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

ABSTRACT

In this work, Box-Behnken"s Response Surface Methodology (RSM) was applied to study the esterification reaction effectiveness of Ngbo pillarred activated clay catalyst. The esterification was monitored based on temperature, time duration, amount of reactant, catalyst weight, and particle size. The Box--Behnken's Response Surface Methodology indicates that the pillarred clay-catalyzed esterification reactions proceed through dual Acid-complex and Alcohol-complex mechanisms, with the Alcohol mechanism dominating. The esterification efficiencies of acetic acid and ethanol by acid-activated Ngbo clay catalyst optimized using RSM models indicated the estimated esterification percentage of >99%. The predicted and experimental values under the same conditions showed less than 5% difference, making the Box-Behnken design approach 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 the correlation coefficient of the regression of 0.8674, implying that 86.74% 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, Pillarred Activated Clay Catalyst, Response Surface Methodology, Box-Behnken design

1. INTRODUCTION

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 has drawbacks of corrosion, loss of catalyst and environmental problems [1, 2]. Therefore, research has been focused on developing eco-friendly heterogeneous catalysts to synthesize fatty acid esters. The most popular solid acids catalyst used to produce esters were ion-exchange organic resins, such as Amberlyst – 15 [3, 4], Zeolites [5 – 6], [7] and Silica-supported heteropoly acid [8] and [9]. Nevertheless, they have shown limitations in the applicability for catalysing esterification reactions due to low thermal stability (Amberlyst-15 < 140^{o}C), mass transfer resistance (Zeolites) [10], [11], or loss of active acid sites in the presence of a polar medium (HPA/silica) [9].

Clay is one of the raw materials in abundance 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 potential of clays, such as the bleaching of palm oil [12, 13], in adsorption of dyes [14 – 16], among others. In a quest to develop green processes, clay is mostly used to synthesize catalysts. However, the use of Nigerian clays from Ngbo, Ohaukwu- Ebonyi State for producing clay catalysts is limited in the literature. However, the kinetics of clay-catalyzed esterification reactions is abundant in literature, but with little or no data on the mechanical and empirical modelling of the use of Ngbo clay in this regard.

Response Surface Methodology (RSM) collects statistical and mathematical techniques that uses quantitative data. Central composite design (CCD), Box-Behnken and Doehlert designs (BBD) are the principal response surface methodologies used in experimental design. This method is suitable for fitting a quadratic surface. It helps optimize the effective parameters with a minimum number of experiments and analyzes the interaction between the parameters [4]. The objective is to optimize a response (output variable) influenced by several independent variables (input

variables). The application of RSM to design optimization aims to reduce the cost of expensive numerous experiments, save time, reduce stress, etc [17 – 20].

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

2. Materials and Methods

2.1 Source of Raw Materials

The clay sample was obtained from Ngbo in Ohaukwu L.G.A. of Ebonyi State (N 06^{o}30$^{'}$ 32.8''), (E 007^{o}58'13.7''). The dye was purchased from a chemical shop at Ogbete main market, Enugu, Enugu State. Other chemicals such as acetic acid, sodium hydroxide, aluminium trichloride ($AlCl_3$), distilled water, etc were of standard grade.

2.2 Physico-Chemical Characterization of Ngbo Clay

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

2.3 Characterisation of the raw clay and Pillarred activated sample

The Ngbo clay sample was characterized using XRF and SEM.

2.4 Clay Pillarring

The pillared clay was prepared according to the method described by Huan-Yan Xu *et al* (2009) with some modification. The pillaring agent used was an alluminium polioxocation prepared by basic hydrolysis of an aluminium trichloride ($AlCl_3$). A 0.20m/dm^3 of sodium hydroxide (NaOH) solution was poured at 4ml/min over the 0.2m $AlCl_3$ salt solution and stirred vigorously until a molar ratio OH/Al of 2 was reached. The final pH was 3.5 and the solution was kept for 1 hour at 50^{o}C.

100g of clay sample were suspended in distilled water and stirred continuously for 30 min after which the pillaring agent solution was added (4ml/min) over the clay suspension while stirred vigorously. The final Aluminium/clay was 2mol/g. The resulting suspension was kept at 80^{o}C for

4 hours. The solid was recovered by filtration and oven-dried at 450^{o}C. The clay sample was pulverized and stored in an airtight container.

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

2.5.1 Sample Preparation/Procedure

The raw clay sample was crushed, sieved at 100microns, 200microns and 300microns. Thereafter, the clay sample was activated using pillaring agent. The activated clay sample was used in esterification reaction to assess the effectiveness. 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 active sites of the catalyst were not blocked by the ethanol. The container was tightly closed, the contents was 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 (^{o}C), 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;

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

2.6 Response Surface Methodology

The response surface technique applying Box-behnken design matrix was applied 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 needed best working conditions in a shorter time and detailed conditions of processes are provided. This was achieved through a designed experimental design applying Box-Behnken Response Surface Methodology design of 46 steps of experiment consisting five factors and three levels (Table 4). The numerical optimization method of RSM was used in the optimization.

3. RESULTS AND DISCUSSIONS

3.1 Physical properties of the raw clay

The result of the physical properties of raw Ngbo clay is presented in table 3. The result showed that the clay has a moisture content of 3.3 % and 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 2: 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

3.2 Characterization of Raw Clay and Pillarred Activated Clay

The chemical properties of the raw Ngbo clay was analysed using XRF and SEM.

The result of the XRF composition analysis of raw Ngbo clay and Pillarred activated Ngbo clay (PLC) is presented in Table 4. The result showed that raw and activated clays have contaminations of oxides and other impurities, but the clay minerals compositions are not meaningfully affected by thermal treatments even under strong conditions and below 500 ℃ as reported in literature by [25, 26] and [27]. This shows that improvement on the properties of the clay by chemical methods below 500 ℃ is difficult due to its low reactivity. This result of the XRF on the Ngbo raw clay and pillarred activated Ngbo clays as shown in table 4 also indicates high content of silicon and aluimium oxides compared to other oxides.

Table 3: Results of XRF analysis of raw Ngbo Clay and Ngbo Pillarred activated clay

Chemical constituent	**Raw clay (Wt. %)**	**Pillarred activated (PLC), (Wt. %)**
SiO_2	62.70	65.395
TiO_2	1.52	1.354
Al_2O_3	19.70	24.562
Fe_2O_3	2.06	5.667
P_2O_3	_	0.000
CaO	0.789	0.359
MgO	0.026	0.586
Na_2O	0.20	0.261
K_2O	0.85	1.196
Mn_2O_3	_	0.148
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	_	0.220
Cl	_	0.217
ZnO	_	0.016
SrO	_	0.007

The SEM image results of the raw clay at 80μm, 20μm and 8μm magnifications are presented in figure 1. The SEM image results of Ngbo raw clay showed cracking or peeling morphology and presence of tubular or rod material attributed to halloysite, clinochlore, mica and muscovites as reported in literature by [28]. The results are in agreement with the XRD results.

