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Comparative Studies of the Effect of CaO and Zeolite Catalyst on Waste Plastics Pyrolysis

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Abstract

The study examines the comparative studies of the effect of calcium oxide (CaO) and zeolite catalyst on waste plastic pyrolysis. The primary objectives of the study are characterization of CaO and zeolite catalyst using XRF and XRD, waste plastic pyrolysis using CaO and zeolite catalyst, and optimization of the parameters of pyrolysis using CaO and zeolite catalyst. The XRD and XRF analysis shows that the crystal structure of zeolite corresponds to those of ZSM-5 a silica to alumina ratio of 29.48 while the CaO catalyst contains mainly CaO in its crystal structure with 98.848% CaO. The waste plastic pyrolysis was successfully carried out. The optimization study shows that the optimum values of pyrolysis temperature, heating rate and catalyst type for maximum oil yield are 597 °C temperature and 29.909 °C/min heating rate using zeolite catalyst type to give a maximum waste plastic pyrolysis oil yield of 58.385% while 600 °C and 30 oC/min using CaO catalyst type give a yield of 54.868% which shows that the yield obtained with CaO as catalyst is relatively comparable to that obtained using zeolite. The study also shows that there was no much significant difference in the yield of CaO and zeolite at the established optimum condition for both catalyst type. Therefore, considering cost of zeolite CaO could be useful as catalyst for waste plastic pyrolysis.

Keywords: *XRD, XRF, CaO, Zeolite, Pyrolysis.*

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Background to the Study

In recent times, there have been rise in environmental concern over plastic waste generation and disposal worldwide, resulting from the rise in population and industrialization. Plastics are materials that comprises of a wide range of synthetic and natural compound, and are malleable and can be molded into different shapes and sizes. Plastics have become an indispensable material used in several countries of the world, due to their durability, lightweight as well as flexibility and are utilized in a range of industrial and domestic areas (Khan *et al.*, 2016). In 2015, global plastics production was about 388 million tonnes and has reached over 407 million tonnes per annum in recent times and this figure is estimated to double in the next 20 years (Morten, Ryberg, and Michael, 2018). In the last decades, the utilization of plastic and its waste generation has continuously grown in several countries of the world and count for a reasonable part of solid waste generation. According to Meidl (2018), nearly 8.3 billion metric tons of plastic have been produced since 1950, and 6.3 billion tons of plastic waste have been generated, of which 9% has been recycled, 12% incinerated, and 79% accumulated in landfills or abandoned in the environment.

In Nigeria, cities and towns are currently facing serious environmental problem arising from solid waste generation. The rate of solid waste generation, particularly plastic waste in Nigeria has increased with rapid urbanization, due to their end-of-life management challenges and a larger fraction of waste plastic end up at dumpsites, landfills and even clogging of drainages (Babayemi *et al.*, 2018). A large proportion of plastics waste is being disposed of in landfills and dumpsites than ever before. Plastic wastes generated in Nigeria are predominantly plastic bottles, bags and packages and remain a large proportion of municipal solid waste. According to the Nigeria Federal Ministry of Commerce and Industry, the production of the most common and cheapest source of drinking water, popularly known as "pure water" is one of the largest contributors to plastic waste generation in the country, and these waste accounts for about 20% of total waste generation (Akinola, Adeyemi and Adeyinka, 2014). These plastic wastes generated are not biodegradable, but take about 100 years to degrade in the environment (World Environment Day, 2018). Added to the degradability challenges are risks of flooding by clogging of drains and degradation of air quality from open dumps, a serious concern of its management. These necessitate the need to source for an effective and sustainable plastic waste management system.

Over the years, different management methods have been developed to mitigate the threat posed by rising amounts of plastic waste generated by conversion to valuable and useful products that will significantly reduce the volume of waste generated. There have been focus on sustainable methods in the conversion of plastic waste to a valuable source of energy and chemical substances, as landfills and burning have resulted in serious environmental and health hazards (Dogan *et al.*, 2012). This makes energy recovery processes the most effective approach to reducing the volume of plastic waste significantly as they focus on potentially converting the plastic waste into other useful products such as fuel products through pyrolysis process (Baiden, 2018). Pyrolysis, as a method of waste conversion, is widely used in recent times for waste conversion to useful product. It simply implies the breaking down of chemically bonded material with the aid of thermal energy in the absence of air and have been carried out in the presence of catalyst to convert waste plastics into fuels and other valuable materials (Bursali, 2014).

Pyrolysis is an environmentally friendly means of plastic waste disposal with the production of valuable products when compared to other disposal methods. This method, in recent times, has become an alternative and sustainable method of waste-to-energy conversion to substitute fossil fuel while also mitigating the environmental degradation challenges caused by plastic waste disposal. Despite the environmental friendliness of the method, energy consumption of the process is high and a wide product distribution occurs for non-catalytic pyrolysis processes, hence, the use of catalyst to influence the product distribution and relatively reduce reaction temperature and time, as well as maximize product efficiency (Bursali, 2014; Osayi, Iyuke and Ogbeide, 2014). The use of catalyst during pyrolysis enhances the reaction by cracking down higher molecular weight hydrocarbon compounds to lighter hydrocarbon products. It has been reported by several authors that catalyst utilization in plastic waste pyrolysis process can greatly influence products yield, composition and quality (Williams, 2013; Osayi *et al.*, 2014; Strydom, 2017). This resulted growing interest in the investigation of catalyst utilization in plastic wastes pyrolysis to enhance selectivity of products through appropriate selection of catalyst type.

