



Empirical Modelling and Optimization of Ngbo Synthetic Zeolite B in Esterification Reaction Using Response Surface Methodology

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ABSTRACT

In this study, Box-Behnken's Response Surface Methodology (RSM) was applied to study the esterification reaction effectiveness of Ngbo synthetic zeolite B (ratio 1:4 of sodium bicarbonate and sodium hexametaphosphate solution) catalyst. The esterification reaction 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 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 Ngbo synthetic zeolite B was optimized using RSM models which indicated the estimated esterification percentage of >85%. 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 synthetic zeolite B was optimized using A-One way ANOVA modelling, which indicated correlation coefficient of the regression of 0.8532, which implies that 85.32% 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 loss of catalyst, corrosion and environmental problems.

Keywords: Optimization, Characterization, Esterification, Empirical Modelling, Synthetic Zeolite, Response Surface Methodology, Box-Behnken design

INTRODUCTION

In the past decades, the high demand for catalysts and zeolites for industrial processes has been of serious concern to developing countries considering the industrialization growth. Also insufficient and unsafe quality of drinking water due to effluents or waste-products from textiles, chemicals, mining and metallurgical industries are considered major water contaminants [1]. Several conventional methods such as precipitation [2], ion exchange [3], membrane filtration technology [4], electrochemical processes [5] and adsorption process [6] have been employed to remove these contaminants from wastewaters. The conventional methods are expensive and sometimes ineffective, especially when the contaminant's concentration is higher than 100mg/l [7].

There are increased researches on the development of solid acid catalysts for adsorption of contaminants in wastewater and other various organic transformations. Even though there are sets of regulations established to aid in the substitution of unfriendly and corrosive liquids used in chemical and petrochemical industries, the use of solid acid catalysts for adsorption of water contaminants are important [8]; [9].

Zeolites are crystalline, hydrated alumina-silicates of groups I and II elements [10]. The zeolites have varying dimension from other adsorbents such as activated carbon, activated alumina and silica gel. Over 150 synthetic zeolites and about 40 naturally occurring zeolites are known [11]. Initially, only natural zeolites were used for various applications, but more recently, synthetic zeolites have been prepared on industrial scale giving rise to tailor-made zeolites that are highly replicable. Zeolites have been exploited commercially due to their accessible pore structure, size, shape and molecular polarity. At present, synthetic zeolites are used commercially more often than natural zeolites due to the purity of crystalline products and the uniformity of particle sizes [10]. However, the preparation of synthetic zeolites from chemical sources of silica and alumina

is expensive and such costs may be reduced by the use of various geological materials like clays or industrial wastes as starting materials. Therefore, in order to reduce costs, zeolite researchers are seeking cheaper raw materials for zeolite synthesis, which include geological materials, such as clay minerals, natural zeolites, volcanic glasses, diatomite, high silica bauxite or oil shale and combustion residues, such as coal ashes, municipal solid waste incineration ashes and industrial slags [12]. Zeolite synthesis has been also developed by the transformation of one zeolite type into others.

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 [13, 14]. 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 [15, 16], Zeolites [17 – 18], [19] and Silica-supported heteropoly acid [20] and [21]. Nevertheless, they have shown limitations in applicability for catalysing esterification reaction due to low thermal stability (Amberlyst-15 < 140°C), mass transfer resistance (Zeolites) [22], [23], or loss of active acid sites in the presence of a polar medium (HPA/silica) [21].

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 [24]. 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 analysis methods [24].

MATERIALS AND METHODS

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 chemicals used such as silica gel, methylene blue dye—molecular formula (C₁₆H₁₈N₃SCl, molecular weight=319.85, λ_{max} = 663 nm), sodium hydroxide, sodium bicarbonate, sodium hexa-metaphosphate, acetic acid, ethanol, deionised water, viju bottles, were all of standard grade and purchased from a chemical shop at Ogbete main market, Enugu, Enugu State. Instruments used include common glasswares, electrical carbolite furnace, water bath shaker, oven and a UV spectrophotometer (JASCO UV/Vis-550).

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).

Characterisation of the raw clay and activated sample

The Ngbo clay sample was characterised using XRF and SEM.

Production of Synthetic zeolite B from Ngbo Clay

The procedure reported by [25] was used in this work with some modifications. In this work, one kilogram of kaolin clay procured from Ngbo, Ohaukwu L.G.A. in Ebonyi State, Nigeria was soaked in deionised water for four days with intermittent manual stirring. The slurry was sieved with 60 meshes size (250 microns). Then 1litre of 1:4 ratios of sodium bicarbonate and sodium hexa-metaphosphate solution respectively was added to the clay slurry sample to allow for deflocculation. The products of deflocculation were allowed to stand for eight hours, after which it was decanted and the excess deflocculant removal. The clay slurry recovered was then dried at 50°C for two days in an oven; cooled and grinded into fine powder and then

characterized. The aluminium to silicon ratio was determined. It was calcined at 600°C for four hours, thereafter it was cooled in a desiccator, packaged in an air tight container prior to use.

Optimization of Process Conditions on the synthetic zeolite Quality Produced Using Esterification Process

Sample Preparation/Procedure

The Ngbo synthetic zeolite B at ratio 1:4 produced was crushed, sieved at 100microns, 200microns and 300microns. The synthetic zeolite 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 Table1. The summary of the reaction equation is:



On titration, the equation becomes:



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 (°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;

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_4 + b_5X_5 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{14}X_1X_4 + b_{15}X_1X_5 + b_{23}X_2X_3 + b_{24}X_2X_4 + b_{25}X_2X_5 + b_{34}X_3X_4 + b_{35}X_3X_5 + b_{45}X_4X_5 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 + b_{44}X_4^2 + b_{55}X_5^2. \quad (3)$$

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

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



Std	Run	Factor A (°C)	Factor B (min)	Factor C (ml)	Factor D(g)	Factor E (mic)	Response (ml)	Yield (%)
37	1	70	30	3.75	0.25	200		
22	2	70	360	2.5	0.38	200		
23	3	70	30	5	0.38	200		
29	4	70	195	2.5	0.38	100		
26	5	90	195	3.75	0.25	200		
1	6	50	30	3.75	0.38	200		
32	7	70	195	5	0.38	300		
46	8	70	195	3.75	0.38	200		
10	9	70	360	3.75	0.38	100		
34	10	90	195	3.75	0.38	100		
21	11	70	30	2.5	0.38	200		
35	12	50	195	3.75	0.38	300		
8	13	70	195	5	0.5	200		
4	14	90	360	3.75	0.38	200		
2	15	90	30	3.75	0.38	200		
11	16	70	30	3.75	0.38	300		
31	17	70	195	2.5	0.38	300		
3	18	50	360	3.75	0.38	200		
24	19	70	360	5	0.38	200		
16	20	90	195	5	0.38	200		
44	21	70	195	3.75	0.38	200		
12	22	70	360	3.75	0.38	300		
36	23	90	195	3.75	0.38	300		
17	24	70	195	3.75	0.25	100		
18	25	70	195	3.75	0.5	100		
45	26	70	195	3.75	0.38	200		
33	27	50	195	3.75	0.38	100		
25	28	50	195	3.75	0.25	200		
20	29	70	195	3.75	0.5	300		
27	30	50	195	3.75	0.5	200		
30	31	70	195	5	0.38	100		
42	32	70	195	3.75	0.38	200		
41	33	70	195	3.75	0.38	200		
39	34	70	30	3.75	0.5	200		
6	35	70	195	5	0.25	200		
43	36	70	195	3.75	0.38	200		
38	37	70	360	3.75	0.25	200		
19	38	70	195	3.75	0.25	300		
40	39	70	360	3.75	0.5	200		
7	40	70	195	2.5	0.5	200		
28	41	90	195	3.75	0.5	200		
14	42	90	195	2.5	0.38	200		
5	43	70	195	2.5	0.25	200		
13	44	50	195	2.5	0.38	200		
9	45	70	30	3.75	0.38	100		
15	46	50	195	5	0.38	200		

