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

Veronica Nnenna Nwobasi [a*], Philomena K. Igbokwe [b] and Chijioke Elijah Onu [b]

[a] *Department of Food Science and Technology, Ebonyi State University, P.M.B. 53, Abakaliki, Ebonyi State, Nigeria.*
[b] *Department of Chemical Engineering, Nnamdi Azikiwe University, P.M.B. 5025, Awka, Anambra State, Nigeria.*

Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

Original Research Article

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.

_____

*Corresponding author: E-mail: nwobasiveronica@yahoo.com, jioke894@gmail.com;

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 [5–7] 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°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

2.1 Source of Raw Materials

The clay sample was obtained from Ngbo in Ohaukwu L.G.A. of Ebonyi State (N 06°30' 32.8''), (E 007°58'13.7''). The dye was obtained from purchased chemical shop at Onitsha, Anambra State. Other chemicals such as tetraoxosulphate VI acid (H_2SO_4), distilled water etc were all of standard grade.

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°C for four hours. 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°C. The dried, activated and washed clay was then pulverized, screened and stored in desiccators prior to use.

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

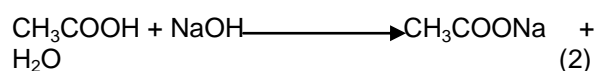| Variables	Natural values			Coded values		
	Low level	Mid-point	High level	Low level	Mid Point	High level
Temperature (^{o}C), A	50	70	90	-1	0	+1
Process duration (minutes), B	30	195	360	-1	0	+1
Excess reactant (ml), C	2.5	3.75	5	-1	0	+1
Catalyst weight (grammes), D	0.25	0.38	0.5	-1	0	+1
Particle size (microns), E	100	200	300	-1	0	+1

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 100 microns, 200 microns and 300 microns. 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:

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O \quad (1)$$
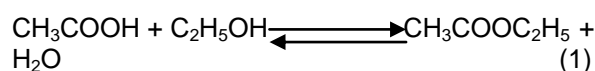
On titration, the equation becomes:

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

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. The numerical optimization method of RSM was used in the optimization.

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.

3.2 Characterization of Raw Clay and Acid Activated Clay

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

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

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 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 contain majorly silicon IV oxide and aluminium oxide among other oxides, but the clay minerals compositions are not meaningfully affected by acid treatments under activating conditions. This is in agreement with the report of [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.

The results of XRD pattern analysis of raw Ngbo clay is presented in Fig. 1. The results of XRD pattern results showed several characteristic peaks due to minerals compositions present. The peak obtained at position corresponding to 2Ө = 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.

The results of XRD pattern analysis of Ngbo acid activated clay, AAC is presented in Fig. 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].

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.

## 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].
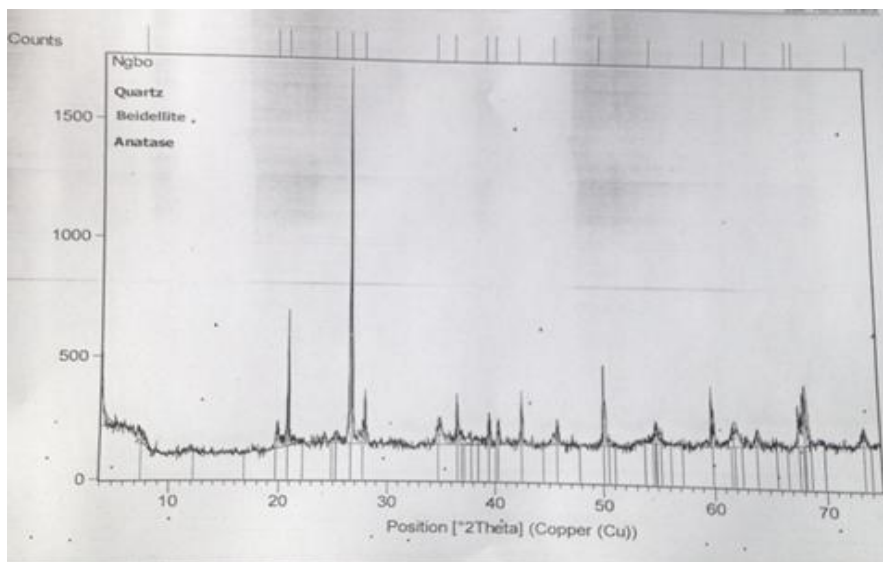
Fig. 1. Results of XRD analysis of Ngbo raw clay
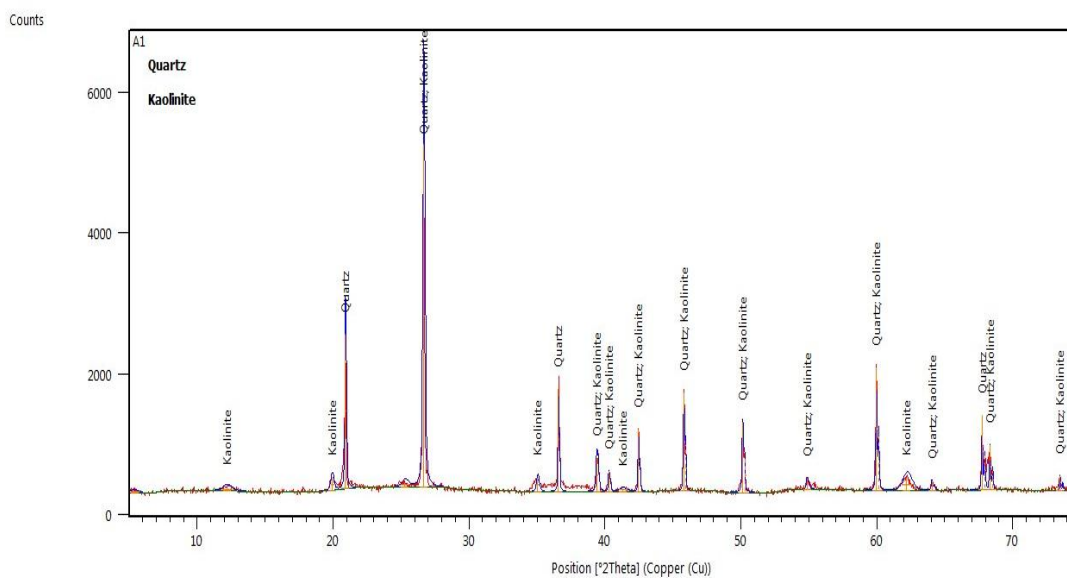
Fig. 2. Results of XRD analysis of acid activated clay

Table 4. Results showing responses and yield of AAC

Std	Run	Factor A (°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

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:

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

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: Yield = 37.26 + 2.91A + 4.84B − 20.46C + 7.89AB   (4).