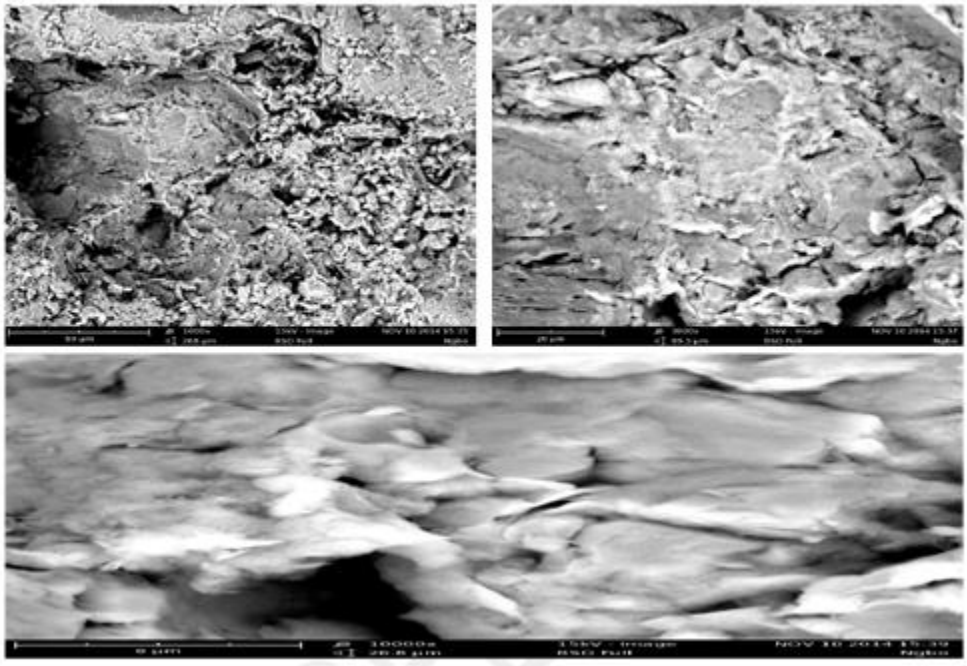

Figure 1: Results of SEM analysis of Ngbo raw clay

The SEM image results of Ngbo Pillarred activated clay at 80μm, 20μm and 8μm magnifications are presented in figure 2. The SEM image results shows retention of kaolinite structure but with noticeable small aggregate particles in between the silica-alumina plate on higher magnification, an indication of impurities on the beneficiated kaolin. The halloysite phase detected in the raw clay SEM image was not in the activated clay SEM image, which is in agreement with the XRF results. The dark and bright patches witnessed in the image were attributed to the presence of imbedded chemicals and completely dried portion of the samples respectively [28].

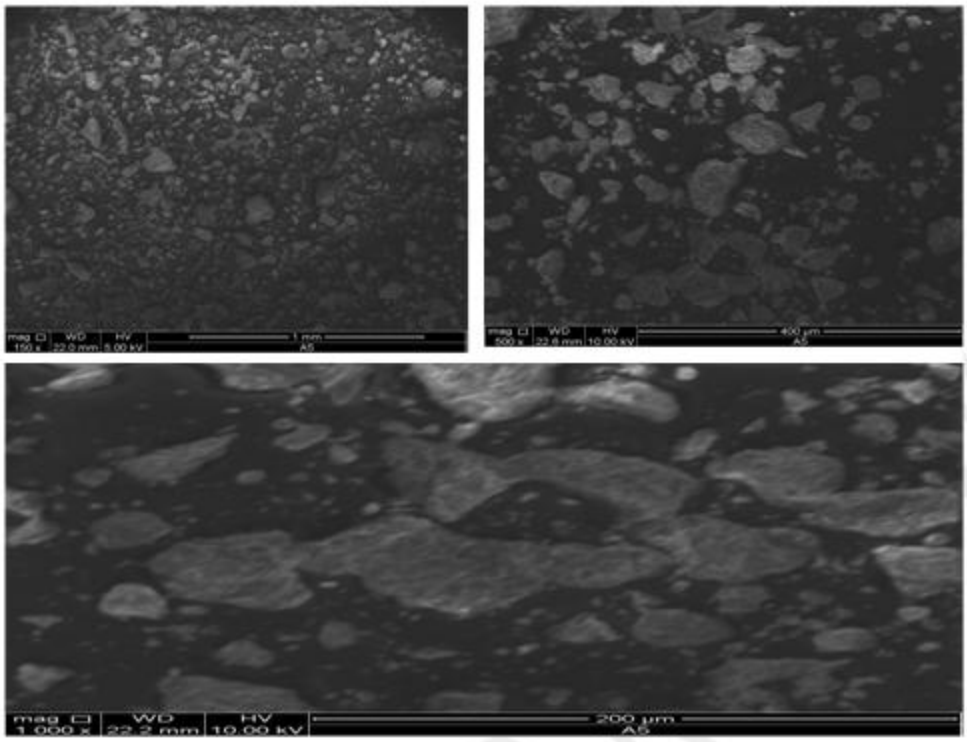

Figure 2: Results of SEM analysis of Ngbo PLC

3.3 Esterification Process Results

Esterification technique was used to obtain the responses and yield of Pillarred Activated Catalyst (PLC) as shown in Table 4

Table 4: Result showing Responses and Yield of PLC

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	30.60	30.93
22	2	70	360	2.5	0.38	200	19.50	55.98
23	3	70	30	5	0.38	200	40.40	8.80
29	4	70	195	2.5	0.38	100	20.80	52.29
26	5	90	195	3.75	0.25	200	27.70	37.47
1	6	50	30	3.75	0.38	200	31.20	29.57
32	7	70	195	5	0.38	300	39.30	8.82
46	8	70	195	3.75	0.38	200	30.40	31.38
10	9	70	360	3.75	0.38	100	29.50	32.34
34	10	90	195	3.75	0.38	100	27.20	37.61
21	11	70	30	2.5	0.38	200	19.90	55.08
35	12	50	195	3.75	0.38	300	28.70	33.41