RESULTS AND DISCUSSIONS

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 [26 – 28] that reported the moisture content of kaolinite clay is between 3.0 – 4.0% and the bulk density is 1.2 – 1.4 g/ml.

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

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

Characterization of Raw Clay and Activated Clay

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

The result of the XRF composition analysis of raw Ngbo clay and Ngbo synthetic zeolite 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 °C as reported in literature by [29, 30] and [31]. This shows that improvement on the properties of the clay by chemical methods below 500 °C is difficult due to its low reactivity. This result of the XRF on the Ngbo raw clay and Ngbo synthetic zeolite as shown in table 4 also indicates high content of silicon and aluminium oxides when compared to other oxides.

The result of the XRF composition analysis of Ngbo clay activated with sodium carbonate and sodium hexa-metaphosphate with chemical ratio of 1:4 is also presented in Table 4. The result indicates silica/alumina ratio of 1.48 was obtained for the clay activated with sodium carbonate and sodium hexa-metaphosphate ratios of 1:4 and which are within literature, theoretical values greater than 1; as reported by [32]. The result shown indicates that Ngbo clay activated with sodium carbonate and sodium hexa-metaphosphate ratios of 1:4 have good silica/alumina ratio for zeolite synthesis.

Table 4: Results of XRF analysis of raw Ngbo Clay and Ngbo Synthetic zeolite ratio 1:4

Chemical constituent	Raw clay (Wt. %)	Chemical Ratio 1:4
		(Wt. %)
SiO ₂	62.7	53.035
TiO ₂	1.52	1.573
Al ₂ O ₃	19.7	25.306
Fe ₂ O ₃	2.06	8.503
P ₂ O ₃	—	3.944
CaO	0.789	0.807
MgO	0.026	0.721
Na ₂ O	0.2	2.924
K ₂ O	0.85	1.546
Mn ₂ O ₃	—	0.093
V ₂ O ₅	0.071	-
Cr ₂ O ₃	0.035	0.016
CuO	0.044	-

BaO	0.19	-
L.O.I	11.82	0.025
SO ₃	—	1.248
Cl	—	0.246
ZnO	—	-
SrO	—	0.014
SiO ₂ /Al ₂ O ₃ ratio		
1.48		

The SEM image results of the raw clay at 80 μ m, 20 μ m and 8 μ m 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, clinocllore, mica and muscovites as reported in literature by [33]. The results are in agreement with the XRD results

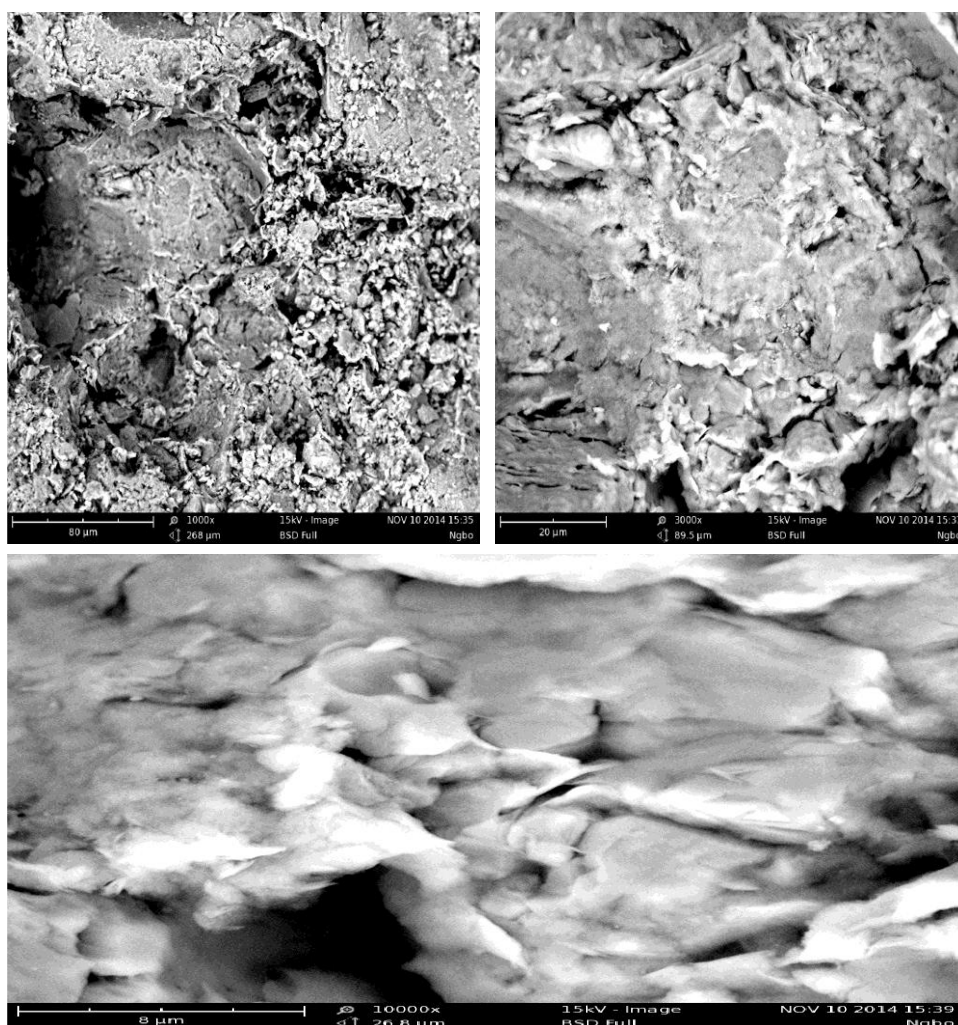
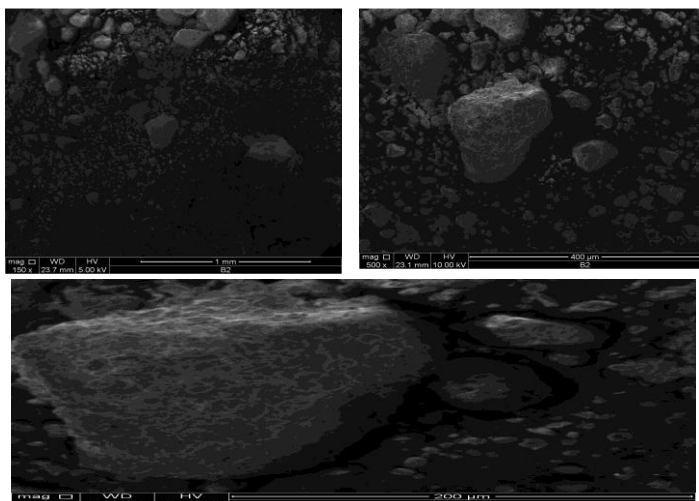


