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Empirical Modelling and Optimization of Zinc Chloride Activated Ngbo Clay Catalysts Using Response Surface Methodology

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Abstract: In this study, Box-Behnken's Response Surface Methodology (RSM) was applied to study the esterification reaction effectiveness of zinc chloride activated Ngbo clay catalyst. The XRF result showed that both raw and activated clay contain contaminations of oxides and other impurities; however, the clay mineral compositions are not significantly affected by zinc chloride treatments. Additionally, it indicates a high content of silicon and aluminium oxides compared to other oxides.XRD pattern results showed several characteristic peaks due to the mineral compositions present. The analysis of the peaks showed sharp peaks with low intensity at $2\theta = 11.300$, which corresponds to the main peak used in the identification of kaolinite clay, as reported in the literature.The esterification was monitored based on the process conditions of temperature, time duration, amount of reactant, catalyst weight and particle size. The Box -Behnken's Response Surface Methodology indicates that the zinc chloride clay-catalysed esterification reactions proceed through dual mechanisms: an Acid-complex and an Alcohol-complex mechanism, with the Alcohol mechanism dominating. The esterification efficiencies of acetic acid and ethanol by zinc chloride activated Ngbo clay catalyst, optimized using RSM models indicated the estimated esterification percentage of >95%. The predicted and experimental values obtained under the same conditions showed a difference of less than 5%, indicating that the Box-Behnken design approach is an efficient, effective, and reliable method for the esterification of acetic acid with ethanol. The produced catalyst was optimized using A-One way ANOVA modelling, which indicated a correlation coefficient of the regression of 0.9551, which implies that 95.51% of the total variation in the esterification reaction was attributed to the experimental variables. The result obtained indicated that the process could be applied in the esterification of acetic acid to avoid the drawbacks of corrosion, loss of catalyst and environmental problems.

Keywords: Optimization, Characterization, Esterification, Zinc Chloride Activated Clay Catalyst, Thermal activated catalyst, Response Surface Methodology, Box-Behnken design

I. Introduction

Clay is one of the abundant raw materials in Nigeria. It is readily available in Nigeria in large deposits, yet its potential has not been fully explored. However, there is recent interest in exploring the potentials of clays, such as in the bleaching of palm oil [1, 2], in the adsorption of dyes [3 – 5], among others. In a quest to develop green processes, clay is mostly used in the synthesis of catalysts, although the use of Nigerian clays from Ngbo, Ohaukwu, Ebonyi State, for producing clay catalysts is limited in the literature. Still, the kinetics of clay-catalysedesterificationreaction is abundant in literature, but with little or no data on the mechanistic and empirical modelling on the use of Ngbo clay in this regard.

Esterification reactions have long been carried out in homogeneous phase in the presence of acid catalysts such as sulphuric acid, hydrochloric acid and p-toluene sulfonic acid (p-TSOH); which have drawbacks of corrosion, loss of catalyst and environmental problems [6, 7]. Therefore, researchers have been focused on developing eco-friendly heterogeneous catalysts for the synthesis of fatty acid esters. The most popular solid acid catalysts used to produce esters were ion-exchange organic resins, such as Amberlyst-15 [8, 9], Zeolites [10 – 11], [12] and Silica-supported heteropoly acid [13] and [14]. Nevertheless, they have shown limitations in applicability for catalysing esterification reaction due to low thermal stability (Amberlyst-15 <140 ˚C), mass transfer resistance (Zeolites) [15], [16], or loss of active acid sites in the presence of a polar medium (HPA/silica) [14].

A cost-benefit and environmental impact analysis of zinc chloride compared to alternative activation methods (thermal, acid, or alkaline treatment) would increase industrial relevance. Additionally, incorporating kinetic modelling could substantiate mechanistic claims more rigorously. Bench marking catalyst performance against established heterogeneous catalysts under identical conditions would also enhance the comparative value, supporting practical adoption in green chemical processes.

Response Surface Methodology (RSM) is a collection of statistical and mathematical techniques that uses quantitative data. Central composite design (CCD), Box-Behnkendesign (BBD), and Doehlert design are among the principal response surface methodologies used in experimental design. This method is suitable for fitting a quadratic surface, and it helps to optimize the effective parameters with a minimum number of experiments, and also to analyze the interaction between the parameters [9]. The objective is to optimize a response (output variable) which is influenced by several independent variables (input variables). The application of RSM to design optimization aims to reduce the cost of numerous expensive experiments, save time, and alleviate stress [17–20].

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This work investigated the use of local clay from Ngbo in Ohaukwu Local Government Area of Ebonyi State, Nigeria for the production of zinc chloride activated catalyst and optimizes the effectiveness of the clay catalyst for the esterification of acetic acid with ethanol using Response Surface Methodology.

II. Materials and Methods

Source of Raw Materials

The clay sample was obtained from Ngbo in Ohaukwu L.G.A. of Ebonyi State (N 06º30˙ 32.8''), (E 007º58'13.7''). Chemicals used, such as Zinc Chloride (aq), NaOH, Acetic Acid, ethanol, distilled water, etc, were all of standard grade. They were purchased in a chemical shop at Ogbete main market Enugu, Enugu State.

Physico-Chemical Characterization of Ngbo Clay

The Ngbo clay sample was subjected to physical analysis to determineits physical properties. The analysis carried out includes: Bulk density, Moisture content, pH and Loss on Ignition (LOI).

Characterisation of the raw clay and Zinc chloride activated sample

The Ngbo clay sample was characterised using XRF and XRD.

Zinc Chloride Activation

The activation method used in this work is as reported by [21]. A 100g of pulverized and screened clay was mixed into a slurry with 50ml of diluted water, 30ml of 1M $ZnCl_2$ (aq) was added and stirred vigorously and placed in an oven where it was maintained at a temperature of 100ºC. The sample was washed thereafter and left to sediment. Complete removal of all residual zinc chloride was achieved by repeating the washing and decanting process until a pH of 6 was obtained. The final slurry was filtered and dried at 100 ˚C. The dried, activated and washed clay was then pulverized, screened and stored in desiccators before use.

Optimization of Process Conditions on the Catalyst Quality Produced Using Esterification Process

Sample Preparation/Procedure

The raw clay sample was crushed and sieved at 100 microns, 200 microns, and 300 microns. Thereafter, the clay sample was activated using zinc chloride. The activated clay sample was used in an esterification reaction to assess the effectiveness. The Predetermined weight of the clay sample was weighed; one mole of Ethanol and acetic acid was each pipetted into the clay sample to ensure that the ethanol did not block the active sites of the catalyst. The container was tightly closed, the contents were shaken vigorously and immersed in a water bath shaker maintained at the conditions of the experimental design in Table 1. The summary of the reaction equation is:

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O \quad (1)$$

On titration, the equation becomes:

$$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O \quad (2)$$

Table 1: The natural and coded values of the independent variables used

VARIABLES	NATURAL VALUES			CODED VALUES		
	Low level	Mid-point	High level	Low level	Mid Point	High level
Temperature (ºC), A	50	70	90	-1	0	+1
Process duration (minutes), B	30	195	360	-1	0	+1
Excess reactant (ml), C	2.5	3.75	5	-1	0	+1
Catalyst weight (grammes), D	0.25	0.38	0.5	-1	0	+1
Particle size (microns), E	100	200	300	-1	0	+1

The clay-catalysed esterification was modelled using Box-Behnken Response Surface Methodology.

For five factors inputs of x_1, x_2, x_3, x_4 and x_5, the equation of the quadratic response is given as;

$$Y = b_o + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_4 + b_5X_5 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{14}X_1X_4 + b_{15}X_1X_5 + b_{23}X_2X_3 + b_{24}X_2X_4 + b_{25}X_2X_5 + b_{34}X_3X_4 + b_{35}X_3X_5 + b_{45}X_4X_5 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 + b_{44}X_4^2 + b_{55}X_5^2. \quad (3)$$

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III. Response Surface Methodology

The response surface technique, applying a Box-Behnken design matrix, was used to study the interaction and effects among the factors and their level of contributions and significance in the clay-catalysed esterification. This method determines the optimal working conditions in a shorter timeframe, and provides detailed information on the conditions of the processes. This was achieved through a designed experimental design applying Box-Behnken Response Surface Methodology design of 46 steps of experiment consisting of five factors and three levels (Table 2). The numerical optimization method of RSM was used in the optimization.