The regression model developed was also tested for by residual plots as shown in Figs. 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.

Figs. 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.

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			
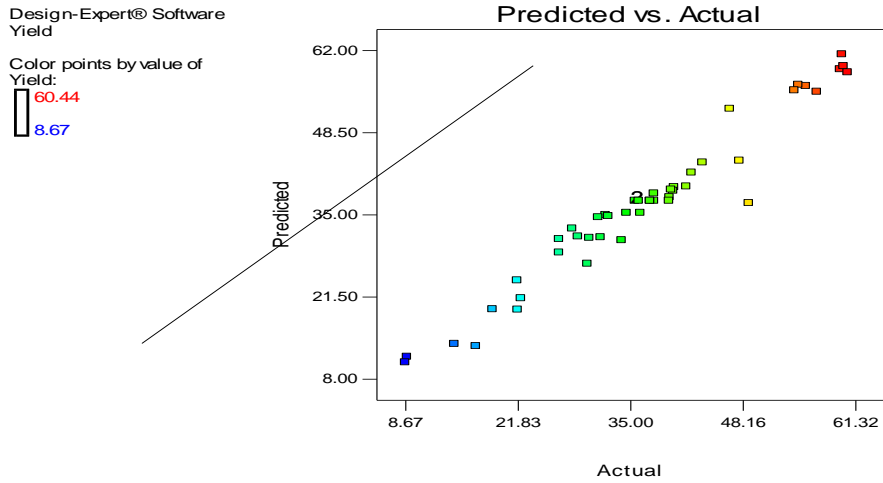
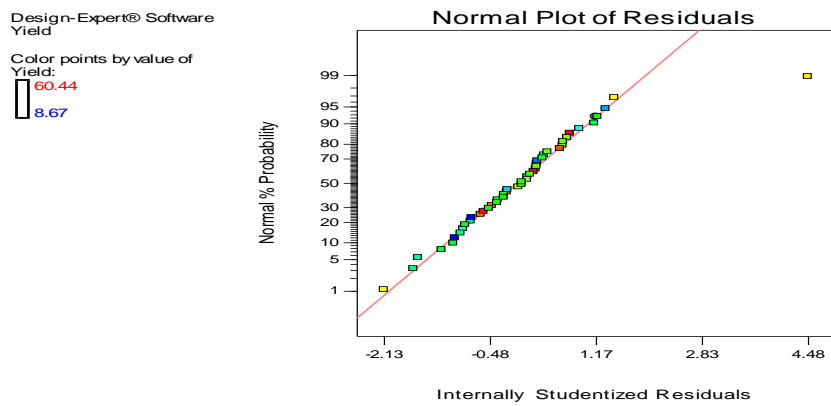**Fig. 3. Residual plot of predicted vs actual for AAC**

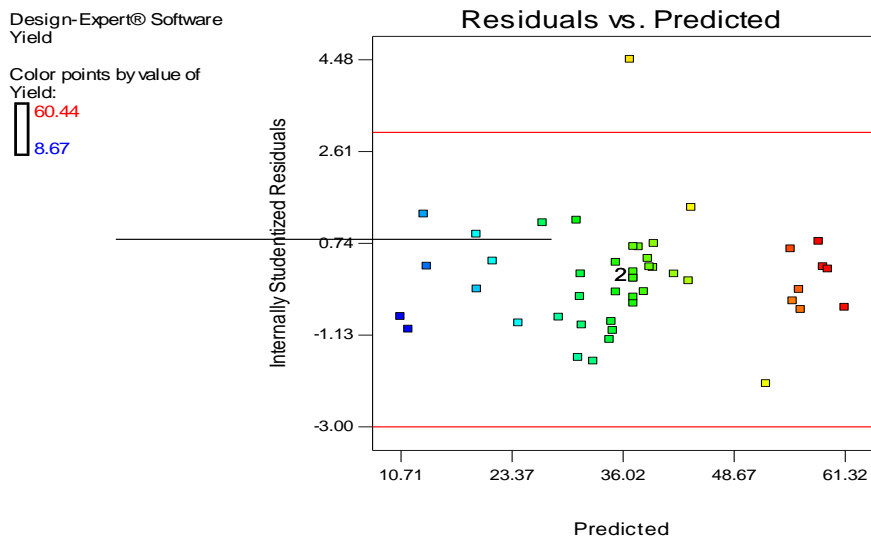**Fig. 4. Normal plot of residuals for AAC**