Several studied have reported the use of zeolite catalyst for plastic waste pyrolysis (Williams, 2013; Osayi *et al.*, 2014; Ryan, 2015; Strydom, 2017). Zeolite catalyst is expensive and would impact cost of pyrolysis, thus the need to source for a cheap and readily available catalyst in Nigeria such as CaO obtainable from $CaCO_3$. This led to the investigation of the comparison between zeolite and kaolin catalytic pyrolysis by Gandidi, Susila and Rustamaji (2018). All this study has deeply examined the effect of zeolite catalyst on pyrolysis oil from different perspectives, however, no studies have been reported to the best of my knowledge on the comparative studies of the effect of a cheaply source catalyst like CaO from $CaCO_3$ which is readilt available in large quantity in Nigeria with zeolite catalyst which is expensive, on waste plastic pyrolysis liquid. These therefore, necessitate the need for this study. The study aims to investigate the comparative studies of the effect of CaO and zeolite catalyst on waste plastic pyrolysis. The objectives are characterization of CaO and zeolite catalyst using XRF and XRD, waste plastic pyrolysis using CaO and zeolite catalyst, and optimization of the parameters of pyrolysis using CaO and zeolite catalyst.

Methodology

Materials

The catalyst zeolite was obtained from zeolist, UK while $CaCO_3$ was obtained from NARICT Zaria and the calcinated at 850 °C to obtained CaO which was used as catalyst in comparison with zeolite for waste plastic pyrolysis. Waste plastic materials were sourced from around Kaduna State metropolis. All other chemical used were of analytical grade.

Characterization of Catalyst Materials

The zeolite and CaO adsorbent were characterized using XRF to determine the elemental and oxide compositions of the catalyst materials and XRD was used to examine the crystal structure of catalyst materials.

Experimental Design

Three factors; pyrolysis temperature, heating rate and catalyst type were considered for the optimization of oil yield from plastic pyrolysis. Full factorial design of experiment method was used for the optimization to determine the effect of pyrolysis temperature, heating rate and catalyst type on the product yield. The effect of the selected factors was studied using full factorial design. The levels of the factors were selected based on preliminary study. The uncoded levels of the factors are presented in Table 1.

Table 1: Code and uncoded level of the independent variables

Factors	Type	Level	
Pyrolysis Temperature (°C)	Numeric	300	650
Heating Rate (°C/min)	Numeric	10	40
Catalyst Type	Text	CaO	Zeolite

The relationship between the responses product yield and selected factors were defined using full factorial method. Design Expert 10.0.1 software package was used for the implementation of the method. Design of experiment for the studied factors are presented in Table 2.

Table 2: Design of Experimental of the factors in uncoded values

Run	Factors			Response
	Pyrolysis Temp. (°C)	Catalyst Type	Heating Rate (°C/min)	Yield (5)
1	600	Zeolite	30	
2	400	CaO	30	
3	400	Zeolite	15	
4	400	Zeolite	30	
5	500	CaO	22.5	
6	500	CaO	22.5	
7	600	CaO	30	
8	500	Zeolite	22.5	
9	400	CaO	15	
10	600	CaO	15	
11	500	Zeolite	22.5	
12	600	Zeolite	15	

Waste Plastic Pyrolysis

An improvised pyrolysis reactor in Chemical Engineering Department, ABU Zaria was used for the waste plastic pyrolysis experiment. The schematic setup of the reactor is as shown in Figure 1. The setup is an improvised reactor system where the temperature was maintained and the desired heating rate set. The condenser attached to the reactor is to condense the vapourized products from the reactor by cooling with water passing through the shell side of the condenser. The waste plastic pyrolysis was carried out using 50g of the cleaned and size reduced waste plastic material with 5g (10%) catalyst according to the conditions of the first run presented in Table 2. That is, the temperature was set to 600°C using 5g of zeolite (10%) at a heating rate of 30°C/min. Subsequent runs was carried out according to the set conditions in Table 3.4 using the same procedure.