Table 2: Box-Benhken's Response Surface Methodology Design of Experiment

Std	Run	Factor A (^{O}C)	Factor B (min)	Factor C (ml)	Factor D(g)	Factor E (mic)	Response (ml)	Yield (%)
37	1	70	30	3.75	0.25	200		
22	2	70	360	2.5	0.38	200		
23	3	70	30	5	0.38	200		
29	4	70	195	2.5	0.38	100		
26	5	90	195	3.75	0.25	200		
1	6	50	30	3.75	0.38	200		
32	7	70	195	5	0.38	300		
46	8	70	195	3.75	0.38	200		
10	9	70	360	3.75	0.38	100		
34	10	90	195	3.75	0.38	100		
21	11	70	30	2.5	0.38	200		
35	12	50	195	3.75	0.38	300		
8	13	70	195	5	0.5	200		
4	14	90	360	3.75	0.38	200		
2	15	90	30	3.75	0.38	200		
11	16	70	30	3.75	0.38	300		
31	17	70	195	2.5	0.38	300		
3	18	50	360	3.75	0.38	200		
24	19	70	360	5	0.38	200		
16	20	90	195	5	0.38	200		
44	21	70	195	3.75	0.38	200		
12	22	70	360	3.75	0.38	300		
36	23	90	195	3.75	0.38	300		
17	24	70	195	3.75	0.25	100		
18	25	70	195	3.75	0.5	100		
45	26	70	195	3.75	0.38	200		
33	27	50	195	3.75	0.38	100		
25	28	50	195	3.75	0.25	200		
20	29	70	195	3.75	0.5	300		
27	30	50	195	3.75	0.5	200		
30	31	70	195	5	0.38	100		

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42	32	70	195	3.75	0.38	200		
41	33	70	195	3.75	0.38	200		
39	34	70	30	3.75	0.5	200		
6	35	70	195	5	0.25	200		
43	36	70	195	3.75	0.38	200		
38	37	70	360	3.75	0.25	200		
19	38	70	195	3.75	0.25	300		
40	39	70	360	3.75	0.5	200		
7	40	70	195	2.5	0.5	200		
28	41	90	195	3.75	0.5	200		
14	42	90	195	2.5	0.38	200		
5	43	70	195	2.5	0.25	200		
13	44	50	195	2.5	0.38	200		
9	45	70	30	3.75	0.38	100		
15	46	50	195	5	0.38	200		

IV. Results and Discussions

Physical properties of the raw clay

The physical properties of raw Ngbo clay are presented in Table 3. The result showed that the clay has a moisture content of 3.3 % and a bulk density of 1.25 g/ml, which are in agreement with the previous research of [22 – 24] that reported the moisture content of kaolinite clay is between 3.0 – 4.0% and the bulk density is 1.2 – 1.4 g/ml.

Table 3: Results of Bulk density, Moisture content, pH, and LOI

Clay type	Bulk density (g/ml)	% moisture content	pH	LOI (%)
Ngbo clay	1.25	3.33	7.5	10.52

Characterization of Raw Clay and Zinc Chloride Activated Clay

The chemical properties of the raw Ngbo clay were analysed using XRF and XRD.

The result of the XRF composition analysis of rawNgbo clay and Zinc Chlorideactivated Ngboclays (ZAC) is presented in Table 4. The result showed that raw and activated clays have contaminations of oxides and other impurities, but the clay mineralcompositions are not meaningfully affected by zinc chloridetreatments even under strong conditionsand below 500 ℃ as reported in literature by [25, 26] and[27]. This indicates that improving the properties of the clay through chemical methods below 500 ℃ is challenging due to its low reactivity. This result of the XRF on the Ngbo raw clay and zinc chlorideactivated Ngbo clays, as shown in Table 4, also indicates high content of silicon and aluminium oxides compared to other oxides.

Table 4: Results of XRF analysis of raw Ngbo Clay and Zinc Chloride activated Ngbo clay

Chemical constituent	Raw clay ($_{Wt.\ \%}$)	Zinc Chloride activated (ZAC), ($_{Wt.\ \%}$)
SiO_2	62.70	65.743
TiO_2	1.52	1.386
Al_2O_3	19.70	23.457
Fe_2O_3	2.06	5.855
P_2O_3	–	0.000

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CaO	0.789	0.232
MgO	0.026	0.522
Na_2O	0.20	0.256
K_2O	0.85	1.149
Mn_2O_3	_	0.135
V_2O_5	0.071	_
Cr_2O_3	0.035	0.011
CuO	0.044	_
BaO	0.19	_
L.O.I	11.82	_
SO_3	_	0.181
Cl	_	0.131
ZnO	_	0.936
SrO	_	0.007

The results of XRD pattern analysis of raw Ngbo clay are presented in Figure 1. The XRD pattern results showed several characteristic peaks due to the mineral compositions present. The peak obtained at a position corresponding to $2\Theta = 22.64°$ indicated the presence of large quantities of quartz. Minor impurities, such as illite, muscovite,haloysite, quartz, hydrated mica, non-cryistalline hydroxide iron and halloysiteare present. The presence of these minor impurities and quartz content in Ngbo clay needs to be reduced to a minimum before its usage for industrial purposes, especially in catalysts development in line with the research of [28 and 29]. The XRD analysis corroborates the results obtained with the XRF analysis.

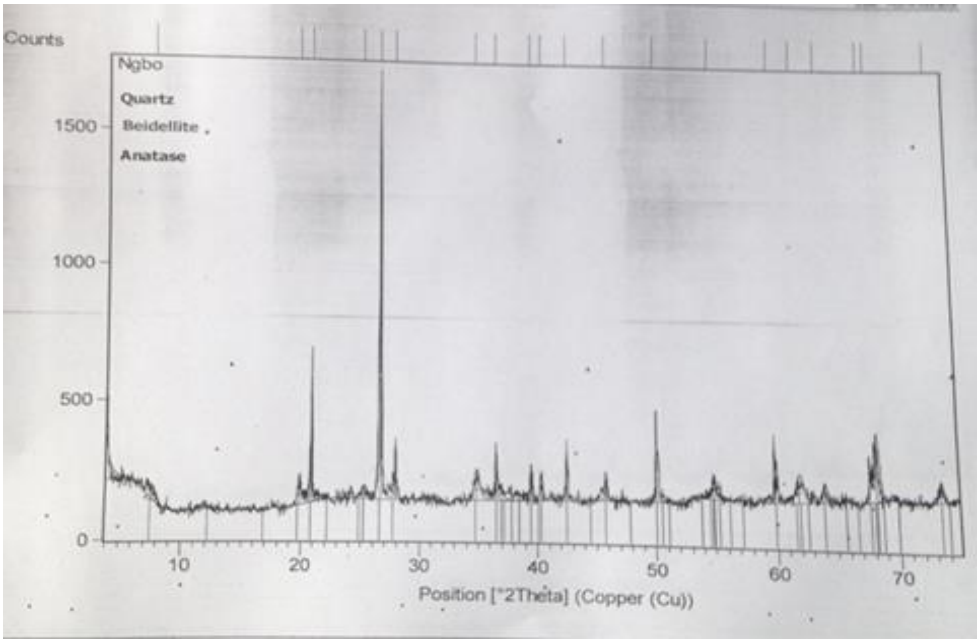

Figure 1: Results of XRD analysis of Ngbo raw clay

The results of XRD pattern analysis of Ngbozinc chloride activated catalyst, ZAC is presented in figure 2. The XRD pattern results showed several characteristic peaks due to the mineral compositions present. The analysis of the peaks showed sharp peaks with low intensity at $2\theta = 11.30^0$, which is the main peak used in the identification of kaolinte clay as reported in literature by [30].