Figure 1: Results of SEM analysis of Ngbo raw clay

The SEM results of Ngbo clay activated with sodium carbonate and sodium hexa-metaphosphate ratios of 1:4 at 80 μ m, 20 μ m and 8 μ m magnifications are shown in figure 2. The results of the SEM images of the activated clay shows retention of clay structure but with noticeable small aggregate particles in between the silica-alumina plate on higher magnification [33]. The dark and bright patches witnessed in the image were attributed to presence of imbedded chemicals on the samples respectively.

1:4



Esterification Process Results

Esterification technique was used to obtain the responses and yield of Ngbo Synthetic zeolite B ratio 1:4 as shown in Table 5.

Table 5: Results showing responses and yield of Synthetic zeolite B ratio 1:4

Std	Run	Factor A (°C)	Factor B (min)	Factor C (ml)	Factor D(g)	Factor E (mic)	Response (ml)	Yield (%)
37	1	70	30	3.75	0.25	200	34.8	28.10
22	2	70	360	2.5	0.38	200	39.3	18.80
23	3	70	30	5	0.38	200	45.6	5.79
29	4	70	195	2.5	0.38	100	22.8	51.18
26	5	90	195	3.75	0.25	200	27.6	42.98
1	6	50	30	3.75	0.38	200	31.5	34.92
32	7	70	195	5	0.38	300	43.5	9.56
46	8	70	195	3.75	0.38	200	35.7	26.24
10	9	70	360	3.75	0.38	100	32.7	29.98
34	10	90	195	3.75	0.38	100	25.8	44.75
21	11	70	30	2.5	0.38	200	24.3	49.79
35	12	50	195	3.75	0.38	300	33.3	30.77
8	13	70	195	5	0.5	200	46.8	3.31
4	14	90	360	3.75	0.38	200	23.1	52.27
2	15	90	30	3.75	0.38	200	28.8	40.50
11	16	70	30	3.75	0.38	300	34.5	28.27
31	17	70	195	2.5	0.38	300	25.5	46.99
3	18	50	360	3.75	0.38	200	31.5	34.92
24	19	70	360	5	0.38	200	39.0	19.42
16	20	90	195	5	0.38	200	30.9	36.16
44	21	70	195	3.75	0.38	200	35.4	26.86
12	22	70	360	3.75	0.38	300	45.6	5.20
36	23	90	195	3.75	0.38	300	24.6	48.86
17	24	70	195	3.75	0.25	100	33.6	28.05
18	25	70	195	3.75	0.5	100	34.2	26.77
45	26	70	195	3.75	0.38	200	33.3	31.20
33	27	50	195	3.75	0.38	100	28.5	38.97
25	28	50	195	3.75	0.25	200	30.6	36.78
20	29	70	195	3.75	0.5	300	36.9	23.28



27	30	50	195	3.75	0.5	200	32.1	33.68
30	31	70	195	5	0.38	100	44.7	4.28
42	32	70	195	3.75	0.38	200	31.5	34.92
41	33	70	195	3.75	0.38	200	35.7	26.24
39	34	70	30	3.75	0.5	200	35.4	26.86
6	35	70	195	5	0.25	200	43.5	10.12
43	36	70	195	3.75	0.38	200	30.3	37.40
38	37	70	360	3.75	0.25	200	34.5	28.72
19	38	70	195	3.75	0.25	300	34.5	28.27
40	39	70	360	3.75	0.5	200	31.8	34.30
7	40	70	195	2.5	0.5	200	22.8	52.89
28	41	90	195	3.75	0.5	200	24.9	48.55
14	42	90	195	2.5	0.38	200	23.7	51.03
5	43	70	195	2.5	0.25	200	24.9	48.55
13	44	50	195	2.5	0.38	200	23.4	51.65
9	45	70	30	3.75	0.38	100	36.9	20.99
15	46	50	195	5	0.38	200	39.6	18.18

Analysis of Variance (ANOVA) for Synthetic zeolite ratio 1:4

The result of the ANOVA for synthetic zeolite ratio 1:4 is shown in table 6. The result showed that RSM model is significant of the experimental results as indicated from the F – value of 2.33 calculated and very low probability value of $P < 0.0001$. The Model F-value of 7.27 implies the model is significant. The "Lack of Fit F-value" of 2.33 implies the Lack of Fit is not significant relative to the pure error and there is a 17.72% chance that a "Lack of Fit F-value" this large could occur due to noise. Non-significant lack of fit is good -- we want the model to fit. 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 [34]. The regression model demonstrates that the model is significant as evident from the calculated F-value and a very low probability value ($P = 0.0001$). If P – value of lack of fit is less than 0.05, there is statistically significant lack of fit at 95% confidence level [35].

The result in table 6 indicates that the significant model terms are A, C, BC, BE, A^2 which imply that only linear effects of temperature, excess reactants, process duration and excess reactants, process duration and particle size, and quadratic effect of temperature were significant. The model accuracy was confirmed by the correlation coefficient of the regression model which is 0.8532. The correlation coefficient showed that 85.32% of the total variation in the final concentration was attributed to the experimental variables considered in this research work. The "Pred R-Squared" of 0.4493 is not as close to the "Adj R-Squared" of 0.7358 as onemight normally expect. This may indicate a large block effect or a possible problem with your model and/or data. Things to consider are model reduction, response tranformation, outliers, etc.(Mohd and Rasyidah, 2010; [34].

The standard deviation for the model was 6.95, which indicated that the predicted values are still considered suitable to correlate the experimental data. Adequate Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. Here it has a ratio of 11.179, which indicates an adequate signal.