8	13	70	195	5	0.5	200	32.00	27.77
4	14	90	360	3.75	0.38	200	25.60	42.21
2	15	90	30	3.75	0.38	200	32.40	26.86
11	16	70	30	3.75	0.38	300	30.40	29.47
31	17	70	195	2.5	0.38	300	20.20	53.13
3	18	50	360	3.75	0.38	200	30.70	30.70
24	19	70	360	5	0.38	200	38.40	13.32
16	20	90	195	5	0.38	200	37.00	16.48
44	21	70	195	3.75	0.38	200	30.40	31.38
12	22	70	360	3.75	0.38	300	29.50	31.55
36	23	90	195	3.75	0.38	300	28.10	34.80
17	24	70	195	3.75	0.25	100	30.90	29.13
18	25	70	195	3.75	0.5	100	30.60	29.82
45	26	70	195	3.75	0.38	200	30.80	30.47
33	27	50	195	3.75	0.38	100	32.20	26.15
25	28	50	195	3.75	0.25	200	32.00	27.77
20	29	70	195	3.75	0.5	300	30.60	29.00
27	30	50	195	3.75	0.5	200	31.70	28.44
30	31	70	195	5	0.38	100	40.00	8.26
42	32	70	195	3.75	0.38	200	30.80	30.47
41	33	70	195	3.75	0.38	200	31.00	30.02
39	34	70	30	3.75	0.5	200	31.10	29.80
6	35	70	195	5	0.25	200	24.00	45.82
43	36	70	195	3.75	0.38	200	30.40	31.38
38	37	70	360	3.75	0.25	200	29.80	32.73
19	38	70	195	3.75	0.25	300	30.30	29.70
40	39	70	360	3.75	0.5	200	29.40	33.63
7	40	70	195	2.5	0.5	200	19.50	55.98
28	41	90	195	3.75	0.5	200	28.00	36.79
14	42	90	195	2.5	0.38	200	17.30	60.95
5	43	70	195	2.5	0.25	200	19.50	55.98
13	44	50	195	2.5	0.38	200	21.00	52.60
9	45	70	30	3.75	0.38	100	31.40	27.98
15	46	50	195	5	0.38	200	42.50	4.06

3.4: Analysis of Variance (ANOVA) for Pillared Clay (PLC)

The result of the ANOVA for Pillared Clay (PLC) is shown in table 5. The result showed that RSM model is significant of the experimental results as indicated from the F – value of 143.88 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 [29]. If P – value of lack of fit is less than 0.05, there is statistically significant lack of fit at 95% confidence level [30].
However, the result in table 5 indicates that the significant model terms A, B, C, AB and C^2, which implies that only linear effects of temperature, process duration, excess reactants, interactive effects of temperature and process duration and quadratic effects of excess reactant were significant. The model accuracy was confirmed by the correlation coefficient of the regression model which is 0.8674. The correlation coefficient showed that 86.74% of the total variation in the final concentration was attributed to the experimental variables considered in this study. 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 [29].

The standard deviation for the model was 6.48, which indicated that the predicted values are still considered suitable to correlate the experimental data."Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Here it has a ratio of 11.341, which indicates an adequate signal.

The Final equation in terms of coded factors gives:

$$\text{Yield} = +30.85 + 3.78A + 2.12B - 19.29C - 1.14D + 0.39E + 3.56AB + 1.02AC - 0.34AD - 2.52AE + 0.92BC + 0.51BD - 0.57BE - 4.51CD - 0.070CE - 0.35DE + 0.62A^2 - 0.62B^2 + 4.74C^2 + 3.53D^2 - 2.08E^2.$$

The coefficient with one factor represents 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:

$$\text{Yield} = +30.85 + 3.78A - 19.29C + 4.74C^2.$$

The regression model developed was further assessed using residual plots as shown in figure 3-6. Residual is the difference between the experimental value and value predicted by the model. This tests the assumption of constant variance of the experimental data.

TABLE 5: ANOVA Table for Pillared Clay (PLC)

Source	Sum of Squares	Df	Mean Square	F – Value	P – Value Prob > F
Model	6864.87	20	343.24	8.18	<0.0001 significant
A – Temperature	228.54	1	228.54	5.44	0.0280
B – Process duration	71.91	1	71.91	1.71	0.2025
C – Excess reactant	5952.5	1	5952.51	141.80	< 0.0001
D – Effect of Catalyst	20.93	1	20.93	0.50	0.4866
E – Particle size	2.48	1	2.48	0.059	0.8099
AB	50.55	1	50.55	1.20	0.2829
AC	4.14	1	4.14	0.099	0.7561
AD	0.46	1	0.46	0.011	0.9179
AE	25.35	1	25.35	0.60	0.4444
BC	3.37	1	3.37	0.080	0.7793
BD	1.03	1	1.03	0.025	0.8768
BE	1.30	1	1.30	0.031	0.8618
CD	81.45	1	81.45	1.94	0.1759
CE	0.020	1	0.020	4.669E-004	0.9829
DE	0.48	1	0.48	0.012	0.9154
A^2	3.40	1	3.40	0.081	0.7784
B^2	3.39	1	3.39	0.081	0.7785
C^2	196.13	1	196.13	4.67	0.0404
D^2	108.84	1	108.84	2.59	0.1199
E^2	37.64	1	37.64	0.90	0.3527
Residual	1049.49	25	41.98		
Lack of fit	1047.67	20	52.38	143.88	< 0.0001 significant
Pure Error	1.82	5	0.36		
Cor Total	7914.36	45			

3.4.1: Residual Plots for PLC

The residual plots are shown in Figure 3 – figure 6. 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.

