

Catalytic Pyrolysis of Polyethylene Wastes into Liquid Fuel using ZSM-5 as catalyst

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Abstract- Polyethylene waste was converted into liquid fuel in the presence of zeolite ZSM-5 catalyst at various conditions (temperature, residence time catalyst weight) for the study of derived fuel yield. TGA and FT-IR analysis was carried out on the polyethylene sample to describe the thermal properties, as well as change in mass of the sample as a function of temperature and the functional groups present respectively. BET and FT-IR analysis was used to characterize zeolite ZSM-5 catalyst to determine the surface area, pore size and pore volume and to identify the functional groups and their assignment. The surface area, pore size and pore volume of ZSM-5 was found to be 688 m²/g, 6.077 nm and 0.2445 cm³/g respectively. The optimal conditions (temperature, residence time and catalyst weight) obtained for a percentage yield of 79.45 % of liquid fuel was found to be 400 °C, 60 min and 200 g respectively. The effects of temperature, residence time and catalyst weight on the conversion yield into liquid product were examined using Response Surface Methodology (RSM). Performance test analysis carried out on the derived liquid fuel with an API gravity of 49.9 ° revealed that the derived liquid fuel is classified as light crude oil. Fuel converted from plastic wastes using pyrolysis can be effectively used as an alternative energy source which is available, viable and equitable for the economy.

KeyWords: Plastic , wastes, Pyrolysis, Polyethylene, Liquid fuel , pyrolysis, technology

1 INTRODUCTION

Waste disposal problem has instigated attention in the biodegradability of polymers as it pose great danger to human health and quality of our environment. In recent years, due to rapid population growth, industrial growth and urbanization, wastes disposal has become a serious concern globally with plastic wastes forming the bulk of the municipal solid wastes. According to a recent study carried out by the United States Environmental Protection Agency (US. EPA), approximately 48 million tons of plastics wastes are generated in the USA alone [1]. Statistics also showed that approximately 10 % of this plastic wastes is recycled, 25 % is incinerated and the remaining 65 % is dumped in landfills [2]. These conventional methods of disposal of plastic wastes are not eco friendly, harmful to human beings and the environment. Incineration is carried out at high temperature ranging from 700 °C to 1100 °C resulting in the emission or release of hazardous and toxic gases and substances [3]. Land filling is another conventional method of plastic wastes disposal with a challenge of limited space for landfills in many countries [4]. Plastic wastes in landfills become a carbon sink because they are non biodegradable materials that resist microbial attack. Landfills results into environmental harm with a long term threat of contamination of groundwater and soil [5],[6]. These methods of plastic wastes disposal result in air pollution, loss of solid wastes, global warming and it is not cost effective. Expenditure incurred on disposal of plastic wastes throughout the world is around US\$2 billion every year [7]. The challenges and problems of convention methods of plastic wastes management have led to the development of new process technology for plastic wastes management such as pyrolysis.

Pyrolysis is the thermal degradation or breakdown of organic materials at elevated temperature in an oxygen-starved or inert atmosphere. There are two types of pyrolysis; these are thermal and catalytic pyrolysis. This research explores the catalytic degradation of plastic wastes with zeolite ZSM-5 used as the catalyst with emphasis on the liquid fuel. The use of zeolite ZSM-5 will help in reducing the temperature and residence time for the production of liquid fuel. Pyrolysis of plastic wastes yields three value added fuel products, which are solid fuel (char), liquid fuel (oil) and gaseous fuel. Some other advantages of pyrolysis include production of storable and transportable fuel, energy is obtained from renewable sources such as municipal solid wastes and the capital cost is low [8].

2.1 problem statement

Plastic are household materials which have formed an integral part of a modern life. Due to increase in population worldwide, there has been an increase in plastic wastes contributing and posing great hazard to human health and environment. The conventional methods of waste management such as incineration, land filling and recycling leads to the destruction of these resources that could be converted to alternative energy source which are eco-friendly. Converting plastic wastes into fuel using pyrolysis technology seems to be a solution to the menace in disposal of plastic wastes. Moreso, due to the depletion of fossil fuel such as carbon petroleum and natural gas, and increase in population leading to increase in fuel consumption, there is a need for conversion of plastic wastes to serve as an alternate energy

source. Hence, these concerns led to the research area of study

2.2 Final Stage Aim and Objectives

The aim of this study is the Catalytic Pyrolysis of Polyethylene Wastes into Liquid Fuel using ZSM-5 as catalyst. This aim can be achieved through the realization of the following objectives:

1. Characterization of Polyethylene using Thermogravimetric Analysis (TGA) and Fourier Transformed Infrared Spectroscopy (FT-IR) analysis.
2. Characterization of ZSM-5 catalyst using Brunauer Emmet Teller (BET) and Fourier Transformed Infrared Spectroscopy (FT-IR) analysis.
3. To study the effect of operating parameters (catalyst weight, temperature and residence time) on the conversion yield into liquid product using Response Surface Methodology (RSM).
4. To characterize the liquid product by carrying out performance test such as density, specific gravity, API gravity, dynamic viscosity, kinematic viscosity, flash and fire point test, aniline point as well as composition analysis of crude oil to determine the sulphur content.
5. Comparative study of oil derived from catalytic pyrolysis with crude oil.

2.0 METHOD AND PROCEDURES

2.1 Characterization of Polyethylene wastes

Polyethylene wastes sample was characterized using Thermogravimetric Analysis (TGA) and Fourier Transformed Infrared Spectroscopy (FT-IR) to describe the thermal properties, as well as change in mass of the sample as a function of temperature and the functional groups present in Polyethylene respectively.

2.2 Characterization of zeolite ZSM-5 catalyst

Zeolite ZSM-5 catalyst used in this experimental study was characterized using Brunauer Emmet Teller (BET) to analyze the textural characteristics and pore size distribution as well as Fourier Transformed Infrared Spectroscopy Analysis (FT-IR) to analyze the functional groups present in ZSM-5 catalyst

2.3 COLLECTION AND PREPARATION OF SAMPLES

Plastic wastes samples were collected from Gwagwalada municipal, Abuja, FCT in Nigeria and separated into different types of plastics such as polyethylene, polypropylene, polystyrene, polyvinyl chloride and polyethylene terephthalate. The desired plastic wastes in this study is polyethylene due to its good properties such as toughness, flexibility, excellent chemical resistance, ease of processing

and excellent electrical insulation [9]. The samples were physically cleaned and rinsed with water to remove any particulate solids. The washed samples were air dried and stored at room temperature in an air tight dry vessel. The stored samples were shredded into small pieces of 3cm to 5cm size to fit into the reactor and to create higher surface area for pyrolysis [10],[11].

2.2 Cracking of feedstock

For catalytic degradation process of polyethylene, Zeolite ZSM-5 catalyst was used. The shredded samples were fed into the pyrolytic chamber, a batch reactor unit and heat was applied to the reactor with the aid of an electrical heater covering the outside part of the surface of the pyrolytic chamber. Nitrogen gas was introduced into the pyrolytic chamber to create an inert atmosphere, such that polyethylene plastic wastes melt and not burn. The temperature of the pyrolytic chamber was set to a designated temperature (250 - 450 °C), and the electrical heater was turned on afterward at a heating rate of 3 °C/min [12]. The heating was maintained for one hour, the feed vapour passes through the catalytic unit and the smaller hydrocarbons pass through the condenser and get condensed to liquid. Simultaneously, cooling water was kept circulating over the experiment. The condensed liquid is collected in a delivery flask. Figure 2.1 summarize the experimental procedure for the conversion of plastic wastes into fuel using pyrolysis technology in the presence of catalyst.

2.3 Optimization of process parameters

The experiment was carried out by loading 500 g of plastic wastes into the pyrolytic chamber (reactor). The ZSM-5 was also loaded into the catalyst chamber with varying catalyst mass between (50 - 200 g), at varying operating temperatures ranging between (250 - 400 °C) and varying residence time ranging between (15 - 60 min) in order to establish optimum temperature, residence time and catalyst mass [13], and the response was the liquid oil yield. The liquid product yield was characterized to determine some properties such as density, specific gravity, API gravity, dynamic viscosity, kinematic viscosity, sulphur content, flash point, fire point and aniline point. This procedure was repeated for the number of experiment generated by the design of experiment (DOE)

