Original Research Article

Optimization of Acid Activated Ngbo Clay Catalysts in Esterification Reaction Using Response Surface Methodology

ABSTRACT

In this study, Box-Behnken"s Response Surface Methodology (RSM) was applied to study the esterification reaction effectiveness of acid activated Ngbo clay catalyst. The esterification were monitored based on the process conditions of temperature, duration, amount of reactant, catalyst weight and particle size. The Box--Behnken's Response Surface Methodology indicates that the acid clay-catalysed esterification reactions proceed through dual mechanisms of 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 thereby 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 correlation coefficient of the regression of 0.9940, which implies that 99.40% 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, Acid Activated Clay Catalyst, Response Surface Methodology, Box-Behnken design

1. INTRODUCTION

Esterification reactions has 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, researches have been focused to develop eco-friendly heterogeneous catalysts for synthesis of 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 applicability for catalysing esterification reaction 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 deposit yet its potentials have not been fully explored. However, there is recent interest in exploring the potentials of clays such in 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 in the synthesis of catalysts, although use of Nigerian clays from Ngbo, Ohaukwu- Ebonyi State for producing clay catalysts is limited in literature. Though the kinetics of clay-catalysed esterification reactions 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.

Response Surface Methodology (RSM) is a collection of statistical and mathematical techniques that uses quantitative data. Central composite design (CCD), Box-Behnken and Doehlert designs (BBD) 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 [4]. 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 is aimed at reducing the cost of expensive numerous experiments, saving time, reducing 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 acid activated catalyst and optimizes the effectiveness of the clay catalyst for esterification of acetic acid with ethanol using Response Surface Methodology.

2. Materials and Methods

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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’’).

2.2 Physico-Chemical Characterization of Ngbo Clay

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

2.3 Characterisation of the raw clay and acid activated sample

The Ngbo clay sample was characterised using XRF and XRD.

2.4 Acid Activation

The acid activation method used in this work is as reported by [21]. A 100g of pulverized and screened clay was mixed into slurry with 50ml of diluted water, 30ml of 1M H_2SO_4 was added and stirred vigorously and placed in an oven where it was maintained at a temperature of 100^{o}C. The sample was washed thereafter and left to sediment. Complete removal of all residual acid was achieved by repeating washing and decanting until a pH of six was obtained. The final slurry was filtered and dried at 100^{o}C. The dried, activated and washed clay was then pulverized, screened and stored in desiccators prior to use.

Comment [A2]: write down the time required for activation

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 acid (H_2SO_4) method. The acid 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:

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

On titration, the equation becomes:

$$CH_3COOH \; + \; NaOH \longrightarrow CH_3COONa \; + \; H_2O \qquad (2)$$

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;

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

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.

3. RESULTS AND DISCUSSION

3.1 Physical properties of the raw clay

The result of the physical properties of raw Ngbo clay is presented in table 2. 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.

Comment [A3]: check the writing format

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 Acid Activated Clay

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

The result of the XRF composition analysis of raw Ngbo clay and Acid activated Ngbo clays (AAC) is presented in Table 3. 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 acid 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 acid activated Ngbo clays as shown in table 4 also indicates high content of silicon and aluimium oxides compared to other oxides.

Comment [A4]: oxide contaminants ?

Comment [A5]: Table 4

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

Chemical constituent	**Raw clay (Wt. %)**	**Acid activated (AAC), (Wt. %)**
SiO_2	62.70	67.030
TiO_2	1.52	1.285
Al_2O_3	19.70	23.924
Fe_2O_3	2.06	4.968
P_2O_3	–	0.149
CaO	0.789	0.143

MgO	0.026	0.646
Na_2O	0.20	0.057
K_2O	0.85	1.109
Mn_2O_3	–	0.079
V_2O_5	0.071	–
Cr_2O_3	0.035	0.012
CuO	0.044	–
BaO	0.19	–
L.O.I	11.82	–
SO_3	–	0.573
Cl	–	0.008
ZnO	–	0.013
SrO	–	0.006

The results of XRD pattern analysis of raw Ngbo clay is presented in figure 1. The results of XRD pattern results showed several characteristic peaks due to minerals compositions present. The peak obtained at position corresponding to 2Ɵ = 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 halloysite present. The presence of these minor impurities and quartz content of Ngbo clay needs to be reduced to minimum before its usage for industrial purpose especially in zeolites/catalysts development in line with researches of [28,29]. The XRD analysis corroborates with the results obtained with the XRF analysis.

Comment [A6]: Figure 1

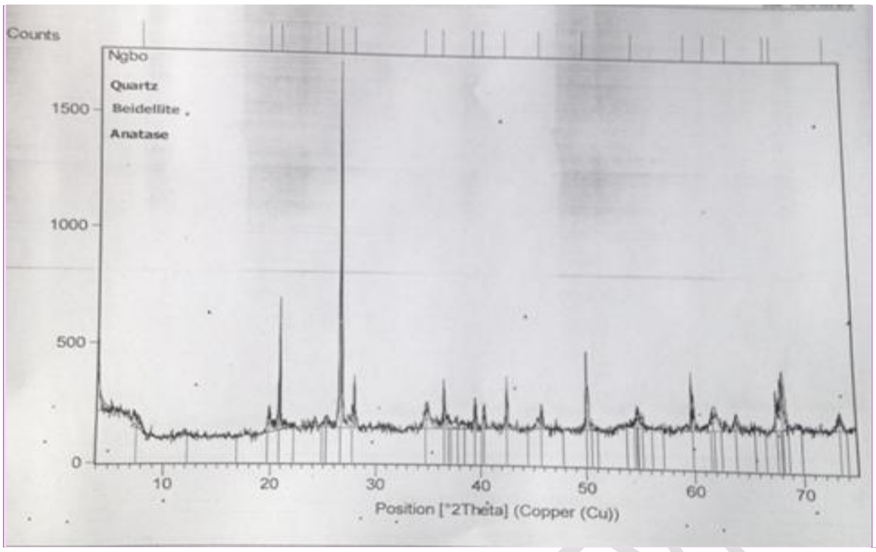

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Figure 1: Results of XRD analysis of Ngbo raw clay

The results of XRD pattern analysis of Ngbo acid activated clay, AAC is presented in figure 2. The results of XRD pattern results showed several characteristic peaks due to minerals 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].