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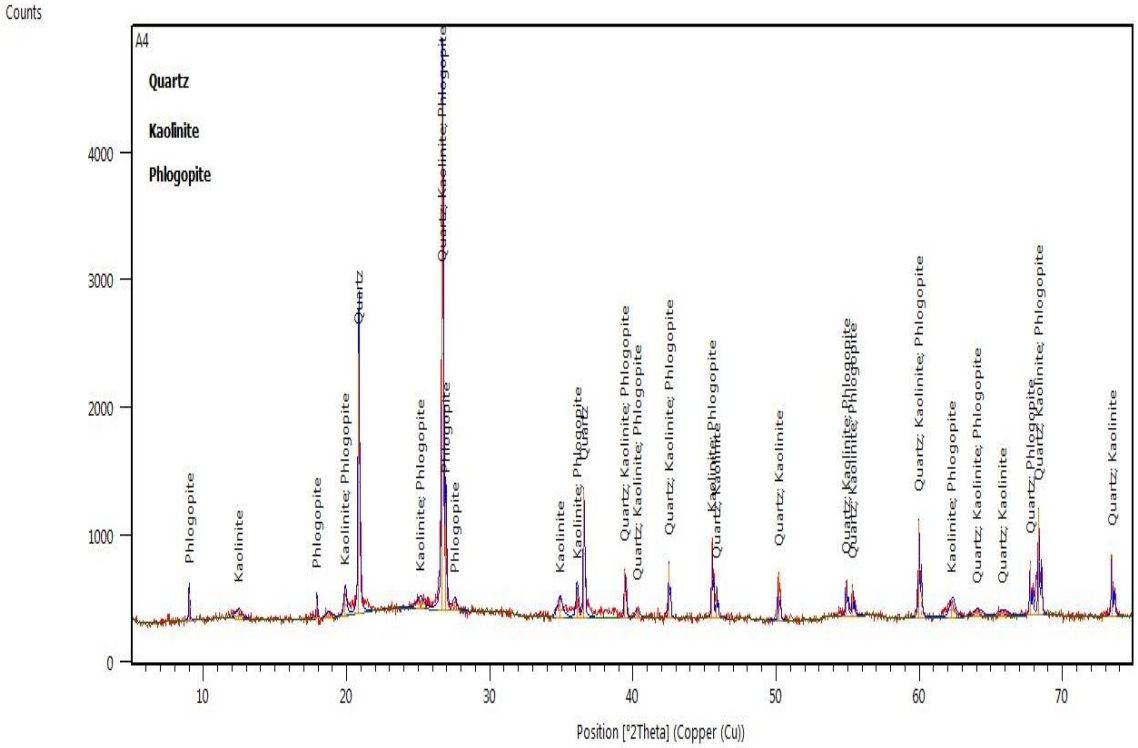

Figure 2: Results of XRD analysis of Zinc Chloride Activated Clay

Esterification Process Results

Esterification technique was used to obtain the responses and yield of Zinc Chloride Activated Catalyst (ZAC) as shown in Table 5.

Table 5: Showing Responses and Yield of ZAC

Std	Run	Factor 1A (^{O}C)	Factor 1B (min)	Factor 1C (ml)	Factor 1D(g)	Factor 1E (mic)	Response (ml)	Yield (%)
37	1	70	30	3.75	0.25	200	31.00	32.61
22	2	70	360	2.5	0.38	200	18.50	59.78
23	3	70	30	5	0.38	200	40.00	13.04
29	4	70	195	2.5	0.38	100	20.00	56.90
26	5	90	195	3.75	0.25	200	26.50	42.39
1	6	50	30	3.75	0.38	200	30.90	32.85
32	7	70	195	5	0.38	300	36.40	20.35
46	8	70	195	3.75	0.38	200	30.00	34.78
10	9	70	360	3.75	0.38	100	28.90	37.72
34	10	90	195	3.75	0.38	100	28.50	38.58
21	11	70	30	2.5	0.38	200	21.20	53.91
35	12	50	195	3.75	0.38	300	31.80	30.42
8	13	70	195	5	0.5	200	39.00	15.22
4	14	90	360	3.75	0.38	200	26.40	42.61
2	15	90	30	3.75	0.38	200	30.60	33.48

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11	16	70	30	3.75	0.38	300	30.50	33.26
31	17	70	195	2.5	0.38	300	20.40	55.36
3	18	50	360	3.75	0.38	200	30.60	33.48
24	19	70	360	5	0.38	200	35.40	23.04
16	20	90	195	5	0.38	200	36.00	21.74
44	21	70	195	3.75	0.38	200	30.40	33.91
12	22	70	360	3.75	0.38	300	27.50	39.82
36	23	90	195	3.75	0.38	300	27.50	39.82
17	24	70	195	3.75	0.25	100	30.30	34.70
18	25	70	195	3.75	0.5	100	30.80	33.62
45	26	70	195	3.75	0.38	200	30.40	33.91
33	27	50	195	3.75	0.38	100	31.50	32.11
25	28	50	195	3.75	0.25	200	32.10	30.22
20	29	70	195	3.75	0.5	300	30.50	33.26
27	30	50	195	3.75	0.5	200	33.00	28.26
30	31	70	195	5	0.38	100	38.50	17.03
42	32	70	195	3.75	0.38	200	30.40	33.91
41	33	70	195	3.75	0.38	200	29.00	36.96
39	34	70	30	3.75	0.5	200	30.50	33.70
6	35	70	195	5	0.25	200	38.50	16.30
43	36	70	195	3.75	0.38	200	30.30	34.13
38	37	70	360	3.75	0.25	200	29.00	36.96
19	38	70	195	3.75	0.25	300	30.50	33.26
40	39	70	360	3.75	0.5	200	28.80	37.39
7	40	70	195	2.5	0.5	200	20.50	55.43
28	41	90	195	3.75	0.5	200	28.00	39.13
14	42	90	195	2.5	0.38	200	18.90	58.91
5	43	70	195	2.5	0.25	200	19.50	57.61
13	44	50	195	2.5	0.38	200	21.00	54.35
9	45	70	30	3.75	0.38	100	31.50	32.11
15	46	50	195	5	0.38	200	38.70	15.87

Result of ANOVA for Zinc Chloride Activated Clay (ZAC)

The result of ANOVA for Zinc Chloride Activated Clay (ZAC) is shown in table 6. The ANOVA result showed that RSM model is significant of the experimental results as indicated from the F – value of 124.44 calculated and very low probability value of P <0.0001. The lack of fit F – value of 8.71 showed that it was significant and there is 23.07% chance that a Lack of Fit F – value this large could occur due to noise. The significant terms of the model was determined by F- value and P- values. The values of "Prob> F" less than 0.0500 indicate the model terms are significant while values greater than 0.100 indicate that the model terms are not significant. ANOVA involves subdividing the total variation of a set of data onto component parts. The F – value is defined as the ratio of the mean square of regression (MRR) to the error (MRe). The smaller the magnitude of the F – value, the more significant is the corresponding coefficient [31]. The regression model demonstrates that the model is highly significant as evident from the calculated F-value (207.52) and a very low probability value (P =0.0001). The lack of fit F-value of 2.50 implies that it

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was not significant relative to the pure error and there is a 15.67% chance that a "Lack of Fit F-value this large could occur due to noise. If P – value of lack of fit is less than 0.05, there is statistically significant lack of fit at 95% confidence level [32].

The result in Table 6 also indicate that the significant model terms A, B, C, AB andC^2implies that only linear effects of temperature, process duration, excess reactants, and interactive effects of temperature and process duration, and quadratic effects of excess reactants were significant. The model accuracy was confirmed by the correlation coefficient of the regression model which is 0.9551. The correlation coefficient showed that 95.51% of the total variation in the final concentration was attributed to the experimental variables considered in this research work. The high value of the R^2 and the "Pred R-Squared" of 0.8236 is in good agreement with the "Adj R – Squared" of 0.9192 as reported in literature by Mohd and Rasyidah, 2010; [31].

Final equation in terms of coded factors gives:

Yield = + 34.60 + 3.69A + 2.86B – 19.35C - 0.50D + 0.17E + 2.13AB + 0.33AC – 0.32 AD + 0.73AE + 1.03BC – 0.17BD + 0.24BE + 0.27CD + 1.21CE + 0.27DE + $0.62A^2$ + $0.75B^2$ + $2.34C^2$ – $0.56D^2$ + $0.13E^2$. (4)

The coefficient with one factor represent the effect of the particular factor, while the coefficients with two factors and those with second order terms represent the interaction between two factors and quadratic effect respectively (Mohd and Rasyidah 2010).