3.0 RESULTS AND DISCUSSION

3.1 Result

Polyethylene waste sample of 14.352 mg weight was heated at a rate of 10 °C/min. with PerkinElmer TGA between 45 °C and 950 °C. The results obtained for polyethylene wastes showing thermal degradation shows three stages of pyrolysis. Stage 1 is referred to as the dehydration stage, stage 2 is referred to as the active pyrolysis and stage 3 is referred to as the passive pyrolysis. The dehydration stage was observed to take place between 45 °C to 250 °C, the active pyrolysis where polyethylene waste sample began to degrade started from 250 °C to 400 °C and the passive pyrolysis was observed to take place above 400 °C. The degradation around 250 °C with 99 % mass left may be attributed to possible trace amount of

plasticizers [14]. The major degradation was observed to take place between 250 °C and 300 °C where 27 % mass of sample was left. At 350 °C, 14 % mass of sample was remaining and at 400 °C, 10 % mass of sample was left. Beyond 400 °C, no significant degradation was observed; this may be attributed to the presence of fillers because fillers increase the stability of polyethylene composites that is needed in many applications [15]. The FT-IR analysis carried out on polyethylene waste sample was found in the range from 500 to 4000 cm⁻¹. Table 3.1 shows corresponding band width of polyethylene waste sample. FT-IR spectrum of polyethylene waste sample displays number of absorptions peaks, the band spectra 3904 – 3601 cm⁻¹ and 1734 – 1507 cm⁻¹ found in the sample shows antioxidant absorption as compared to previous study of [16].

Band (cm ⁻¹)	Assignment	Intensity
2841	CH ₂ symmetric stretching	Strong
2663	C-CH ₃ stretching	Weak
2345 - 2018	C=C stretching	Very weak
1463	CH ₂ bending deformation	Strong
1368	CH ₃ symmetric bending deformation	Medium
1304	Acyl group C-O	Weak
1080	Cyclic alcohols alkoxy C-O	Very weak
908	Monosubstituted alkene - CH=CH ₂	Very weak
729 - 719	Disubstituted alkene - CH=CH	Strong

Table 3.2 shows the result of BET analysis of zeolite ZSM-5 catalyst to analyze the textural characteristics and pore size distribution.

Table 3.2: BET analysis result for ZSM-5 catalyst

Surface (m ² /g)	Area	Pore (cm ³ /g)	Volume	Pore (nm)	Size
688		0.2445		6.077	

The result obtained shows that zeolite ZSM-5 catalyst possess good surface area, pore size and pore volume necessary to make it an effective catalyst for high yield of liquid fuel. The determined surface area is significantly larger than those for natural porous materials, such as clay (10 – 100 m²/g), activated graphite (119 m²/g) and other types of zeolite and porous carbons [17]. ZSM-5 catalyst is highly active in liquefaction of plastic wastes to give high yield of very light gasoline-like oil with high aromatic content. The high activity may be attributed to high acidity strength, high pore size and high surface area [18]. FT-IR characterization of zeolite ZSM-5 shows a spectra band of

amorphous silica, silanol groups and bridging hydroxyl group Si(OH)Al which is considered the strongest Bronsted acid sites as compared with previous study by [19],[20].

To study the effect of process parameters (temperature, residence time and catalyst weight) on the yield of the derived fuel, the responses was subjected to numerical optimization using Design Expert software. The process parameters variables and responses percentage yield were simultaneously optimized within the upper and lower limits of the experimental data. The aim is to determine the optimal process parameters for optimal response percentage yield. Table 3.3 shows the process variables and their coded variables for optimization.

Table 3.3: Independent variables and their coded levels for optimization

Variables (Factors)	Code	Unit	Coded variable levels		
			-1	0	+1
Temperature	A	°C	250	325	400
Residence time	B	min	15	37.5	60
Catalyst weight	C	g	50	125	200

Quadratic model developed fitted well between the response percentage yield and the process variables: Temperature (A), Time (B) and Catalyst weight (C). Therefore, the quadratic models were selected as suggested by the software and the response surface model equations for the liquid fuel percentage yield in their actual values is:

$$\text{Percentage Yield (\%)} = + 65.26 + 14.31 A + 3.92 B + 3.61 C - 2.22 AB - 0.7750 AC + 4.20 BC - 7.78 A^2 + 0.1736 B^2 - 0.8268 C^2 \quad 3.1$$

Equation 3.1 in terms of coded factors can be used to make predictions about the response for given levels of each factor. Table 3.4 shows the correlation between the experimental and predicted percentage yield of liquid fuel.

