



Optimization of Process Parameters for Catalytic Pyrolysis of Waste Tyre using Reactivated Fluid Catalytic Cracking Catalyst

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ABSTRACT

This work investigated the optimization of process parameters for catalytic pyrolysis of waste tyre using reactivated spent Fluid catalytic cracking (FCC) catalyst. The waste tyre pyrolysis used design expert software as the optimization tool for this study. A 3-factor level CCD with 20 experimental runs was used with temperature, time and catalyst as the input parameters while oil yield, density and viscosity were the output variables. Thereafter, an experimental validation of the optimized parameters, which were not among the original experimental runs, was carried out. Pyrolysis was also carried out at the optimized conditions with un-activated catalyst and without catalyst to ascertain the contributions of the catalyst and its reactivation. Based on the optimum parameters, 48.5 wt. % oil (0.79 g/ml and 2.05 cSt) was produced with the reactivated catalyst, 43.4 wt. % (0.86 g/ml and 3.52 cSt) was produced with spent catalyst, and 51 wt. % oil (0.95 g/ml and 4.24 cSt) was produced without catalyst. The oil yield without catalyst was higher than with reactivated catalyst (R-CAT); but it however had the lowest fuel qualities while oil produced with catalyst in turn had higher quantity and quality compared to oil produced with catalyst. Therefore, the incorporation of density and viscosity of the oil in the optimization of the catalytic pyrolysis of waste tyre enhanced the improvement of yield and quality of the oil produced.

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INTRODUCTION

Waste tyres, defined as tyres that have reached the end of their useful life continue to increase on a regular basis around the world, with a global production rate of about 1-1.5 billion tyres annually and a generation of waste tyre stock estimated to be around 17 million tons in 2016 [1-2]. They are either discarded in landfills or recycled [3]. There are rising concerns to mitigate environmental impacts of a fire outbreak in landfills which produces hazardous chemicals such as biphenyl and benz(α)pyrene which are carcinogens [3-4].

Waste tyre management options includes reuse (retreading and recycling), energy recovery (incineration), thermochemical conversion (pyrolysis and gasification) and landfilling, which is the least desired option for waste tyre disposal [5-7]. Tyres are made up of more than 90% organic matter and can produce excellent

calorific fuel with calorific value of about 31,400 kJ/kg, higher than that of coal (26,200 kJ/kg) and slightly less than crude oil (39,500 kJ/kg). This huge energy potential of the waste tyres, coupled with its recovery resulting to a lower impact of the waste tyres on human and environmental health encouraging researchers to the energy recovery potential of waste tyre [8].

Pyrolysis, which is the most recommended thermochemical waste tyre treatment method, generates oil, char, and syngas. The derived oils and syngas can be used as fuels or as feedstock for refining crude oil or chemical products, which is why pyrolysis is widely applied for waste tyre treatment [9]. Pyrolysis is an endothermic reaction with temperature and heating rate as the most important kinetic parameters [10]. Depending on the type of pyrolysis (fast, slow, flash and catalytic) with changes in process parameters, product distributions are significantly affected [11-13].

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Fluid catalytic cracking (FCC) catalysts are used in refining processes to convert heavy feed into lighter products such as LPG, gasoline, and diesel, with a global consumption of approximately 750 MT per year [14]. It is made up of Y zeolite which has a well-defined lattice structure with Silica and Alumina tetrahedral as its basic building block. Oxidation states of Si and Al are +4 and +3, making Si neutral and leaving Al with a net charge of -1 which is balanced during synthesis with positive ions and thus making Al the source of active sites responsible for activity and selectivity [15]. The catalyst is rapidly deactivated due to sintering and high temperature in the regenerator, steam in the stripper which reducing crystallinity and deposition of carbon and contaminant metals like Ni, V, and Co on the catalyst's surface [16]. After some regeneration cycles, spent catalyst are withdrawn for disposal. Contaminant metals in the spent catalyst are listed as hazardous wastes, making landfilling a less recommended option [17].

It has been reported that the use of catalyst in tyre pyrolysis systems can have a significant impact on the composition, quality, and yield of products [12]. Studies have used both alkaline and acidic catalysts for catalytic pyrolysis of waste tyre. While alkaline catalysts like MgO, CaCO₃, NaOH and CaO improved the quantity of oil yield, acidic catalysts like zeolites improved the quality of the oil produced [1,12]. Ramirez-Canon et al. [2] used a hydrogen stream to enhance the physical properties of used tyre pyrolysis and products were similar to diesel fuel with maximum oil yield of 37 wt.% at 550°C, densities were in the range of 0.83-0.88 g/cm³, viscosities were in the range of 1.59-3.07 cSt, flash point values were in the range of 31.0-35.5 °C, while HHV values were in the range of 45.95-48.67 MJ/kg. Osayi and Osifo [9] used synthesized zeolite NaY catalyst for pyrolysis of waste tyre and got maximum oil yield of 21.3 wt.% at a catalyst-to-tyre ratio of 7.5%. While the oil yield from non-catalyzed pyrolysis was higher at 34.4 wt.%, the quality in terms of chemical compositions and hydrocarbon range from the GC-MS analysis was lower than that of catalyzed pyrolytic oil. The catalyst displayed the potential of improving the carbon range of gasoline (C₆-C₁₂) and kerosene (C₁₁-C₁₄), with lower yields of diesel and fuel oil (C₁₁-C₂₀) when compared to non-catalyzed pyrolytic oil. Kordoghli et al. [18] used MgO and CaO as catalysts for pyrolysis of waste tyre and found that oil yields were in the range of 27.14 wt.% for MgO and 27.5 wt.% for CaO. Although the liquids were not characterized, the gas analysis showed that CaO catalyst favored the formation of C₂H₄, C₂H₆ and C₃H₈ while MgO only increased CH₄ from 30 to 38 wt.%. Wang et al. [12] utilized the residual activity of spent FCC catalyst in pyrolysis of waste tyre and found that the oil yield using spent FCC catalyst was 40.71 wt.% which was lower than oil yield of 42.68 wt.% without catalyst. However, pyrolytic oil produced using the spent FCC catalyst had

