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# Optimization of Pyrolysis Oil Yield from Low and High Density Polyethylene and Polypropylene Wastes

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## ABSTRACT

*The work explored the thermal degradation of waste plastics from Asaba metropolis in a locally fabricated batch unit for pyrolysis of the waste feeds and the optimization of pyrolysis yield. Special attention was given to Low Density Polyethylene (LDPE), High Density Polyethylene (HDPE) and Polypropylene (PP) because of their ability to randomly degrade, giving rise to waxy hydrocarbons that are suitable for fuel applications. Proximate and ultimate analyses of waste samples were carried out. The effects of time and temperature on the quantity of the pyrolysis products were studied and three (3) quadratic models were developed to explain the process. The LDPE liquid fraction obtained was analyzed for the functional groups present using Fourier Transform Infrared Spectroscopy (FTIR). The fuel analysis was carried out based on chemical and physical properties to characterize the liquid product from the pyrolysis process. A 3-D plot of interaction was plotted to visualize the surface effects of these process variables. The results of the proximate and ultimate analyses of HDPE, LDPE and PP revealed high carbon contents of 89.93%, 84.10%, 82.81% respectively and volatile matter 96.88%, 98.10%, 82.81% respectively showing the suitability of the materials as a potential fuel source.. The process was optimized using Response Surface Methodology with the highest yield of 62% for LDPE obtained at 600$^{o}$C and 60 minutes. The density of the fuel gotten existed in the range of regular gasoline, the fire point,120-180$^{0}$C and flash point,341-350$^{0}$C were within the standard limits of regular gasoline. This research work, through pyrolysis of waste polymers, has significantly reduced the environmental concern by turning waste polymers into wealth generating, bio-degradable and environmentally friendly pyrolysis oil. Model equations were developed for the process and the optimum conditions were established.*

**Keywords**: Pyrolysis, Optimization, Polyethylene, LDPE, HDPE, PP.

## 1.0 INTRODUCTION

Plastic products in developing countries are growing by the day and it is driven by economic necessity and human demand. While only a fraction of the total plastic wastes are being recycled in many developed nations, approximately 95-75% of them emerge to be retrieved in developing countries (Hassanpour and Unnisa, 2017). Global plastic generation reported around 230 and 299 Mt in 2009 and 2013 respectively, 3.9% rise from 2012 (Comanita *et. al*, 2015). In 2012, according to the European Association of Plastics Recycling and Recovery (EPRO), 5.4 metric tons were recycled, 34.7%, of all the plastic packaging waste (Siddique *et. al*, 2008). In Nigeria thousands of tons of plastics are manufactured to meet plastic demand. This much production and consumption of plastic is a threat to environment as it takes several years to decompose naturally; hence the plastics waste disposal is the biggest concern of the country. The poor implementation of relevant environmental laws and regulations or complete absence of waste management resources and facilities within and around major urban cities in developing countries and Nigeria in particular has promoted indiscriminate generation of plastic wastes (Karibo, 2008). Many processes, including pyrolysis and catalytic degradation, have been developed to depolymerize plastic wastes into liquid hydrocarbon fuel. The conversion of plastic waste into volatile hydrocarbon is known as pyrolysis. Pyrolysis involves degradation of plastic by heating it at high temperatures in the absence of oxygen, leading to the formation of a volatile fraction which will be separated into condensable hydrocarbon fuel and char (Ali *et al*, 2011, Antoniou and Zabaniotou, 2013, Churkunti *et al*, 2016). Plastics can be converted into hydrocarbon fuel since it contains hydrogen and carbon and one of the methods of this conversion is pyrolysis. This resource-saving goal is very important for most cities, where rapid industrialization and economic development put a lot of pressure on natural resources. Pyrolysis may be either by fluidized-bed or fixed-bed. Fluidized-bed pyrolysis is more complex than fixed-bed pyrolysis. In fixed-bed pyrolysis, a fixed-bed reactor is used. Fixed-bed reactors are easy to operate compared to other sorts of reactors, and are considered very economical due to its manageable maintenance and operation (Hall *et al*, 2009).

Waste management system in Nigeria does not include energy recovery from generated wastes (including plastic), as it relies solely on landfill and open burning. However, in many developed cities in the world, energy is recovered from non-recycled plastic (NRP) which could have been sent to landfills at waste-to-energy (WTE) facilities by combustion to generate steam and electricity (GBB, 2013; Wienenergie, 2014); by pyrolysis to produce oil and by gasification to produce syngas. There are a number of technical challenges facing the production of bio-oil using pyrolysis in Nigeria. These challenges can be categorized as design, fabrication, operational, and analytical challenges. In the light of seeking solution for energy and environmental issues, pyrolysis has been found the foremost effective technique of conversion of waste plastics to fuels. However, there is limited literature focused on the recovery of monomers or valuable chemicals from waste plastics pyrolysis in Nigeria. This study has been conducted as such to determine pyrolysis conditions enabling valuable chemicals recovery from waste polyethylene (PEs) and polypropylene (PP) plastics. Although, there are few commercial fast pyrolysis plants within the world, the varied process technologies are not fully developed (Mictchell, 2011). Hence further studies are required to improve its reliability, performance, product consistency and product characteristics.