Fig. 5. Residuals vs predicted for AAC

3.4.1 Contour plot of AAC

The contour plots were depicted in Fig. 6 to Fig. 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.
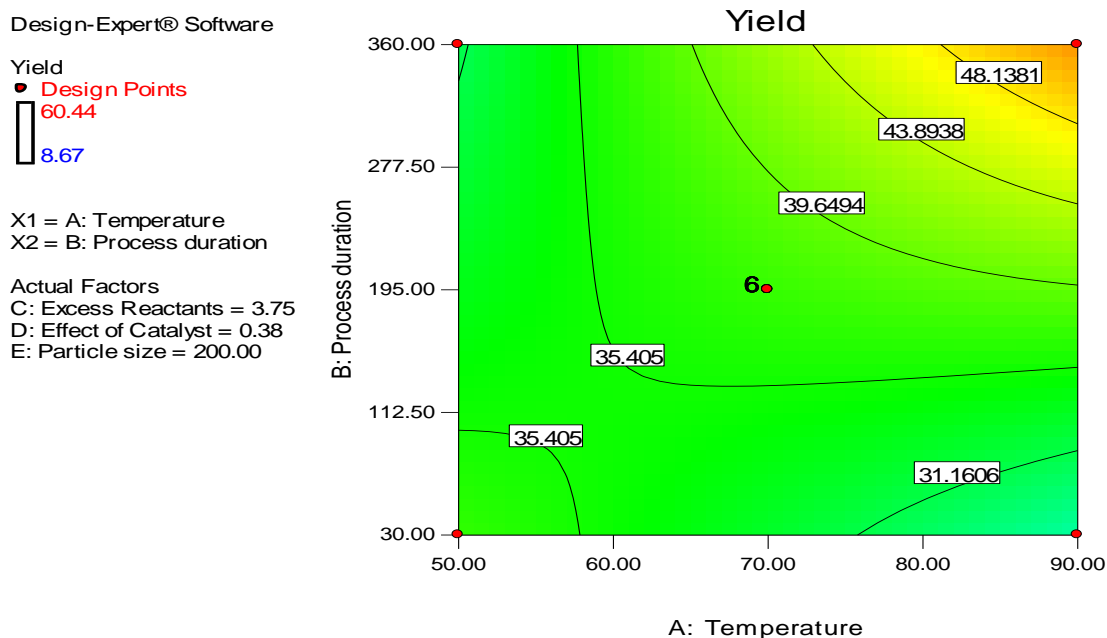
Fig. 6. The contour plots for process duration against temperature and yield of AAC
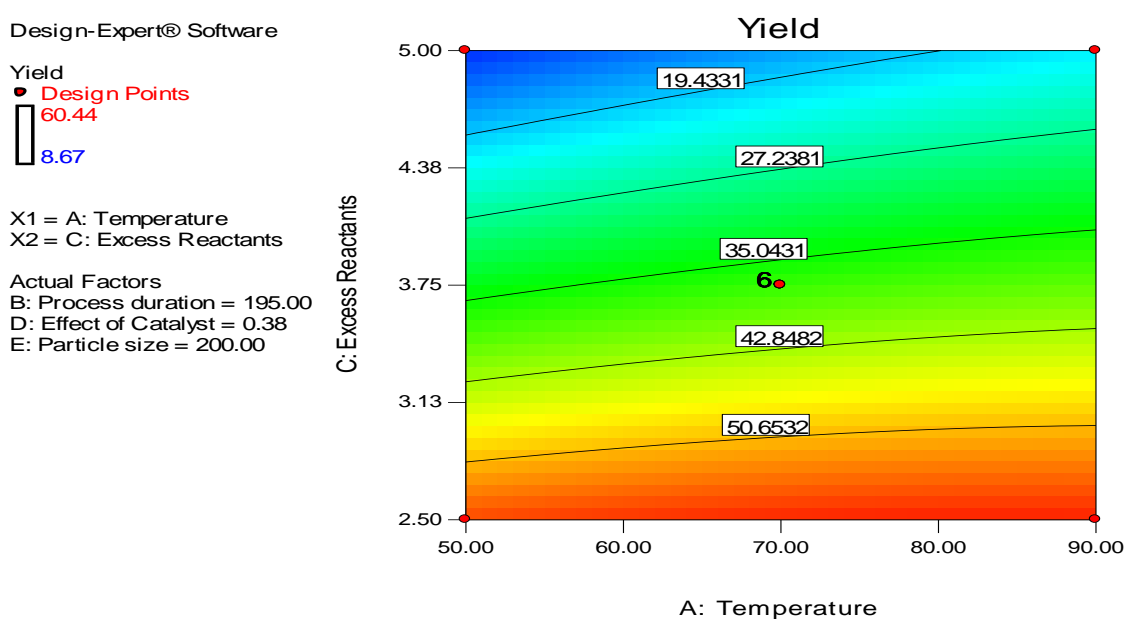
Fig. 7. The contour plots for excess reactant against temperature and yield of AAC
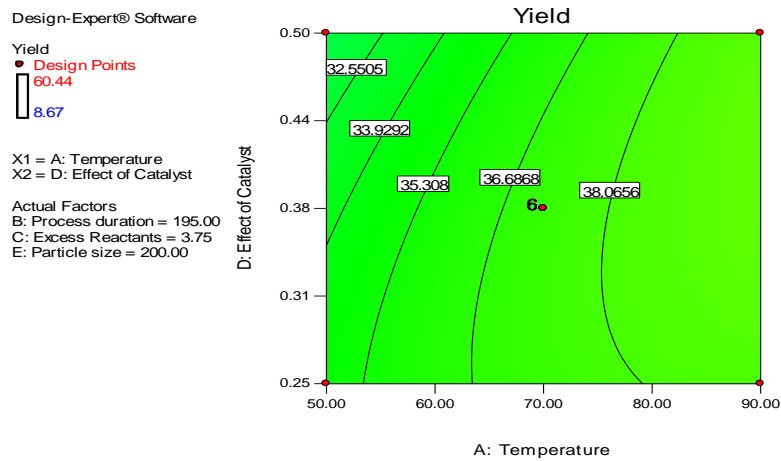
Fig. 8. The contour plots for effect of catalyst against temperature and yield of AAC
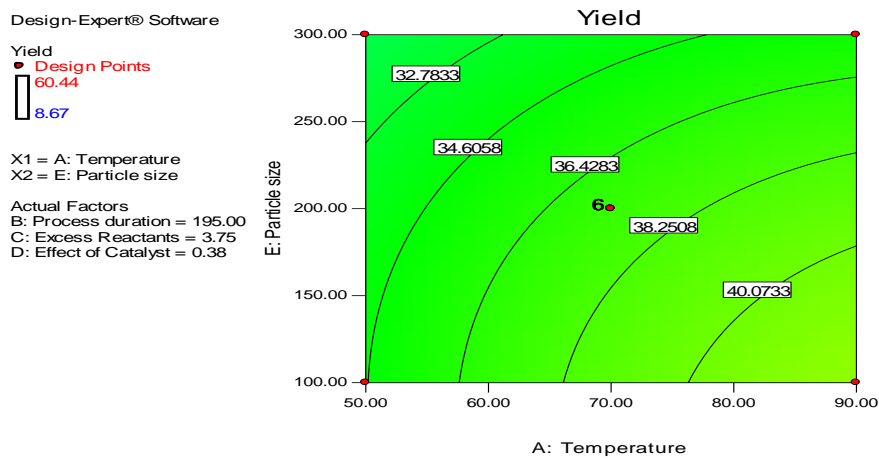
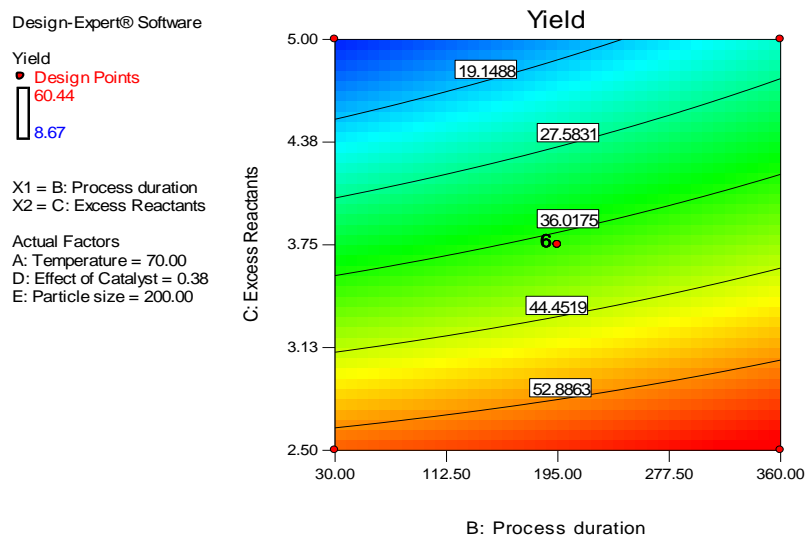**Fig. 9. The contour plots for particle size against temperature and yield of AAC**