improved qualities with density of 0.844 g/cm³ and viscosity of 0.8497 mm²/s when compared to oil produced without catalyst with density of 0.9308 g/cm³ and viscosity of 5.556 mm²/s. Again, the pyrolytic oils were not analyzed but the analysis of gas showed that C₄H₈ (65.58 %) was the main gas component in the presence of the spent FCC catalyst while C₄H₆ (48.07%) was the main gas component in the absence of the catalyst. Hossain and Rahman [19] investigated the effect of a zeolite catalyst on the production of liquid fuel from waste tire and discovered that the presence of the catalyst resulted in higher yield of gas at the expense of the oil. However, the presence of the catalyst favored an increase in the concentration of light naphtha in the pyrolytic oil. Hossain et al. [20] also investigated the influence of ZSM-catalyst/tire ratio on pyrolysis of waste tire products. They found that char and oil were increased with an increase in catalyst-to-tire ratio while reverse was the case with the gas. The CHNS analysis revealed an increase in carbon content from 86.81 to 88.60% and a decrease in sulfur content from 1.325 to 1.064% when the catalyst-tire ratio was increased from 0.1 to 0.15. Liquid fuels can also be produced from pyrolysis of other hydrocarbon wastes like polyethylene plastics wastes and biomass wastes [21, 22].

Recently, optimization of process parameters using various statistical modelling and optimization techniques has been of significant importance to researchers. Response surface methodology (RSM) is one of such technique that can be used to optimize process conditions by analyzing the effects of process variables [23-28]. Central composite design (CCD) and Box-Behnken are mostly used to execute RSM design matrices to fit experimental data and can accurately predict optimized conditions for experiments with minimum number of experimental runs [29]. Three different points define the CCD design: center points used to determine experimental errors and replication range from 4 to 6 with 6 being ideal for best predictions, axial (star) points usually projected from the center point and list factor levels in coded units, and factorial points containing all possible combinations from low to high levels [30].

Beside the use of other types of catalysts, most of the reported studies regarding the catalytic pyrolysis of waste tires used either fresh or spent FCC catalysts. In addition, there were few studies that were devoted to the optimization of process parameters for catalytic waste tyre pyrolysis. Therefore, this study was focused on optimizing the production of oil from pyrolysis of waste tyre in the presence of reactivated spent FCC catalyst, which possessed high activity than the untreated spent catalyst. The optimization process provided the opportunity of incorporating parameters such as oil viscosity and density that helped in the determination of the oil quality.

MATERIALS AND METHODS

Materials

Waste tyre obtained from dumpsite in Zaria, Kaduna, Nigeria; reactivated FCC catalyst designated as R-CAT obtained from Kaduna Refining and Petrochemical Company (KRPC), Kaduna, Nigeria. Equipment used includes digital weighing balance, heating mantle, improvised reactor, thermocouple, viscometer and oxygen bomb calorimeter.

Methods

Spent FCC catalyst reactivation

Spent FCC (E-CAT) was calcined at 550 °C for 1hr, followed by acid washing with lactic acid at 80°C, time of 60 mins, pH of 2 and solution (ml)-to-catalyst (g) ratio of 15.

Waste tyre preparation

Waste tyre was reduced to sizes of 6 -10mm sizes to ensure constant heat transfer through the material during pyrolysis. The tyre sample was washed to remove debris and sand followed by drying to remove moisture.

Experimental design

A pyrolysis batch reactor from Chemical Engineering Department, ABU Zaria was used for the pyrolysis experiment. The setup consisted of a reactor and a condenser attached to the reactor to condense the vapour from the reactor. 60 g of prepared waste tyre sample and a constant heating rate of 15 °C/min and atmospheric pressure were used for all experimental runs in the pyrolysis reactor. Design ranges for input parameters are presented in Table 1. To optimize the oil yield, density and viscosity of the pyrolyzed fuel oil (output responses), a 3-factor RSM, CCD was used requiring 20 experimental runs with three input and three output parameters.

In analysis of experiments, models are fit based on a response or quality of a set of controllable variables. These models can be linear or first order (Equation (1)) in which case they model the average effect of a control variable or factorial (two-factor interactions) (Equation (2)) in which case they allow the interaction of two variables. They can also be quadratic or second order (Equation (3)) in which case they allow for higher interactions involving more than 2 factors and for curvature in the effect of a control on the response. This quadratic model is widely used in optimization

experiments. used in optimization experiments. It is worth to be mentioned that there is a fourth model known as the cubic model which is aliased; that is the design points are too few to determine all terms in the model [30-31].