This study focuses on Asaba metropolis of Delta state, Nigeria. The method of waste disposal generally practiced in Delta State is the landfill method which is visibly seen located in various parts of the State with some towns having up to five landfill sites. Incineration is additionally administered not as a sort of recycling (down-cycling) but as a means of reducing the quantity of waste on the landfill sites. Pyrolysis of plastic waste can make it possible to collect and dispose of plastic waste in an environmentally friendly way, as well as turn it into a resource. This study will significantly expose policy makers in Delta state on the potential of this method of converting plastics waste to an alternative energy source and to reduce the negative impact of indiscriminate waste management. The process parse can be used in designing an effective waste management procedure and in other hand generate alternative energy. The materials considered for this are currently landfilled, it is anticipated that there would be a lot of economic and environmental benefits. The use of the gas and char products would be critical to the viability of the pyrolysis process as both products could be utilized for fuel application. Fishing is one of the major occupation of people in the riverine area of the state and effective removal of plastics from the environment will help to ensure a recurring source of income for the locale and also help to maintain balance in the ecosystem.

## 2.0 LITERATURE REVIEW

There is absence of literature on pyrolysis of waste plastics from Asaba metropolis. Merve. al,(2017) studied the effects of type of plastic, pyrolysis temperature and plastic waste prewashing on pyrolysis liquid product fraction, with HDPE producing the highest oil yield while PET and PP produced the lowest oil yield. Ahmad et al. (2014) conducted the pyrolysis of HDPE using a steel reactor at a temperature range of 300–400°C. The fluidizing medium used was nitrogen. 80.88 wt% of liquid was obtained and the total conversion was at 350°C. 33.05 wt. % solid residues were obtained at 300°C. Thermal pyrolysis study of HDPE was conducted by Kumar and Singh (2011) using a semi batch reactor at higher temperature of 400 – 550°C. The highest liquid yield and gaseous product (79.08 wt. % and 24.75 wt. % respectively) was obtained at a temperature of 550°C.Beltrán et al. (2009) also conducted pyrolysis of HDPE plastics at 550°C. The liquid oil yield obtained was 84.7 wt. % and gaseous product was found to be 16.3 wt. %. This results show that higher liquid oil yield is possible from HDPE at higher temperature. However, too high temperature would reduce the liquid oil yield and would increase the gaseous product yield as the process may go beyond the maximum thermal degradation point of HDPE. This result was proved by the experiment on HDPE pyrolysis in a fluidized bed reactor at 650°C by Mastral et al (2001). The experiments provided a liquid oil production of around 68.5 wt. % and 31.5 wt. % of gaseous product. So it can be concluded that at high temperature above 550°C, the liquid was cracked to gaseous state.

Bagri and Williams (2001) conducted LDPE pyrolysis in fixed-bed reactor at a temperature of 500°C. The experiment was conducted for a duration of 20 min and nitrogen gas was used as fluidizing medium. The liquid yield obtained was 95 wt% with low gas yield and negligible amount of char. 93.1 wt% of liquid oil was obtained when the same experiment was conducted in a batch reactor at a temperature of 550°C by Marcilla et al. (2011). Aguado et al. (1996) obtained 74.7 wt% of liquid oil when using a batch reactor at a temperature of 450°C. Onwudili et al. (2009) conducted pyrolysis of LDPE at a temperature of 425°C in a pressurized batch reactor (0.8 – 4.3 MPa). The liquid oil yield obtained was 89.5%, gas obtained was 10 wt% and char was 0.5 wt%. Many researchers have studied the process of pyrolysis of PP by altering the parameters to optimize the liquid oil yield. One experiment conducted by Ahmad et al. (2014) on PP pyrolysis was done at 250 – 400°C temperature. From the experiments it was found that 69.82 wt% of liquid oil was achieved at temperature of 300°C. Pyrolysis of PP was conducted by Sakata et al. (1999) on PP at temperature of 380°C and obtained a liquid yield of 80.1 wt%, gas yield of 6.6 wt% and 13.3 wt% solid residue. Fakhrhoseini and Dastanian (2013) conducted PP pyrolysis at 500°C and obtained 82.12 wt% of liquid yield. The liquid yield was reduced when the temperature was more than 500°C. Demirbas (2004) conducted pyrolysis of PP at 740°C in a batch reactor and 48.8 wt% liquid, 49.6 wt% gas and 1.6 wt% char yield were obtained. This experiment inferred a reduction in liquid yield with increasing temperature.

## 3.0 MATERIALS AND METHODS

The materials utilized for this study are waste HDPE, LDPE and PP from municipal dumpsite in Asaba metropolis. For the pyrolysis experiment, a locally fabricated semi-batch reactor as shown in Plate 1 was employed for the study. The feeds were properly washed and dried after which they were subjected to proximate and ultimate analysis using ASTM D5373-08 method.

### Experimental Procedure

1.02 kg of the sample was prepared and fed into the reactor. The temperature was set by adjusting the controller for the pyrolysis to start, The temperature at the first drop of the liquid was noted . The condensable liquid products were collected through the water cooled condenser and weighed. The pyrolysis experiment was repeated for different constituents of the plastics wastes and operating conditions according to the design matrix of Table 2. The weight of the waxy residue left inside the reactor after each process was noted. Hot steam was used for purging the reactor batch wise. The obtained fluid was separated from accompanying impurities through gravity separation process and then filtered before characterization.