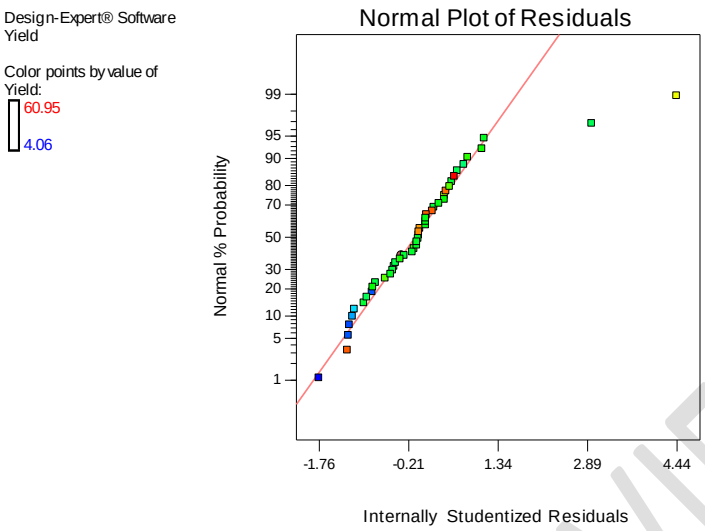

Figure 3: Normal plot of residuals for PLC

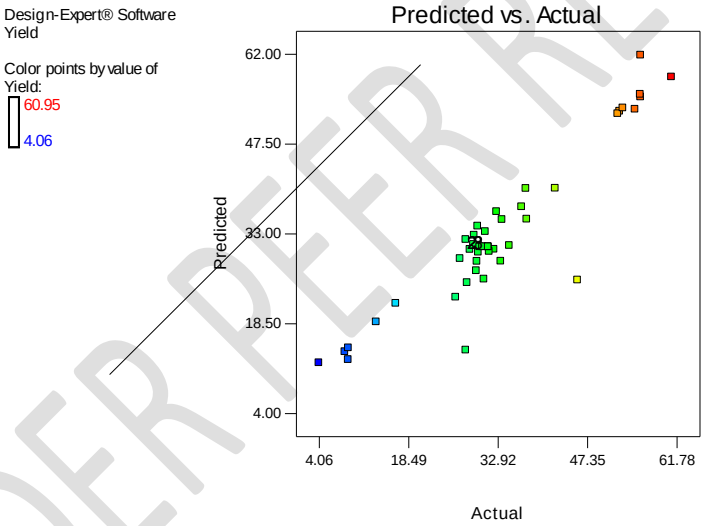

Figure 4 : Plot of predicted verse actual for PLC

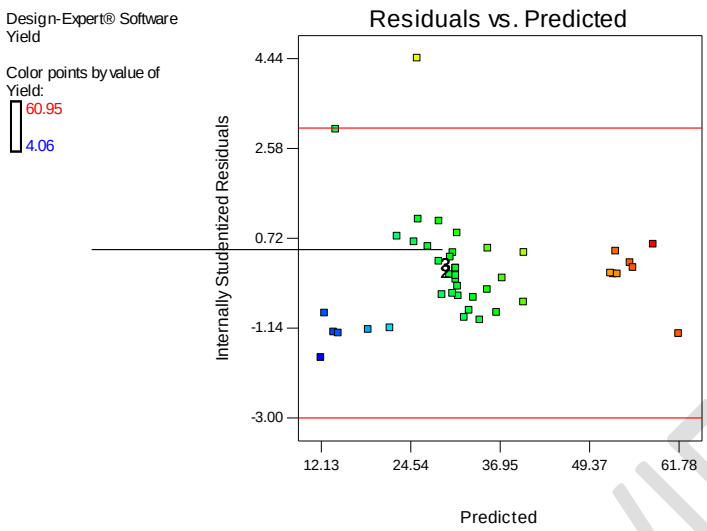

Figure 5: Plot of residuals verse predicted for PLC

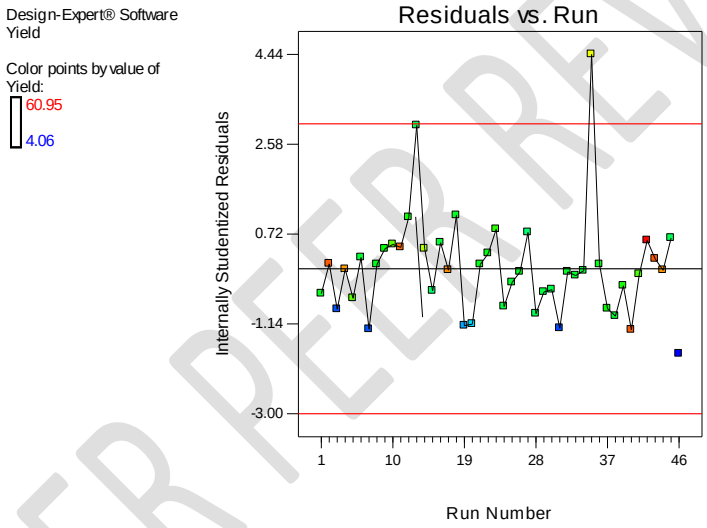

Figure 6: Plot of residuals verse run for PLC

3.4.2: Contour Plots for PLC

The contour plots for PLC are shown in figure 7 to figure 16. The circular nature of the contour plots signifies that the interactive effects between the variables are not significant and the optimum values of the test process variables cannot be easily obtained [31, 29]. 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.

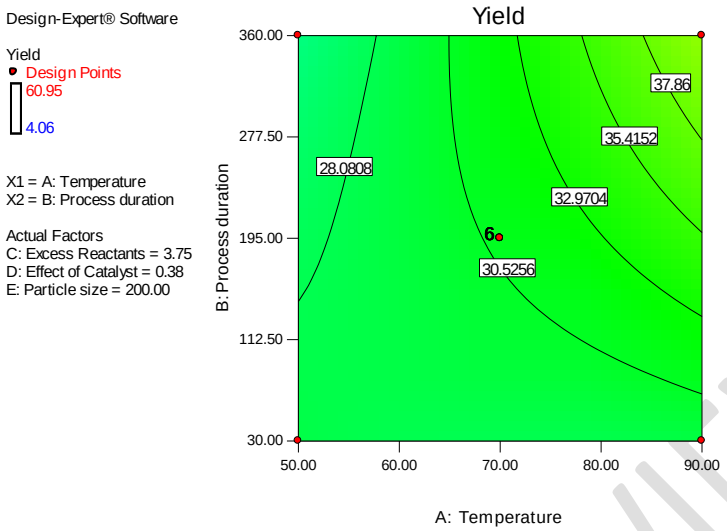

Figure 7: The contour plots for process duration against Temperature and yield of PLC

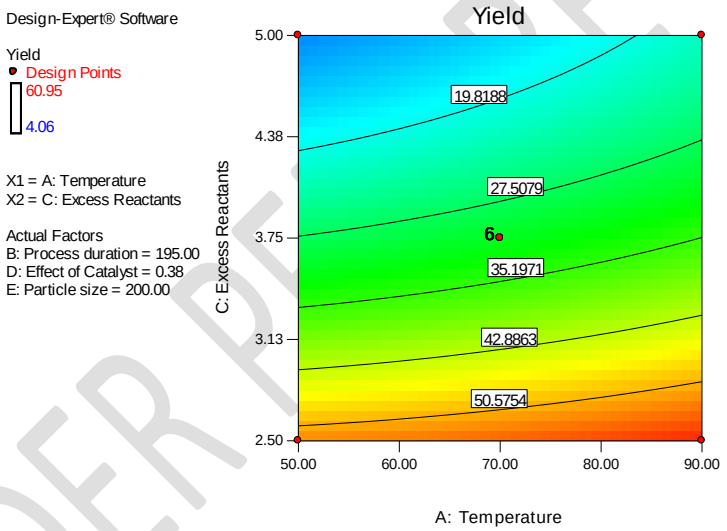

Figure 8: The contour plots for excess reactants against Temperature and yield of PLC