Linear model:

$$Y = \beta_0 + \beta_1x_1 + \beta_2x_2 \dots + \beta_nx_n + \varepsilon \quad (1)$$

Factorial model:

$$Y = \beta_0 + \beta_1x_1 + \beta_2x_2 + \beta_{12}x_1x_2 + \dots + \beta_{1n}x_1x_2 \dots x_n + \varepsilon \quad (2)$$

Quadratic model:

$$Y = \beta_0 + \beta_1x_1 + \beta_2x_2 + \beta_{12}x_1x_2 + \beta_{11}x_1^2 + \beta_{22}x_2^2 + \dots + \beta_{nn}x_n^2 + \varepsilon \quad (3)$$

where Y = response, x_1 and x_2 = process variables, β_0 = constant coefficient, β_1 = coefficient for linear interaction, β_{11} , β_{12} and β_{12} = coefficient for quadratic interaction, n = nth coefficient and ε = error.

Depending on which model best fits the design, Equations (1)-(3) can be written in terms of actual or coded factors that could be used to reproduce experimental data [32].

As the pyrolysis progressed, the gaseous product formed was continuously transported through a condenser and the condensed oil product was collected at the bottom of the condenser tube. The process was stopped at the elapse of the required time. The char, oil and gaseous products were weighed to determine the yield of the oil using Equation (4) after which the density and viscosity of the oil were measured for each run.

$$\text{Oil Yield (\%)} = \frac{W}{W_0} \times 100 \quad (4)$$

here W = weight of the oil produced (g), W_0 = weight of the tyre sample (g).

The oil produced was then analyzed to measure its density and viscosity. The measured responses (oil yield, density and viscosity) for all the 20 runs were inputted into the RSM to determine the optimum conditions. Thereafter, the optimum values of input variables (temperature, time and feed-to-catalyst ratio) predicted by the RSM was experimentally validated as these optimum values were not among the experimental runs. Finally, the yield and quality of the oil were also determined with unreactivated catalyst and without catalyst at the same optimum values of the input parameters to determine the effect of the catalyst and its reactivation.

Table 1. Coded and uncoded level of the independent variables

Type	Factors	Units	-level	+level
A	Temperature	°C	350	500
B	Time	Min	60	120
C	Catalyst	%	1	10

RESULTS AND DISCUSSION

Detailed experimental runs and their respective responses are presented in Table 2. The experiment is endothermic and it was observed that an increase in temperature led to a corresponding increase in products formation. For

instance, increasing the temperature from 350 to 425 °C at 90 mins and catalyst-to-feed ratio of 5.5 % led to an increase in the oil yield from 16.72 to 48.98 wt. % and density from 0.75 to 0.79 g/ml but a reduction in viscosity from 6.23 to 3.54 cSt. However, further increase in temperature from 425 to 500 °C led to an increase in non-condensable gas yield, which resulted in to a decrease in oil yield with an increase in density and viscosity. This may be due to secondary reactions enabling the formation of gases at high temperatures. It was also observed that initial increase in the catalyst-to-feed ratio from 1 to 5 wt. % at constant temperature and time increased the oil yield while further increase in from 5 to 10 wt. % enhanced the formation of non-condensable gas yield at the detriment of the oil yield. Lastly, an increase in the time at constant temperature and catalyst-to-feed ratio also increased liquid yield up to 90 minutes but a subsequent decrease in oil yield was observed from 90 to 120 minutes. The condition that gave the highest oil yield of 48.98 wt. % with density and viscosity of 0.79 g/ml and 3.56 cSt, respectively was observed at temperature of 425 °C, catalyst-to-feed ratio of 5 wt. %, and time of 90 minutes, respectively. Similarly, the condition for the lowest oil yield of 10.63 wt. % with density and viscosity of 0.64 g/ml and 7.67 cSt, respectively was observed at temperature of 350 °C, catalyst-to-feed ratio of 1 wt. % and time of 60 minutes.

Optimization analysis and model equations

Analysis of variance (ANOVA) results for this pyrolysis study are presented in Tables 3, 4 and 5 for the three responses. The statistical results for the pyrolysis study are summarized in Table 6. The values of the regression coefficient R^2 , adjusted R^2 and predicted R^2 values for oil yield, density and viscosity were close to 1 and all the "Predicted R^2 " were in reasonable agreement with the "Adjusted R^2 " of less than 20% difference. A quadratic model was suggested for oil yield and viscosity while a linear model was suggested for density. The model equations in terms of coded factors are presented in Equations 5a, 6a and 7a for the three responses while Equations 5b, 6b and 7b represent the actual factors respectively. These models can be used to recreate the experimental data for oil yield, density and viscosity from pyrolysis of waste tyre using the reactivated spent FCC catalyst and they were in line with the predicted values from the model equations.