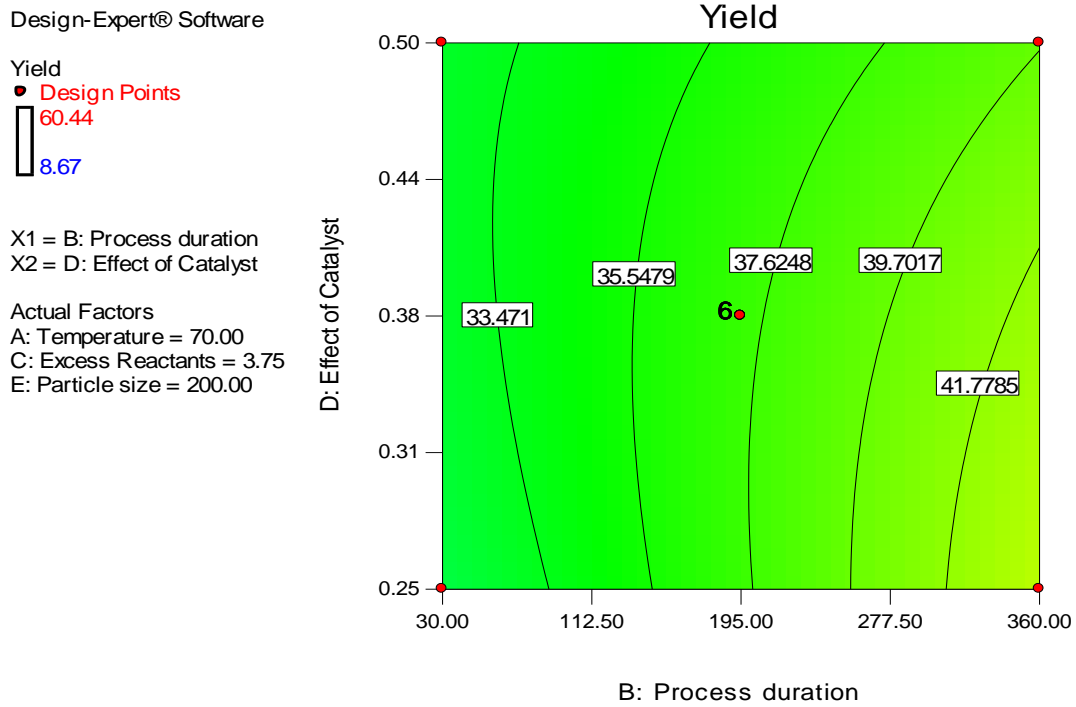**Fig. 10. The contour plots for excess reactant against process duration and yield of AAC**

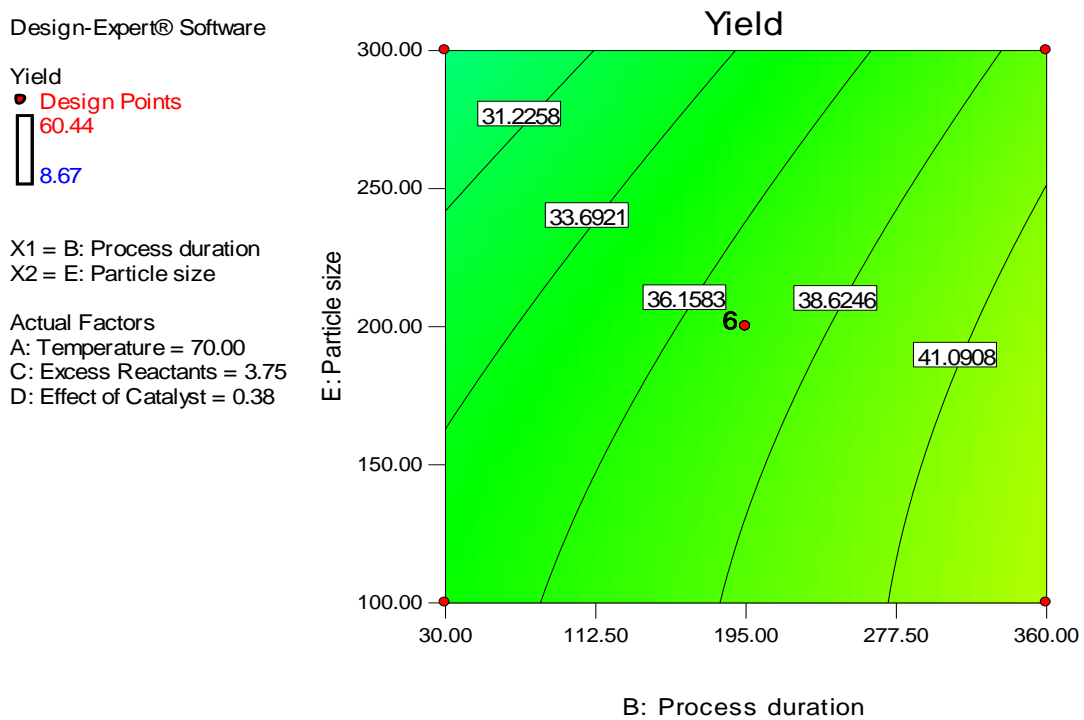**Fig. 11. The contour plots for effect of catalyst against process duration and yield of AAC**