Final model equation after eliminating the insignificant terms in terms of coded variables:

Yield = + 34.60 + 3.69A + 2.86B – 19.35C + 2.13AB + $2.34C^2$ (5)

Table 6: ANOVA Table for Zinc Chloride Activated Clay (ZAC)

Source	**Sum of Squares**	**df**	**Mean Square**	**F - Value**	**P – Value Prob> F**
Model	6443.58	20	322.18	124.44	<0.0001 significant
A - Temperature	218.30	1	218.30	84.32	<0.0001
B – Process duration	131.33	1	131.33	50.72	<0.0001
C – Excess reactant	5993.08	1	5993.08	2314.73	<0.0001
D – Effect of Catalyst	4.04	1	4.04	1.56	0.2232
E – Particle size	0.48	1	0.48	0.19	0.6695
AB	18.06	1	18.06	6.98	0.0140
AC	0.43	1	0.43	0.17	0.6874
AD	0.42	1	0.42	0.16	0.6897
AE	2.15	1	2.15	0.83	0.3713
BC	4.26	1	4.26	1.65	0.2111
BD	0.11	1	0.11	0.042	0.8392
BE	0.23	1	0.23	0.087	0.7703
CD	0.30	1	0.30	0.12	0.7353
CE	5.90	1	5.90	2.28	0.1435
DE	0.29	1	0.29	0.11	0.7400
A^2	3.38	1	3.38	1.31	0.2639
B^2	4.92	1	4.92	1.90	0.1803
C^2	47.82	1	47.82	18.47	0.0002
D^2	2.71	1	2.71	1.05	0.3159
E^2	0.15	1	0.15	0.058	0.8121
Residual	64.73	25	2.59		
Lack of fit	57.48	20	2.87	1.98	0.2307 not significant

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Pure Error	7.25	5	1.45		
Cor Total	6508.31	45			

Residual Plots for ZAC

The regression model developed was further assessed using residual plots. Residual is the difference between the experimental value and value predicted by the model. Some of the residual plots used were: plot of residual vs. predicted values which tests the assumption of constant variance of the experimental data, plot of residuals vs. run which checks for lurking variables that may have influenced the response during the experiment, normal plot of residuals which indicates whether the residuals follow a normal distribution, and plot of predicted vs. Actual response values which helps to detect a value, group of values that the model does not easily predict.

The residual plots for ZAC are shown in Figure 3 – 4. The trends of the residual plots indicate that the model can be considered as a good fit and that the regression equations follow the experimental results with a good accuracy. The plots indicate values that are not easily predicted by the model. The plot of residuals against run checks for lurking variables that may have influenced the response during the experiment. The normal plot of residuals indicates whether the residuals follow a normal distribution, and the plot of predicted against actual response values helps to detect a value, group of values that are not easily predicted by the model.

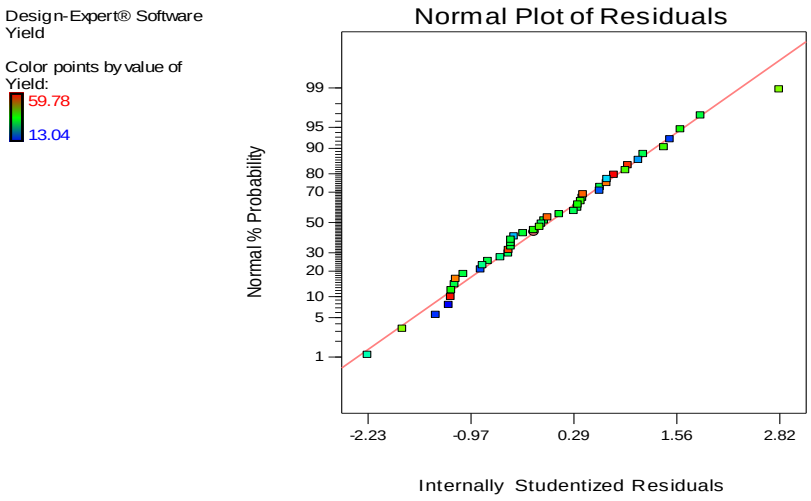

Figure 3: Normal plot of residual for ZAC

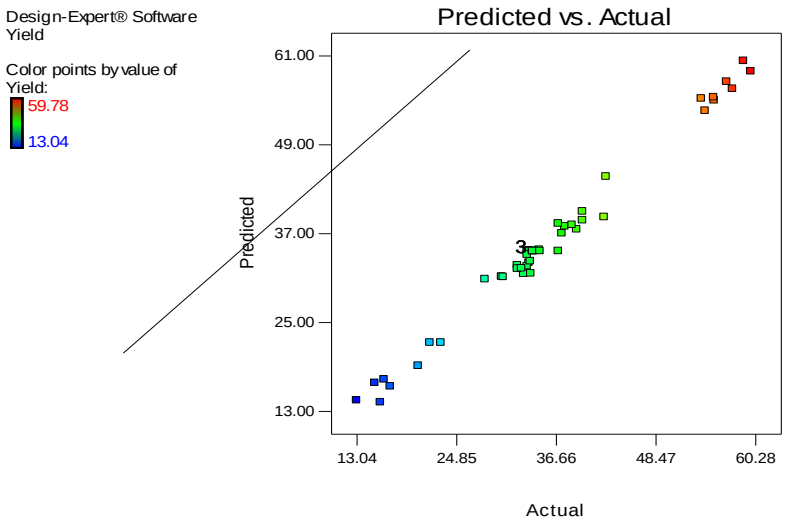

Figure 4: Plot of predicted verse actual for ZAC

Contour Plots of ZAC

The contour plots of ZAC were depicted in Figures 5 to 14. The circular nature of the contour plots indicates that the interactive effects between the variables are not significant, and the optimum values of the test process variables cannot be easily

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determined[33,31]. The non-circular nature of the contour plots reveals that there is an interaction between the process variables studied, and the optimum value of the process variables can be easily obtained.

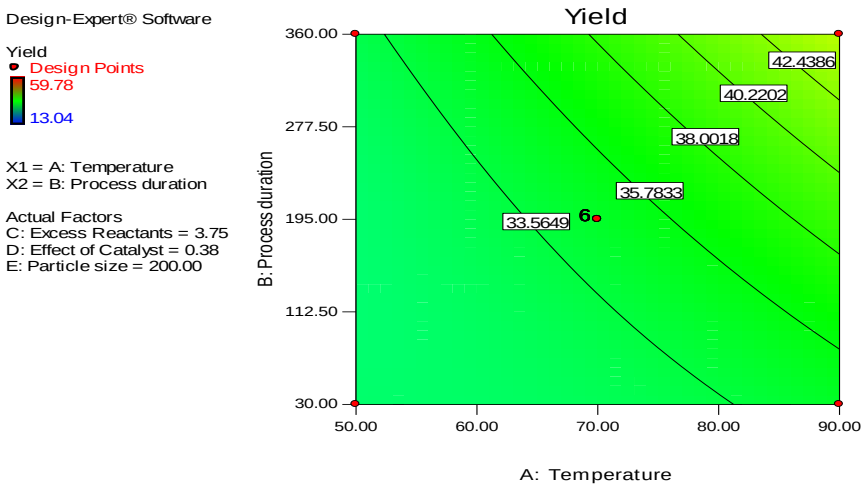

Figure 5: The contour plots for process duration against temperature and yield of ZAC

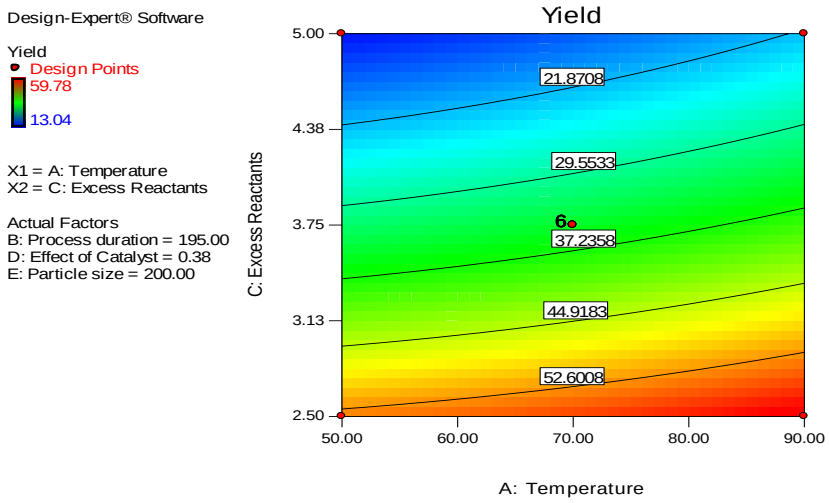

Figure 6: The contour plots for excess reactants against temperature and yield of ZAC