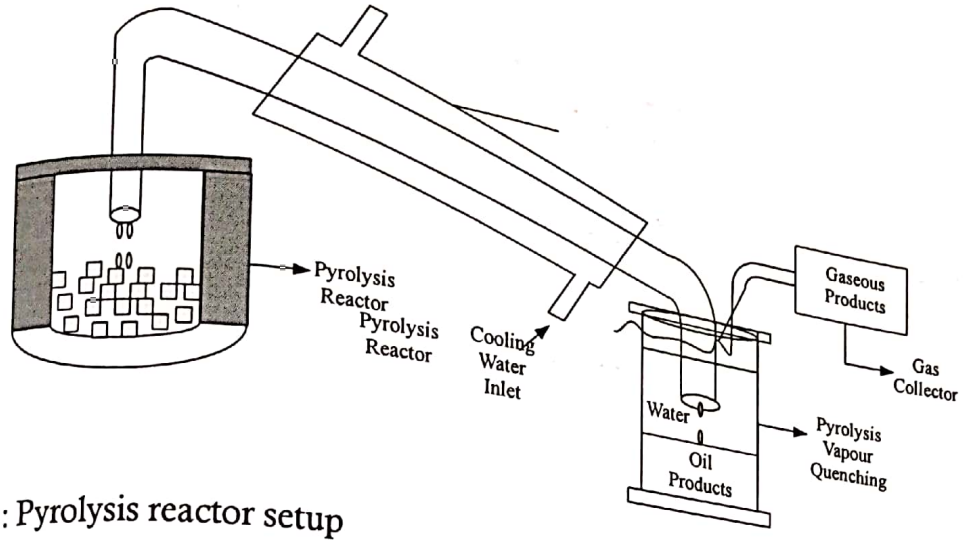


Figure 1: Pyrolysis reactor setup

Results and Discussion

XRD Analysis of Catalyst

The crystal structure of the CaO and zeolite catalyst was characterized by XRD. Figure 2 and 3 presents the XRD pattern of the CaO and zeolite catalyst respectively. From Figure 2, it can be seen that the diffraction peak at 2θ angle of 32.340°, 37.487°, 54.005°, 64.483° and 67.503° was the typical diffraction peak of lime and shows that the CaO catalyst comprises mainly of lime with the main peak appearing at 2θ angle of 37.487°. These peaks correspond to (111), (200), (220), (311) and (222) planes of CaO phase assigned to respectively. The XRD result of the CaO catalyst is consistent with those reported for CaO/g-C_3N_4 composites and synthesis of Nano-Calcium Oxide (Ramacharyulu *et al.*, 2017; Habte *et al.*, 2019). However, the diffraction peak at 2θ angle of 18.054°, 28.952°, 34.309°, 47.229°, 51.011°, and 64.483° was the typical diffraction peak of portlandite and shows that the CaO catalyst contains small quantity of $Ca(OH)_2$. The XRD analysis shows that the CaO catalyst contains mainly CaO and small quantity of $Ca(OH)_2$ as shown in Figure 2.

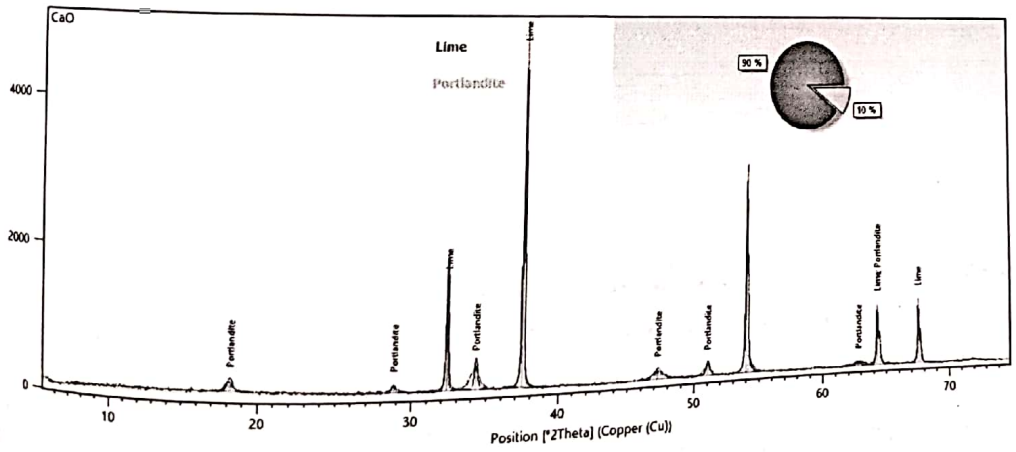


Figure 2: XRD analysis of CaO catalyst

From the XRD analysis zeolite catalyst was also analysed. From Figure 3, it can be seen that the diffraction peak at 2θ angle of 8.101°, 8.968°, 23.254°, 24.094°, 29.477°, 30.108°, 45.260° and 45.654° was similar to the diffraction peak of zeolite ZSM-5 and beta zeolite type. These

peaks are similar to those reported by Heman *et al.* (2019). It also shows that the crystalline structure of the zeolite catalyst contains mainly silicate crystals. As can be seen, all the peaks show the presence of a highly crystalline zeolitic structure with well-defined diffraction peaks of a high structural order that are comparable to XRD pattern of ZSM-5 from JCPDS card No. 44-0002 (Phan *et al.*, 2017). The presence of other non-zeolitic phases was not detected, which indicated the purity of the zeolite catalyst samples.

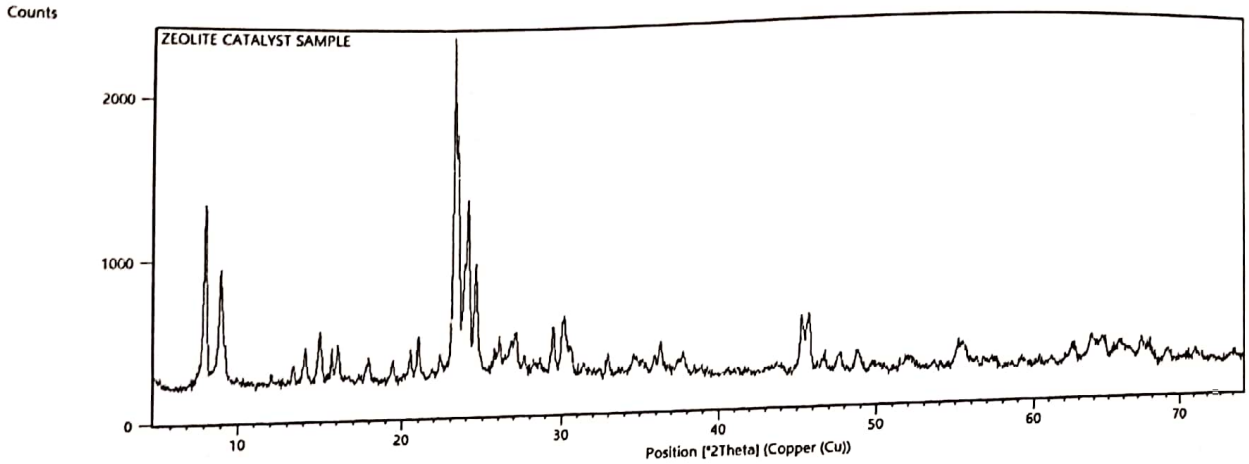


Figure 3: XRD analysis of zeolite catalyst

XRF Analysis of Catalyst

The CaO and zeolite catalyst used were characterized for their chemical compositions using XRF. table 3 shows the chemical composition of the catalyst samples. From table 3, it was observed that the zeolite catalyst contains 3.133% Al_2O_3 and 92.356% SiO_2, to give a silica to alumina ratio of 29.48. This also confirms the high silicate presence from the XRD analysis. The dominating oxides in the zeolite catalyst are; SiO_2 and Al_2O_3, while other oxides present in the zeolite catalyst samples were <1%. It was also observed that CaO catalyst contains mainly, 98.848% CaO and all other oxide were <1%. This further confirms the high presence of CaO form the XRD analysis of CaO catalyst.