The F-test values validated the models developed for the oil yields with corresponding densities and viscosities and showed that these models could govern the design space. The F values of the models from ANOVA were 20.14, 14.73 and 27.88 for the oil yield, density and viscosity, respectively indicating that the models were significant. The lack of fit tests was found to be insignificant implying the difference between the residual

Table 2. Experimental runs for CCD with respective responses

Std	Run	Temperature (°C)	Time (mins)	Catalyst-to-feed ratio (%)	Oil Yield (wt. %)	Density (g/ml)	Viscosity (cSt)
12	1	425	120	5.5	41.27	0.81	3.93
14	2	425	90	10	42.28	0.84	2.78
10	3	500	90	5.5	44.32	0.83	2.74
18	4	425	90	5.5	46.55	0.77	2.63
19	5	425	90	5.5	38.05	0.82	3.56
13	6	425	90	1	36.33	0.78	2.79
5	7	350	60	10	25.35	0.73	5.47
15	8	425	90	5.5	45.55	0.78	2.69
9	9	350	90	5.5	16.72	0.75	6.23
20	10	425	90	5.5	46.27	0.77	2.48
17	11	425	90	5.5	48.98	0.79	3.54
11	12	425	60	5.5	44.3	0.82	2.75
6	13	500	60	10	42.13	0.82	1.96
16	14	425	90	5.5	48.55	0.78	2.6
4	15	500	120	1	42.18	0.82	2.75
7	16	350	120	10	22.95	0.76	6.3
8	17	500	120	10	41.15	0.83	2.97
2	18	500	60	1	38.8	0.8	2.14
3	19	350	120	1	17.13	0.7	6.53
1	20	350	60	1	10.63	0.64	7.67

and pure error was insignificant. The signal-to-noise ratio was found to be 13.23, 14.22 and 16.83 for the oil yield, density and viscosity and these ratios are greater than the minimum required (4) for adequate precision value [33]. From the ANOVA of each response, temperature was found to be the factor with the highest influence on the pyrolysis process because of its low p-value, large coefficient value in the uncoded models as well as its large F-test value compared to the other factors.

Coded model for the oil yield

$$Oil\ Yield\ (\%) = 44.39 + 11.58A + 0.35B + 2.88C - 0.21AB - 2.28AC - 1.66BC - 11.96A^2 + 0.31B^2 - 3.17C^2 \quad (5a)$$

Actual model for the oil yield

$$Oil\ Yield\ (\%) = -437.22 + 2.01A + 0.06B + 6.34C - 9.44AB - 0.007AC - 0.01BC - 0.002BA^2 + 3.41B^2 - 0.16C^2 \quad (5b)$$

Coded model for the density

$$Density\ (g/ml) = 0.78 + 0.052A + 0.011B + 0.024C \quad (6a)$$

Actual model for the density

$$Density\ (g/ml) = 0.43 + 0.0007A + 0.0004B + 0.005C \quad (6b)$$

Coded model for the viscosity

$$Viscosity\ (cSt) = 2.96 - 1.96A + 0.25B - 0.24C + 0.24AB + 0.31AC + 0.30BC + 1.46A^2 + 0.31B^2 - 0.24C^2 \quad (7a)$$

Actual model for the viscosity

$$Viscosity\ (cSt) = 70.24 - 0.26A - 0.11B - 0.51C + 0.0001AB - 0.0009AC - 0.0022BC - 0.00026A^2 + 0.00035B^2 - 0.011C^2 \quad (7b)$$

Table 3. ANOVA for oil yield

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	2454.457	9	272.717474	20.1365	< 0.0001	Significant
A-Temperature	1340.964	1	1340.964	99.0119	< 0.0001	
B-Time	1.20409	1	1.20409	0.08891	0.7717	
C-Catalyst	82.88641	1	82.88641	6.12003	0.0329	
AB	0.36125	1	0.36125	0.02667	0.8735	
AC	41.5872	1	41.5872	3.07065	0.1103	
BC	21.97845	1	21.97845	1.62281	0.2315	
A^2	393.2149	1	393.214914	29.0336	0.0003	
B^2	0.259645	1	0.25964545	0.01917	0.8926	
C^2	27.68205	1	27.6820455	2.04394	0.1833	
Residual	135.4346	10	13.5434625			
Lack of Fit	56.97174	5	11.3943482	0.7261	0.6330	not significant
Pure Error	78.46288	5	15.6925767			
Cor Total	2589.892	19				

Table 4. ANOVA for density

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	0.03401	3	0.01133667	14.7349	< 0.0001	Significant
A-Temperature	0.02704	1	0.02704	35.1454	< 0.0001	
B-Time	0.00121	1	0.00121	1.57271	0.2278	
C-Catalyst	0.00576	1	0.00576	7.4866	0.0146	
Residual	0.01231	16	0.00076937			
Lack of Fit	0.01056	11	0.00096	2.74286	0.1376	not significant
Pure Error	0.00175	5	0.00035			
Cor Total	0.04632	19				

Table 5. ANOVA for viscosity

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	53.28354	9	5.92039351	27.877	< 0.0001	Significant
A-Temperature	38.57296	1	38.57296	181.626	< 0.0001	
B-Time	0.62001	1	0.62001	2.91941	0.1183	
C-Catalyst	0.576	1	0.576	2.71218	0.1306	
AB	0.465613	1	0.4656125	2.1924	0.1695	
AC	0.762613	1	0.7626125	3.59087	0.0873	
BC	0.702113	1	0.7021125	3.306	0.0991	
A^2	5.847309	1	5.84730909	27.5329	0.0004	
B^2	0.269728	1	0.26972784	1.27005	0.2861	
C^2	0.160809	1	0.16080909	0.75719	0.4046	
Residual	2.123753	10	0.21237534			
Lack of Fit	0.89682	5	0.17936402	0.73094	0.6304	not significant
Pure Error	1.226933	5	0.24538667			
Cor Total	55.4073	19				