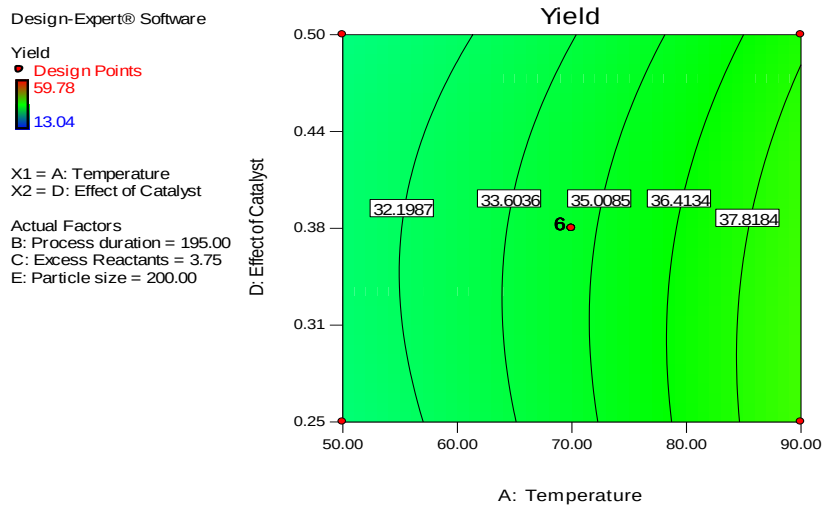

Figure 7: The contour plots for effect of catalyst against temperature and yield of ZAC

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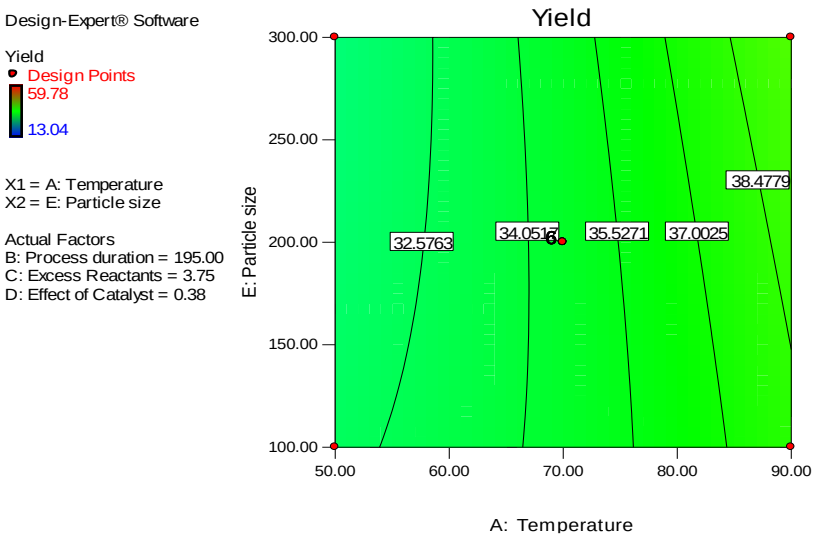

Figure 8: The contour plots for particle size against temperature and yield of ZAC

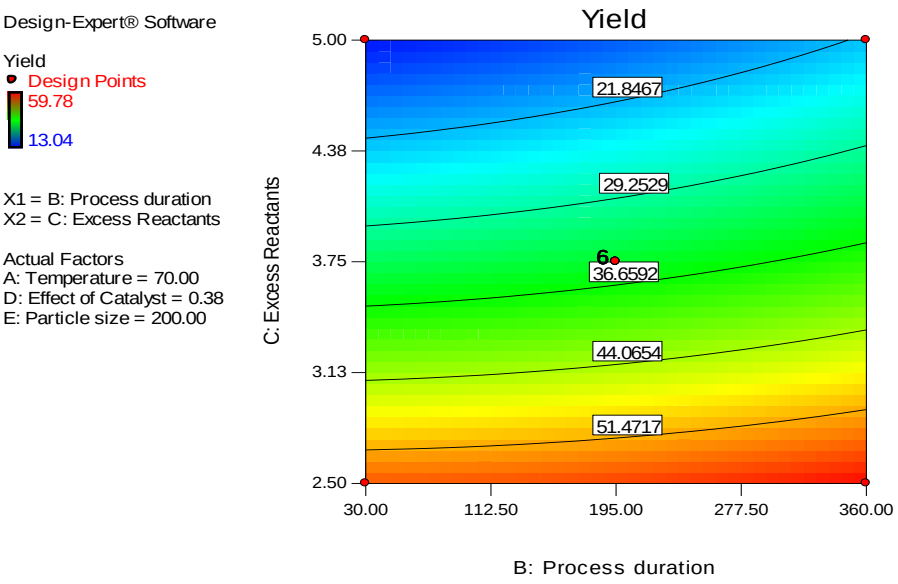

Figure 9: The contour plots for exces reactants against process duration and yield of ZAC

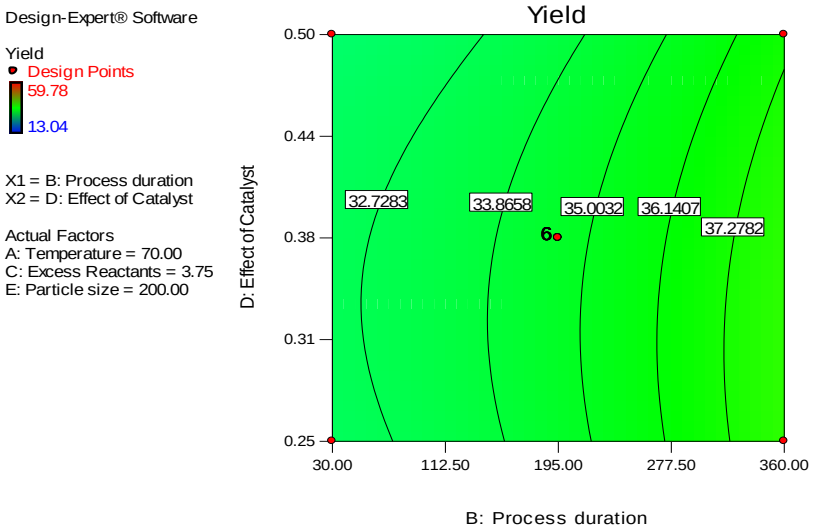

Figure 10: The contour plots for effect of catalyst against process duration and yield of ZAC

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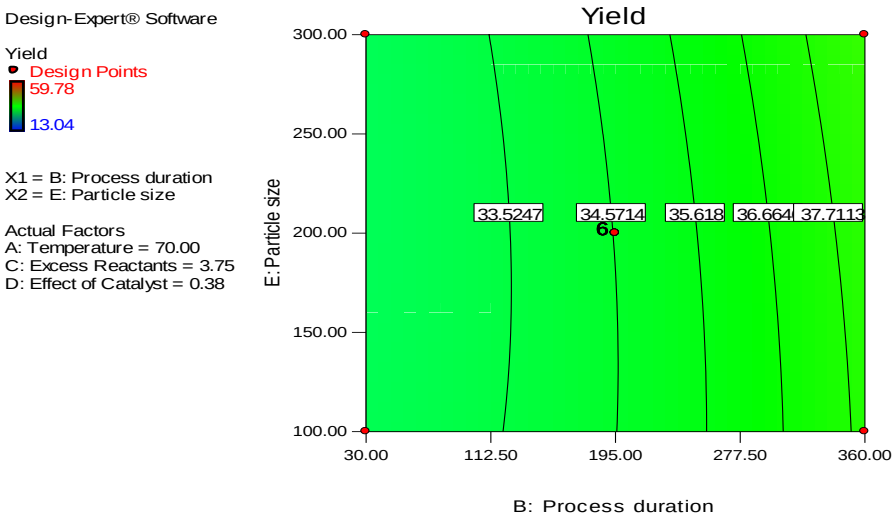

Figure 11: The contour plots for particle size against process duration and yield of ZAC