Table 3: Chemical Compositions of Catalyst

Metal Oxide	Zeolite	CaO
Fe_2O_3	0.048	0.026
Al_2O_3	3.133	0.000
CaO	0.021	98.848
Cl	0.050	0.069
Cr_2O_3	0.005	0.000
CuO	0.001	0.000
K_2O	0.000	0.001
MgO	0.950	0.630
MnO	0.001	0.003
Na_2O	0.000	0.051
Nb_2O_5	0.002	0.002
NiO	0.341	0.000
P_2O_5	0.229	0.004
PbO	0.004	0.000
S	0.000	0.103
SiO_2	92.356	0.505
SrO	0.000	0.563
SO_3	0.223	0.000
Ta_2O_5	0.000	0.001
TiO_2	0.010	0.001
WO_3	0.003	0.000
Y_2O_3	0.000	0.002
ZnO	0.005	0.001

Optimization of Plastic Pyrolysis Oil Yield

The result of the production and optimization of plastic pyrolysis oil parameter for maximum oil yield are presented in table 4. Design Expert ® 12 software package was used for the implementation of the 3 factor 2-level full factorial experimental design. The optimization study was executed using Full Factorial experimental design approach. The results of the plastic pyrolysis oil yield for each experimental run of the input parameters (temperature, catalyst type and heating rate) are presented in table 4 The experimental values for the response parameter (pyrolysis oil yield) and the three factors in actual form are also presented in table 4.

Table 4: Experimental design and response factor of full factorial analysis of oil yield

Run	Factors			Response (Oil Yield)		
	Temperature	Catalyst Type	Heating Rate	Actual	Predicted	Deviations
	°C		°C/min	%	%	
1	600	Zeolite	30	58.34	58.77	-0.4317
2	400	CaO	30	25.16	26.54	-1.38
3	400	Zeolite	15	45.24	45.67	-0.4317
4	400	Zeolite	30	40.56	39.18	1.38
5	500	CaO	22.5	43.54	43.42	0.1167
6	500	CaO	22.5	45.2	43.42	1.78
7	600	CaO	30	55.3	54.87	0.4317
8	500	Zeolite	22.5	57.78	58.46	-0.6767
9	400	CaO	15	19.94	19.51	0.4317
10	600	CaO	15	19.9	21.28	-1.38
11	500	Zeolite	22.5	57.24	58.46	-1.22
12	600	Zeolite	15	40.08	38.70	1.38

From the production and optimization of plastic pyrolysis oil yield, the t-distribution, coefficients and p-values for the experimental results were obtained. The sum of squares and the F-distribution were also determined. The 95% confidence level was used for the statistical calculations. The regression equation coefficients were also established from the fit of the pyrolysis oil yield. The statistical significance of a particular result based on the sample means were determined using F and T distributions. Values for the t- and F-distributions were compared to tabulated values based on the number of degrees of freedom 1and 95% confidence interval. Also, the p-value was also used to established the statistical significance of the model and the parameters. The p-value is the smallest level of significance that would lead to the rejection of the null hypothesis and the conclusion that data is statistically significant (Montgomery, 2004). If the p-value is <0.05, then the factor is statistically significant at the 95% confidence level.

Analysis of Variance (ANOVA)

Statistical analysis of the model was performed to evaluate the ANOVA and check the adequacy of the empirical model. The results of ANOVA for fitting the quadratic response model by a mean square method are summarized in Table 5. The coefficients of the full factorial method model in actual factor were also evaluated. The significance of each of the coefficients were checked from p-values, which also indicate the interaction strength of each parameter.

Table 5: ANOVA for factor of full factorial analysis of oil yield

Source	Sum of Squares	Df	Mean Square	F-value	p-value	Remark
Model	**1755.64**	**6**	**292.61**	**87.00**	**0.0003**	**significant**
A-Temperature	228.12	1	228.12	67.83	0.0012	significant
B-Catalyst Type	678.00	1	678.00	201.59	0.0001	significant
C-Heating Rate	367.20	1	367.20	109.18	0.0005	significant
AB	38.19	1	38.19	11.36	0.0280	significant
AC	352.72	1	352.72	104.87	0.0005	significant
BC	91.40	1	91.40	27.17	0.0065	significant
Residual	13.45	4	3.36			
Lack of Fit	**11.93**	**2**	**5.96**	**7.83**	**0.1133**	**not significant**
Pure Error	1.52	2	0.7618			
Cor Total	2211.13	11				

The p-value which is an index measuring the discrepancy of the fit of a model or the strength of evidence against the null hypothesis (the hypothesis that there is no association between the factors and response variable) was examined for the response factor (pyrolysis oil yield) (Gelman, 2013; Maqsood and Ibrahim, 2015). To quantify the strength of evidence against null hypothesis, $p < 0.05$ (5% significance) is used as a standard level for concluding that there is evidence against the hypothesis tested. The significance of the regression coefficients was tested using F-value and the p-values, and was also used to test the significance of the effect of each variable in the model. From Table 5, it can be seen that the model p-value is 0.0003 ($p<0.05$), which implies that the oil yield model is significant (Gelman, 2013; Sedgwick, 2014; Maqsood and Ibrahim, 2015). It was also observed that the p-value for all model term are significant ($p<0.05$).