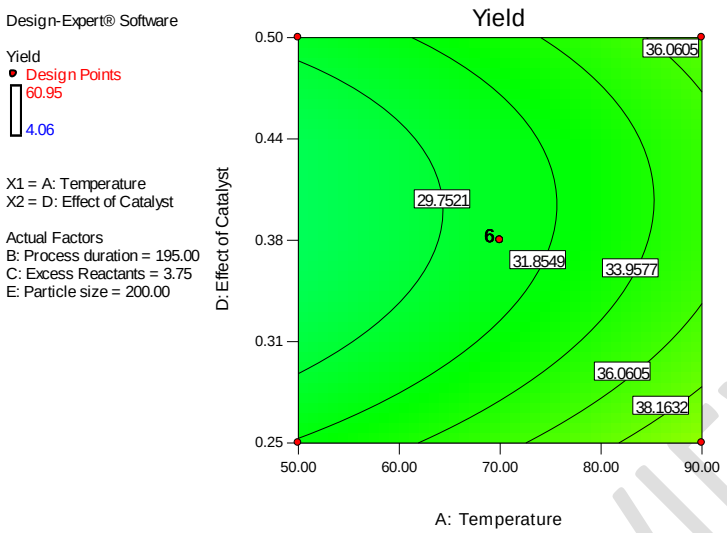

Figure 9: The contour plots for effect of catalyst against Temperature and yield of PLC

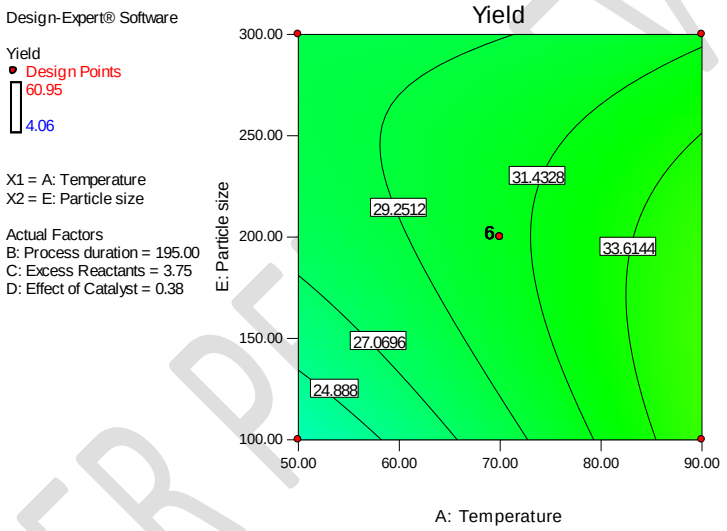

Figure 10: The contour plots for excess reactants against Temperature and yield of PLC

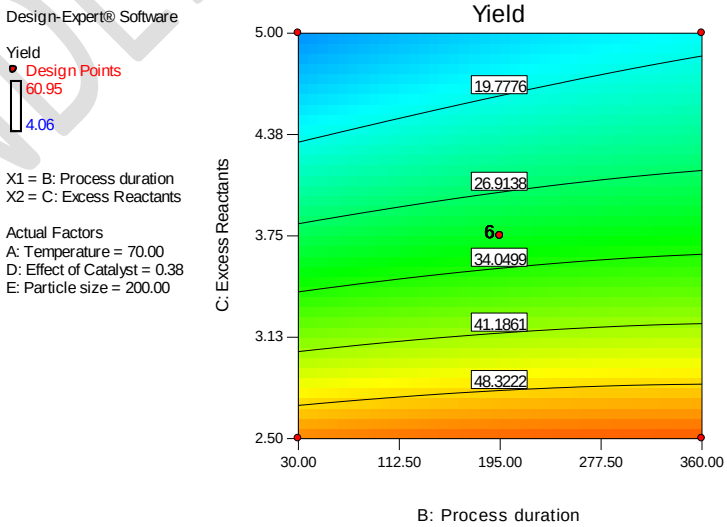

Figure 11: The contour plots for excess reactants against process duration and yield of PLC

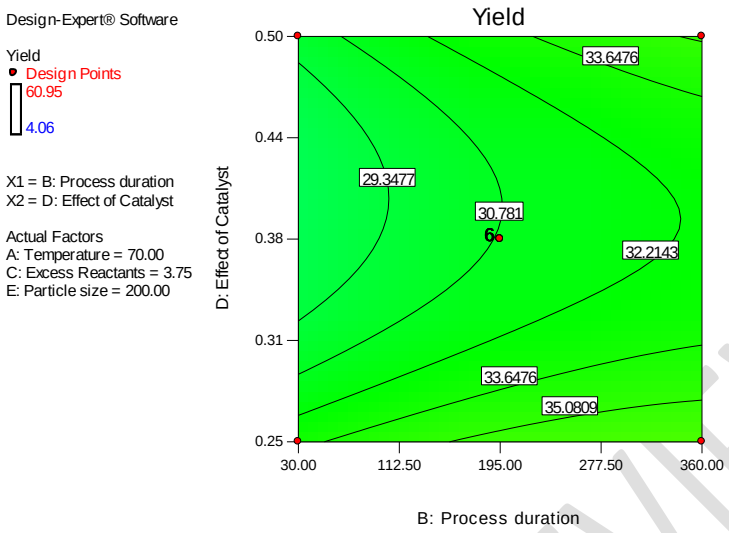

Figure 12: The contour plots for effect of catalyst against process durationand yield of PLC

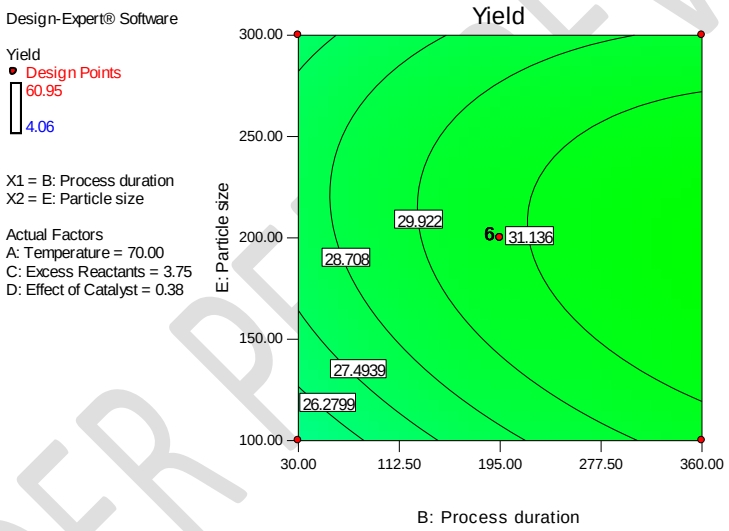

Figure 13: The contour plots for particle size against process duration and yield of PLC