**Plate 1: The Pyrolysis set-up employed for the thermal degradation of waste polymers.**

### Experimental Design & Optimization Studies

Mat Lab® 2015a software was used to design the experiment and to statistically analyze the data. A Full Factorial Design (FFD) with five (5) levels and two (2) factors (Table 1) was used for the experimental design of the pyrolysis process. A complete description of the experimental suggestions as provided by the Mat Lab® 2015a software is presented in Table 2. These suggested experiments involve different combination of factors. Out of these 20 runs 2n i.e. 8 are factorial points and 2n i.e. 6 are axial points. Total number of center points is 6. These center points in principle are required to evaluate the experimental errors. These center points are also used to measure the reproducibility of output. Hence higher numbers of center points are required to ensure high accuracy and reproducibility of the results. Statistical analysis of the results obtained from the experiments was carried out using ‘analysis of variance’ (ANOVA) regression model. Equation 1 was used to calculate the empirical model for pyrolysis fuel yield.

$$Linear\ regression\ model:$$

$$Y = \beta o + \sum_{j=1}^{k} \beta_j X_j + \sum_{j=1}^{k} \beta_{jj} X_j^2 + \sum_{i<} \sum_{j=2}^{k} \beta_{ij} X_I X_J + \varepsilon \qquad (1)$$

Where; Y is the response or output, $\beta_{ij}$ and $\beta_{jj}$ are linear and quadratic coefficients respectively, $\beta o$ is regression coefficient, ε is the random error in the experiment, κ is the number of factors.

Table 1**: Experimental Range and Levels for the Design**

| Factors | Levels | | | | |
|---|---|---|---|---|---|
| | -2 | -1 | 0 | 1 | 2 |
| Time, $X_1$ (mins) | 20 | 30 | 40 | 50 | 60 |
| Temperature, $X_2$ ($^0$C) | 200 | 300 | 400 | 500 | 600 |

Table2**: Design template for the optimization of the effect of process variables on the pyrolysis of the polymer samples.**

| STD | RUNS | TIME(mins) | TEMP ($^0$C) |
|---|---|---|---|
| 1 | 11 | 20 | 200 |
| 2 | 1 | 30 | 200 |
| 14 | 26 | 40 | 200 |
| 15 | 18 | 50 | 200 |
| 3 | 8 | 60 | 200 |
| 16 | 21 | 20 | 300 |
| 17 | 25 | 30 | 300 |
| 4 | 9 | 40 | 300 |
| 5 | 5 | 50 | 300 |
| 6 | 12 | 60 | 300 |
| 7 | 6 | 20 | 400 |
| 18 | 19 | 30 | 400 |
| 9 | 4 | 40 | 400 |
| 19 | 24 | 50 | 400 |
| 20 | 22 | 60 | 400 |
| 21 | 17 | 20 | 500 |
| 22 | 20 | 30 | 500 |
| 23 | 23 | 40 | 500 |
| 10 | 10 | 50 | 500 |
| 11 | 13 | 60 | 500 |
| 26 | 16 | 60 | 600 |
| 12 | 7 | 20 | 600 |
| 13 | 2 | 30 | 600 |
| 24 | 14 | 40 | 600 |
| 25 | 15 | 50 | 600 |
| 26 | 16 | 60 | 600 |

## 4.0 RESULTS AND DISCUSSION

### 4.1 Fuel Potential Analysis of the Waste Polymers

The ultimate and proximate analysis of the various polymer samples were carried out to determine their suitability as pyrolysis feedstock. Ultimate analysis provides a convenient method for reporting the major organic elemental composition of a sample. The results of the analysis are as presented in Tables 3 & 4.

Table 3**: Experimental Results of the Proximate Analysis of the Feedstock**.

| PROPERTY | POLYMER SAMPLE | | |
|---|---|---|---|
| | HDPE | LDPE | PP |
| Moisture Content (%) | 0.41 | 0.32 | 0.48 |
| Ash Content (%) | 2.43 | 1.31 | 5.45 |
| Volatile Content (%) | 96.88 | 98.10 | 93.82 |
| Fixed Carbon (%) | 0.28 | 0.27 | 0.25 |

The volatile matter was 96.88% for HDPE, 98.10% for LDPE and 93.82% for PP in the proximate analysis. It can be seen that LDPE contains the most volatile component and less ash correspondingly (1.31%). Due to the presence of ash in waste LDPE sample in small quantity; its degradation occurs with minimal formation of residue. PP contains the least volatile matter and correspondingly highest ash content of 5.45%. The decomposition of PP occurs with a reasonable formation of residue as seen during the pyrolysis process. The volatile matter is the quantity of matter that can be thermally degraded in a given substance. This is a measure of the amount of matter that can be recovered upon cracking (Sharma *et. al* 2014). High combustible content indicates high energy and matter recovery from a material. The volatile matter for the three feedstocks is high enough. This result indicates that high amount of fuel products can be obtained upon thermal cracking. This value is in close range to most reported work; 89.65% [Panda, 2011], 91.48% [Khaing and Chaw, 2015], and 94.59% [Gao, 2010]; however, the value obtained was significantly different from another study [Sonawale *et.al* 2015) where a value of 83.56% was reported. This considerable variation can be attributed to differences in the polymeric material used.