Table 3.4: Actual- predicted values and residual for percentage liquid fuel yield

Ru ns	Actual Value	Predicted Value	Residual
1	65.00	65.26	0.2597
2	79.45	79.86	0.4128
3	69.67	68.07	1.60
4	68.66	69.35	0.6949
5	67.98	65.26	2.72
6	58.22	57.24	0.9842
7	66.87	65.26	1.61
8	58.34	61.51	3.17
9	65.66	68.04	2.38
10	37.56	36.18	1.38
11	70.78	70.80	0.0178

12	65.34	65.26	0.08
13	39.45	40.08	0.6298
14	36.77	36.56	0.2132
15	66.56	65.81	0.7532
16	65.00	65.26	0.2597
17	69.87	71.79	1.92
18	41.22	43.17	1.95
19	59.34	60.82	1.48
20	66.10	65.26	0.8403

The experimental values were the result obtained, while the predicted values were obtained by calculation from the quadratic equation. It is shown in Figure 3.1 that the data points on the plot are distributed near to the straight line, indicating a good relationship between the experimental and predicted values of the response. The result also suggests that the quadratic model was adequate in predicting the response variables for the experimental data

From the results obtained, the highest percentage yield of liquid fuel from catalytic pyrolysis was 79.45 % with gas 13 % and char 7.55 %. Equation 3.2 shows the calculation for percentage yield. The mass of liquid fuel derived was measured to be 397.25 g, while the mass of char was measured to be 37.75 g. This gives a corresponding percentage yield from a 500 g feedstock of polyethylene waste to be 79.45 % and 7.55 % for liquid fuel and char respectively. The remaining 13 % is attributed to the gaseous fuel. A similar yield of fuel with zeolite ZSM-5 was reported by [18]. Zeolite ZSM-5 catalyst has high activity attributed to high acidity strength, addition of catalyst up to 200 g increased the activity, enhancing liquid fuel of percentage yield of 79.45 % at a reduced degradation temperature of 400 °C and residence time of 60 min. in the reactor. Similar trends of products yield with increase in catalyst weight was reported by [21], [22] to increase overall liquid fuel yield with decrease in char and increase in gas production. The effect of process parameters temperature, residence time and catalyst weight is as shown in figure 3.2, 3.3 and 3.4 respectively.