Comment [A8]: Figure 2

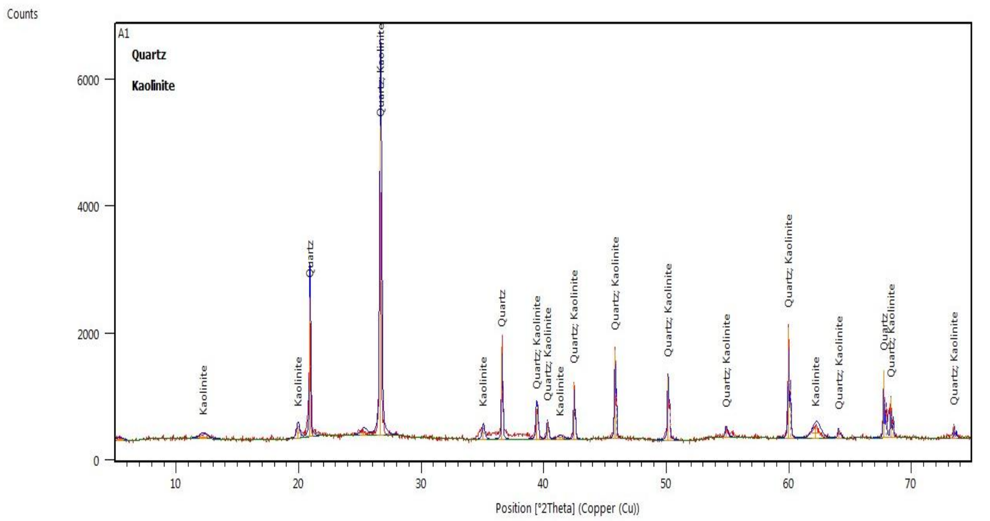

Figure 2: Results of XRD analysis of Acid Activated Clay

3.3 Esterification Process Results

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

Table 4: Results showing responses and yield of AAC

Std	Run	Factor A (^{O}C)	Factor B (min)	Factor C (ml)	Factor D(g)	Factor E (mic)	Yield (%)
37	1	70	30	3.75	0.25	200	28.89
22	2	70	360	2.5	0.38	200	59.78
23	3	70	30	5	0.38	200	8.67
29	4	70	195	2.5	0.38	100	59.96
26	5	90	195	3.75	0.25	200	37.78
1	6	50	30	3.75	0.38	200	48.89
32	7	70	195	5	0.38	300	16.94
46	8	70	195	3.75	0.38	200	36.00
10	9	70	360	3.75	0.38	100	43.47
34	10	90	195	3.75	0.38	100	42.18
21	11	70	30	2.5	0.38	200	54.22
35	12	50	195	3.75	0.38	300	26.68
8	13	70	195	5	0.5	200	14.44
4	14	90	360	3.75	0.38	200	46.67
2	15	90	30	3.75	0.38	200	30.00
11	16	70	30	3.75	0.38	300	26.68
31	17	70	195	2.5	0.38	300	56.84
3	18	50	360	3.75	0.38	200	34.00
24	19	70	360	5	0.38	200	21.78
16	20	90	195	5	0.38	200	22.22
44	21	70	195	3.75	0.38	200	37.33

12	22	70	360	3.75	0.38	300	40.14
36	23	90	195	3.75	0.38	300	34.57
17	24	70	195	3.75	0.25	100	39.61
18	25	70	195	3.75	0.5	100	40.04
45	26	70	195	3.75	0.38	200	37.33
33	27	50	195	3.75	0.38	100	31.26
25	28	50	195	3.75	0.25	200	32.44
20	29	70	195	3.75	0.5	300	31.55
27	30	50	195	3.75	0.5	200	30.22
30	31	70	195	5	0.38	100	21.84
42	32	70	195	3.75	0.38	200	35.56
41	33	70	195	3.75	0.38	200	37.78
39	34	70	30	3.75	0.5	200	28.22
6	35	70	195	5	0.25	200	18.89
43	36	70	195	3.75	0.38	200	39.56
38	37	70	360	3.75	0.25	200	47.78
19	38	70	195	3.75	0.25	300	36.19
40	39	70	360	3.75	0.5	200	41.56
7	40	70	195	2.5	0.5	200	59.56
28	41	90	195	3.75	0.5	200	39.78
14	42	90	195	2.5	0.38	200	60.44
5	43	70	195	2.5	0.25	200	55.56
13	44	50	195	2.5	0.38	200	54.67
9	45	70	30	3.75	0.38	100	32.12
15	46	50	195	5	0.38	200	8.89

3.4 Analysis of Variance (ANOVA) for AAC

The ANOVA result in table 5 showed that RSM model is significant of the experimental results as indicated from the F – value of 26.60 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 1.23% 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 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].

However, the result in table 6 indicates that the significant model terms A, B, C, and AB, implies that only linear effects of temperature, process duration, excess reactants, and interactive effects of temperature and process duration 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 [31].

The final equation in terms of coded factors of A, B, C, and AB that indicates effects of temperature, process duration, excess reactants, and interactive effects of temperature and process duration gives:

$$\text{Yield} = +37.26 + 2.91A + 4.84B - 20.46C - 0.74D - 2.56E + 7.89AB + 1.89AC + 1.05AD - 0.76AE + 1.89BC - 1.39BD + 0.53BE - 2.11CD - 0.45CE - 1.27DE - 0.77A^2 + 0.25B^2 + 0.40C^2 - 0.62D^2 - 0.82E^2.$$

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 gives: $\text{Yield} = + 37.26 + 2.91A + 4.84B – 20.46C + 7.89AB$ (4).