The Final Equation in Terms of Coded Factors:

$$\text{Yield} = + 30.48 + 5.33 * A - 1.58 * B - 15.65 * C - 0.12 * D - 1.49 * E + 2.94 * A * B + 4.65 * A * C + 2.17 * A * D + 3.08 * A * E + 7.75 * B * C + 1.71 * B * D - 8.02 * B * E$$



$$-2.79 * C * D + 2.37 * C * E - 0.93 * D * E + 11.67 * A^2 - 2.70 * B^2 - 1.13 * C^2 - 0.31 * D^2 - 3.23 * E^2$$

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 = + 30.48 + 5.33*A - 15.65 * C + 7.75 * B * C - 8.02 * B * E + 11.67 * A²

Table 6: ANOVA for Synthetic zeolite ratio 1:4

Source	Sum of Squares	df	Mean Square	F - Value	P – Value Prob> F
Model	7027.72	20	351.39	7.27	< 0.0001 significant
A - Temperature	454.01	1	454.01	9.39	0.0052
B – Process duration	39.82	1	39.82	0.82	0.3729
C – Excess reactant	3919.70	1	3919.70	81.05	< 0.0001
D – Effect of Catalyst	0.23	1	0.23	4.814E-003	0.9452
E – Particle size	35.31	1	35.31	0.73	0.4009
AB	34.63	1	34.63	0.72	0.4055
AC	86.49	1	86.49	1.79	0.1932
AD	18.79	1	18.79	0.39	0.5387
AE	37.88	1	37.88	0.78	0.3846
BC	240.10	1	240.10	4.96	0.0351
BD	11.63	1	11.63	0.24	0.6282
BE	256.96	1	256.96	5.31	0.0297
CD	31.08	1	31.08	0.64	0.4303
CE	22.42	1	22.42	0.46	0.5022
DE	3.44	1	3.44	0.071	0.7919
A ²	1189.45	1	1189.45	24.59	<0.0001
B ²	63.69	1	63.69	1.32	0.2620
C ²	11.12	1	11.12	0.23	0.6357
D ²	0.82	1	0.82	0.017	0.8977
E ²	90.80	1	90.80	1.88	0.1828
Residual	1209.0	25	48.36		
Lack of fit	1091.91	20	54.60	2.33	0.1772 not significant
Pure Error	117.18	5	23.44		
Cor Total	8236.81	45			

Residual Plot for ratio 1:4

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

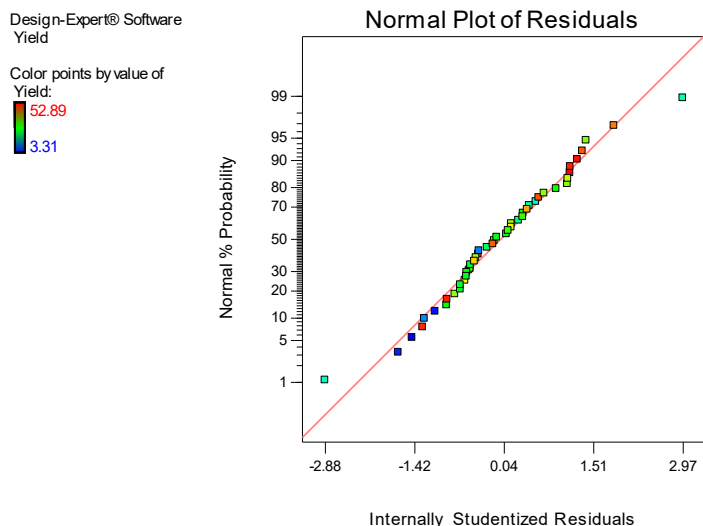


Figure 3: Normal plot of Residuals

Contour Plots for chemical ratio 1:4

The contour plots for ratio 1:4 are shown in figure 4 to figure 13. 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 [36, 34]. 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.