However, model p-value of 0.0003 demonstrating high significance of the model in predicting the response values of the oil yield and the suitability of the model (Montgomery, 2006, Maqsood and Ibrahim, 2015). Furthermore, from Table 5, it was observed that the model F-value is 87.00, which also implies that the model is significant and that there is only a 0.03% chance that an F-value this large could occur due to noise in the experiments (Adepoju and Olawale, 2015; Maqsood and Ibrahim, 2015). The model F-value with low probability value 0.0003 ($p<0.05$) indicated the high significance of the fitted model (Scheffe, 2005). Additionally, the Lack of Fit is also an important index to evaluate the reliability of model. From Table 5, the Lack of Fit F-value of 7.83 implies the Lack of Fit is not significant relative to the pure error and that there is a 11.33% chance that a Lack of Fit F-value this large could occur due to noise (Jia *et al.*, 2018). Non-significant lack of fit is good well fitted model.

Factorial Method Modelling of Pyrolysis Oil Yield

The relationships of the response (pyrolysis oil yield) with the input factor (independent variables) were explored by using the regression model. The regression model was evaluated with a 2 way linear-linear interaction of the factors. The regression model in terms of coded factors that correlates the pyrolysis oil yield to the various input factors are presented in Table 6.

Table 6: Model coefficient in terms of coded factor for pyrolysis oil yield

Factor	Coefficient Estimate	Df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	38.07	1	0.6484	36.26	39.87	
A-Temperature	5.34	1	0.6484	3.54	7.14	1.0000
B-Catalyst Type	-7.52	1	0.5294	-8.99	-6.05	1.0000
C-Heating Rate	6.77	1	0.6484	4.97	8.58	1.0000
AB	2.19	1	0.6484	0.3848	3.99	1.0000
AC	6.64	1	0.6484	4.84	8.44	1.0000
BC	3.38	1	0.6484	1.58	5.18	1.0000
R^2	**0.9924**					
Adjusted R^2	**0.9810**					
Predicted R^2	**0.8237**					

The regression modeled in term of coded factors as shown in Table 4.4 is therefore expressed as Equation 1.

$$Yield = 38.07 - 5.34A - 7.52B + 6.77C + 2.19AB + 6.64AC + 3.38BC \quad \text{Eq. 1}$$

The coefficient estimate in table 6 represents the expected change in response per unit change in factor value when all remaining factors are held constant. The intercept in an orthogonal design is the overall average response of all the runs. The coefficients are adjustments around that average based on the factor settings. When the factors are orthogonal the VIFs are 1 while VIFs greater than 1 indicate multi-collinearity. The higher the VIF the more severe the correlation of factors as such VIFs less than 10 are tolerable and acceptable. Also, the regression model in terms of coded factors (Eq 4) can be used to make predictions about the response for given levels of each factor which by default, the high levels of the factors are coded as +1 and the low levels of the factors are coded as –1. The coded equation is useful for identifying the relative impact of the factors by comparing the factor coefficients. Conversely, this equation is not suitable for make predictions about the response in actual term. The regression model in terms of actual factor for pyrolysis oil yield is therefore, expressed as Equation 2 and 3 for CaO and zeolite catalyst respectively.

$$Oil\ Yield\ (CaO\ Catalyst) = 62.05833 - 0.12395 * Temperature - 3.07267 * Heating\ Rate + 0.008853 * Temperature * Heating\ Rate \quad \text{Eq.2}$$

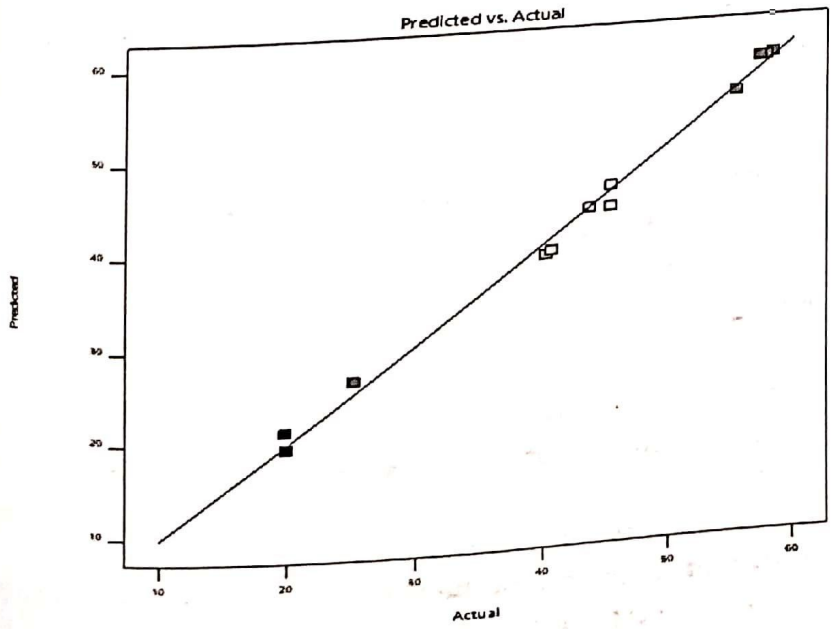
$$Oil\ Yield\ (Zeolite\ Catalyst) = 119.22167 - 0.16765 * Temperature - 3.974 * Heating\ Rate + 0.008853 * Temperature * Heating\ Rat \quad \text{Eq.3}$$

The model equations in terms of actual factors are presented in Eq. 2 and 3 for catalyst type o CaO and zeolite respectively. The equation in terms of actual factors suitable for mak predictions about the response for given levels of each factor in its actual term. A such, th levels are specified in the original units for each factor. However, this equation is not suitable i determining the relative impact of each factor because the coefficients are scaled t accommodate the units of each factor and the intercept is not at the center of the design space.