Table 4**: Experimental result of the ultimate analysis of the feedstock**

| PROPERTY | POLYMER SAMPLE | | |
|---|---|---|---|
| | HDPE | LDPE | PP |
| Carbon Content (%) | 83.93 | 84.10 | 82.81 |
| Hydrogen Content (%) | 12.84 | 12.10 | 11.93 |
| Nitrogen Content (%) | 0.50 | 0.48 | 0.41 |
| Oxygen Content (%) | 0.80 | 0.71 | 0.73 |
| Sulphur Content (%) | 6.03 | 6.44 | 5.72 |

The ultimate analysis result, as presented in Table 4, shows the suitability of HDPE, LDPE and PP as feedstock for the pyrolysis process based on their high carbon content. Again, LDPE presented the highest carbon content of 84.10% of the three feedstocks. PP has the least; 82.81 and HDPE has 83.93%. The presence of Oxygen, Sulphur, Hydrogen, and Nitrogen might be attributed to additives added during polymer processing. The presence of Sulphur in particular can be traced back to natural gas which is the starting raw material for the polymerization processes. The ratio of Carbon to Hydrogen obtained in this study is as expected judging from the chemical composition of the feed stocks, $(C_2H_4)n$ (LDPE, HDPE), and $(C_3H_6)n$ (PP). The ratio of % weight of Carbon to that of Hydrogen is about 85:14 which is very close to the obtained values of 84:6, 84:6 and 82:5 for HDPE, LDPE and PP respectively. The little variation might be due to the presence of other elements as revealed by the ultimate analysis results.

Other properties determined were in consonance to most documented work on the proximate analysis of plastic materials (Mi-Jin *et. al,* 2011, Rui *et. al*, 2006).

Table 5**: Physico-chemical analysis of the various waste polymers.**

| | HDPE | LDPE | PP |
|---|---|---|---|
| Density (Kg/m$^3$) | 945 | 923 | 905 |
| Flash point ($^0$C) | 341 | > 341 | > 350 |

| | | | |
|---|---|---|---|
| Fire point ($^0$C) | 120 – 180 | 120 – 180 | 266 |
| Calorific value | 44,000 | 45,000 | 43,000 |

Table 6**: Experimental Result for the Pyrolysis of LDPE, HDPE and PP**

| STD | RUNS | TIME | TEMPERATURE | YIELD% | | |
|---|---|---|---|---|---|---|
| | | | | LDPE | HDPE | PP |
| 3 | 8 | 60 | 200 | 15.0 | 9.0 | 9.1 |
| 6 | 12 | 60 | 300 | 28.6 | 15.1 | 15.5 |
| 11 | 13 | 60 | 500 | 51.1 | 38.2 | 39.7 |
| 26 | 16 | 60 | 600 | 62.0 | 53.0 | 51.1 |
| 12 | 7 | 20 | 600 | 8.2 | 8.0 | 7.1 |
| 13 | 2 | 30 | 600 | 15.3 | 15.0 | 14.2 |
| 24 | 14 | 40 | 600 | 18.4 | 18.1 | 24.1 |
| 25 | 15 | 50 | 600 | 38.8 | 38.1 | 36.2 |
| 26 | 16 | 60 | 600 | 62.0 | 54.0 | 52.1 |