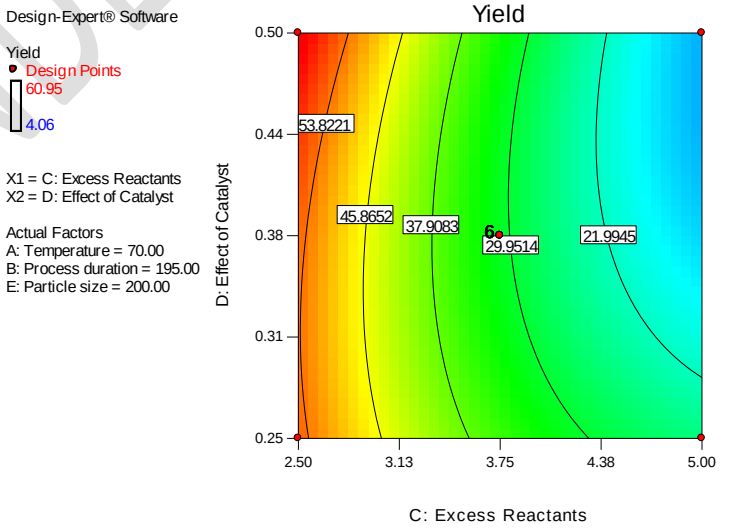

Figure 14: The contour plots for effect of catalyst against excess reactants and yield of PLC

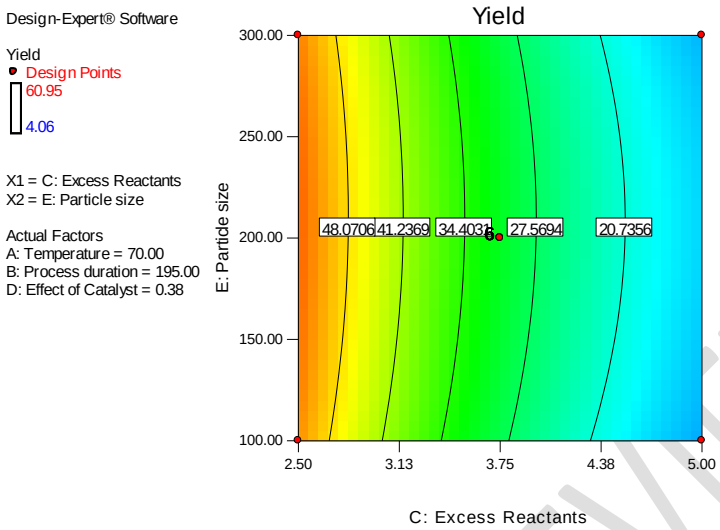

Figure 15: The contour plots for particle size against excess reactants and yield of PLC

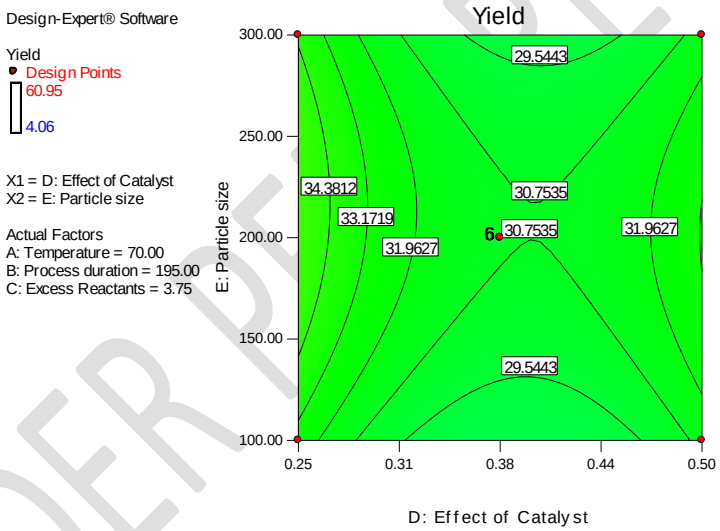

Figure 16: The contour plots for particle size against effect of catalyst and yield of PLC

3.4.3: The 3 - D Plot for PLC

The 3 – Dimensional plots of the response surface model are shown in figures 17 to 26. The results showed that the optimum value of the conversion was 42 for the process variabless studied; which are similar to results obtained by [29, 23, 24, 30]. The excess reactants increases 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 behavior of the system within the experiment design, facilitate an examination of the effects of the experimental factors on the responses and contour plots between the factors [31, 34, 35]. The 3-D plots were generated by continually varying any two variables while maintaining all other input variables constant at their null point. The 3-D curves were observed to have elliptical nature with any two concerned variables. This denotes that the quadratic model chosen was appropriate with significant correlation between the two variables [36, 37].

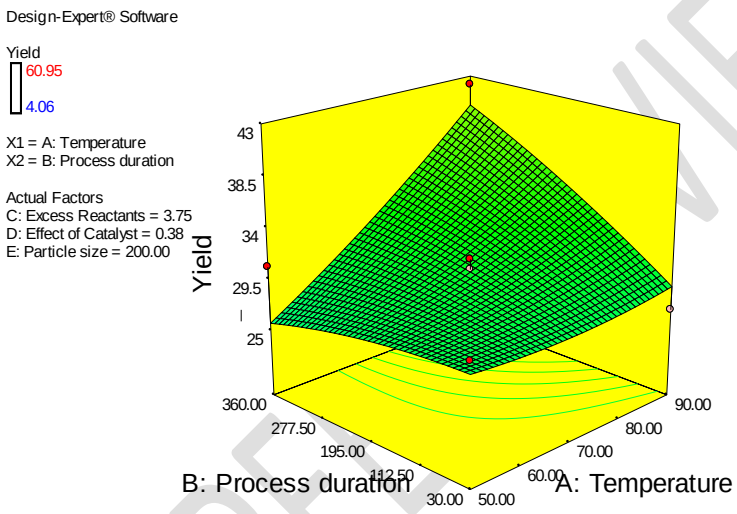

Figure 17: The 3 - D Plot for process duration against temperature and yield of PLC

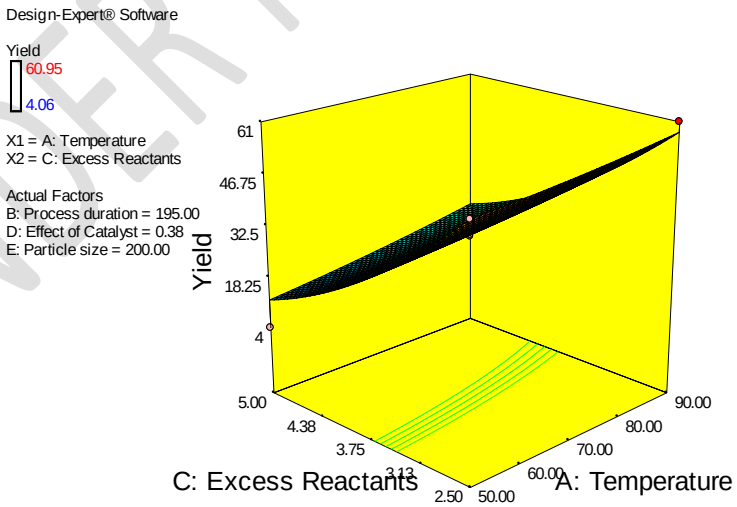

Figure 18: The 3 - D Plot for excess reactants against temperature and yield of PLC