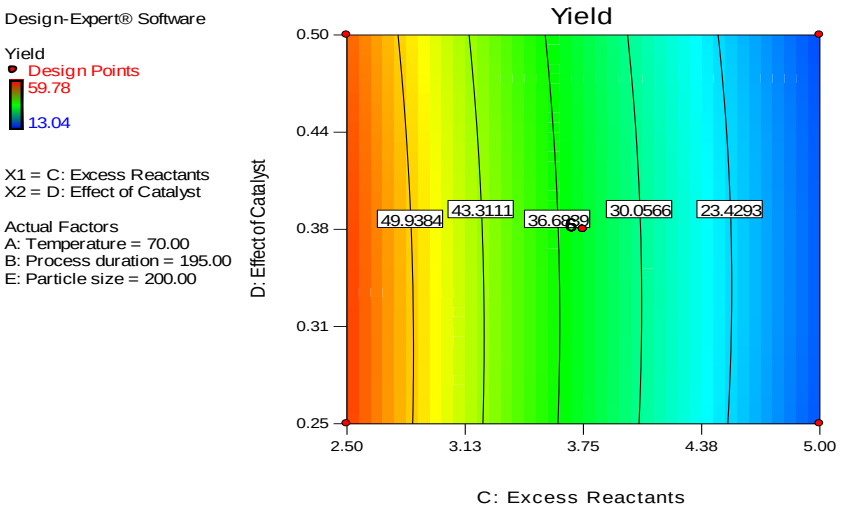

Figure 12: The contour plots for effect of catalyst against excess reactants and yield of ZAC

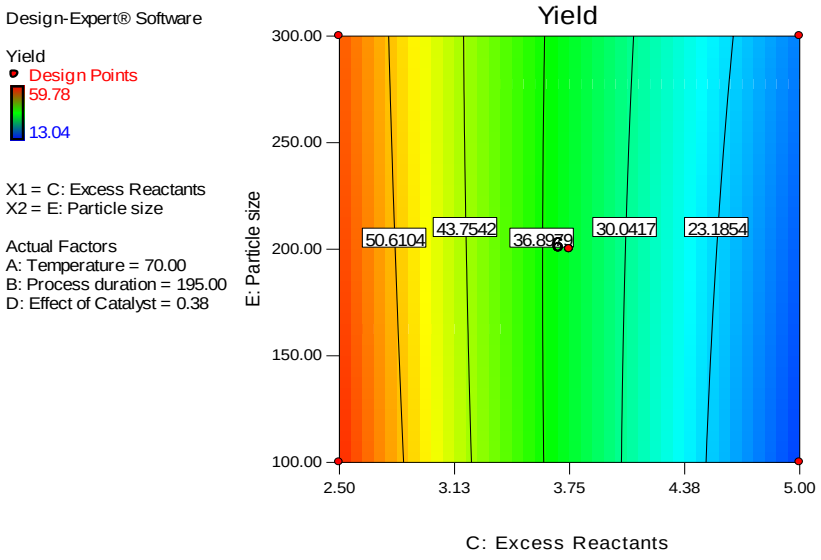

Figure 13: The contour plots for particle size against excess reactants and yield of ZAC

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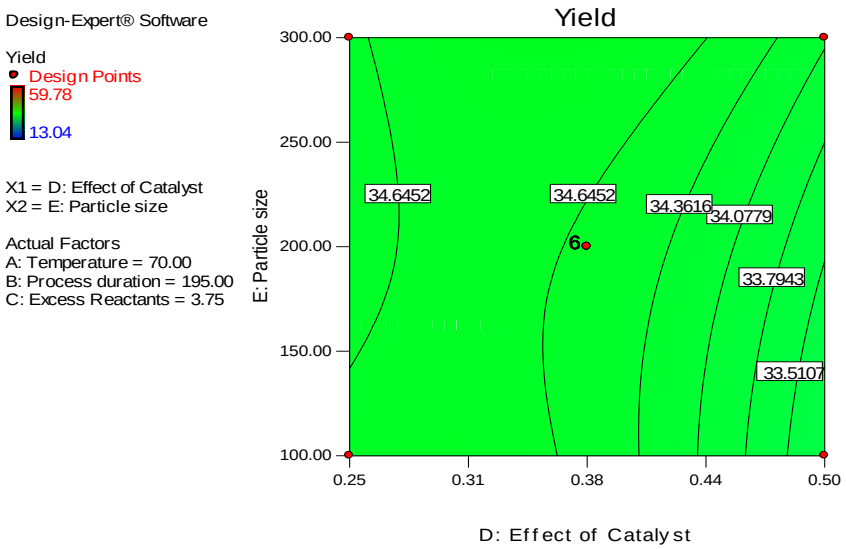

Figure 14: The contour plots for particle size against the effect of catalyst and yield of ZAC

3-D Plot of ZAC

The 3 – Dimensional plots of the response surface model for ZAC are shown in figures 15 to 24. The results showed that the optimum value of the conversion was 42 for the process variables studied, which is similar to the results obtained by [34,23,24,35]. The excess reactants increase with process duration as the yield also increases.The response surface plots showed clear peaks, implying that the maximum values of the response were attributed to the factors in the design space. The three-dimensional surfaces provide useful information about the behaviour of the system within the experiment design, facilitating an examination of the effects of the experimental factors on the responses and contour plots between the factors [33,36,37]. The 3D plots were generated by continually varying any two variables while maintaining all other input variables constant at their null point. The 3D curves were observed to have an elliptical nature with any two concerned variables. This denotes that the quadratic model chosen was appropriate, with significant correlation between the two variables [38,39].

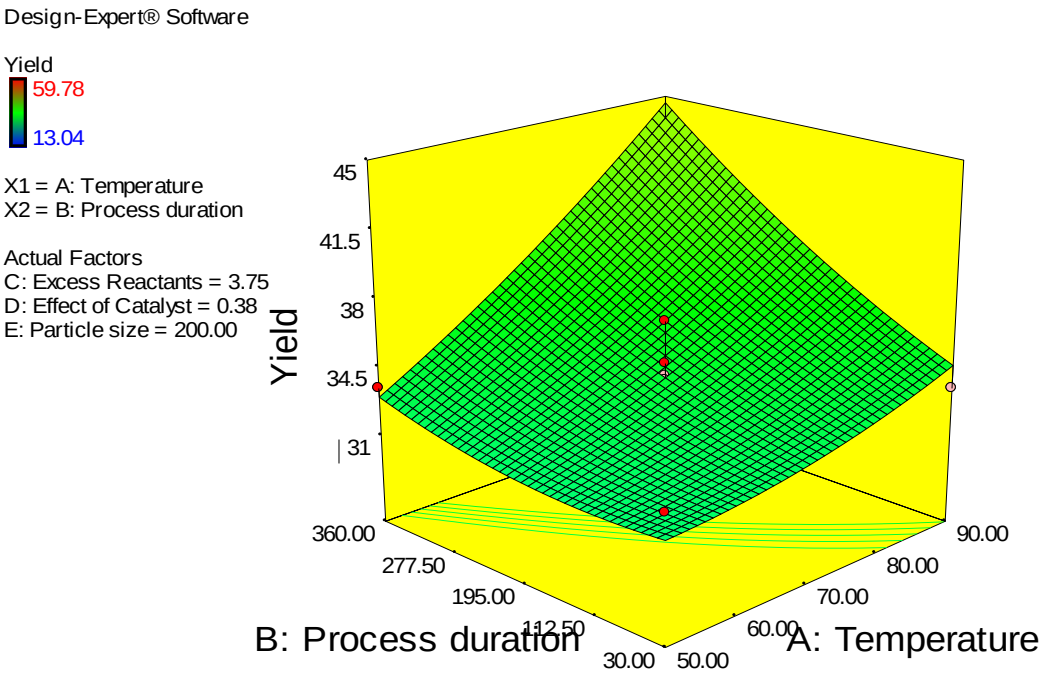

Figure 15: The 3 - D Plotfor process duration against temperature and yield of ZAC

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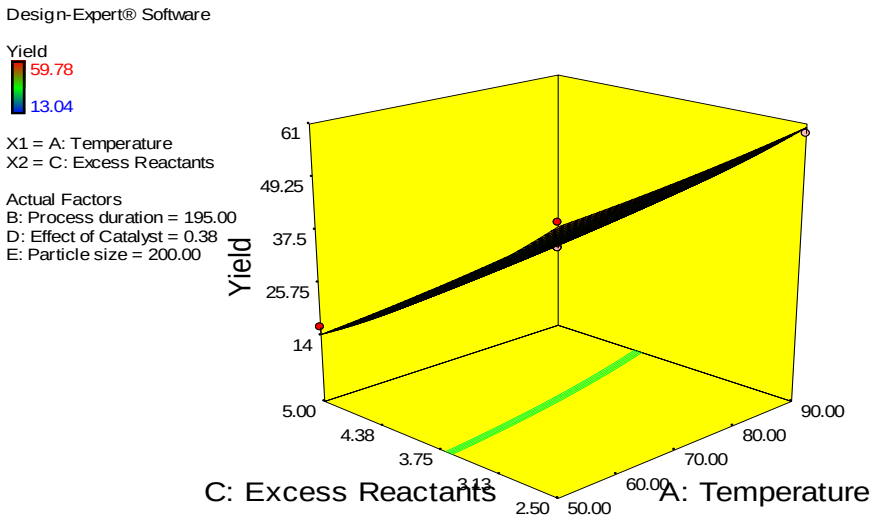