Comment [A9]: No need to add (+) at the beginning of the coefficient

Table 5: ANOVA for Acid Activated Clay (AAC) catalyst

Source	**Sum of Squares**	**df**	**Mean Square**	**F - Value**	**P – Value Prob> F**
Model	7658.64	20	382.93	26.60	< 0.0001 significant
A - Temperature	135.66	1	135.66	9.42	0.0051
B – Process duration	375.29	1	375.29	26.07	< 0.0001
C – Excess reactant	6697.79	1	6697.79	465.18	< 0.0001
D – Effect of Catalyst	8.66	1	8.66	0.60	0.4453
E – Particle size	104.50	1	104.50	7.26	0.0124
AB	249.01	1	249.01	17.29	0.0003
AC	14.29	1	14.29	0.99	0.3287
AD	4.45	1	4.45	0.31	0.5831
AE	2.30	1	2.30	0.16	0.6931
BC	14.25	1	14.25	0.99	0.3293
BD	7.70	1	7.70	0.53	0.4714
BE	1.11	1	1.11	0.077	0.7833
CD	17.85	1	17.85	1.24	0.2761
CE	0.79	1	0.79	0.055	0.8165

DE	6.43	1	6.43	0.45	0.5102
A^2	5.16	1	5.16	0.36	0.5549
B^2	0.53	1	0.53	0.037	0.8495
C^2	1.39	1	1.39	0.096	0.7588
D^2	3.32	1	3.32	0.23	0.6351
E^2	5.87	1	5.87	0.41	0.5288
Residual	359.96	25	14.40		
Lack of fit	349.91	20	17.50	8.71	0.0123 significant
Pure Error	10.05	5	2.01		
Cor Total	8018.59	45			

The regression model developed was also tested for by residual plots as shown in figure 3 - 5. 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.

Figure 3 - 5 showed the plots of predicted vs Actual response values. 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.