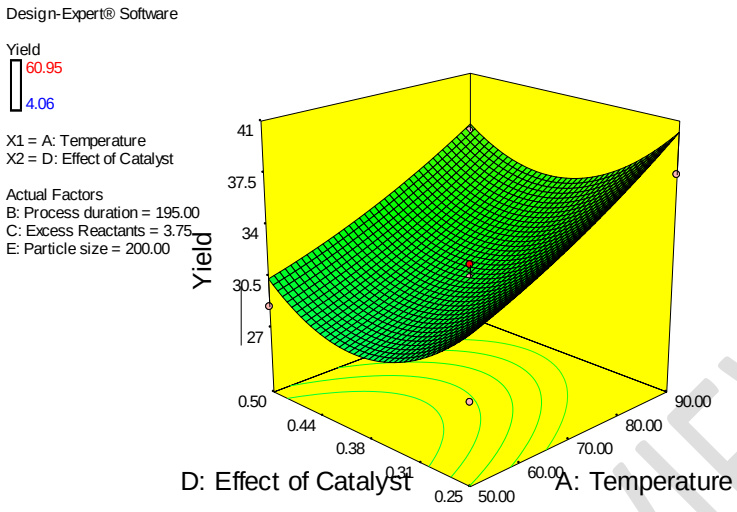

Figure 19: The 3 - D Plot for effect of catalyst against temperature and yield of PLC

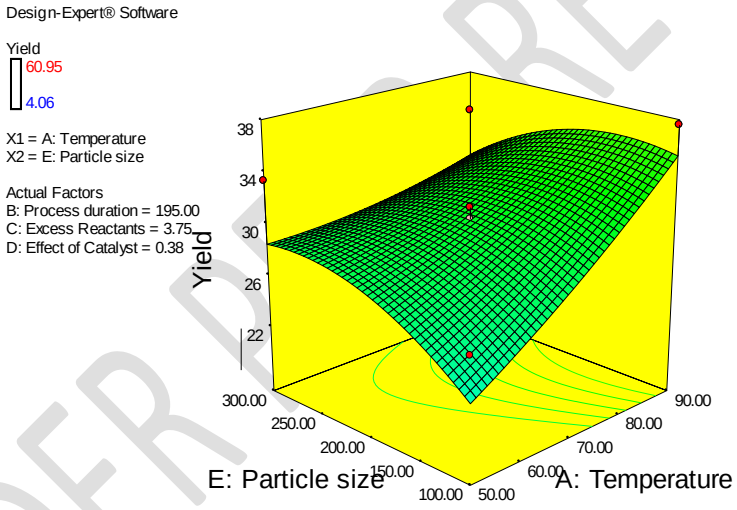

Figure 20: The 3 - D Plot for particle size against temperature and yield of PLC

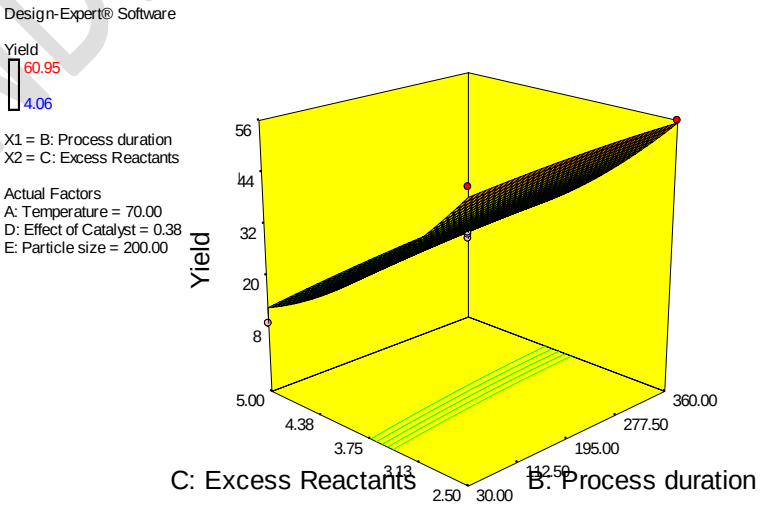

Figure 21: The 3 - D Plotf or excess reactants against duration and yield of PLC

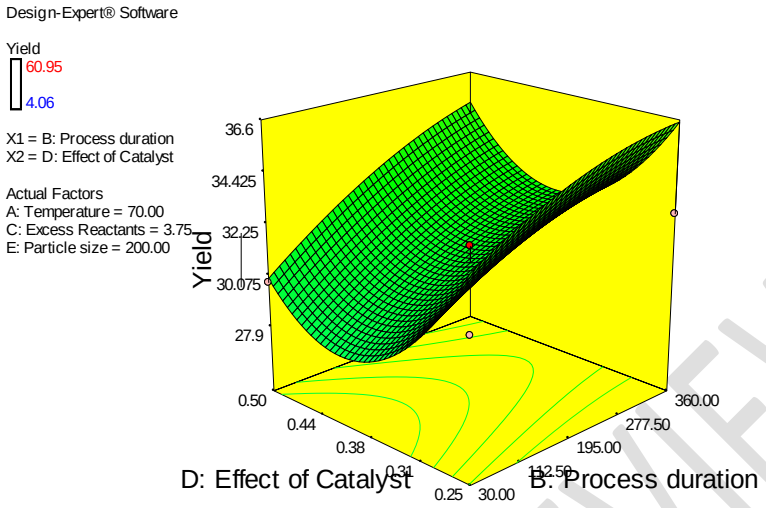

Figure 22: The 3 - D Plot for effect of catalyst against process duration and yield of PLC

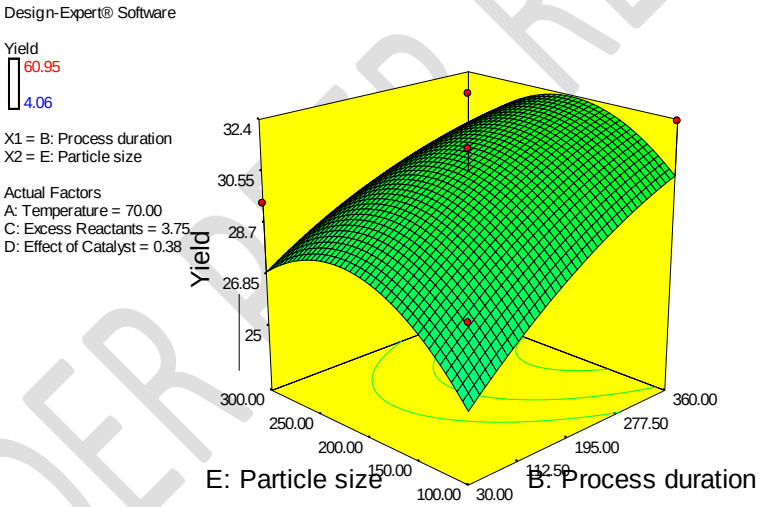

Figure 23: The 3 - D Plot for particle size against process duration and yield of PLC