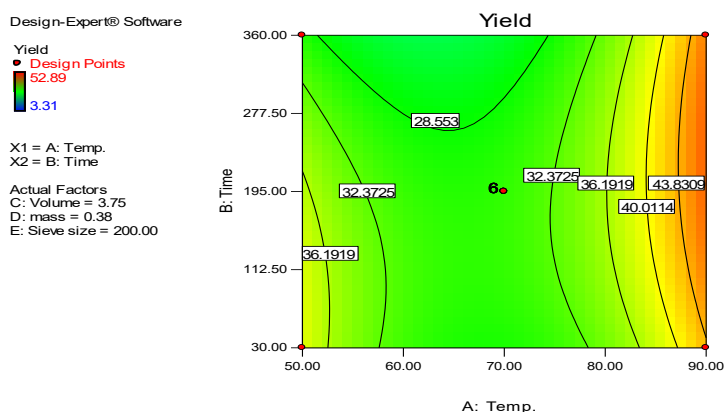


Figure 4: Contour plot of Time vs Temp and yield

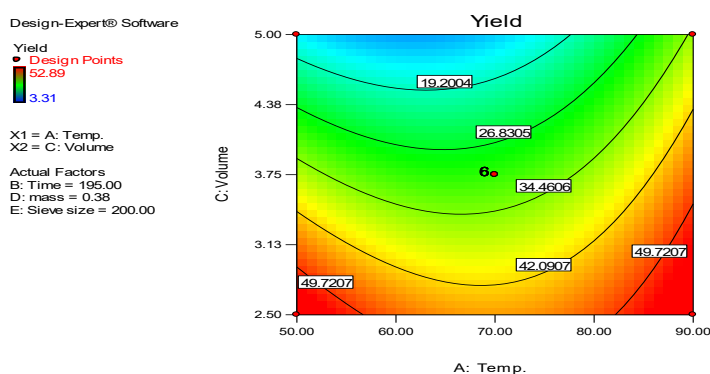


Figure 5: Contour plot of excess reactant vs Temp and yield

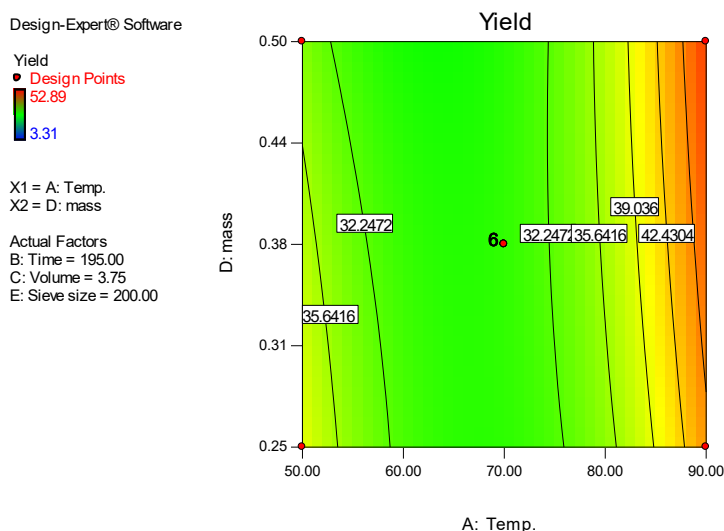


Figure 6: Contour plot of effect of catalyst vs Temp and yield

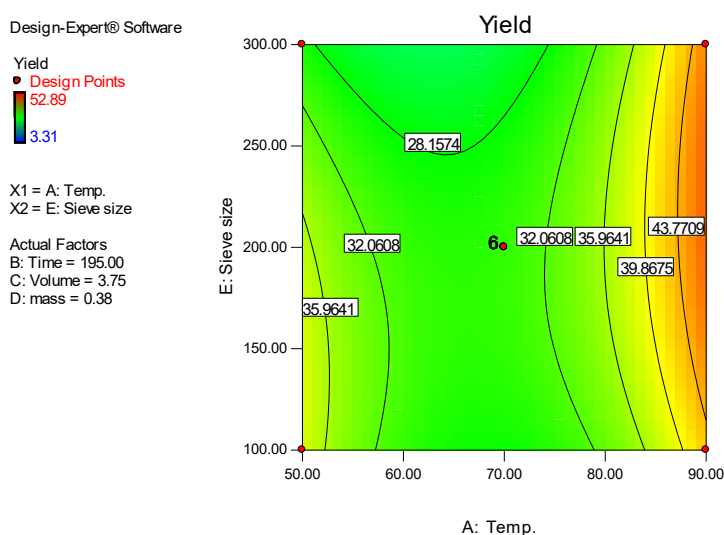


Figure 7: Contour plot of particle size vs Temp and yield

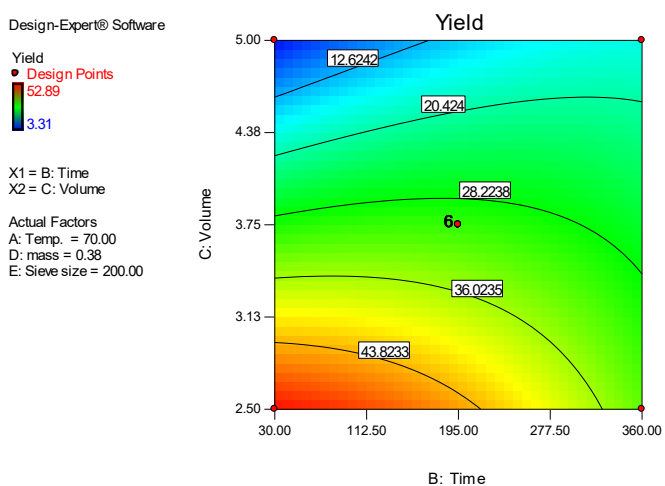


Figure 8: Contour plot of excess reactant vs Time and yield

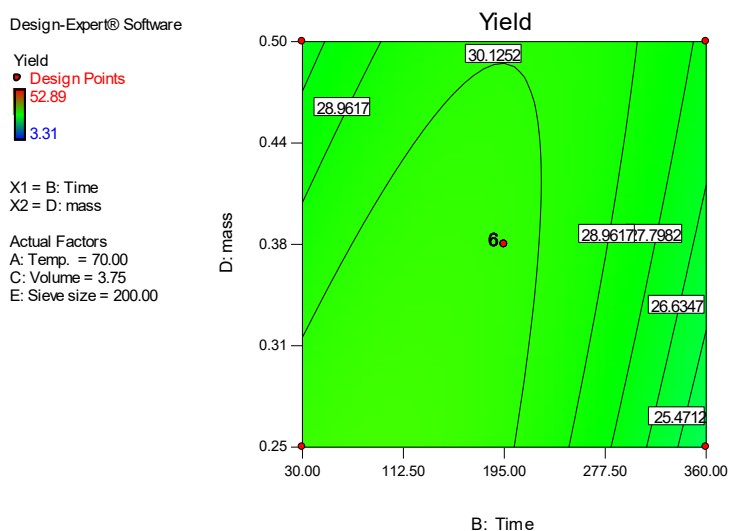


Figure 9: Contour plot of effect of catalyst vs Time and yield

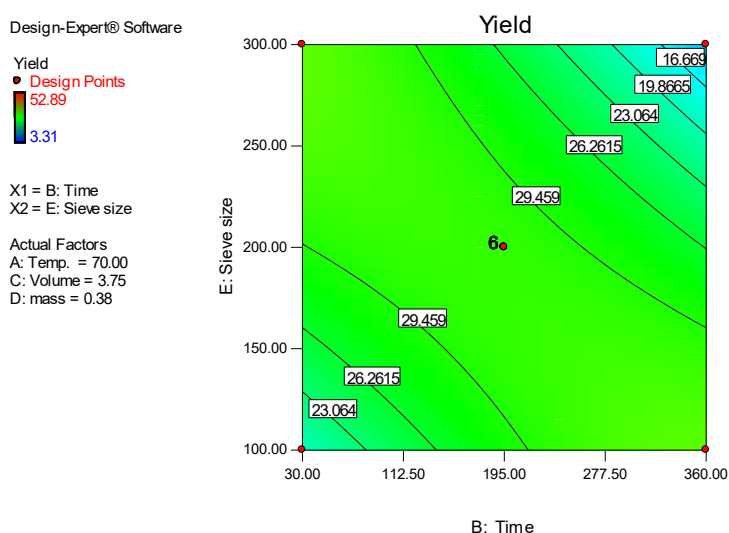


Figure 10: Contour plot of particle size vs Time and yield

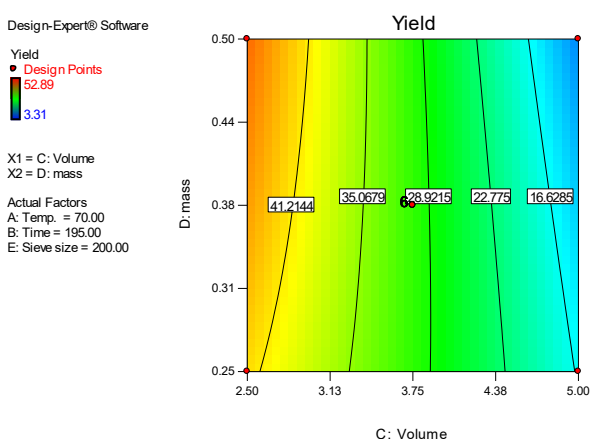


Figure 11: Contour plot of effect of catalyst vs excess reactant and yield

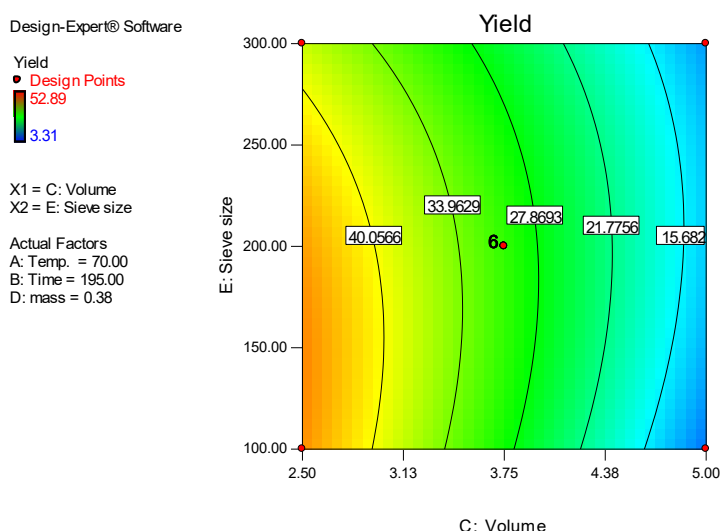


Figure 12: Contour plot of particle size vs excess reactant and yield

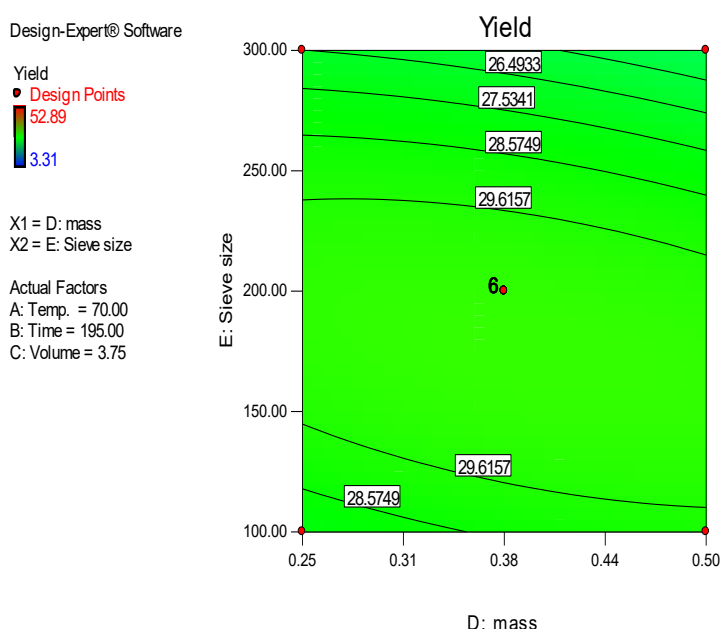


Figure 13: Contour plot of particle size vs effect of catalyst and yield

The 3 - D Plot for chemical ratio 1:4

The 3 – Dimensional plots of the response surface model are shown in figures 14 to 23. The results showed that the optimum value of the conversion was 52 for the process variables studied; which are similar to results obtained by [37, 27, 28, 38]. The excess reactants increase with process duration as the yield also increases. The response surface plots showed clear peaks, implying that the maximum values of the response were attributed to the factors in the design space. The three-dimensional surfaces provide useful information about the behaviour of the system within the experiment design, facilitate an examination of the effects of the experimental factors on the responses and contour plots between the factors [36, 39, 40]. 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 an elliptical nature with any two concerned variables. This denotes that the quadratic model chosen was appropriate with significant correlation between the two variables [41, 42].