Table 6. Statistical result for oil yield, density and viscosity

Source	Linear			2FI			Quadratic			Cubic		
	Oil yield	Density	Viscosity	Oil yield	Density	Viscosity	Oil yield	Density	Viscosity	Oil yield	Density	Viscosity
Std. Dev.	8.53	0.028	0.99	9.20	0.027	1.03	3.68	0.024	0.46	4.32	0.028	0.45
R-Squared	0.55	0.73	0.72	0.57	0.79	0.75	0.94	0.87	0.96	0.95	0.89	0.98
Adjusted R-Squared	0.47	0.68	0.66	0.37	0.69	0.64	0.90	0.76	0.93	0.86	0.68	0.98
Predicted R- Squared	0.26	0.52	0.51	-1.32	-0.1	-0.36	0.82	0.47	0.76	-14.87	-77.83	0.08
PRESS	1913	0.022	26.93	6012	0.052	75.52	463	0.024	13.21	41119	3.65	50.77
		S					S		S	A	A	A

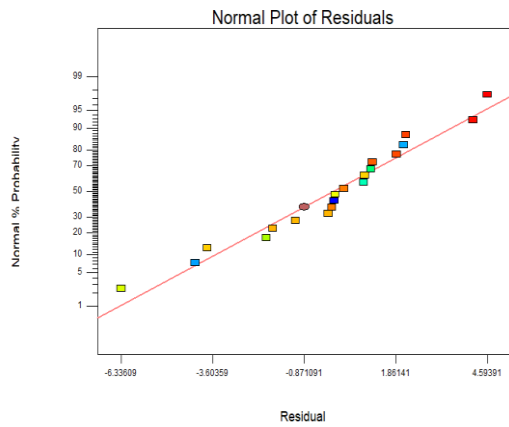
2FI is 2 factor interaction model, S-Suggested, A-Alias

Figures 1a, 1b and 1c present the plots of normal probability versus studentized residuals for oil yield, density and viscosity, respectively. These diagnostics plots provided by Design Expert software confirms that the model selected provides adequate approximation of the real system plot for evaluating the models. Data points are approximately linear and followed a normal distribution pattern with no S-shape curve, indicating normality in the error term. However, some scattering is expected even with normal data [34]. There is therefore no requirement of actual data transformation to improve the fit.

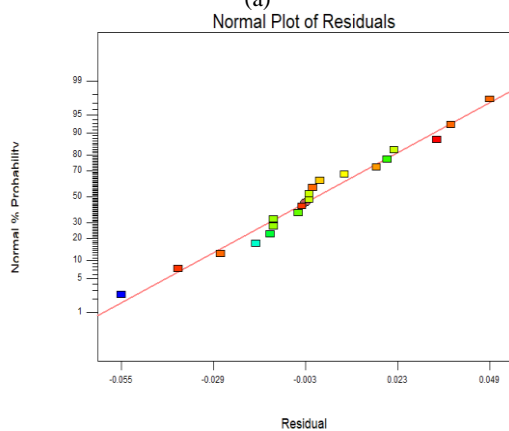
Similarly, Figures 2a, 2b and 2c present the actual versus predicted model percentage for oil yield, density and viscosity of the experimental runs, respectively. These plots help to detect a value, or group of values, that are not easily predicted by the model. For example, runs

3 and 9 Figure 2b were not easily predicted, as such the points were not captured in the plot. It is required that the data points are split evenly by the 45° line, as presented in these figures. This means that there is also no need for a transformation to improve the fit.

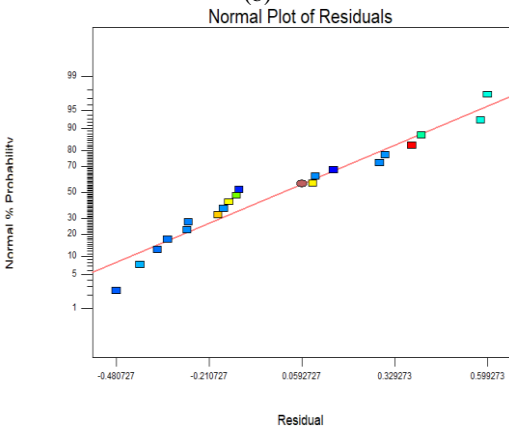
The three-dimensional response surfaces that show the effects of different experimental variables for oil yield, density and viscosity are presented in Figures 3 -5. Figures 3(a) - 3(c) show the interacting effect of temperature (A) and Time (B) on oil yield, density and viscosity, respectively. It was observed that the oil yield increased with an increase in temperature and time. While time had a gradual increase, temperature on the other hand increased up to a certain point (around 425 °C) and then started dropping. This is comparable with data reported in literature [34]; as reported data, maximum oil yield at a temperature of 470 °C without catalyst and



(a)