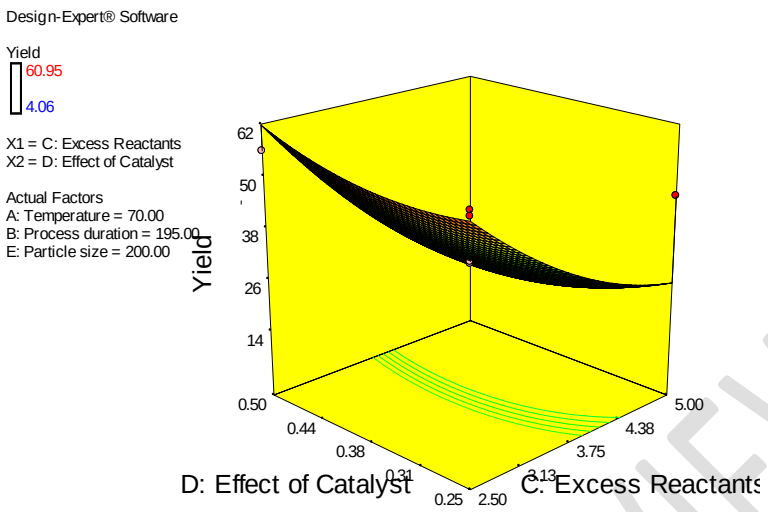

Figure 24: The 3 - D Plot for effect of catalyst against excess reactants and yield of PLC

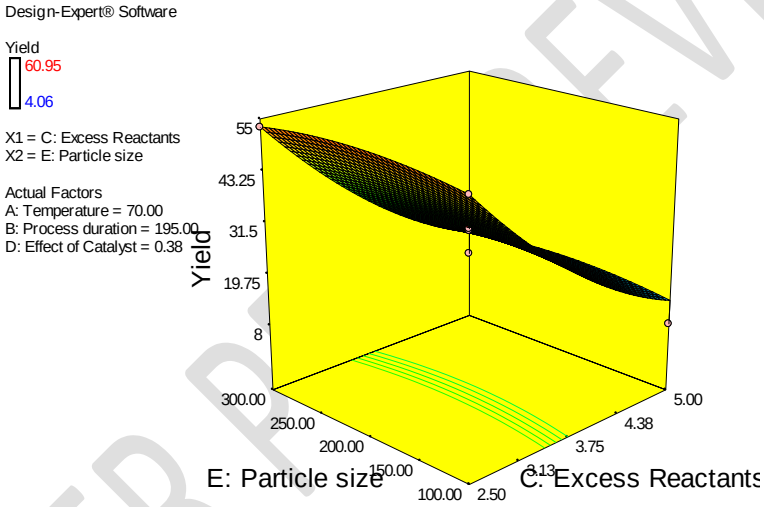

Figure 25: The 3 - D Plot for particle size against excess reactants and yield of PLC

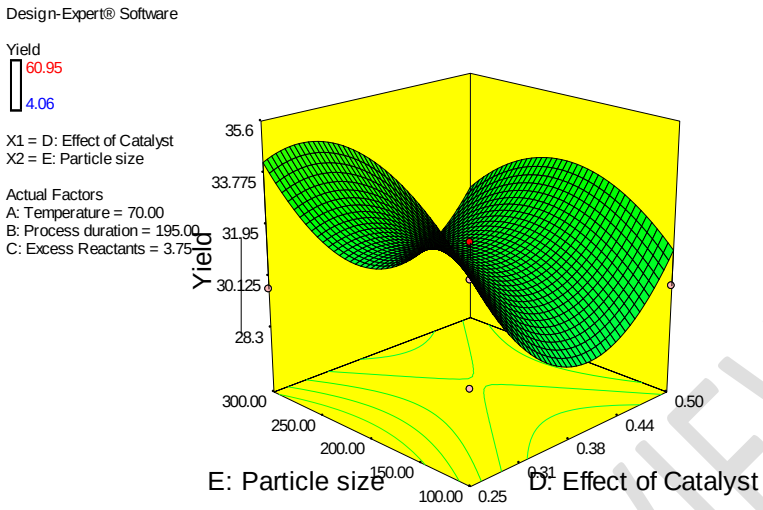

Figure 26: The 3 - D Plot for particle size against effect of catalyst and yield of PLC

3.4.3 Process Optimization

In the process optimization for PLC at table 6, 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 359.93 min, 90^{o}C, 4.40ml, 0.50g, and 299.92 microns for time, temperature, excess reactant, catalyst weight and particle size respectively. The predicted conversion yield was 27.5361. The optimization was validated at those experimental conditions and conversion yield of 45.65 was obtained.

Table 6: Validation of Optimization Results

Catalysts	Model Desirability	Temp (^{o}C)	Time (min)	Excess Reactant (ml)	Catalyst Weight (g)	Particle Size (microns)	Yield (ml)	% Conversion	% Error
PLC	27.5361	90	359.93	4.40	0.50	299.92	25.00	45.65	2.54

The summary of the model validation for the catalyst produced (PLC) is shown in table 6. The result indicates that Ngbo PLC is a good catalyst produced when compared to other catalyst produced from Ngbo as a result of its less percentage error and its pH being alkaline.

4. CONCLUSIONS

The study presented the optimum conditions for esterification reaction of acetic acid and ethanol using Ngbo pillarred activated clay catalyst. The optimum conditions for esterification reaction for the process conditions of temperature, time duration, amount of reactant, catalyst weight and particle size was determined using Response Surface Methodology (RSM) approach. The optimum process conditions for the variables studied for time, temperature, excess reactant, catalyst weight and particle size were 359.93 min, 90^{o}C, 4.40ml, 0.50g, and 299.92 microns respectively. The maximum predicted esterification yield was 27.5361. The XRF analysis showed that the clay was made of mainly SiO_2 and aluminium while SEM results indicated crystalline nature suitable for esterification. The model validation showed that the experimental value obtained at the optimal conditions was in good agreement with the values predicted from the model with relatively small error of 2.54% between them. The predicted and experimental values from the model showed less than 5% difference thereby making the Box-Behnken design approach an efficient, effective and reliable method for the esterification of acetic acid and ethanol using Ngbo Pillarred activated clay catalyst.

DISCLAIMER:

Authors have declared that no competing interests exist. The products used for this research are commonly and predominantly use products in our area of research and country. There is absolutely no conflict of interest between the authors and producers of the products because we do not intend to use these products as an avenue for any litigation but for the advancement of knowledge. Also, the research was not funded by the producing company rather it was funded by personal efforts of the authors.

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