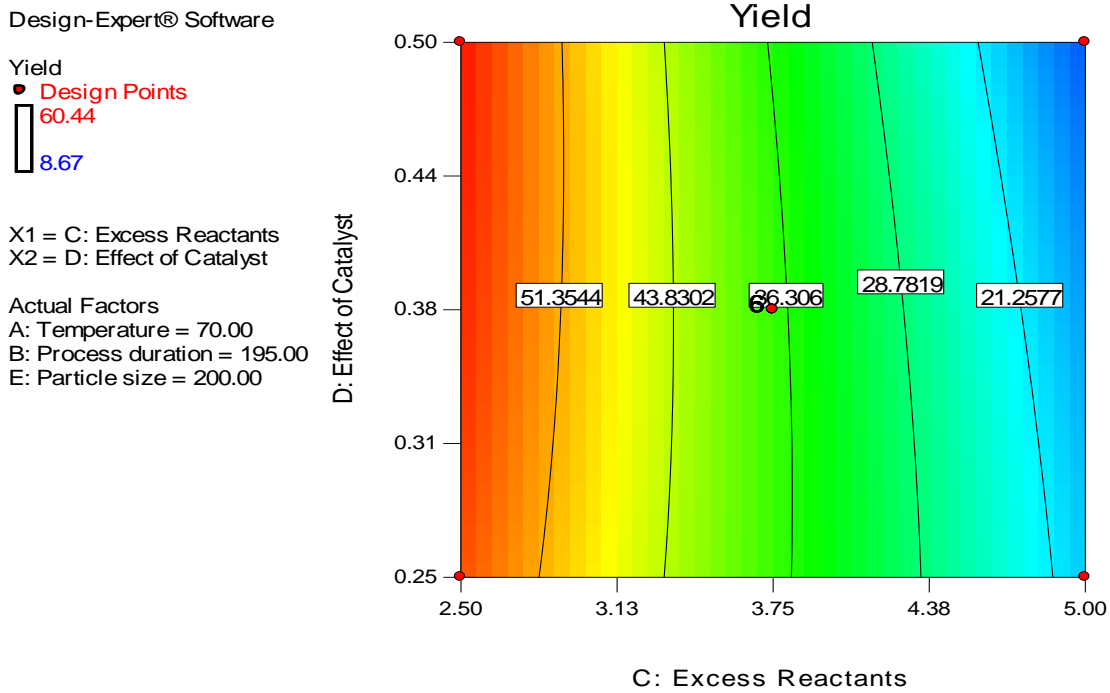**Fig. 12. The contour plots for particle size against process duration and yield of AAC**

Design-Expert® Software

Yield
● Design Points
60.44

8.67

X1 = C: Excess Reactants
X2 = D: Effect of Catalyst

Actual Factors
A: Temperature = 70.00
B: Process duration = 195.00
E: Particle size = 200.00

Yield

Fig. 13. The contour plots for effect of catalyst against process duration and yield of AAC

Design-Expert® Software

Yield
● Design Points
60.44

8.67

X1 = D: Effect of Catalyst
X2 = E: Particle size

Actual Factors
A: Temperature = 70.00
B: Process duration = 195.00
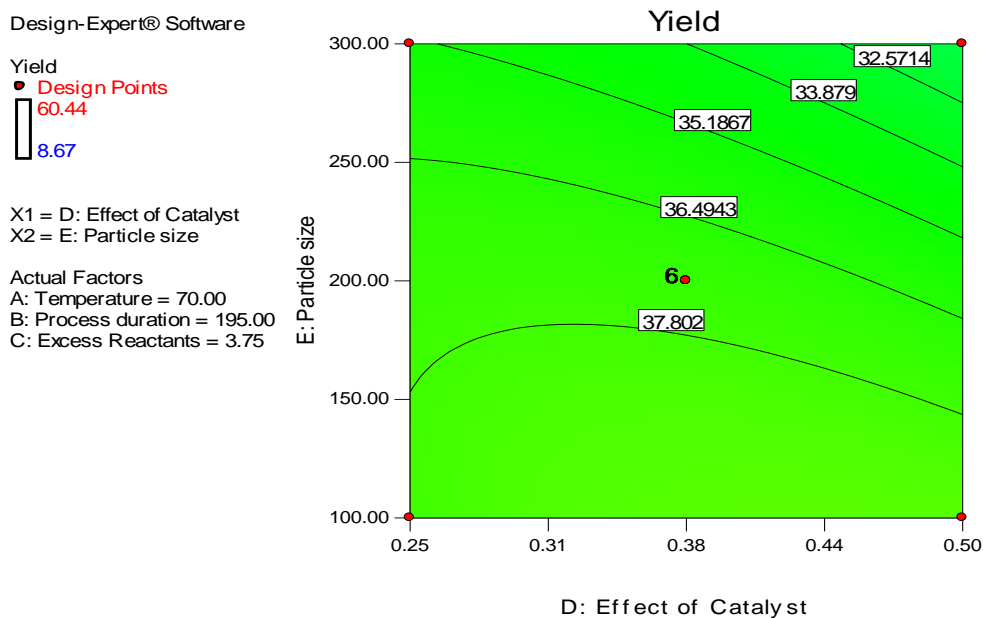C: Excess Reactants = 3.75

Yield

Fig. 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 Figs. 15 to 20. The results showed that the optimum value of the conversion was 42 for the process variabless 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].

3.4.3 Process optimization

In the Process Optimization for AAC, desirability function was used to obtain the optimum value.

The time and temperature were set at minimum while the catalyst weight, particle sizee and excess reactant were set in range. The conversion yield was set at maximum. The optimum process conditions for the variables 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 yield was 37.5983. The optimization was validated at those experimental conditions and conversion yield of 39.223 was obtained.
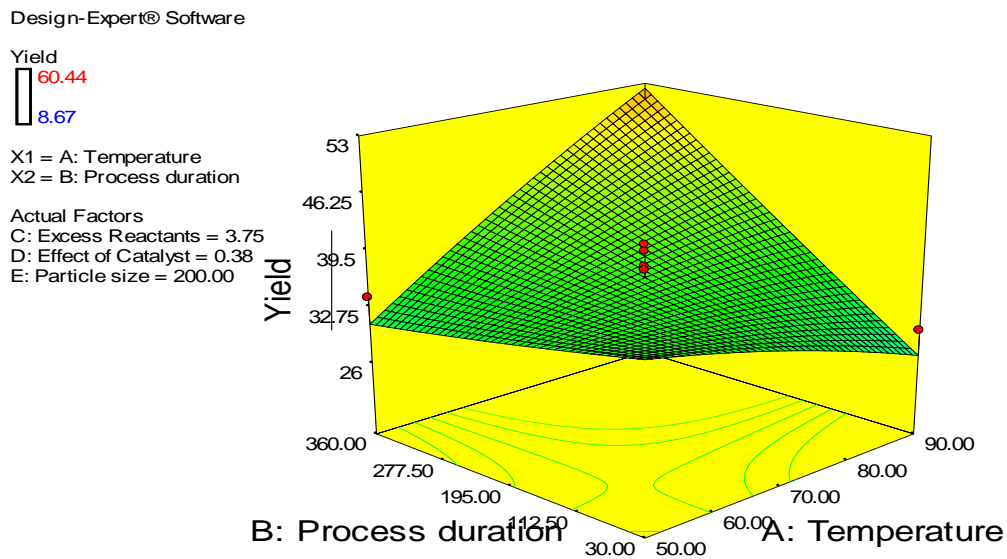