Design-Expert® Software

Yield
52.89
3.31

X1 = A: Temp.
X2 = B: Time

Actual Factors
C: Volume = 3.75
D: mass = 0.38
E: Sieve size = 200.00

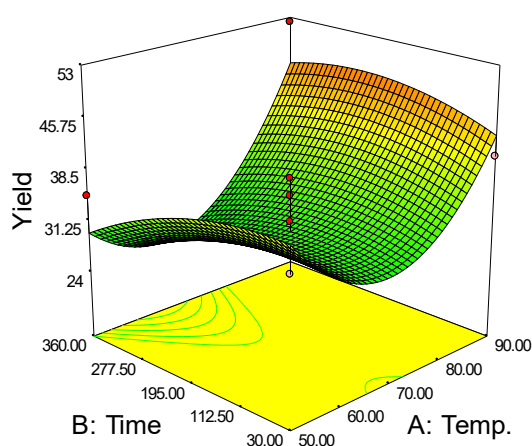


Figure 14: 3 – D Plot of Time vs Temp and Yield

Design-Expert® Software

Yield
52.89
3.31

X1 = A: Temp.
X2 = C: Volume

Actual Factors
B: Time = 195.00
D: mass = 0.38
E: Sieve size = 200.00

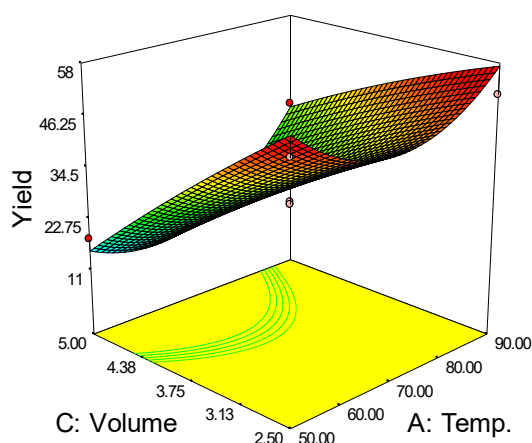


Figure 15: 3 – D Plot of Excess reactant vs Temp and Yield

Design-Expert® Software

Yield
52.89
3.31

X1 = A: Temp.
X2 = D: mass

Actual Factors
B: Time = 195.00
C: Volume = 3.75
E: Sieve size = 200.00

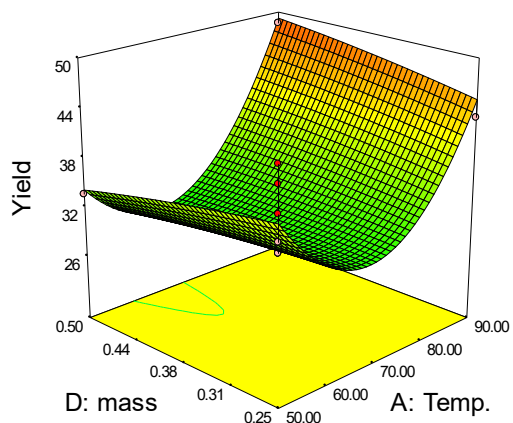


Figure 16: 3 – D Plot of Effect of catalyst vs Temp and Yield

Design-Expert® Software

Yield
52.89
3.31

X1 = A: Temp.
X2 = E: Sieve size

Actual Factors
B: Time = 195.00
C: Volume = 3.75
D: mass = 0.38

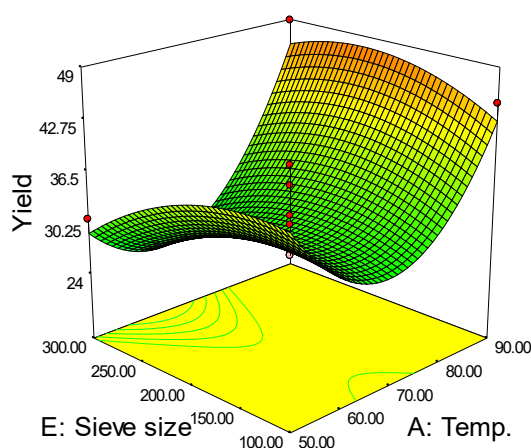


Figure 17: 3 – D Plot of Particle size vs Temp and Yield

Design-Expert® Software

Yield
52.89
3.31

X1 = B: Time
X2 = C: Volume

Actual Factors
A: Temp. = 70.00
D: mass = 0.38
E: Sieve size = 200.00

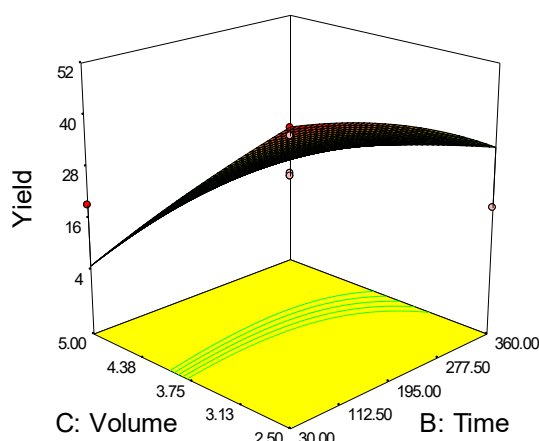


Figure 18: 3 – D Plot of Excess reactant vs Time and Yield

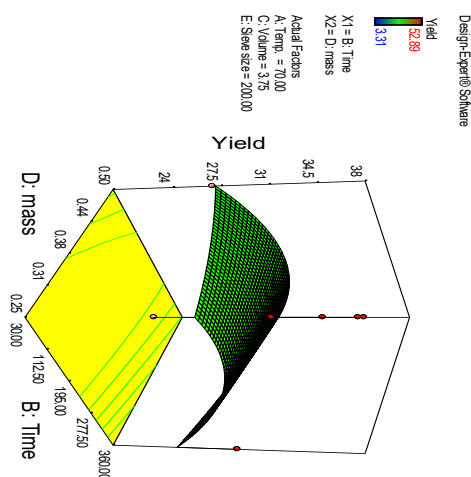


Figure 19: 3 – D Plot of Effect of catalyst vs Time and Yield

Design-Expert® Software

Yield
52.89
3.31

X1 = B: Time
X2 = E: Sieve size

Actual Factors
A: Temp. = 70.00
C: Volume = 3.75
D: mass = 0.38

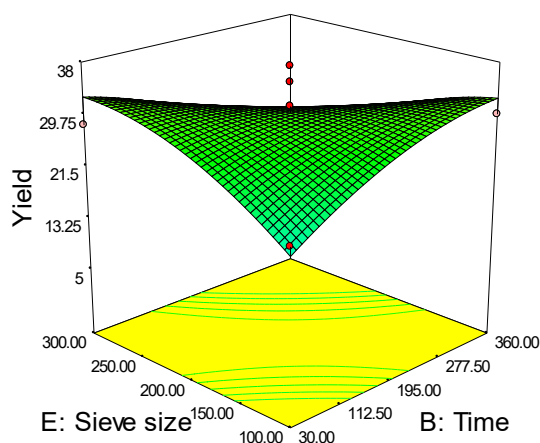


Figure 20: 3 – D Plot of Particle size vs Time and Yield

Design-Expert® Software

Yield
52.89
3.31

X1 = C: Volume
X2 = D: mass

Actual Factors
A: Temp. = 70.00
B: Time = 195.00
E: Sieve size = 200.00

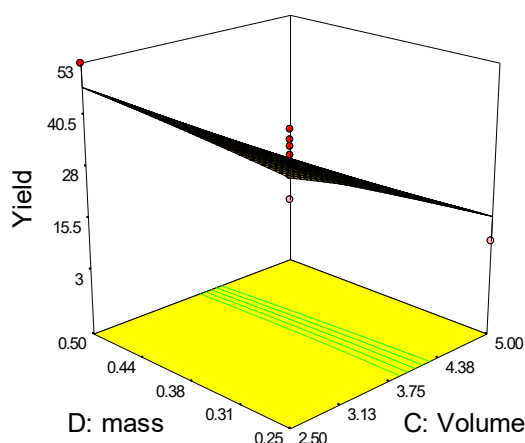


Figure 21: 3 – D Plot of Effect of catalyst vs Excess reactant and Yield

Design-Expert® Software

Yield
52.89
3.31

X1 = C: Volume
X2 = E: Sieve size

Actual Factors
A: Temp. = 70.00
B: Time = 195.00
D: mass = 0.38

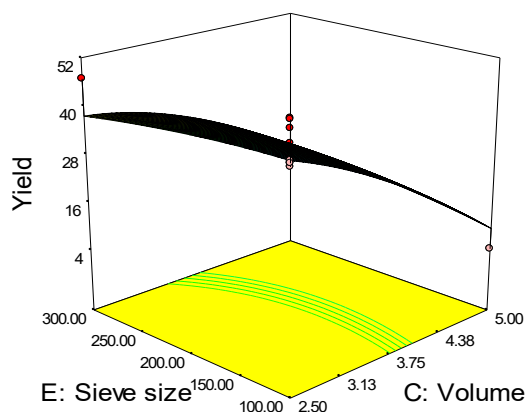


Figure 22: 3 – D Plot of Particle size vs Excess reactant and Yield

Design-Expert® Software

Yield
52.89
3.31

X1 = D: mass
X2 = E: Sieve size

Actual Factors
A: Temp. = 70.00
B: Time = 195.00
C: Volume = 3.75

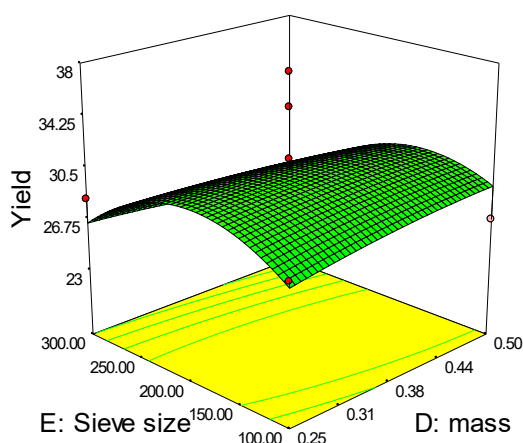


Figure 23: 3 – D Plot of Particle size vs Effect of catalyst and Yield

Process Optimization

In the process optimization for Ngbo synthetic zeolite for ratio 1:4, 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 73.64min, 86°C, 2.61ml, 0.26g, and 227.41 microns for time, temperature, excess reactant, catalyst weight and particle size respectively. The predicted conversion yield was 54.1058. The optimization was validated at those experimental conditions and conversion yield of 55.65 was obtained.

CONCLUSIONS

The study presented the optimum conditions for esterification reaction of acetic acid and ethanol using Ngbo synthetic zeolite B ratio 1:4 as 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 73.64min, 86°C, 2.61ml, 0.26g, and 227.41 microns respectively. The maximum predicted esterification yield was 54.1058. The XRF analysis showed that the clay was made of mainly SiO₂ 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 1.56% 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 synthetic zeolite B ratio 1:4 as catalyst.

Competing Interests

Authors have declared that no competing interests exist.

REFERENCES

1. Gómez-Álvarez, A.; Valenzuela-García, J.L.; Meza-Figueroa, D.; De, M.; O-Villanueva, L.A.; Ramírez-Hernández, J.; Almendariz-Tapia, J.; Pérez-Segura E. Impact of mining activities on sediments in a semi-arid environment: San Pedro River, Sonora, Mexico. *Appl. J. Geochem.* **2011**, 26, 2101-2112.