Figure 16: The 3 - D Plotfor excess reactants against temperature and yield of ZAC

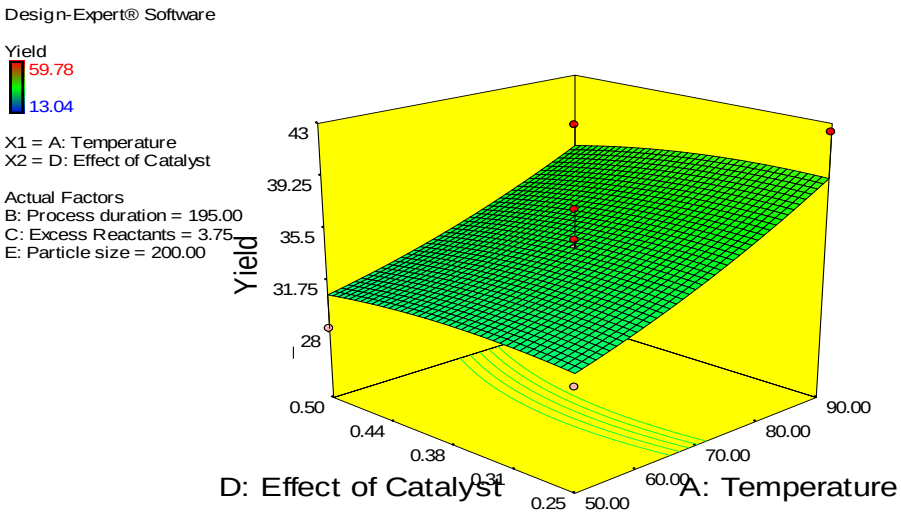

Figure 17: The 3 - D Plotfor effect of catalyst against temperature and yield of ZAC

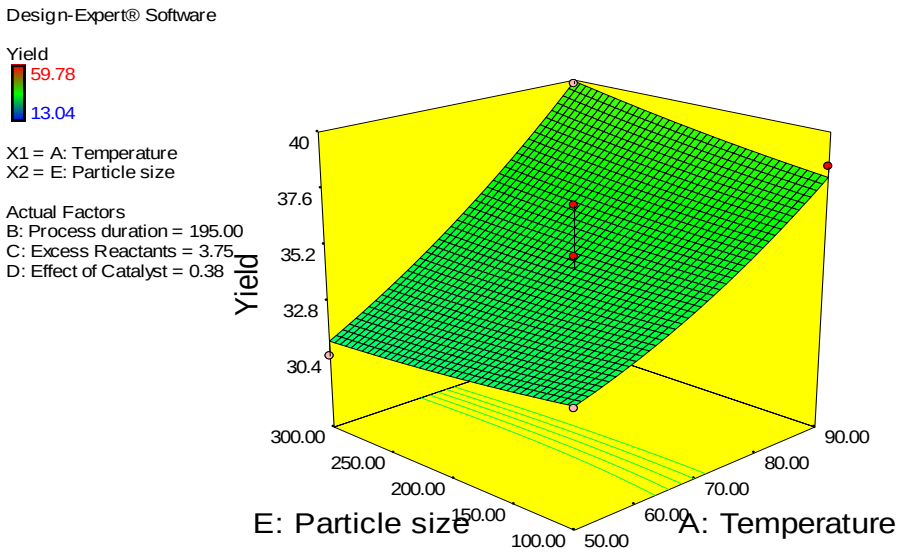

Figure 18: The 3 - D Plotfor particle size against temperature and yield of ZAC

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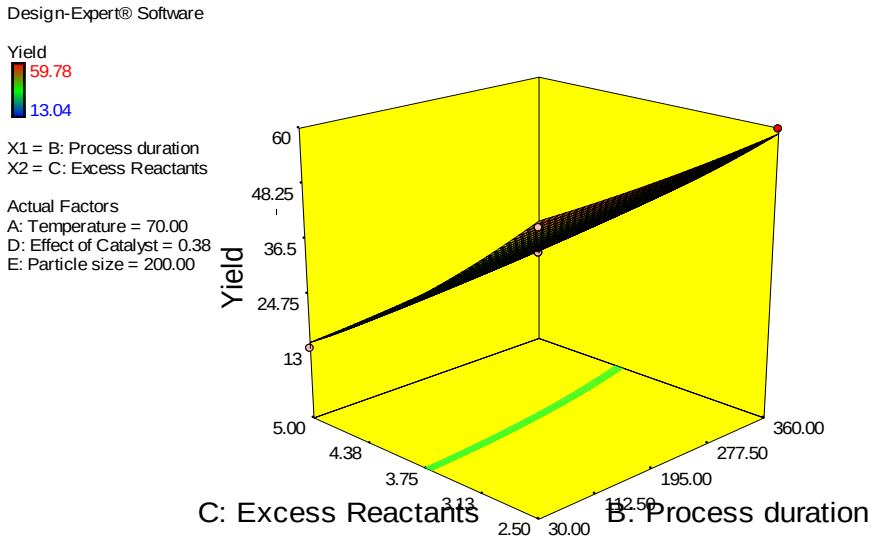

Figure 19: The 3 - D Plot for excess reactants against process duration and yield of ZAC

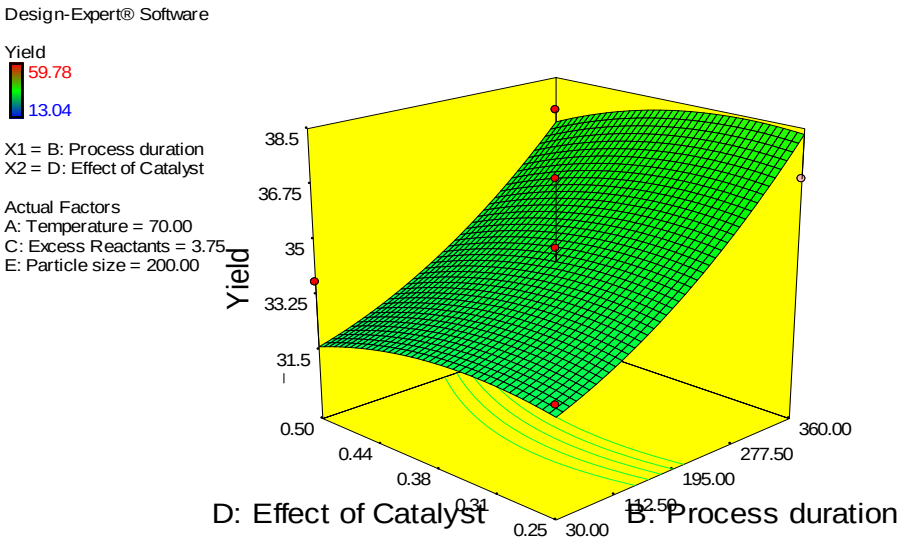

Figure 20: The 3 - D Plotfor effect of catalyst against process duration and yield of ZAC

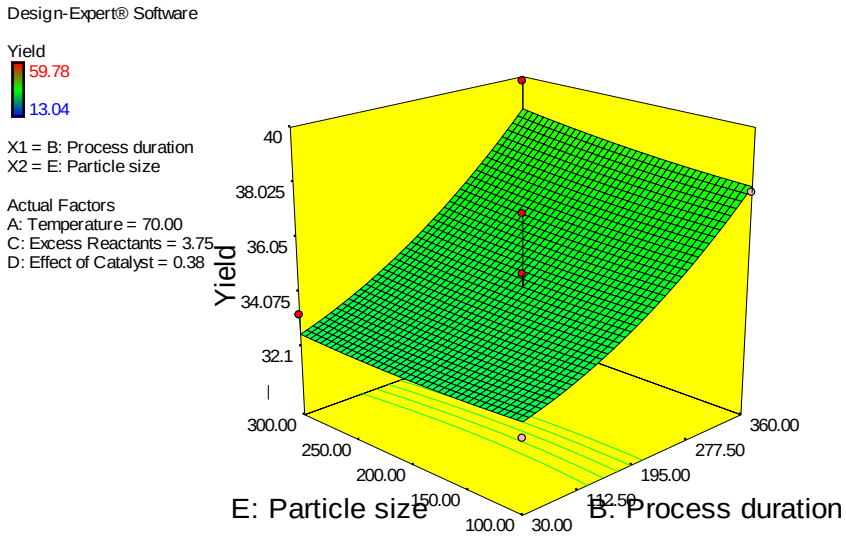

Figure 21: The 3 - D Plotfor particle size against process duration and yield of ZAC