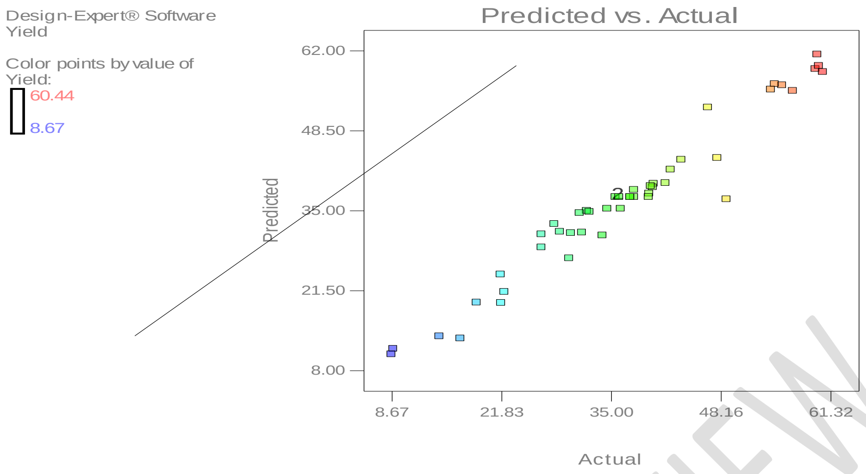

Figure 3: Residual plot of predicted vs actual for AAC

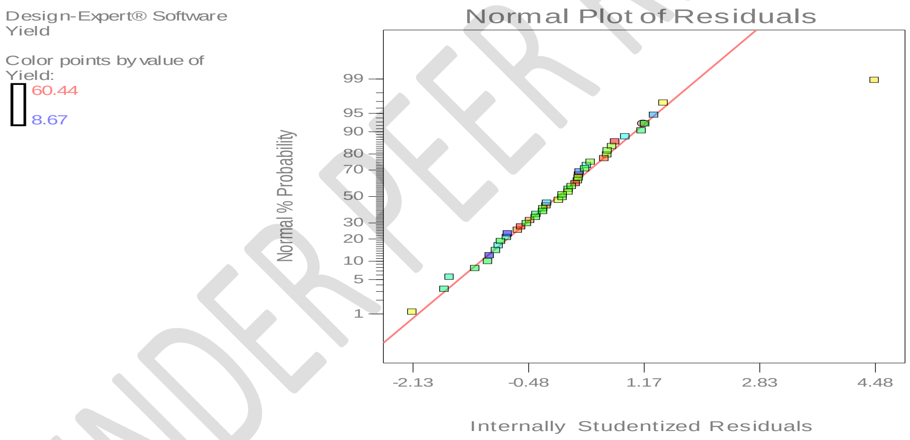

Figure 4: Normal plot of residuals for AAC

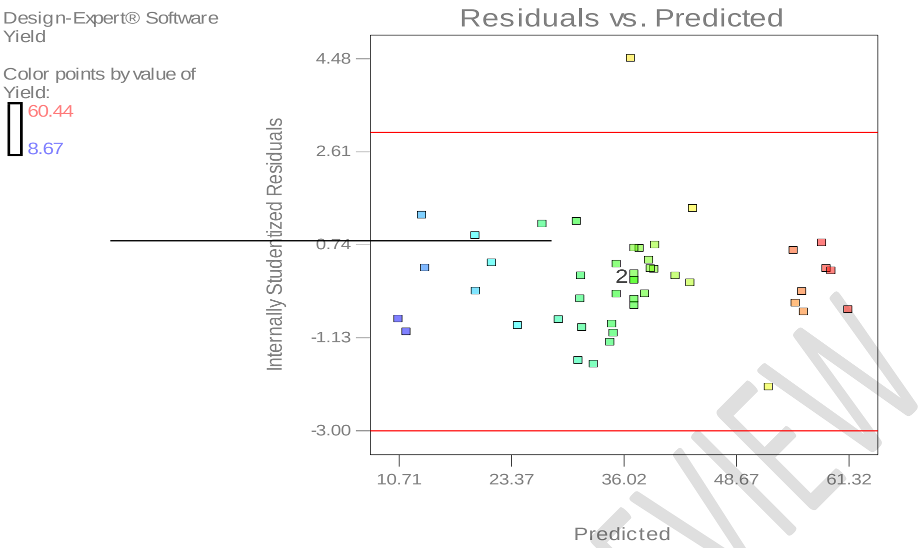

Figure 5: Residuals vs predicted for AAC

3.4.1 Contour plot of AAC

The contour plots were depicted in figure 6 to figure 14. 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 [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.

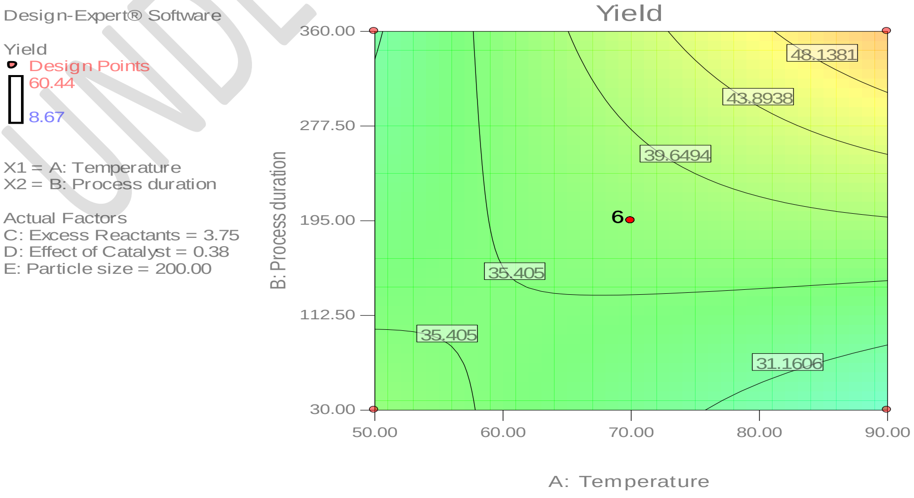

Figure 6: The contour plots for process duration against temperature and yield of AAC

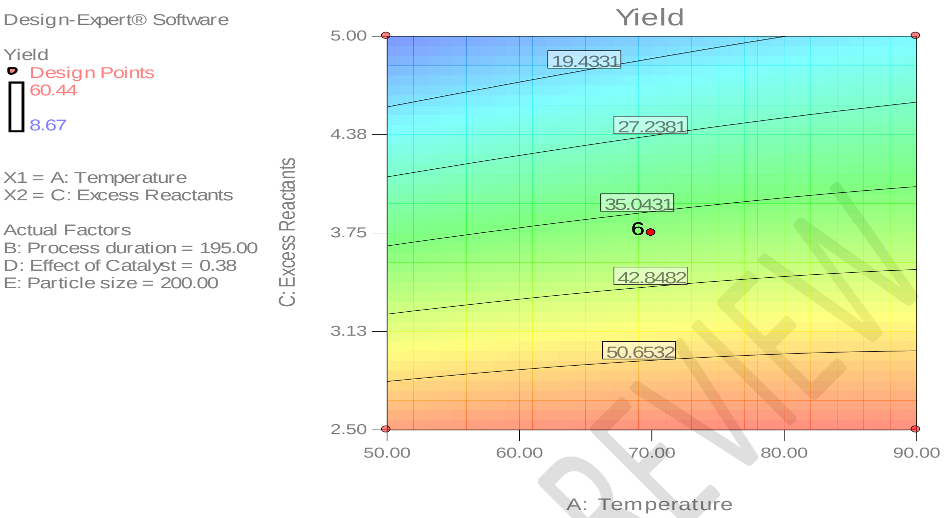

Figure 7: The contour plots for excess reactant against temperature and yield of AAC

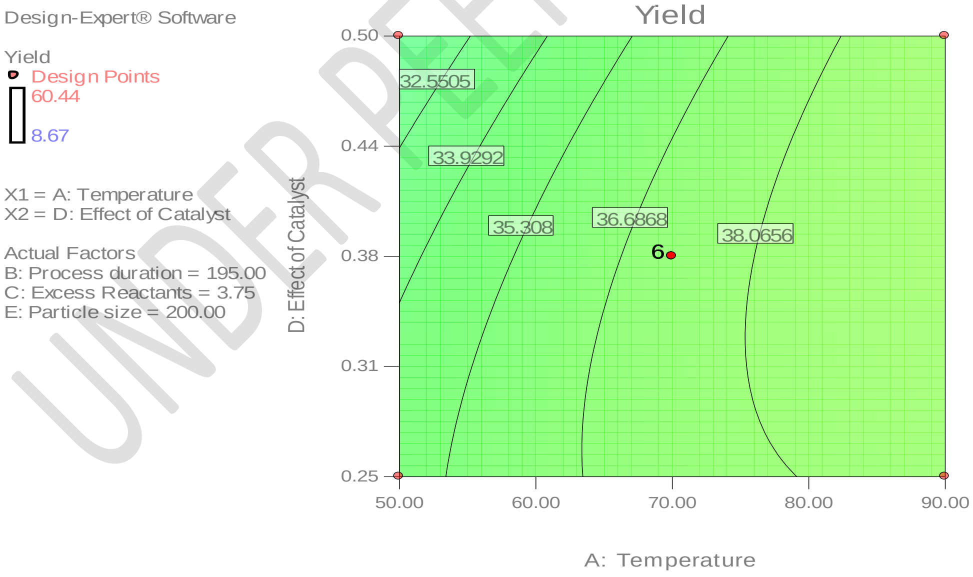

Figure 8: The contour plots for effect of catalyst against temperature and yield of AAC