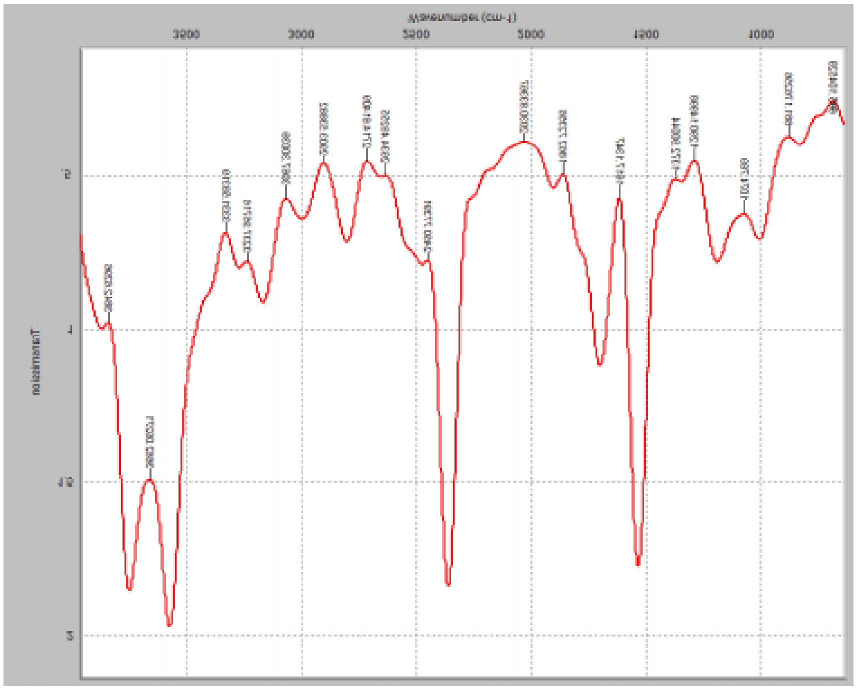

Figure 1**: Fourier Transform Infrared Spectrograph of the LDP Fuel Oil.**

FTIR (Fourier Transform Infra-Red Spectroscopy) was used to analyze the liquid product as presented in Figure 1. FTIR analysis of the liquid hydrocarbon components from waste polymer (LDPE) was in accordance with the wave number and following types of functional groups appeared in the analysis. The material sample has aromatic compounds such as benzene, toluene, ethyl benzene, styrene, α-methylstyrene, propyl-benzene, 2-propenyl-benzene, pentyl-benzene, heptyl-benzene. The wave number values of the most important peaks are summarized in Table 7.

Table 7**: Physical Properties of the LDPE fuel sample**

| Property | LDPE Fuel | Standard Limits | Test Standard |
|---|---|---|---|
| Color | Brownish Yellow | Bright Yellow | ASTM D1500 |
| Density (Kg/m3) | 775.28 | 850 | ASTM D1655 |

| | | | |
|---|---|---|---|
| Flash Point ($^{o}$C) | 36 | 55-110.7 | EN ISO 2719 (19) |
| Ash Content (%) | 0.15 | <0.01 | ASTM D482 |
| Kinematic Viscosity (mm2/s) | 3.8 | 2.0-4.5 | EN ISO 3104 (13) |
| Acid Value (mgKOH/g) | 38.63 | 42.9-110.0 | ASTM D664 |
| Moisture Content (mg/Kg) | 172 | <200 | EN 1S 12937 (27) |
| Iodine Value (gI/100g) | 128.08 | <93.91 | EN 14111 |
| Refractive Index | 1.604 | <1.5 | AOAC 921 |
| Saponification Value (mgKOH/g) | 182.7 | 54.6-115.0 | ASTM D4052 |
| Cetane No | 48 | 47.5-51 | EN15195 |

In a study to classify and compare the municipal solid waste (MSW) based on thermochemical characteristics, the cluster analysis of MSW components was applied based on proximate and ultimate analysis and heating value results. The results showed that PE, PP, and PS could be clustered as a category (Hui et. al, 2014). Thus, the characterization of the pyrolysis oil properties was based on the waste sample having the highest pyrolysis yield. Table 14 shows the results for the physical properties of the LDPE oil from the pyrolysis process. By comparing the corresponding value of LDPE oil and diesel using the above listed parameters, it can be observed that LDPE oil has a density that is within the range for diesel as postulate by the ASTM and is less dense than diesel. The density is 775.28kg/m$^3$ which is lesser than that of diesel. The flash point of the oil was gotten at 36$^{o}$C which gives it good flammability but poses risk to environment. The flash point for the LDPE oil obtained is lower than the ASTM recommendation for diesel; hence the fuel is flammable and combustible above room temperature. The LDPE oil can be improved to suite the standard requirements of diesel. The test results also show that LDPE oil is less viscous than diesel and this implies that the rate of consumption of the LDPE oil will be higher than that of diesel. The fuel has an ash content of 0.15% as compared to diesel that has an ash content of less than 0.01%, and this is a result of being unable to trap or separate non-condensable gases. The kinematic viscosity of the oil was found to be 3.8mm$^2$/s and shows that the oil gotten from the pyrolysis of LDPE is light hence flow easily. The pyrolysis fuel meets the EN 590 standard for the Cetane number but the value is slightly higher than the minimum value. Cetane No presents auto-ignition ability of a fuel sample, high values desirable for improved engine performance. Generally, the LDPE oil has an objectionable odor, with low flash point which requires careful handling so as to avoid flash fire. Figure 2 is a bar chart which compares between some of the properties of the fuel obtained from thermal decomposition of LDPE and standard fuel. It can be seen that most of the various properties of the oil from the pyrolysis process fell within the limits for standard diesel.