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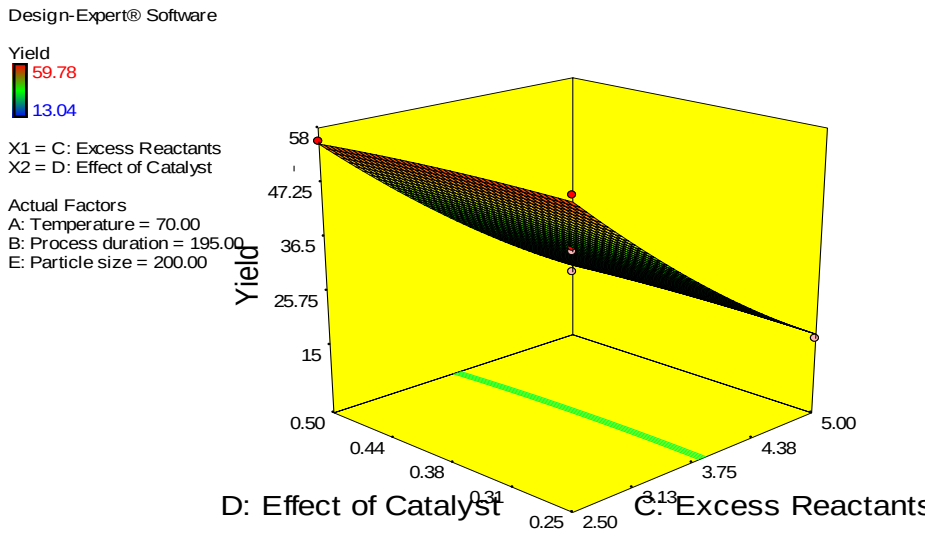

Figure 22: The 3 - D Plotfor effect of ctalyst against excess reactants and yield of ZAC

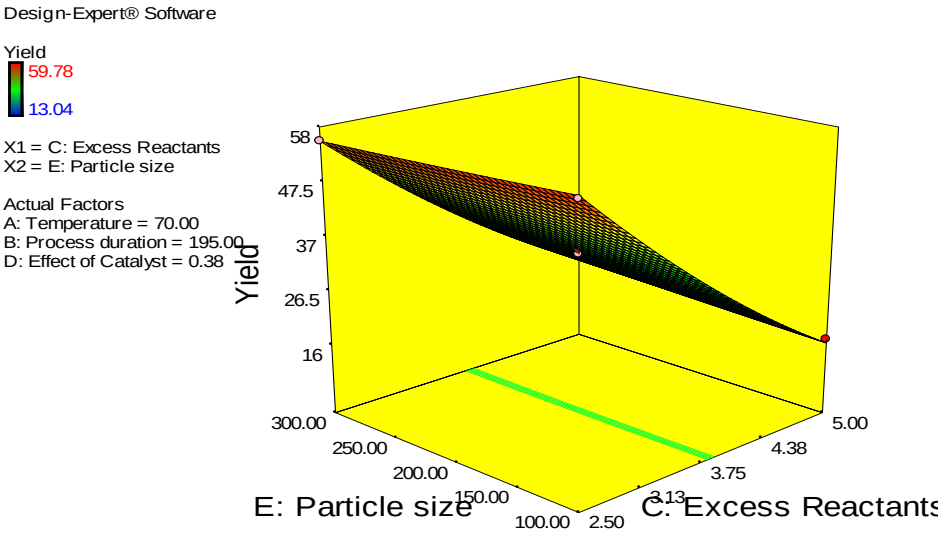

Figure 23: The 3 - D Plotfor particle size against excess reactants and yield of ZAC

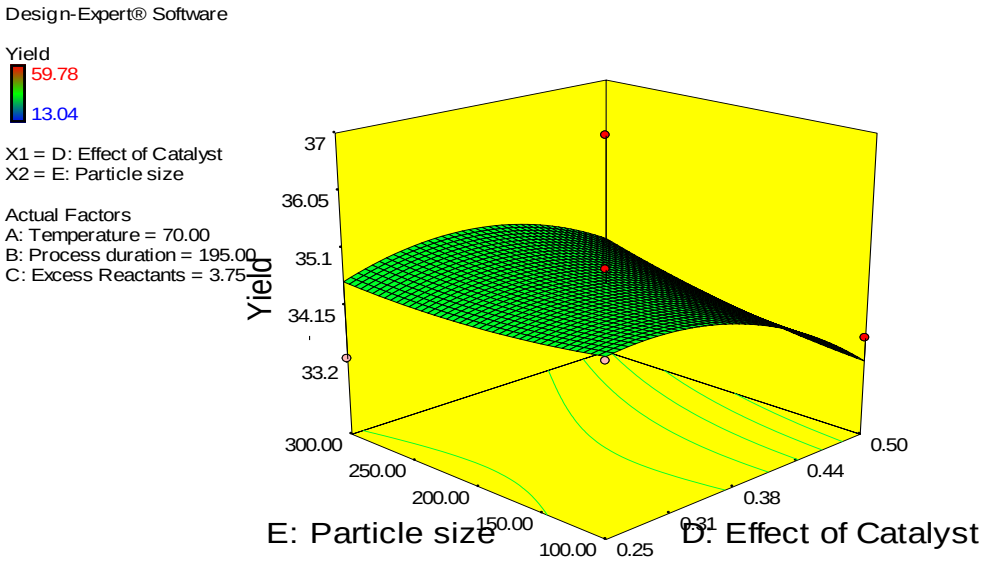

Figure 24: The 3 - D Plotfor particle size against effect of catalystand yield of ZAC

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Process Optimization

In the process optimization for ZAC at table 7, desirability function was used to obtain the optimum value. The time and temperature were set at minimum while the catalyst weight, particle size and excess reactant were set in range. The conversion yield was set at maximum. The optimum process conditions for the variables were 360 min, 90ºC, 4.63ml, 0.50g, and 298.67 microns for time, temperature, excess reactant, Catalyst weight and particle size respectively. The predicted conversion yield was 34.1841. The optimization was validated at those experimental conditions and conversion yield of 48.40was obtained.

Table 7: Validation of Optimization Results

Catalysts	Model Desirability	Temp (ºC)	Time (min)	Excess Reactant (ml)	Catalyst Weight (g)	Particle Size (microns)	Yield (ml)	% Conversion	% Error
ZAC	34.1841	90	360	4.63	0.50	298.67	23.00	48.40	23.00

The summary of the model validation for the catalyst produced (ZAC) is shown in Table 7. The result indicates that Ngbo ZAC isa good catalyst produced when compared to other catalysts produced from Ngbo as a result of its lower percentage error and its pH being alkaline.

V. Conclusions

The study presented theoptimum conditions forthe esterification reaction of acetic acid and ethanol using Zinc Chloride activated Ngbo clay catalyst. The optimum conditions for esterification reaction for the process conditions of temperature, duration, amount of reactant, catalyst weight and particle sizewasdetermined using Response Surface Methodology (RSM) approach. The optimum process conditions for the variables studied including time, temperature, excess reactant, catalyst weight and particle size were 360 min, 90 °C, 4.63ml, 0.50g, and 298.67 microns, respectively. The maximum predicted esterification yield was 34.1841. The XRF analysis revealed that the clay was primarily composed of SiO2 and aluminium, while the XRD analysis indicated quartz as the major component. The predicted and experimental values from the model showed less than 5% difference thereby making the Box-Behnkendesign approach an efficient, effective and reliable method for the esterification of acetic acid and ethanol using Ngbo Zinc Chloride activated clay catalyst.

Competing Interests

Authors have declared that no competing interests exist.

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