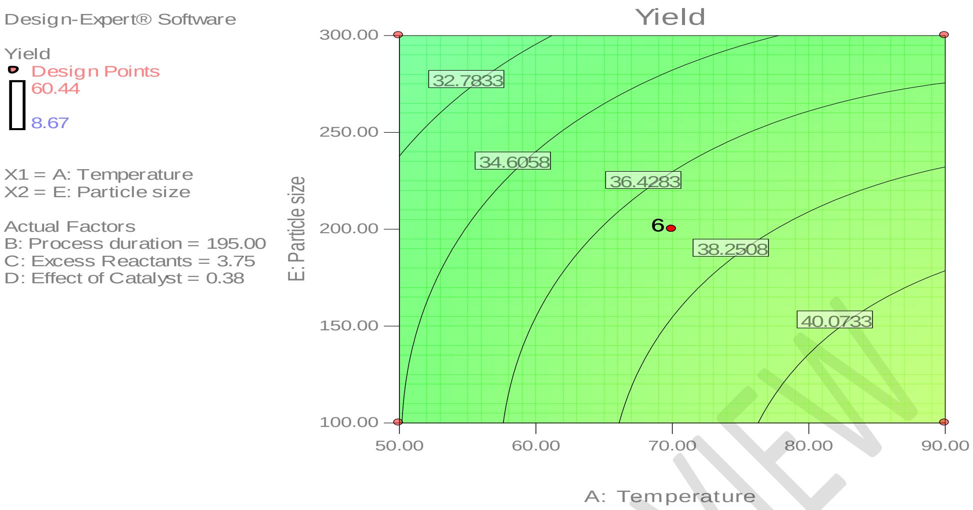

Figure 9: The contour plots for particle size against temperature and yield of AAC

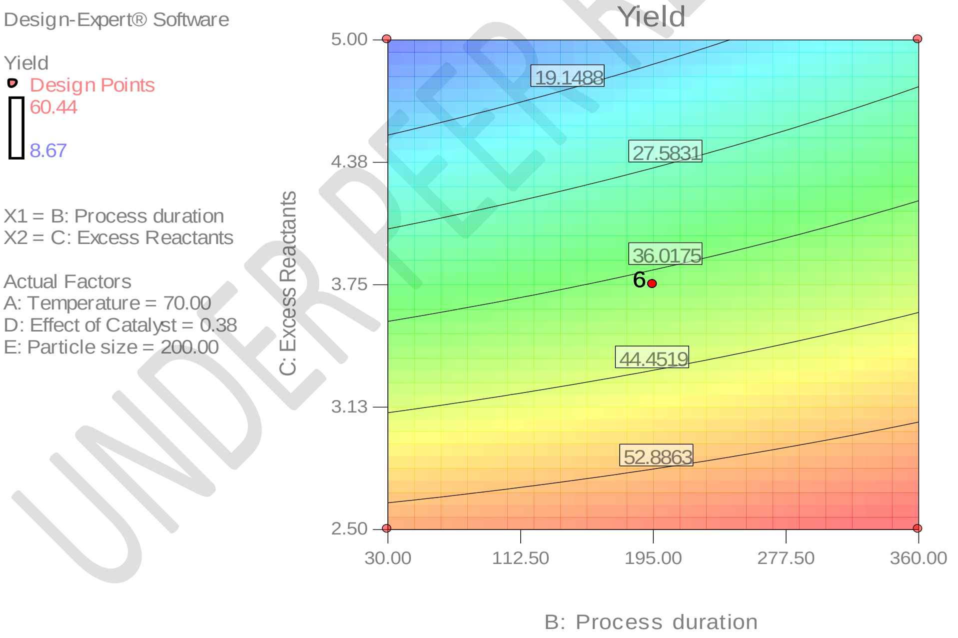

Figure 10: The contour plots for excess reactant against process duration and yield of AAC

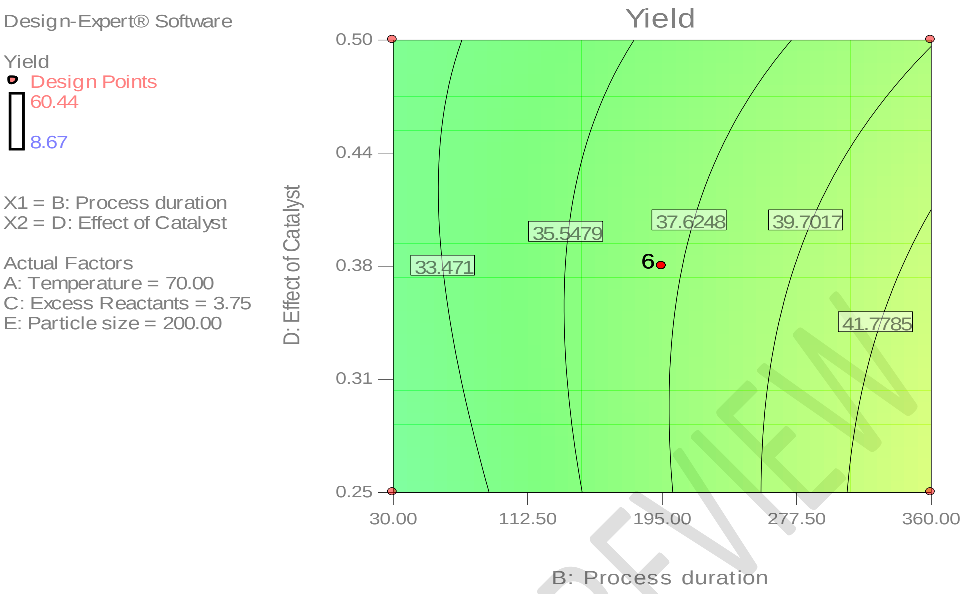

Figure 11: The contour plots for effect of catalyst against process duration and yield of AAC