The model's equations were also evaluated based on the regression coefficients, R^2, Adjusted R^2 and Predicted R^2 of the model. R^2 value is a measure of the goodness of fit of a model. R^2 value lies between 0 and 1, and the closer the R^2 value is to 1, the better the model prediction (Doddapaneni *et al.*, 2007; Jia *et al.*, 2018). This is because as R^2 value approaches 1, the model gets fitted at almost all points. The Adjusted R^2 plateaus when insignificant terms are added to the model, and the Predicted R^2 will decrease when there are too many insignificant terms, therefore, a rule of thumb is that the difference between Adjusted and Predicted R^2 values should be within 0.2 of each other (Montgomery, 2006).

The goodness of fit of the model was checked using the regression coefficient of determination. The R^2, Adjusted R^2 and Predicted R^2 for pyrolysis oil yield model are 0.9924, 0.9810 and 0.8237 respectively (Table 6) which implies that 99.24% of the experimental data are explainable by the model and the high value of R^2 (0.9924) further indicates high significance of the model in predicting the response variable (Akossou and Palm, 2013). From Table 6, it can be seen that the difference between the Adjusted R^2 value Predicted R^2 value are less than 0.2, which further implies that there is good agreement between the experimental data and predicted data for pyrolysis oil yield (Adepoju and Olawale, 2015; Jia *et al.*, 2018). This confirms that the accuracy and general ability of the model was good, and analysis of the associated response trends was reasonable

Furthermore, the validity of the model was checked using the plot of actual against predicted. Figure 4 presents the plot of the actual or experimental responses against the predicted responses. It can be seen from Figure 4 that the waste plastic pyrolysis oil yield both experimental and predicted results are very close with R^2 of 0.9924. This further suggest that the model's equation generated can be used to predict waste plastic pyrolysis oil yield and indicate that the models adequately represents the experimental data (Akossou and Palm, 2013; Adepoju and Olawale, 2015). Therefore, the developed models provide good predictions for average outcomes.



igure 4: Plot of Actual against Predicted pyrolysis oil yield.

Factorial Optimization of Waste Plastic Pyrolysis Oil Yield

The result of the factors that will maximize the pyrolysis oil yield was also evaluated using surface plot. Surface plot was use to explore the relationship between three variables and to view the combinations of x and y factors that produce desirable response values (Saleem and Somá, 2015; Gul, 2016). A typically 3D surface plot consists of an x-axis and y-axis representing values of a continuous predictor variable. The surface plots are useful in regression analysis for viewing the relationship among a dependent and two independent variable or factors. The surface plot shown in Figure 5 and 6 was used to describe the interaction of different variables on plastic waste pyrolysis oil yield.

Figure 5 presents the effect of the temperature, heating rate and CaO catalyst type on waste plastic pyrolysis oil yield at the center level of the parameters. It can be seen that oil yield increases with the increase in the temperature and heating rate. Moreover, waste plastic pyrolysis oil yield is more sensitive to both temperature and heating rate. Hence, high oil yield is obtained at high temperature and heating rate, and decrease as temperature and heating rate decreases for CaO catalyst. This is attributed to the fact that increasing pyrolysis temperature and heating rate tends to accelerate chemical degradation of hydrocarbon molecule into oil. Also, the high yield at relatively low temperature could be attributed to fact that CaO could the rate of degradation of the plastics (Zhang *et al.*, 2008). This corroborate with the fact that plastic waste pyrolysis depends upon sets of parameters such as catalyst type, temperature etc. (Alfa, Zubairu and Alhassan, 2019).

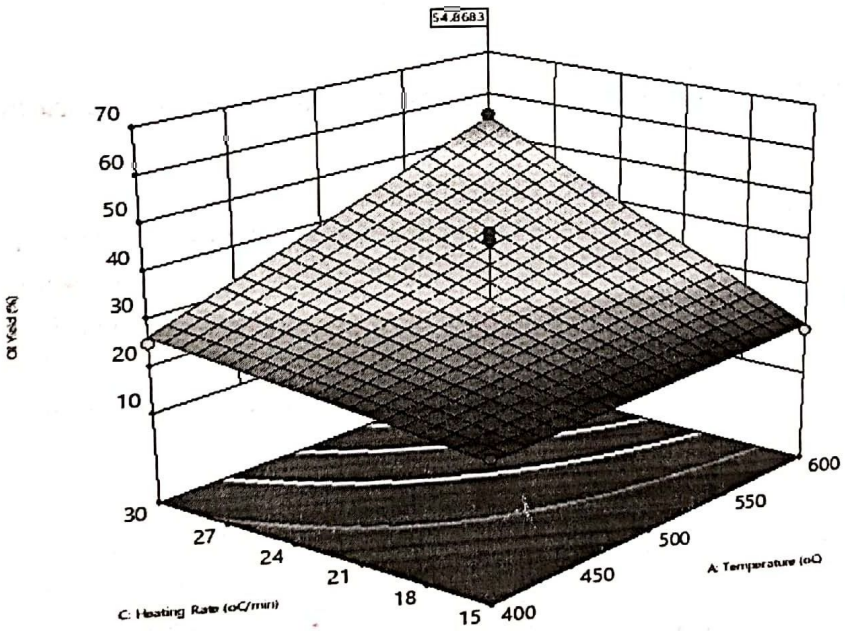


Figure 5: 3D surface plot effect of temperature and heating value on oil yield using CaO catalyst.

Figure 6 presents the effect of the temperature, heating rate and zeolite catalyst type on waste plastic pyrolysis oil yield at the center level of the parameters. It was also observed that oil yield

creases with the increase in the temperature and heating rate using zeolite catalyst. This also confirms that waste plastic pyrolysis oil yield is also sensitive to both temperature, heating rate and catalyst type. Hence, high oil yield is obtained at high temperature and heating rate, and decrease as temperature and heating rate decreases for zeolite catalyst. This corroborate with the fact that plastic waste pyrolysis depends upon sets of parameters such as catalyst type, temperature etc. (Alfa, Zubairu and Alhassan, 2019).