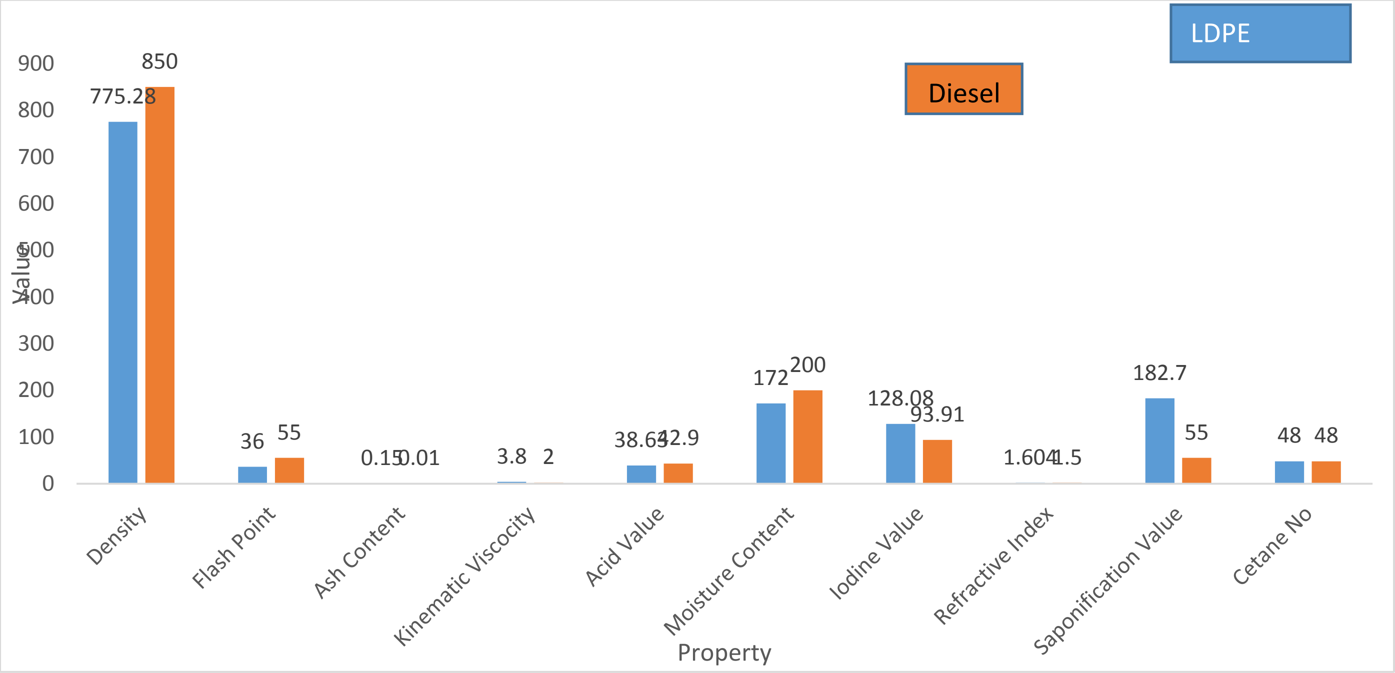

Figure 2**: Bar Chart Comparison of Properties of the LDPE oil against Standard Diesel**

### 4.2 Optimization and Development of the Regression Model

MatLab® 2015a software was used to optimize the process parameters for pyrolysis of LDPE, HDPE and PP. MatLab® 2015a was also used to derive an empirical model for the three processes. The software provided the levels for each of the factors under investigation. The input range

of values given to the software are listed in Table 1. With the help of these limiting values the software designed a series of experiments. The software provided us a set of process parameters for each experiment. Overall 10 set of experiments were used of the total runs provided by the software. The operating parameters for these 10 set of experiments were given by the software. The software selects the operating parameters in such a way that it carries certain number of factorial points, axial points and center points. Table 6 provides detailed information of the process parameters and the response for each set of experiment.

Table 8**: Regression Model Parameters for LDPE Pyrolysis.**

| Model terms | Estimate | SE | t-statistics | p value |
|---|---|---|---|---|
| Intercept | 0 | 0 | | |
| $X_1$ | -0.021424 | 0.0049366 | -4.3399 | 0.012254 |
| $X_2$ | 6.5528e-05 | 0.00049366 | 0.13274 | 0.90081 |
| $X_1X_2$ | 9.9356e-06 | 4.8486e-06 | 2.0492 | 0.10979 |
| $X_1^2$ | 0.00035817 | 7.9004e-05 | 4.5335 | 0.010549 |
| $X_2^2$ | 6.1263e-07 | 7.9004e-07 | 0.77544 | 0.48137 |

Number of observations: 10, Error degrees of freedom: 5
Root Mean Squared Error: 0.0323, R-squared: 0.985, Adjusted R-Squared 0.973
F-statistic vs. constant model: 83.2, p-value = 9.23e-05.
After a regressive analysis of the experimental data, developed mathematical model obtained to predict the LDPE, HDPE and PP fuel yield can be written as Eq. (2) Eq.(3) and Eq.(4) respectively.

$$Yield_{LDPE} = -0.21424X_1 + 6.5528e^{-5}X_2 + 9.9356e^{-6}X_1X_2 + 3.5817e^{-4}X_1^2 + 6.1263e^{-7}X_2^2 \quad (2)$$

$$Yield_{HDPE} = -0.013803X_1 - 4.9026e^{-4}X_2 + 1.058e^{-5}X_1X_2 + 2.3478e^{-4}X_1^2 + 1.2065e^{-6}X_2^2 \quad (3)$$

$$Yield_{PP} = -0.0083057X_1 - 6.6901e^{-4}X_2 + 1.3681e^{-5}X_1X_2 + 1.4117e^{-4}X_1^2 + 1.1626e^{-6}X_2^2 \quad (4)$$

### 4.3 Regression Model for LDPE, HDPE and PP Oil Yield

Equation 2 is the model equation for the pyrolysis of LDPE using the fabricated Pyrolysis setup. Here, $Yield_{LDPE}$ is LDPE oil yield, $X_1$ and $X_2$ are time and temperature respectively. In equation 2, the terms with single factor indicates the effect of that individual factor on the response. Those terms which carry two factors indicate the combined effect of the two factors on the response. A positive sign prior to any term represents the synergic effect of that particular term while the negative sign prior to a particular tem represents the antagonistic effect on response. Also it is worth noting here that the mathematical models represented by Equation 2 have been developed considering the units of $X_1$ and $X_2$ to be minutes and $^0$C respectively. If the units of either of the process parameters will be changed the mathematical models discussed above will not yield the correct results. A similar trend is followed with Eq.(3) and Eq.(4) for HPDE and PP respectively