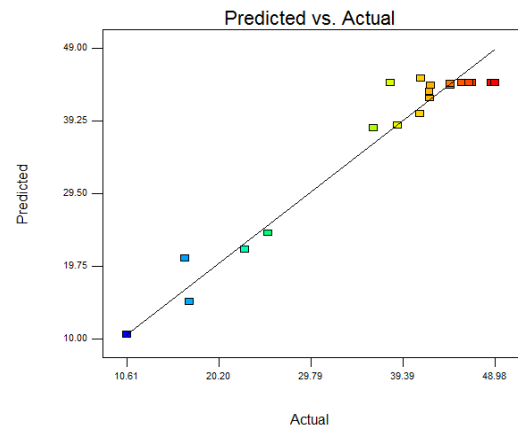


(b)

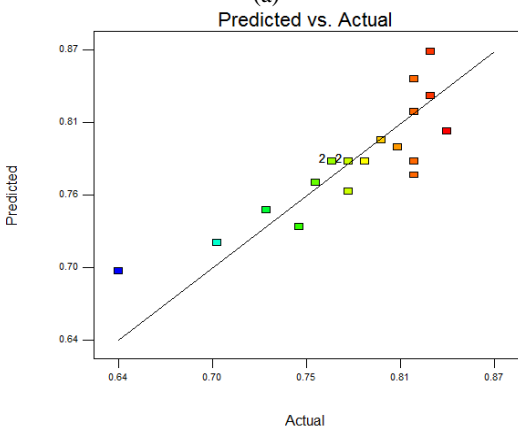


(c)

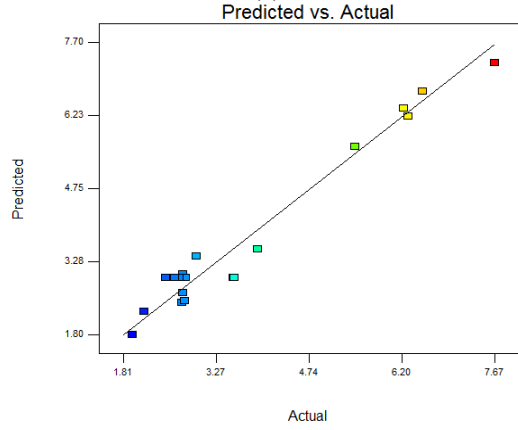
Figure 1. The normal probability vs studentized residual plot for (a) oil yield (b) density (c) viscosity



(a)



(b)



(c)

Figure 2. Actual vs predicted plot for (a) oil yield (b) density (c) viscosity

optimization tools. The reduction at higher temperatures is due to secondary reactions, leading to increase in the formation of non-condensable gases during the pyrolysis process. In addition, density increased with increase in temperature while viscosity on the other hand decreased with increase in temperature according to literature [35]. Figure 4 demonstrated the mutual effect of temperature (A) and Catalyst (C) for the pyrolysis process. There was

a corresponding increase in oil yield and density for the combined effects of temperature and catalyst while for viscosity, increase in temperature reduced the viscosity and increase in catalyst increased the viscosity from 1% up to 7.75% after which further increase saw a drop from 7.75 to 10 %.

Lastly, Figures 5 presents the combined effect of time (B) and catalyst (C). It was observed that with an increase

in time, the percentage increase oil yield increased progressively while an increase in catalyst led to an increase in oil yield up to 8.5% then to a decrease till 10%. For density, the combined effects of catalyst and time led to a corresponding increase in density. Viscosity saw a decrease with an increase in catalyst and a gradual decrease when the time increased from 60 to 90mins with an increase in after 90 mins.

Prediction of optimum parameters

Table 7 presents the predictions of input parameters (temperature, time and catalyst) and the corresponding output parameters (oil yield, density and viscosity) from the design expert software. Experimental runs were carried out to validate these predictions since they were

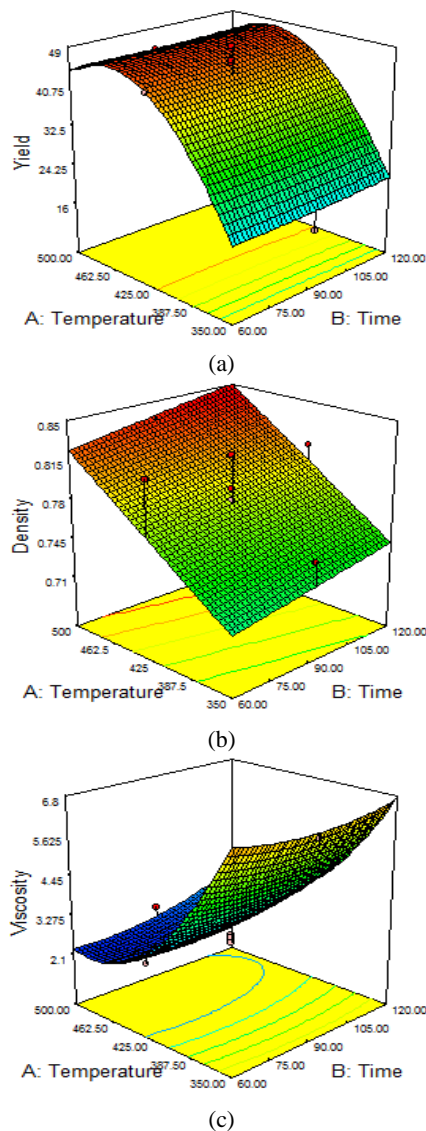


Figure 3. Interacting effects of temperature and time for (a) oil yield (b) density (c) viscosity