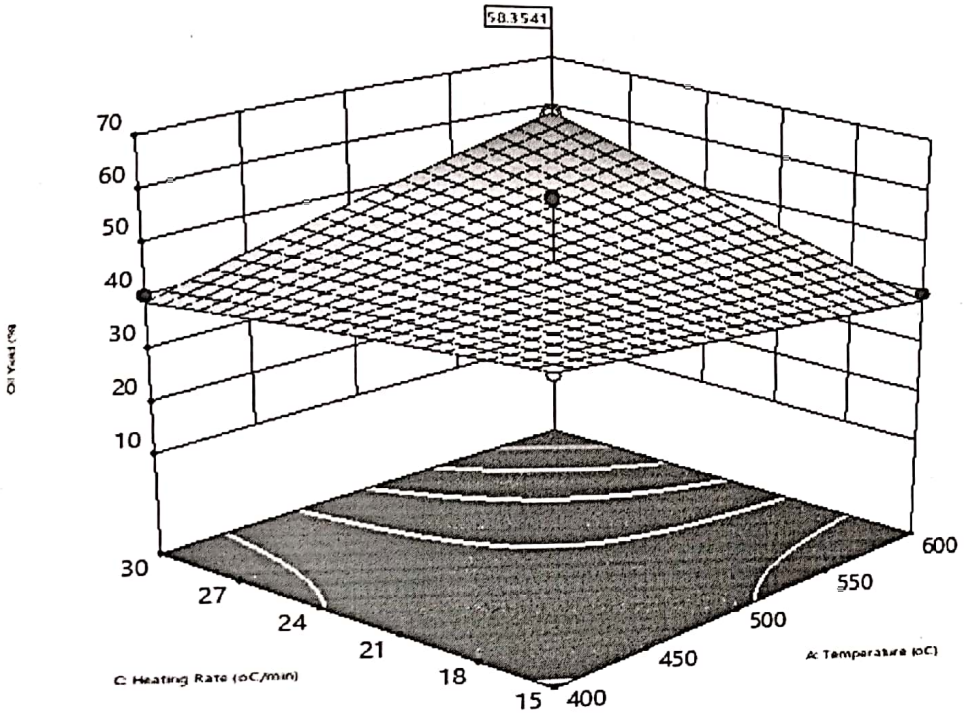


Figure 6: 3D surface plot effect of temperature and heating value on oil yield using zeolite catalyst.

Comparatively, it was observed that waste plastic pyrolysis oil yield using zeolite catalyst was slightly higher that yield that CaO catalyst. This could be attributed to the fact that high Si/Al ratio in zeolite portends acid site which decreases with increase in Si/Al ratio and affect product distribution while higher Si/Al ratio increases crystallinity. The Si/Al ratio in the zeolite used as catalyst has 29.5 Si/Al ratio, which is attributed to the high oil yield obtained with zeolite.

Table 7 presents the yield of oil obtained from waste plastic pyrolysis in the absence of catalyst. It can be seen that, though the oil yield increases from 12.18 – 31.24% as the temperature increases rom 450 – 600 °C, however, the yield was very low when compared to those with catalyst (Table 4). The performance of pyrolysis process can be improved by using catalyst because it will enhance the rate of plastic molecule degradation (Kolsoom *et al.*, 2017; Alfa *et al.*, 2019). Hence, shows the influence of the presence of catalyst on pyrolysis is significant.

Table 7: Plastic pyrolysis oil yield without catalyst

No.	Temperature (^{o}C)	Yield (%)
1	450	12.18
2	500	21.42
3	600	31.24

Optimum Waste Plastic Pyrolysis Parameter

The primary objective of optimization in this study was to find the conditions which gave the maximum waste plastic pyrolysis oil yield. table 8 present the optimization result of the parameters that maximum waste plastic pyrolysis oil yield using optimum desirability function with the setup constraint for temperature, heating rate and catalyst type to be in range between the lower and upper limit while the constraint for the response (waste plastic pyrolysis oil yield) was set at maximum. Desirability is an optimization function that is used to determine the optimum result (region) that satisfied the set criteria or optimization goal. It reflects the desirable ranges for each response. The desirable ranges are from zero to one (least to most desirable, respectively). The simultaneous objective function is a geometric mean of all transformed responses. The optimum factors and corresponding response generated for optimization study are presented in table 8.

Table 8: Factorial Optimization Result for Pyrolysis oil yield

Number	Temperature	Catalyst Type	Heating Rate	Oil Yield	Desirability	
1	**597.269**	**Zeolite**	**29.909**	**58.385**	**1.000**	**Selected**
2	600.000	Zeolite	30.000	58.772	1.000	
3	598.171	Zeolite	29.820	58.354	1.000	
4	599.467	Zeolite	29.857	58.529	1.000	
5	598.389	Zeolite	29.975	58.581	1.000	
6	596.915	Zeolite	29.992	58.459	1.000	
7	596.164	Zeolite	29.979	58.369	1.000	
8	598.387	Zeolite	29.902	58.484	1.000	
9	599.198	Zeolite	29.735	58.341	1.000	
10	599.888	Zeolite	29.789	58.478	1.000	
11	599.949	Zeolite	29.718	58.390	1.000	
12	599.101	Zeolite	29.796	58.412	1.000	
13	599.494	Zeolite	29.937	58.638	1.000	
14	594.010	Zeolite	30.000	58.185	0.996	
15	581.715	Zeolite	30.000	56.981	0.965	
16	**600.000**	**CaO**	**30.000**	**54.868**	**0.910**	**Selected**
17	598.995	CaO	30.000	54.726	0.906	
18	600.000	CaO	29.718	54.237	0.893	
19	587.057	CaO	30.000	53.035	0.862	
20	563.695	CaO	30.000	49.726	0.776	

From table 8, it was observed that the established optimum values for maximum waste plastic pyrolysis oil yield are 597 °C temperature, zeolite catalyst type and 29.909 °C/min heating rate to give a maximum waste plastic pyrolysis oil yield of 58.385% at a desirability of 1. However, 600 °C, CaO catalyst type and 30 oC/min to obtained a yield of 54.868% at 0.9097 desirability function. Figure 6 shows the optimization plot of the established optimum from table 8.