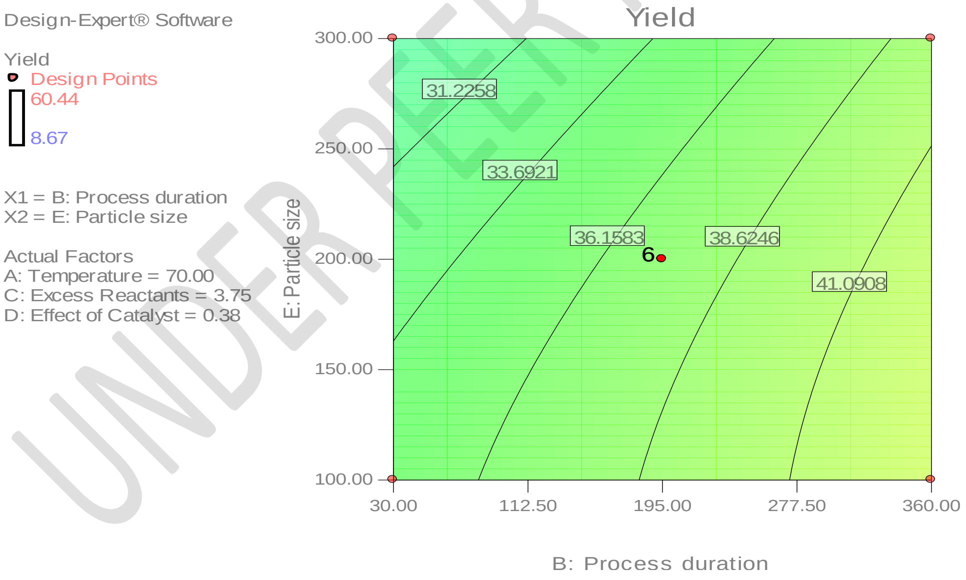

Figure 12: The contour plots for particle size against process duration and yield of AAC

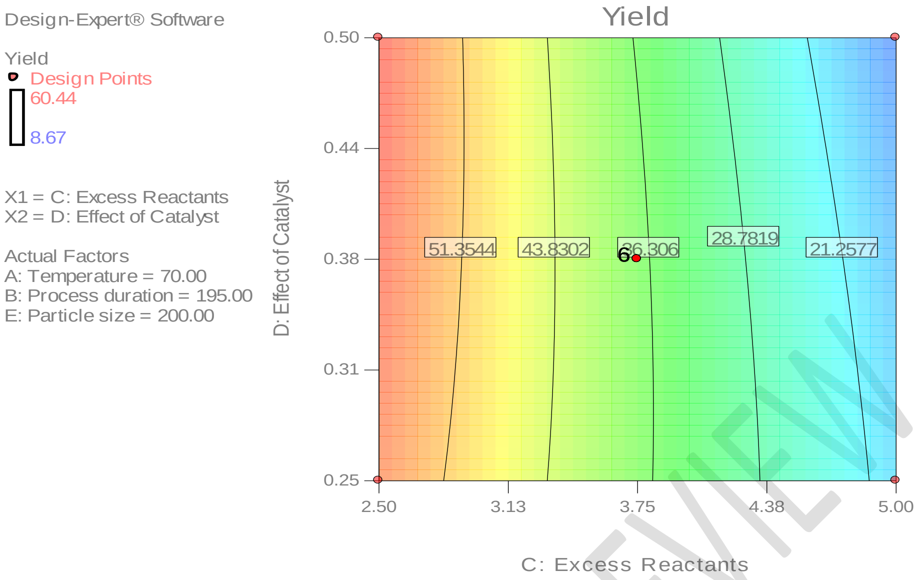

Figure 13: The contour plots for effect of catalyst against process duration and yield of AAC

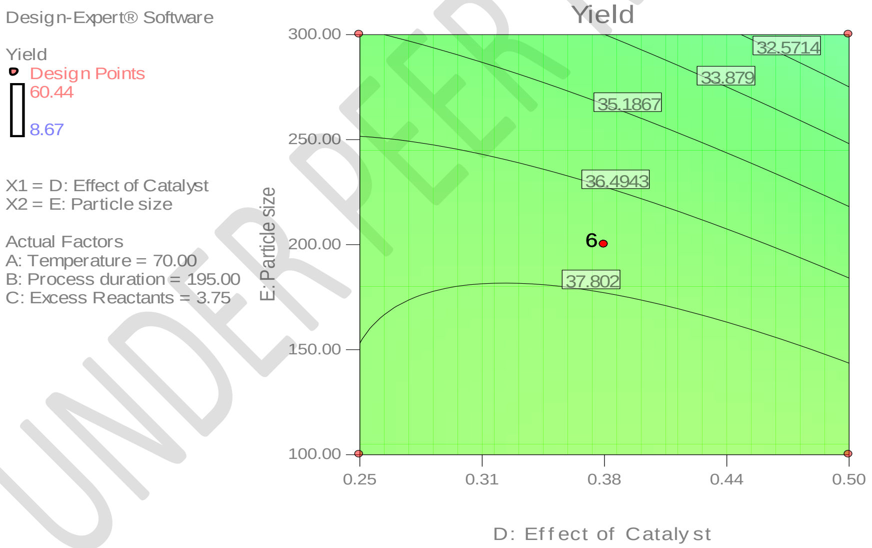

Figure 14: The contour plots for effect of catalyst against process duration and yield of AAC

3.4.2 3 – D Plot for AAC

The 3 – Dimensional plots of the response surface model are shown in figures 15 to 20. The results showed that the optimum value of the conversion was 42 for the process variables studied; which are similar to results obtained by [34, 23, 24, 35]. The three-dimensional surfaces can 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 [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 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].