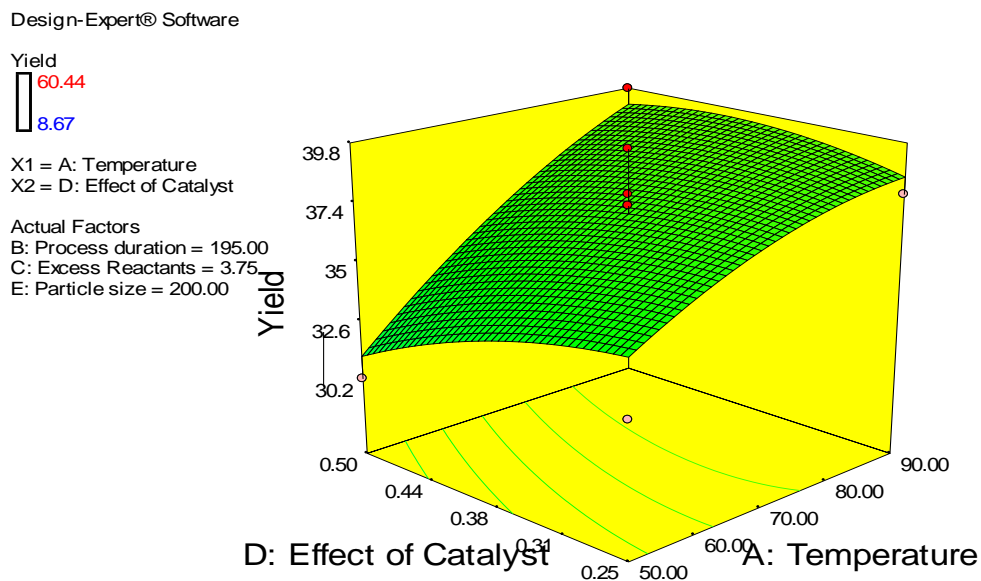**Fig. 15. The 3 - D Plotfor process duration against yield and temperature of AAC**

Fig. 16. The 3 - D Plotfor effect of catalyst against yield and temperature of AAC
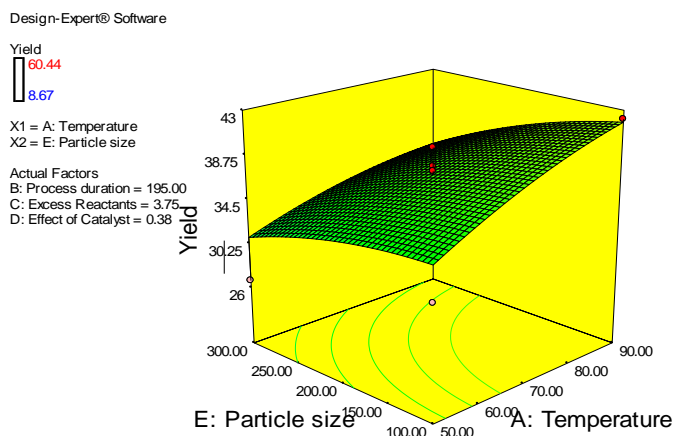
Fig. 17. The 3 - D Plotfor particle size against yield and temperature of AAC
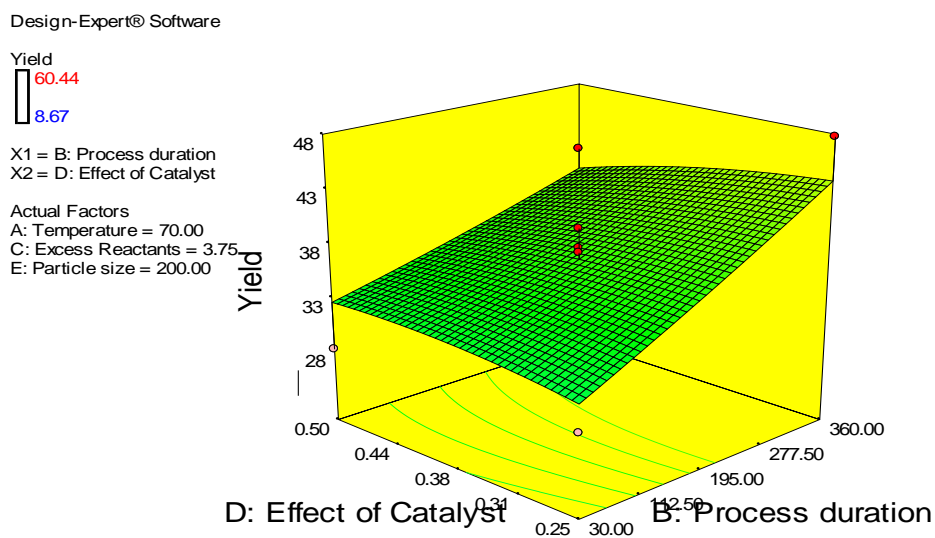