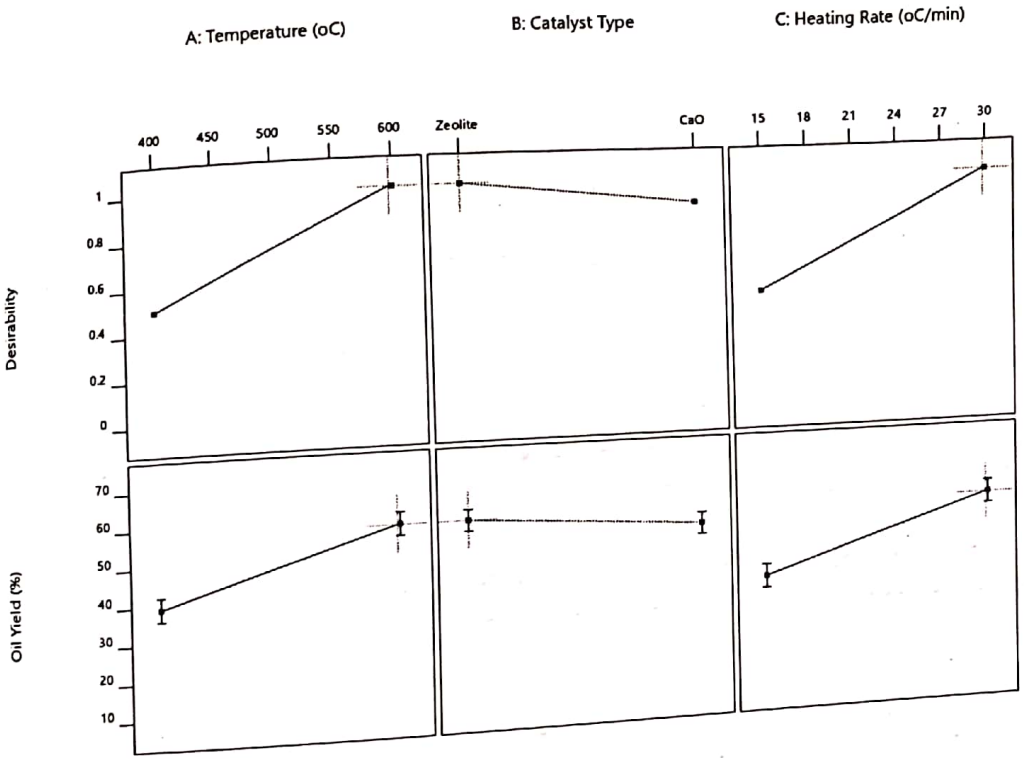


Figure 7: Factorial Optimization plot

A validation experiment was conducted to determine the reliability of the optimum factors for the waste plastic pyrolysis oil yield. Waste plastic pyrolysis was carried out using zeolite catalyst type at 597 °C temperature and 29.909 °C/min heating rate according to the procedure highlighted in the methodology. To establish the validity of the optimum conditions, 3 experiments were conducted. The obtained waste plastic pyrolysis oil yields for the 3-validation experiment conducted are 58.60%, 57.94% and 58.56% with an average oil yield of 58.367%. The waste plastic pyrolysis oil yield obtained for the validation experiment was found to be very close to the predicted maximum of 58.385% using zeolite. The results clearly indicated that no much significant difference was observed between the predicted optimum and validate value. This therefore, indicated that the optimization achieved in the present study was reliable.

Conclusion

The XRD analysis, shows that the crystal structure of zeolite corresponds to those of ZSM-5 diffraction peak and the crystalline structure of the zeolite catalyst contains mainly silicate crystals while the XRD analysis of the CaO catalyst shows that it contains mainly crystal of CaO and small quantity of $Ca(OH)_2$ in its crystal structure. The XRF analysis shows that the

zeolite catalyst contains 3.133% Al_2O_3 and 92.356% SiO_2, to give a silica to alumina ratio of 29.48, confirming the high silicate presence from the XRD analysis while the CaO catalyst contains mainly, 98.848% CaO and all other oxide were <1%, confirms the high presence of CaO form the XRD analysis of CaO catalyst.

Pyrolysis of waste plastic for the production of fuel oil was successful. The optimization study shows that the optimum values of pyrolysis temperature, heating rate and catalyst type for maximum oil yield are 597 °C temperatures and 29.909 °C/min heating rate using zeolite catalyst type to give a maximum waste plastic pyrolysis oil yield of 58.385%. However, 600 °C and 30 oC/min using CaO catalyst type give a yield of 54.868%. This shows that the yield obtained with CaO as catalyst is relatively comparable to that obtained using zeolite. The validation of the established optimum parameters shows that the plastic pyrolysis oil yield for the 3-validation experiment are 58.60%, 57.94% and 58.56% with an average oil yield of 58.367%. Whereas, the validation of the established optimum parameters for CaO catalyst shows that the plastic pyrolysis oil yield for the 3-validation experiment are 54.60%, 54.94% and 53.96% with an average oil yield of 54.50%. The results clearly indicated that no much significant difference was observed between the predicted optimum and validate value for both CaO and zeolite catalyst. This therefore, indicated that the optimization achieved in the present study was reliable. The study also shows that there was no much significant difference in the yield of CaO and zeolite at the established optimum condition for both catalyst type. Therefore, considering cost of zeolite CaO could be useful as catalyst for waste plastic pyrolysis.

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