### 4.4 Statistical Analysis of the LDPE Oil Yield.

To understand the reliability, reproducibility and efficiency of the developed regression models, ANOVA of the experimental data was carried out. Tables 9, 10, 11 summarize the results of ANOVA of the experimental data for the LDPE, HDPE and PP oil yield respectively. Probability value and Fischer test value (formally termed as p-value and F-value respectively) are used to analyze the validity, significance and acceptance for a mathematical model developed using regression technique. F-value evaluates the comparison between the mean square values of the mathematical model developed using regression technique and the mean square value of residuals (i.e. error). Higher F-value will imply a reliable and reproducible mathematical model while a lower F-value will raise a doubt about the reliability and reproducibility of regression model. P-value evaluates the significance of the developed mathematical model. Models with lower P-values enjoy higher significance as compared to the models with higher P-values.

Table 9: **ANOVA Table for LDPE Model Estimation**

| Model Parameters | SumSq | DF | MeanSq | F | PValue |
|---|---|---|---|---|---|
| $X_1$ | 0.27417 | 1 | 0.27417 | 263.15 | 1.6228e-05 |
| $X_2$ | 0.18677 | 1 | 0.18677 | 179.26 | 4.1588e-05 |
| $X_1X_2$ | -2.9261e-33 | 0 | -inf | -inf | NAN |
| $X_1^2$ | 0.021413 | 1 | 0.021413 | 20.553 | 0.0062054 |
| $X_2^2$ | 0.00062648 | 1 | 0.00062648 | 0.60131 | 0.47314 |
| Error | 0.0052093 | 5 | 0.0010419 | | |

Table 10**: ANOVA Table for HDPE Model Estimation**

| Model Parameters | SumSq | DF | MeanSq | F | PValue |
|---|---|---|---|---|---|
| $X_1$ | 0.19571 | 1 | 0.19571 | 281.64 | 1.373e-05 |
| $X_2$ | 0.17852 | 1 | 0.17852 | 256.91 | 1.7214e-05 |
| $X_1X_2$ | -3.0945e-33 | 0 | -inf | -inf | NaN |
| $X_1^2$ | 0.009201 | 1 | 0.009201 | 13.241 | 0.014922 |
| $X_2^2$ | 0.0024298 | 1 | 0.0024298 | 3.4967 | 0.12042 |
| Error | 0.0034744 | 5 | 0.00069488 | | |

Table 11**: ANOVA Table for PP Model Estimation**

| Model Parameters | SumSq | DF | MeanSq | F | PValue |
|---|---|---|---|---|---|
| $X_1$ | 0.18339 | 1 | 0.18339 | 1323.9 | 2.9522e-07 |
| $X_2$ | 0.1696 | 1 | 0.1696 | 1224.4 | 3.587e-07 |
| $X_1X_2$ | -2.6876e-33 | 0 | -Inf | -Inf | NaN |
| $X_1^2$ | 0.0033264 | 1 | 0.0033264 | 24.014 | 0.0044728 |
| $X_2^2$ | 0.0022563 | 1 | 0.0022563 | 16.289 | 0.0099625 |
| Error | 0.00069259 | 5 | 0.00013852 | | |

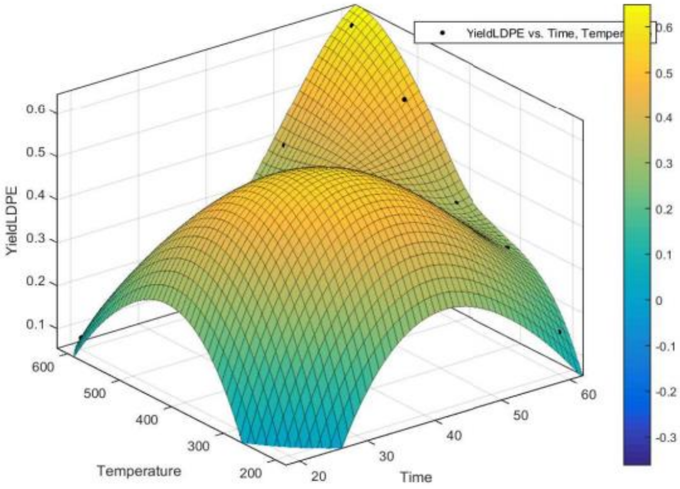

Figure 3: **Response Surface Plot for LDPE yield**.

Figure 3 is a surface plots representing the combined effect of the two process parameters (time, temperature) on LDPE oil yield. It is observed that within the investigated time and temperature ranges, LDPE oil yield increased to 62.0%. Also Figure 3 depicts that very large heating & pyrolysis time are not suitable for LDPE oil through thermal degradation of the polymer. Initially the oil yield increases on increasing either the parameters but after a certain point as any increase in both parameters lowers the oil yield. The highest oil yield was at 60mins and 600$^0$C. The shape of the curve for the combined effect of time and temperature is convex, and within the investigated ranges of time and temperature, the oil yield from LDPE is high when the pyrolysis time lies between 50 and 60 min. It is seen that the surface curve takes a fold for time between 50 and 60 min (depending upon the temperature), indicating that this range of pyrolysis time is suitable for higher LDPE oil production. These observations are in accordance with the previous studies made on the other biomass materials (Kumar and Singh (2011); Adil *et. al* (2007)).