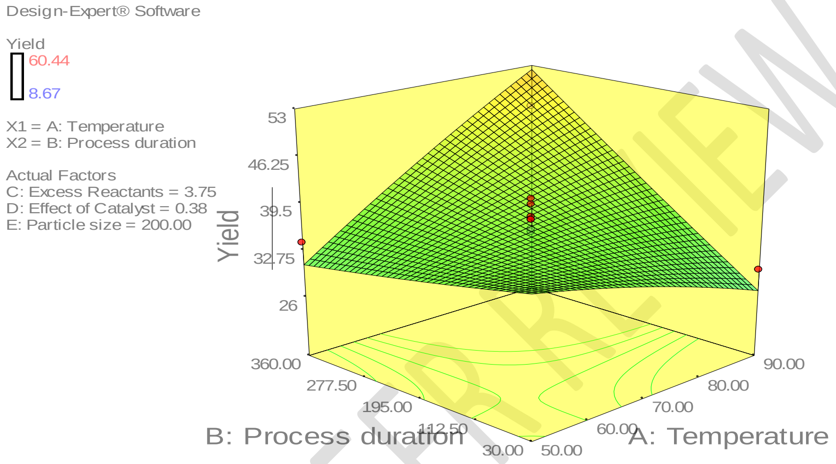

Figure 15: The 3 - D Plotfor process duration against yield and temperature of AAC

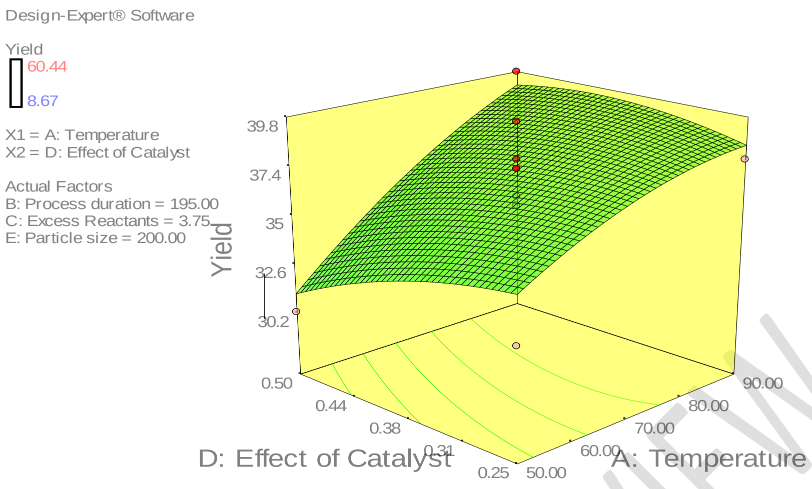

Figure 16: The 3 - D Plotfor effect of catalyst against yield and temperature of AAC

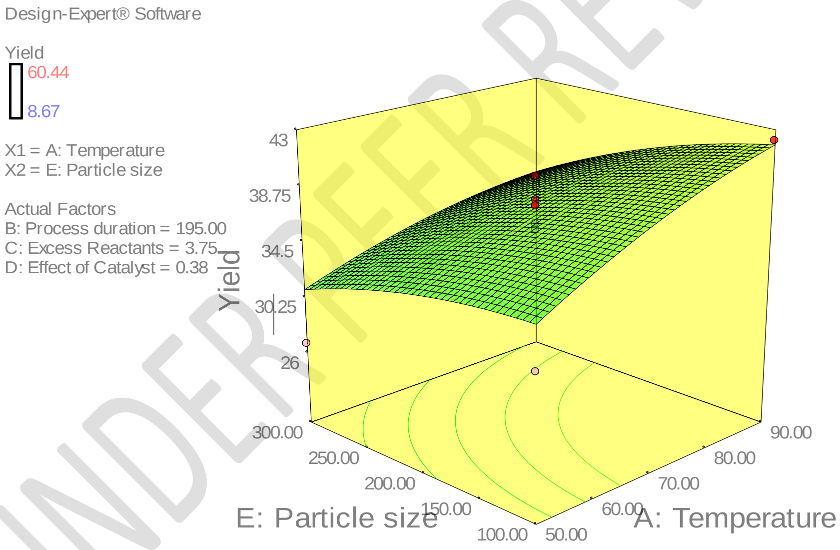

Figure 17: The 3 - D Plotfor particle size against yield and temperature of AAC

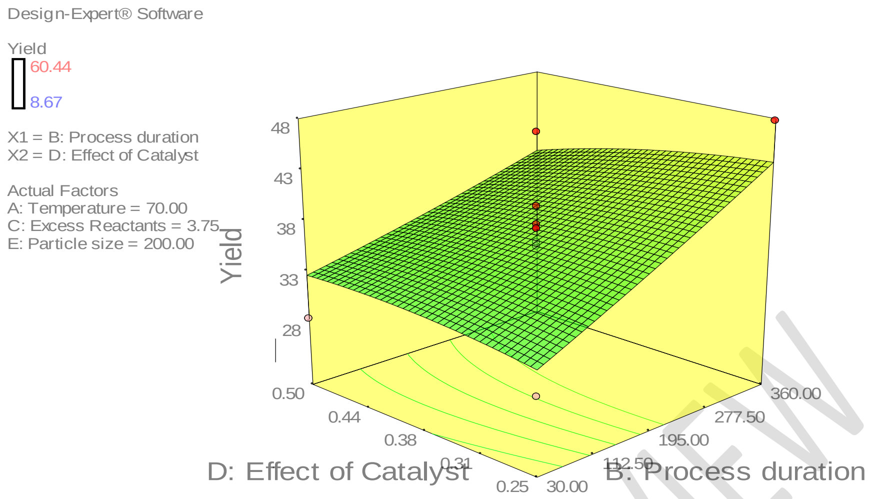

Figure 18: The 3 - D Plotfor effect of catalyst against yield and process duration of AAC