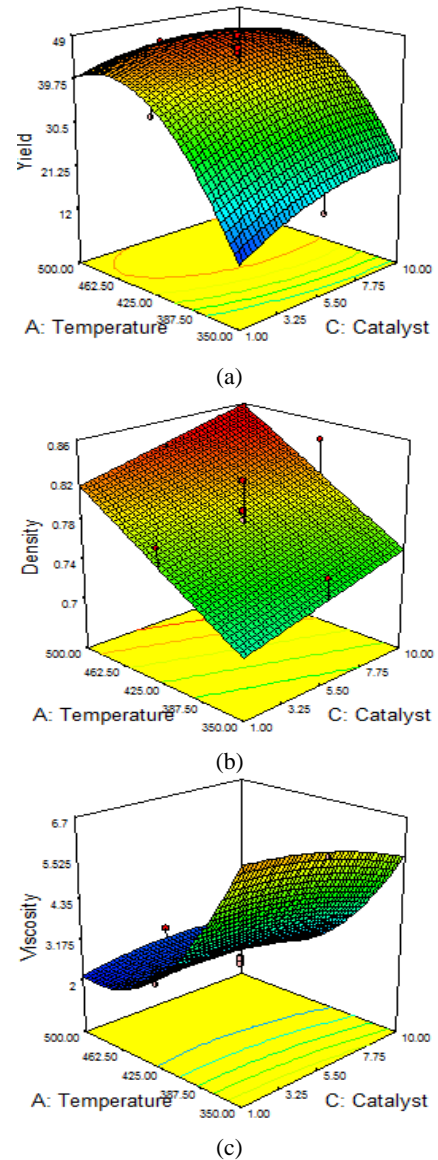


Figure 4. Interacting effects of temperature and catalyst for (a) oil yield (b) density (c) viscosity

not among the original experimental runs. The similarity in these results is quite high and this shows that design expert software was a good predictor and can also be used for product selectivity and desirability.

Output parameters using the spent catalyst and without catalyst were also determined experimentally to compare with those obtained from the reactivated catalyst and results are presented in Table 8. Flash points, pour point and higher heating value (HHV) of the optimum fuel produced were also analyzed. Although oil yield without catalyst was higher, the quality of the oil was however very low, indicating that the use of reactivated catalyst increased the quality of the oil tremendously. Also, the use of R-CAT increased both the quantity and

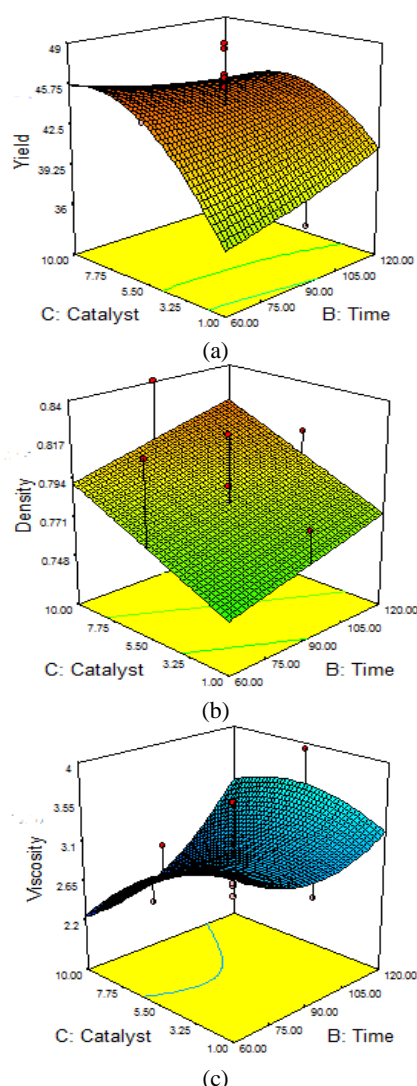


Figure 5. Interacting effects of catalyst and time for (a) oil yield (b) density and (c) viscosity

quality of the oil compared to oil produced with spent catalyst [9]. Optimum oil produced with R-CAT is comparable to kerosene fuel while oils produced with E-CAT and without catalyst are comparable to diesel fuel although with lower HHV. This is in agreement with literature [36].

GC-MS analysis of the oil at optimum conditions

Compositional analysis of the optimized pyrolysis liquids was carried out by GC-MS. Table 9 gives the summary of the PONA composition from GC-MS analysis. The number of compounds identified for pyrolysis oil using reactivated catalyst (Poil 1), spent catalyst (Poil 2) and without catalyst (Poil 3) were 51, 34 and 65, respectively. This analysis revealed that oil produced using reactivated catalyst has less paraffins and olefins than those produced using spent catalyst and in the absence of catalyst. However, the use of catalyst favored the production of aromatics with reactivated catalyst producing the highest quantity. In contrast, the hetero compounds were substantially reduced in the presence catalyst. The analysis also revealed that limonene was the dominant compound with 39.58, 44.04 and 14.12% in the Poil 1, Poil 2 and Poil 3, respectively. It can be inferred that the fuel produced using the treated catalyst were in the range of gasoline and kerosene [37, 38]. Comparatively, the aromatic content for gasoline is 35 according to literature [37, 38]. In terms of hydrocarbon range, the reactivated and spent catalysts displayed the potential to increase yield of carbon in the range of (C_6 - C_{15}) which is within the range of gasoline (C_6 - C_{12}) and kerosene (C_{11} - C_{14}) compared with non-catalyzed pyrolytic oil, which had more carbon more in the diesel and fuel oil range (C_{11} - C_{20}).

