the cup, the gas burner was put on to raise its temperature at a rate of about 3°C per minute, pilot and the test flame was later ignited and the stirrer turned manually until a momentary bluish light flash was seen on the surface. When the oil vapours burn for about 5 seconds the temperature was taken as fire point.

viii) Thermal Properties
Specific Heat
The Bureau of Standard formula;
Specific heat = $\frac{1}{\rho}(0.4024 + 0.00081\,t)$
Specific heat = {[0.355 + 1280 (°API) 10^{-6} + (503 + 1.17 X °API) 32 + 1.8t) 10^{-4}] (0.05 k + 0.41)}
Watson and Fallon also gave;
Specific heat = {(0.045 k 0.233) + (0.44 + 0.01777 k) (1.8t+32)10^{-3} 0.153) X (1.8 t+32)^2 X 10^{-6}}
Where;
k = characterization factor
t = temperature °C

ix) Heat of Combustion
Sherman Kropff gave the relationship;
Heating Value (kJ/kg) = 43,434 + 93.2 9 (API -10) in (Bhaskara 1990), and a corresponding chart given in (Hougen, 1964)

x) Heat of Vapourization
The value was determined from chart of heat of vapourization in appendix of (Hougen, 1964).

xi) Boiling range
This was determined from the true boiling point curve (Figure 2).

RESULTS AND DISCUSSIONS

This section presents the results and discussions from the destructive distillation of the polyethylene based waste materials.

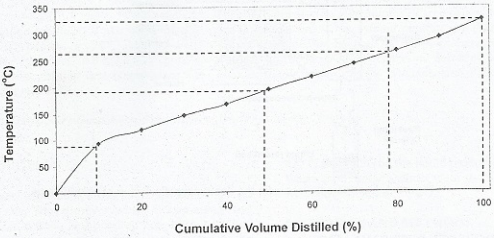


Figure 2: True Boiling Point (TBP) Curve of the Liquid Product

From Figure 2, the mean average boiling point (MABP) was calculated using the formula given in Rao, 1990 as;

$$T_B = \frac{t10 + t20 + t30 + \ldots + t90}{9} = 193.89°C$$

From Figure 2, 10% of the liquid was distilled between 0-90°C, which lies in the light straight run gasoline, while heavy straight run gasoline (90-185°C), kerosine/jet fuel (185-260°C), and gas oil (260-340°C) all correspond to 37%, 33% and 20% respectively of the liquid product distilled.

The mean average boiling point was used to calculate the characterization factor k given by the formula;

$$k = \frac{^3TB(K)}{0.827 \times \text{Specific gravity}} \quad \text{(Rao,1990)}$$

The k value was found to 10.90 which implied that it's constituents were gasoline, kerosene and gas oils.

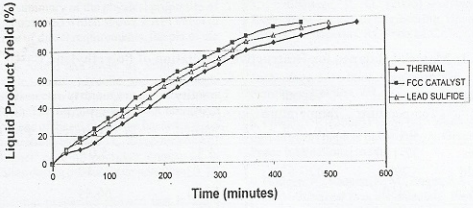


Figure 4: Effects of Reaction Time on yield at 420°C

Figure 4 and 5 are similar in that the reactor temperature was kept constant and FCC catalyst and lead sulfide catalyst were also introduced to see improvements. i.e. Figure 4 shows the reactor temperature kept constant at 420°C while Figure 5 shows its temperature kept constant at 450°C. In the reaction carried out at 420°C, the reaction was fastest with the introduction of FCC catalyst which had a reaction time of 450 minutes followed by the reaction with lead sulfide which took 500 minutes, the reaction without catalyst was the slowest with reaction time of 550 minutes.

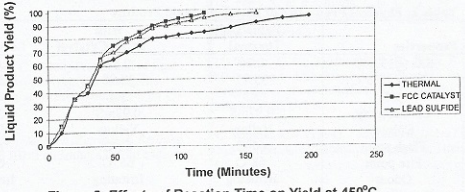


Figure 5: Effects of Reaction Time on Yield at 450°C

There was improvement when the reaction was carried out at 450°C; the reaction with the FCC catalyst was also the fastest with reaction time of 120 minutes followed by the reaction with lead sulfide with reaction time of 160 minutes then the reaction without catalyst with reaction time of 230 minutes.

It was observed in Figure 5 that at 450°C, the reaction without the catalyst, which was the slowest, was even faster that the reaction with the catalyst at 420°C implying that the temperature has a more prominent role to play compared to the two catalysts in the destructive distillation of polyethylene based waste materials at temperatures between 420 and 450°C.

Table 1: Material Balance for Destructive Distillation of Polyethylene Based Waste Materials

Products	Internal Temperature θ_1(°C)	Vapour Temperature θ_2(°C)	Quantity (wt%) Thermal	Quantity (wt%) with FCC Catalyst	Quantity (wt%)with PbS Catalyst
Gases	27-180	27	1.35	5.07	4.80
Liquid	290	42 - 62	21.03	25.12	23.45
Residue	≥450	> 63	75.31	66.44	68.22
Losses			2.31	3.37	3.53
Total			100.00	100.00	100.00

Table 1 shows the material balance for the reaction, the thermal reaction without catalyst had the lowest liquid and gaseous product but the highest residue while with the FCC catalyst, there was high liquid product and gas but lowest residue while the lead sulfide residue had results in ranges between that of thermal and the FCC catalyst.

Table 2: Physical Properties of Distilled Liquid Product

Properties	Value/Units Thermal	with FCC Catalyst	with Lead Sulfide
S.G @15.6°C	0.86	0.83	0.85
API @ 15.6°C	33.17	38.98	34.97
pH	3.5	3.4	3.5
Conductivity	0.97mS	0.98mS	0.98mS
Colour	Yellow	Yellow	Yellow
Flash point	65°C	62°C	63°C
Fire point	68°C	65 °C	66 °C
Odour	Irritating	Irritating	Irritating
Specific heat	0.4826	0.5111	0.4991
k	10.90	11.30	11.04
Hydrogen content	11.50%	12.20%	11.50%
Carbon content	88.5%	87.8%	88.5%
C/H ratio	7.69	7.19	7.69
Heat of combustion	44 425.4766 kJ/kg	45 262.8154 kJ/kg	44 658.0707 kJ/kg
Heat of vaporization	297.7205 kJ/kg	279.1129 kJ/kg	295.3945 kJ/kg
Constituents fractions	Gasoline, kero, gas oils	Gasoline, kero, gas oils	Gasoline, kero, gas oils
Boiling range	42°C-325°C	42°C-325°C	42°C-325°C

Table 2 shows the summary of the physical properties of the liquid product obtained which shows it API value to be within the range of diesel requirements, the pH of the product to be about 3.5
implying that it is acidic and owes its acidity to the presence of formic, acetic, glycolic and malic acids which should be taken care of to prevent gum formation (Totten et al 2003). The flash and fire point are above 62°C are close to those of diesel fuels. Fire hazards can be prevented at temperatures below 60°C. The pour point of 10°C implies higher cost of pumping compared to kerosene or gasoline during product transportation.

The product's thermal properties showed that it had a good potential for energy sources and therefore could be used as an alternative energy source to fossil fuels. Its boiling range which was derived from Figure 2 showed it contained volatile constituents with boiling point up to 325°C.

CONCLUSIONS

1. Temperature has a more significant effect on the rate of degradation than the catalysts.

2. Variation of temperature and the use of catalysts had no significant effect on the products' physical properties.

3. At constant temperatures, the FCC catalyst showed a faster rate of polyethylene degradation than the lead sulfide catalyst.

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