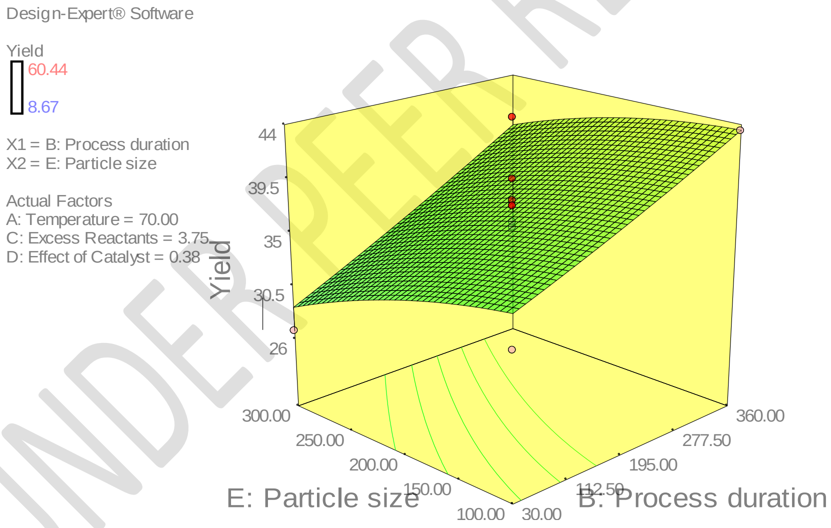

Figure 19: The 3 - D Plotfor particle size against yield and process duration of AAC

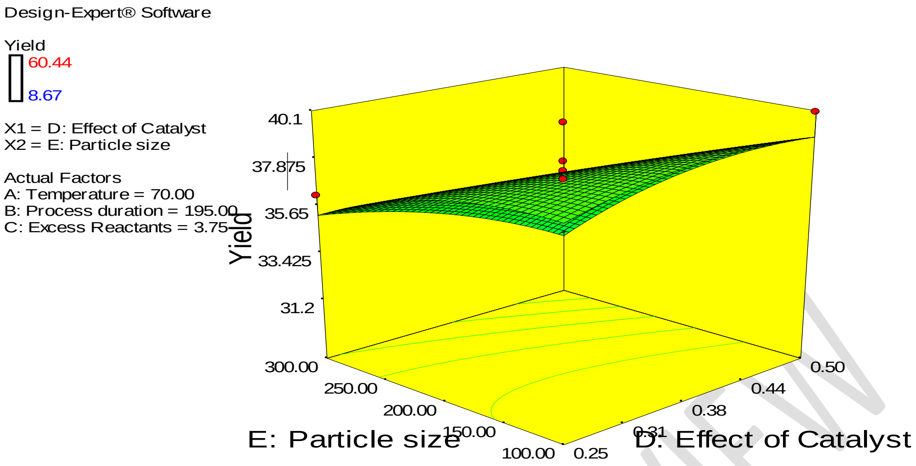

Figure 20: The 3 - D Plotfor particle size against yield and effect of catalyst of AAC

3.4.3 Process Optimization

Comment [A10]: It's better if there is an optimized parameter validity

In the Process Optimization for AAC, desirability function was used to obtain the optimum value. The results of process optimisation AAC is shown in figure 21. The optimum process conditions for the variables studied were; 359.99 min, 90 ^{o}C, 4.30ml, 0.50g, and 297.63 microns for time, temperature, excess reactants, catalyst weight and particle size respectively. The predicted conversion yeild was 37.5983.

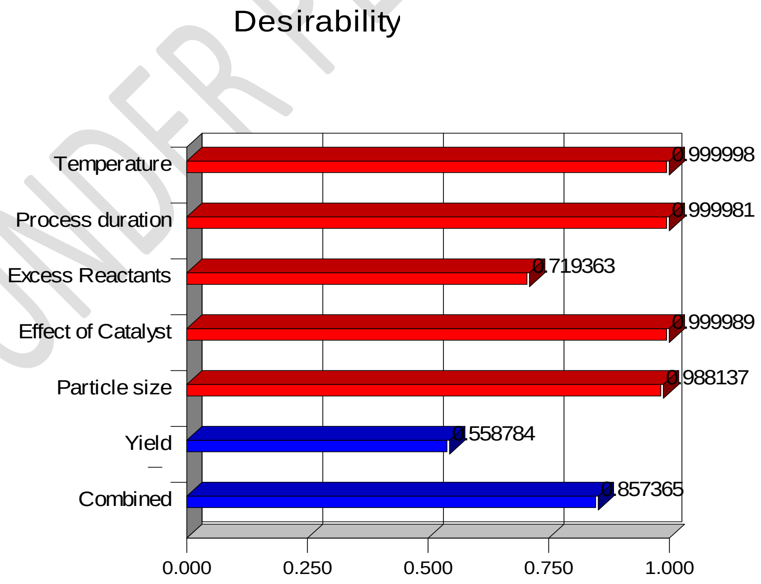

Figure 21: Process optimization for AAC

4. CONCLUSIONS

Comment [A11]: Include the optimum condition in the conclusion

The study presented the optimum conditions for esterification reaction of acetic acid and ethanol using acid activated Ngbo clay catalyst. The optimum conditions for esterification reaction for the process conditions of temperature, duration, amount of reactant, catalyst weight and particle size was determined using Response Surface Methodology (RSM) approach. The XRF analysis showed that the clay was made of mainly SiO_2 while the XRD indicated quartz as the major composition. 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 acid activated clay catalyst.

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Comment [A12]: check and correct the reference writing format

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