Fig. 18. The 3 - D Plotfor effect of catalyst against yield and process duration of AAC
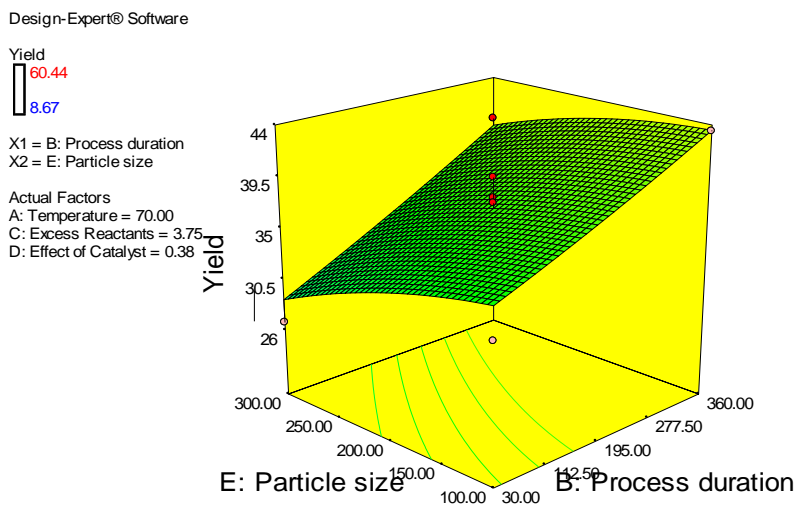

Fig. 19. The 3 - D Plotfor particle size against yield and process duration of AAC

Design-Expert® Software

Yield
60.44
8.67

X1 = D: Effect of Catalyst
X2 = E: Particle size

Actual Factors
A: Temperature = 70.00
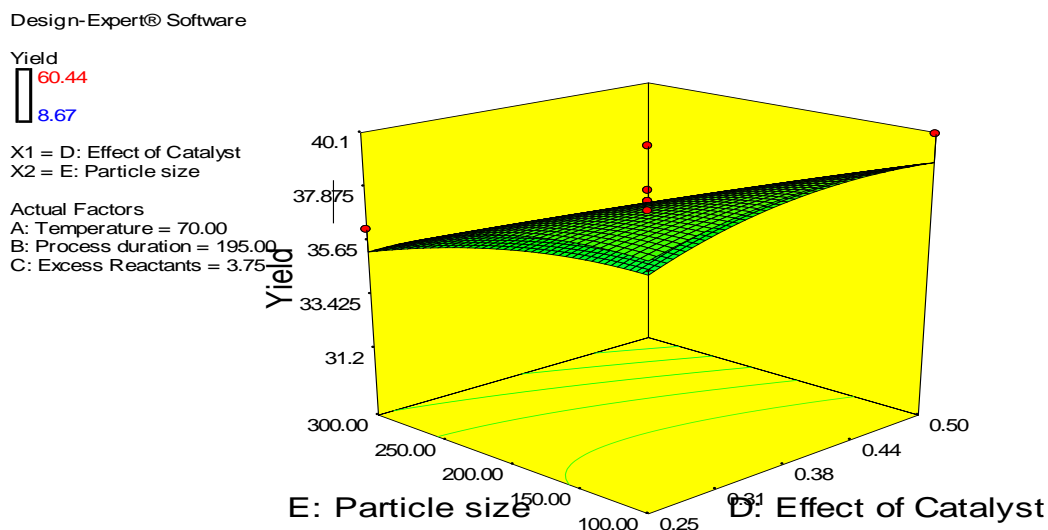B: Process duration = 195.00
C: Excess Reactants = 3.75

Fig. 20. The 3 - D Plotfor particle size against yield and effect of catalyst of AAC

4. CONCLUSIONS

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 optimum process conditions for the variables studied for time, temperature, excess reactants, catalyst weight and particle size were 359.99 min, 90°C, 4.30ml, 0.50g, and 297.63 microns respectively. The maximum predicted estrification yield was 37.5983. The XRF analysis showed that the clay was made of mainly SiO_2 and aluminium 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.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Ravendra Reddy C, Lyengar P, Nagendrappa G, Jai Prakash BS. Esterification of dicarboxylic acids to diesters over Mn^+-montmorillonite clay catalysts. Catalyst Letter. 2005;101:87–91.
2. Chen CC, Hayes KF. X-ray absorption spectroscopy investigation of aqueous Co(II) and Sr(II) sorption at clay-water interfaces. GeochimCosmochimActa. 1999;63:3205–3215.
3. Yadav GD, Thagathar MB. Esterification of maleic acid with ethanol over cation-exchange resin catalyst. React. Funct.Polym. 2002;52:99–110.
4. Zang Y, Ma L, Yang J. Kinetics of esterification of lactic acid with ethanol catalysed by cation-exchange resins" React. Funct.Polym. 2004;61:101–114.
5. Kirumakki SR, Nagaraju N, Chary KVR. Esterification of alcohols with acetic acid over zeolites Hβ, HY and HZSM5. Applied Catalysis A. General. 2006;299:185–192.
6. Kirumakki SR, Nagaraju N, Narayanan SA. Comparative esterification of benzyl alcohol with acetic acid over zeolites Hβ, HY and HZSM5. Applied Catalysis A: General. 2004;273:1–9.
7. Wu K, Chen Y. An efficient two-phase reaction of ethyl acetate production in modified ZSM- 5 zeolites. Applied Catalysis A: General. 2004;257:33–42.
8. Chu W, Yang X, Ye X, Wu Y. Vapour phase esterification catalysed by immobilized dodecatungstosilicic acid (SiW_{12}) on activated carbon. Applied Catalysis A: General. 1996;145:125–140.

9. Sepulvega JH, Yori JC, Vera CR. Repeated use of supported $H_3PW_{12}O_{40}$ catalysts in the liquid phase esterification of acetic acid with butanol. Applied Catalysis A: General. 2005;288:18–24.

10. Jermy BR, Pandurangan A. Catalytic application of Al-MCM-41 in the esterification of acetic acid with various alcohol. Applied Catalysis A: General. 2005;288:25–33.

11. Kirumakki SR, Nagaraju N, Chary KVR, Narayanan S. Kinetics of esterification of aromatic carboxylic acids over zeolites Hβ and HZSM5 using dimethyl carbonate. Applied Catalysis A: General. 2003;248:161–167.

12. Nwabanne Joseph T, Onu Chijioke E, Nwankwoukwu Okwudili C. Equilibrium, kinetics and thermodynamics of the bleaching of palm oil using activated nando clay. Journal of Engineering Research and Reports. 2018;1(3):1-13.
DOI: 10.9734/JERR/2018/42699

13. Ajemba RO, Onukwuli OD. Process optimization of sulphuric acid leaching of alumina from Nteje clay using central composite rotatable design. International Journal of Multidisciplinary Sciences and Engineering. 2012;3(5):1–6.