Table 7. Predicted and validated response from optimized parameters

Optimum Parameters		Predicted Responses		Validated Responses		Difference (%)
Temperature ($^{\circ}$ C)	458	Oil Yield (wt. %)	48.2	Oil Yield (wt. %)	48.5	0.62
Time (min)	60	Density (g/ml)	0.81	Density (g/ml)	0.79	2.47
Catalyst (wt. %)	8	Viscosity (cSt)	2.03	Viscosity (cSt)	2.05	0.97

Table 8. Properties of the oil at optimum conditions

Optimum Oil	Oil Yield (wt%)	Density (g/ml)	Viscosity (cSt)	Flash point ($^{\circ}$ C)	Pour point ($^{\circ}$ C)	HHV (MJ/Kg)
Oil (R-CAT)	48.5	0.79	2.05	50	-18	42.6
Oil (E-CAT)	43.4	0.86	3.52	33	-12	41.2
Oil (No CAT)	51.3	0.95	4.24	28	-3	41.4
Diesel	-	0.82 – 0.86	2–4	>60	-35 – -15	40 – 55
Kerosene	-	0.76 – 0.82	1.8 – 2.5	>38	<-17	46.2

Table 9. PONA composition from GC-MS analysis

Sample	Poil 1	Poil 2	Poil 3 (control)
Paraffins (%)	3.34	9.65	8.07
Olefins (%)	2.69	4.6	8.93
Naphthenes (%)	46.51	50.56	28.11
Aromatics (%)	29.4	20.86	3.06
Hetero compounds (%)	14.74	14.32	51.86
TOTAL	99.99	99.99	100.03

CONCLUSION

Three variable central composite RSM design was used to optimize oil yield from waste tyre pyrolysis using reactivated spent FCC catalyst and conclusions were drawn as follows:

- The predicted condition for optimum oil yield of 48.2 wt. % with density of 0.806 g/ml and viscosity of 2.03 cSt was at a temperature of 457.98°C, contact time of 60 minutes and catalyst-to-feed ratio of 8.01%. The validated optimum oil yield at the same condition was 48.4 wt. % with density of 0.79 g/ml and viscosity of 2.05 cSt.
- A second-order quadratic model was best suited for oil yield and viscosity while a linear model was best suited for density.
- Temperature had the most significant effect on oil yield, density and viscosity based on the F values while contact time had the least effect.
- Pyrolysis of waste tyre without catalyst had highest oil yield but with lowest fuel qualities.
- From GC-MS analysis, the oil produced was more in the range of gasoline and kerosene.

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**Persian Abstract****چکیده**

این کار بهینه‌سازی پارامترهای فرآیند را برای تجزیه در اثر حرارت کاتالیزوری لاستیک زباله با استفاده از کاتالیزور ترک خوردگی کاتالیستی سیال مصرف شده مجدد (FCC) مورد بررسی قرار داد. تجزیه در اثر حرارت تایلر زباله از نرم‌افزار متخصص طراحی به عنوان ابزار بهینه‌سازی برای این مطالعه استفاده کرد. یک CCD سطح ۳ فاکتوری با ۲۰ دوره آزمایشی با دما، زمان و کاتالیزور به عنوان پارامترهای ورودی استفاده شد در حالی که بازده روغن، چگالی و ویسکوزیته متغیرهای خروجی بودند. پس از آن، یک اعتبار سنجی تجربی از پارامترهای بهینه شده، که در میان اجرای آزمایشی اصلی نبودند، انجام شد. پیرولیز هم‌چنین در شرایط بهینه با کاتالیزور فعال نشده و بدون کاتالیزور برای تعیین سهم کاتالیزور و فعال شدن مجدد آن انجام شد. بر اساس پارامترهای بهینه، ۴۸/۵ درصد وزنی روغن (۰/۷۹ g/ml و ۲/۰۵ cSt) با کاتالیزور فعال شده مجدد، ۴۳/۴ درصد وزنی (۰/۸۶ g/ml و ۳/۵۲ cSt) با کاتالیزور مصرف شده، ۵۱ درصد وزنی (۰/۹۵ و ۴/۲۴ cSt) بدون کاتالیست تولید شد. بازده روغن بدون کاتالیزور بیشتر از کاتالیزور راکتیو بود. اما کمترین کیفیت سوخت را داشت در حالی که نفت تولید شده با کاتالیزور به نوبه خود کمیت و کیفیت بالاتری نسبت به نفت تولید شده با کاتالیزور داشت. بنابراین، ادغام چگالی و ویسکوزیته روغن در بهینه‌سازی پیرولیز کاتالیزوری لاستیک‌های زائد باعث بهبود عملکرد و کیفیت روغن تولید شده می‌شود.