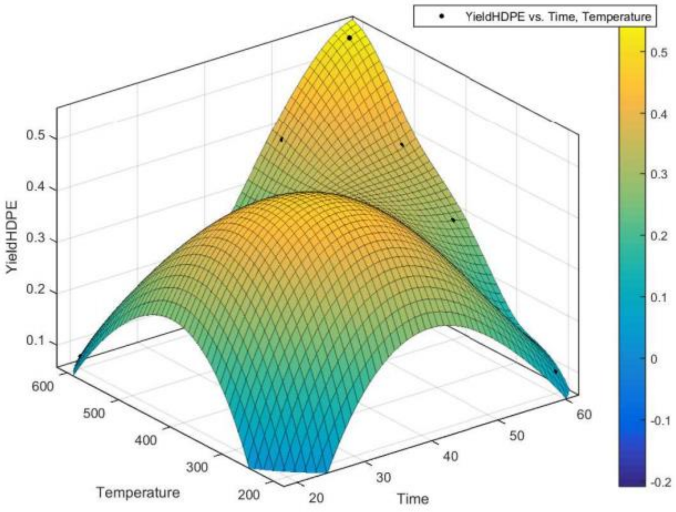

Figure 4**: Response Surface Plot for HDPE Yield.**

Figure 4 is a surface plot representing the combined effect of the two process parameters (time, temperature) on HDPE oil yield. It is observed that within the investigated time and temperature ranges, HDPE oil yield increased to 54.0%. Also Figure 2 depicts that very large heating & pyrolysis time are not suitable for LDPE oil through thermal degradation of the polymer. Initially the oil yield increases on increasing either the parameters but after a certain point as any increase in both parameters lowers the oil yield. The highest oil yield was at 60mins and 600$^0$C similar to that of LDPE. The shape of the curve for the combined effect of time and temperature is convex, and within the investigated ranges of time and temperature, the oil yield from LDPE is high when the pyrolysis time lies between 50 and 60 min.

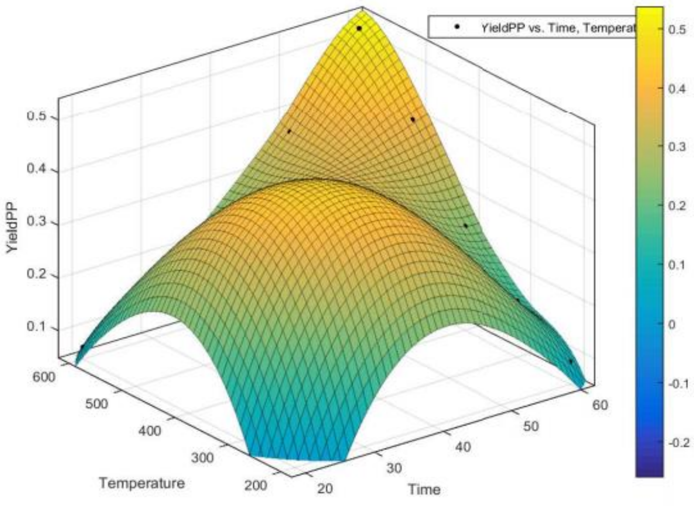

Figure 5**: Response Surface Plot for PP Yield**.

Figure 5 is a surface plots representing the combined effect of the two process parameters (time, temperature) on PP oil yield. It is observed that within the investigated time and temperature ranges, PP oil yield increased to 52.1%. Also, the highest oil yield was at 60mins and 600$^0$C. The shape of the curve for the combined effect of time and temperature is convex, and within the investigated ranges of time and temperature, the oil yield from LDPE is high when the pyrolysis time lies between 50 and 60 min. It is seen that the surface curve takes a fold for time between 50 and 60 min (depending upon the temperature), indicating that this range of pyrolysis time is suitable for higher LDPE oil production.

## CONCLUSION

The present experiment studied the cracking nature of waste HDPE, LDPE and PP from Asaba metropolis. The reaction temperature for the cracking ranges from 400ºC-600ºC and the percentage yield of 62.0% was achieved for LDPE. Time taken for complete reaction was very high about one hour. The experiments were conducted in a locally fabricated semi-batch reactor without any application of a stirrer. The analysis of the selected physical and chemical properties for the pyrolysis oil revealed its suitability for fuel application. The density of the obtained fuel existed in the range of regular gasoline. Pour point and flash point were also tested and found satisfactory as per general requirements of regular gasoline. The solid residue was about 1.6% of the LDPE fed. This technology would significantly reduce the environmental concern since the rapid rate of plastic waste generation in Asaba metropolis has led to greater difficulties for waste disposal. The sustainability of the process is established With the pyrolysis method, the waste management becomes more efficient, and cost effective. Moreover, with the existence of pyrolysis method to decompose plastic into valuable energy fuel, the dependence on fossil fuel as the non-renewable energy can be reduced and this solves the rise in energy demand.

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