14. Onu CE, Nwabanne JT. Application of response surface methodology in malachite green adsorption using nteje clay. Open Journal of Chemical Engineering and Science. 2014;1(2):19 – 33.

15. Nwobasi Veronica Nnenna, Igbokwe Philomena K, Onu Chijioke Elijah. Removal of methylene blue dye from aqueous solution using modified ngbo clay. Journal of Materials Science Research and Reviews. 2020;5(2):33-46.

16. Onu CO, Nwabanne JT. Adsorption kinetics for Malachite green removal from aqueous solution using Nteje clay. Journal of Environment and Human. 2014;1(2):133–150.
DOI: 10.15764/EH.2014.02015

17. Ezedinma Henry C, Nwabanne Jospeh T, Onu Chijioke E E, Nwajinka Charles O. Optimum process parameters and thermal properties of moisture content reduction in water yam drying. Asian Journal of Chemical Sciences. 2021;9(4):44-54.
DOI:https://doi.org/10.9734/AJOCS/2021/v9i419080

18. Onyekwelu Ijeoma U, Nwabanne Jospeh T, Onu Chijioke E. Characterization and optimization of biodiesel produced from palm oil using acidified clay heterogeneous catalyst. Asian Journal of Applied Chemistry Research. 2021;8(3):9-23..
DOI: https://doi.org/10.9734/AJACR/2021/v8i330192

19. Onu CE, Igbokwe PK, Nwabanne JT, Ohale PE. ANFIS, ANN, and RSM modeling of moisture content reduction of cocoyam slices. Journal of Food Processing and Preservation. 2021;00:e16032.
Available:https://doi.org/10.1111/jfpp.16032

20. Iheanacho Chamberlain Ositadinma, Nwabanne Joseph Tagbo, Onu Chijioke Elijah. Optimum process parameters for activated carbon production from rice husk for phenol adsorption. Current Journal of Applied Science and Technology. 2019;36(6):1-11.
Available:https://doi.org/10.9734/CJAST/2019/v36i630264

21. Igbokwe PK, Nwokolo SO, Ogbuagu JO. Catalytic esterification of stearic acid using a local kaolinitic clay mineral. NJERD. 2005;4:1.

22. Igbokwe PK, Olebunne FL. On the catalytic esterification of acetic acid with ethanol, using Nigerian montmorillonite clay: Effect of reaction variables on catalyst efficiency. Journal of the University of Chemical Technology and Metallurgy. 2011;46(6):389-394.

23. Igbokwe PK, Ugonabo VI, Obarandiku E, Ochili A. Characterization and use of catalyst produced from local clay resources. Journal of Applied Sciences (JAS). 2008;2:2.

24. Igbokwe PK, Olebunne FL, Nwakaudu MS. Effect of activation parameters on conversion in clay – Catalysed esterification of acetic acid. International Journal of Basic and Applied Sciences. 2011;11(5):1–8.

25. Murat M, Amokrane A, Bastide JP, Montanaro L. Synthesis of zeolites from thermally activated kaolinite. Some observations on nucleation and growth. Clay Minerals. 1992;27(1):119.

26. Akolekar D, Chaffee A, Howe RF. The transformation of kaolin to low-silica X zeolite. Zeolites. 1997;1(9):5–6,359–365.

27. Demortier A, Golbeltz N, Letlieur JP, Duhayon C. Infrared evidence for the formation of an Intermediate compound,

during the synthesis of Zeolite Na – A from metakaolin. International Journal of Inorganic materials. 1999;1(2):129–134.

28. Tracy MMJ, Higgins JB. Collection of simulated XRD powder patterns of Zeolites. Fourth revised edition ed. 2001, Amsterdam Elsevier 379; 2001.

29. Evamako O Yusuf, Efeovbokhan VE, Babalola R. Development and characterization of zeolite – A from Elefun kaolin. Journal of physics conference, series. 2001;1378–032016.

30. Ramirez JH, Maidonaldo – Hedar FJ, Ferez AF, Moremo C, Costa CA, Madeira LM. Azo-dye orange II degradation by heterogeneous Fenton-like reaction using carbón – Fe catalysts. Applied catalysis B: Environmental. 2007;75(3–4):312–323.

31. Ejikeme ME, Ejikeme PCN, Abalu BN. RSM optimization process for uptake of water from ethanol water solution using oxidized starch. Pacific Journal of Science and Technology. 2013;14(2):319-329.

32. Azargohar R, Dalai AK. Production of activated carbon from luscar char: Experimental and modeling studies. MicroporMesopor. Mater. 2005;85:219–225.

33. Anupam K, Dutta S, Bhattacharjee C, Datta S. Adsorption removal of chromium (VI) from aqueous solution over powdered activated carbon: Optimization through response surface methodology. Jornal of Hazard.Mater. 2011;173:135–143.

34. Igbokwe PK, Ugonabo VI, Iwegbu NA, Akachukwu PC, Olisa CJ. Kinetics of the catalytic esterification of propanol with ethanoic acid using catalyst obtained from Nigerian clays. Journal of the University of Chemical Technology and Metallurgy. 2008;345–348.

35. Olebunne FL, Igbokwe PK, Onyelucheya OE, Osoka EC, Ekeke IC. Mechanistic modeling of clay-catalysed liquid-phase esterification of acetic acid. Journal of Emerging Trends in Engineering and Applied Sciences. 2011;2(4):631-635.

36. Panesar PS. Application of response surface methodology in the permeabilitation of yeast cells for lactose hydrolysis. Biochem. Eng. J. 2008;39:91–96.

37. Ahmad AA, Hameed BH. Effect of preparation conditions of activated carbon from bamboo waste for real textile waste water. Joural of Hazard Mater. 2010;173:487–493.

38. Onu Chijioke Elijah, Igbokwe PK, Nwabanne JT, Nwanjinka OC, Ohale PE. Evaluation of optimization techniques in predicting optimum moisture content reduction in drying potato slices. Artificial intelligence in Agriculture. 2020;4; 39–47.
Available:https://doi.org/10.1016/j.aiia.2020.04.001

39. Onu CE, Nwabanne JT, Ohale PE, Asadu CO. Comparative analysis of RSM, ANN and ANFIS and the mechanistic modeling in eriochrome black-T dye adsorption using modified clay. South African Journal of Chemical Engineering. 2021;36:24–42.
Available:https://doi.org/10.1016/j.sajce.2020.12.003