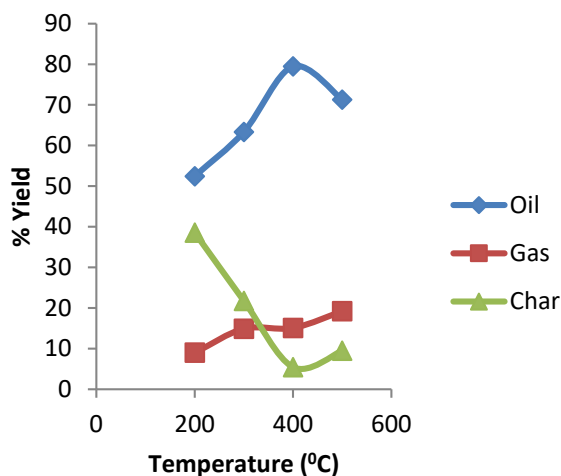


Figure 3.2: Effect of temperature on the percentage yield of fuel

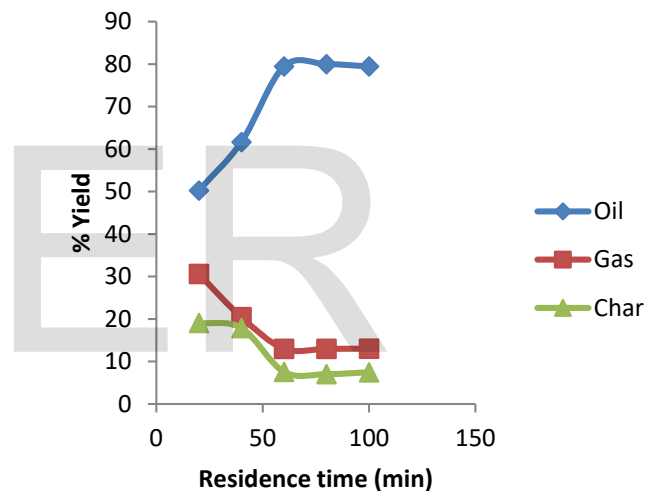


Figure 3.3: Effect of residence time on the percentage yield of fuel

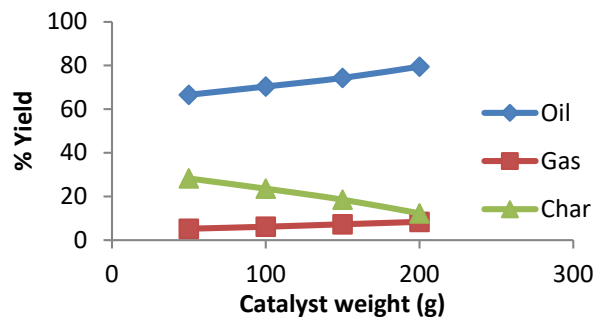


Figure 3.4: Effect of catalyst weight on the percentage yield of fuel

Temperature has the greatest impact on reaction rate that influence product composition of liquid, gaseous and char for all plastics. The operating temperature required is dependent on the product fuel preference. If gaseous or char product fuel was

preferred, higher temperature above 500 °C was suggested. It was observed that liquid fuel increase with temperature for liquid fuel as shown in figure 3.2 up to 400 °C. Beyond this temperature, the liquid fuel begins to decrease with increase in gas and char. From figure 3.3, it was observed that higher liquid fuel yield was obtained at a longer residence time of 60 min. when the temperature was not more than 400 °C, the yield remains constant after 60 min. Increase in catalyst weight increases the yield of liquid and gas but decrease the yield of char as shown in figure 3.4. This result is attributed to the surface area and microporous structure of zeolite ZSM-5. Catalysts with higher acidity increase the cracking process and as result increase the production of liquid fuel and gases [23].

Liquid fuel produced was subjected to test analysis for characterization, to determine the pyrolysed liquid fuel physical properties, such as density, specific gravity, API gravity, sulphur content, flash point, fire point, viscosity, dynamic viscosity, kinematic viscosity and aniline point. A comparative data analysis between derived liquid fuel and crude oil sample from Niger Delta, Nigeria as shown in table 3.5

Table 3.5: Physical properties of liquid fuel from polyethylene and comparative data of crude oil from Niger Delta, Nigeria

Properties	Liquid fuel	Crude Oil Sample (Niger Delta)	Unit
Density @ 15 °C	0.78	0.944	g/cm ³
Specific gravity @ 15 °C	0.78	0.945	-
API gravity @ 15 °C	49.9	18.2	o
Sulphur content	-	-	wt %
Flash point	38	95	°C
Fire point	41	-	°C
Dynamic viscosity	1.54	75.9	mPa.s
Kinematic viscosity @ 40 °C	1.98	80.4	cSt
Aniline point	77	-	°C

Comparative data analysis of derived liquid fuel and crude oil from Niger Delta in Nigeria was carried out. Analysis conducted revealed values of properties tested such as density, specific gravity, API gravity, flash point, fire point, dynamic viscosity, kinematic viscosity and aniline point of liquid fuel of 0.78 g/cm³, 0.78 and 49.9 °, 38 °C, 41 °C, 1.54 mPa.s, 1.98 cSt and 77 °C respectively. Results from crude oil samples collected in Niger Delta, Nigeria shows varying values such as density, specific gravity, API gravity, flash point, dynamic viscosity and kinematic viscosity to be 0.944 g/cm³, 0.945, 18.2 °, 95, 75.9 and 80.4 cSt respectively [24]. The difference in values is attributed to the classification of oil

according to the API degree. The liquid fuel derived with API gravity of 49.9 ° is classified as light crude oil (API gravity higher than 31.1 °, less than 870 kg/m³), while the crude oil sample with API gravity of 18.2 ° is classified as heavy crude oil (API gravity from 22.3 ° to 10 °, 920 kg/m³ to 1000 kg/m³) [25]. The API degree indicates the density and viscosity of crude oil. It shows whether crude floats on water or sink. Light crude flows easily and volatile, while heavy crude is more viscous with high density.

4.0 CONCLUSION

The physical properties of pyrolysed liquid fuel produced shows it is classified as light crude oil with a high percentage yield. This shows that liquid fuel from plastic wastes is an alternative energy source to conventional crude oil and can be utilized in various applications where conventional crude oil dominates. The high percentage yield shows that plastic wastes can be harnessed to fuel to solve environmental pollution caused by plastic wastes.

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