2. Martins, A.; Mata, T.M.; Gallios, G.P.; Vaclavikova, M.; Stefusova, K.(2010) Modeling and simulation of heavy metals removal from drinking water by magnetic zeolite. *Water Treatment Technologies for the Removal of High-Toxicity Pollutants.Project*; No. APVT 51, 017104, 61-84. Available at: <https://link.springer.com/book/10.1007/978-90-481-3497-7>.
3. Yuan, P.; Liu, D.; Fan, M.; Yang, D.; Zhu, R.; Ge, F.; Zhu, J.X.; He, H (2010).“Removal of hexavalent chromium [Cr(VI)] from aqueous solutions by the diatomite supported/unsupported magnetite nanoparticles”*Journal of. Hazard Mater*, 173, 614-621.
4. Song, J.; Oh, H.; Kong, H.; Jang, J. Polyrhodanine modified anodic aluminum oxide membrane for heavy metal ions removal. *J. Hazard. Mater.***2011**, 187, 311-317.
5. Karami, H.(2013).“Heavy metal removal from water by magnetite nanorods”.*Journal of Chemical Engineering*, 219, 209-216.
6. Chiban, M.; Soudani, A.; Sinan, F.; Persin, M. Single, binary and multi-component adsorption of some anions and heavy metals on environmentally friendly *Carpobrotusedulis* plant. *Colloids Surf. B* **2011**, B 82, 267-276.
7. Miretzky, P.; Saralegui, A.; Cirelli, A.F. Simultaneous heavy metal removal mechanism by deadmacrophytes. *Chemosphere* 2006, 62, 247-254
8. Igbokwe, P.K., and Ogbuagu, J.O., Effects of Process parameters on the Yield of Alumina from Indigenous Kaolinitic Clay Deposit, *Nigerian Journal of Engineering Research and development*, vol. 2, no.2, pp.23 – 26, 2003.
9. Shanmugan S; Viswanathan B.; and Varadarajan T. K. (2004).“Esterification by solid acid catalysts – a comparison”.*Journal of molecular catalysis A: Chemical* 223, 143 – 147.
10. Breck D.W. (1974) Zeolite Molecular Sieves.Structure, Chemistry and Uses; JohnWiley and Sons, New York, pp. 313-320 and pp. 731-738
11. Marcus, B.K and W.E. Cormier, (1999).Going Green with Zeolites. *Chemical Engineering.Progress*, 95(6), 47-53
12. Boukadir, D., Bettahar N. and Derriche, Z. (2002) Synthesis of zeolites 4A and HS from natural materials. *Annales de Chimie - Science des Materiaux*. 27,pp. 1-13.
13. Ravendra Reddy, C; Lyengar, P; Nagendrappa, G; Jai Prakash, B.S (2005).” Esterification of dicarboxylic acids to diesters over Mn⁺-montmorillonite clay catalysts” *Catalyst Letter*, 101, 87 – 91.
14. Chen C-C, Hayes KF (1999) X-ray absorption spectroscopy investigation of aqueous Co(II) and Sr(II) sorption at clay-water interfaces. *GeochimCosmochimActa* 63:3205–3215
15. Yadav, G.D;Thagathar, M.B(2002). “Esterification of maleic acid with ethanol over cation-exchange resin catalyst” *React. Funct.Polym*, 52, 99 – 110.
16. Zang, Y; Ma, L; Yang, J (2004). Kinetics of esterification of lactic acid with ethanol catalysed by cation-exchange resins” *React. Funct.Polym*, 61, 101 – 114.
17. Kirumakki S.R.; Nagaraju N; Chary, K.V.R (2006). “Esterification of alcohols with acetic acid over zeolites H β , HY and HZSM5” *Applied Catalysis A: General*, 299, 185 – 192.
18. Kirumakki S.R.; Nagaraju N; Narayanan, S.A(2004).” Comparative esterification of benzyl alcohol with acetic acid over zeolites H β , HY and HZSM5” *Applied Catalysis A: General*, 273, 1 – 9.
19. Wu, K; and Chen, Y (2004).“An efficient two-phase reaction of ethyl acetate production in modified ZSM- 5 zeolites” *Applied Catalysis A: General*, 257, 33 – 42.
20. Chu, W. Yang, X; Ye, X; Wu, Y(1996). “Vapour phase esterification catalysed by immobilized dodecatungstosilicic acid (SiW₁₂) on activated carbon”*Applied Catalysis A: General*, 145, 125 – 140.
21. Sepulveda, J.H; Yori, J.C; Vera, C.R (2005). “Repeated use of supported H₃PW₁₂O₄₀ catalysts in the liquid phase esterification of acetic acid with butanol” *Applied Catalysis A: General*, 288, 18 – 24.
22. Jermy, B.R;Pandurangan,A (2005).” Catalytic application of Al-MCM-41 in the esterification of acetic acid with various alcohol”. *Applied Catalysis A: General*, 288, 25 – 33.
23. Kirumakki S.R.; Nagaraju N; Chary, K.V.R; Narayanan, S (2003). “Kinetics of esterification of aromatic carboxylic acids over zeolites H β and HZSM5 using dimethyl carbonate” *Applied Catalysis A: General*, 248, 161 – 167.
24. Azargohar, R, and A.K. Dalai(2005) “Production of Activated Carbon from Luscar Char: Experimental and Modeling Studies”. *MicroporMesopor. Mater*:85:219 – 225.
25. Kovo A.S and Edoga M.O (2005).“Production and characterization of zeolite from Ahako clay in Kogi State, Nigeria” *Journal of Practices and Technologies*, 4, 7, 31 – 40 (10).



26. Igbokwe P. K and Olebunne F. L,(2011). 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*, 46, 6, 389-394.
27. Igbokwe P. K, Ugonabo V. I, Obarandiku E, Ochili A, (2008) ‘‘Characterization and use of catalyst produced from local clay resources’’ *Journal of Applied Sciences (JAS)*, 2, 2.
28. Igbokwe, P.K., Olebunne, F.L., and Nwakaodu, M.S (2011)., Effect of Activation Parameters on Conversion in Clay – Catalysed Esterification of Acetic Acid, *International Journal of Basic and Applied Sciences*, 11,.5, 1 – 8,
29. Murat, M., A. Amokrane, J.P. Bastide, and L. Montanaro,(1992). ‘‘Synthesis of zeolites from thermally activated kaolinite. Some observations on nucleation and growth’’.*Clay Minerals*, 27, 1, 119.
30. Akolekar, D., A. Chaffee, and R.F. Howe (1997), ‘‘The transformation of kaolin to low-silica X zeolite’’. *Zeolites*, 19, 5–6, 359–365.
31. Demortier A., Golbeltz N., Letlieur J.P., Duhayon C.(1999). Infrared evidence for the formation of an Intermediate compound, during the synthesis of Zeolite Na – A from metakaolin. *International Journal of Inorganic materials*. Volume 1, issue 2, August 1999, pages 129 – 134
32. Ajayi, O. A, Adefila S. S. Aderemi B. O,(2010), ‘‘Novel method of metakaolindealumination-preliminary investigation’’. *Journal of Applied Science Research*, 6(10), 1539-1546
33. Davies J, Haq S, Hawke T, Sarjent J.P (2009). A practical approach to the development of a synthetic Gecko tape. *International journal of Adhesion and Adhesives*. Volume 29, issue-4, June 2009, pages 380 – 390.
34. Ejikeme, M.E., P.C.N. Ejikeme, and B.N. Abalu.(2013). ‘‘RSM Optimization Process for Uptake of Water from Ethanol Water Solution Using Oxidized Starch’’. *Pacific Journal of Science and Technology*. 14, 2 :319-329.
35. Azargohar, R, and A.K. Dalai(2005) ‘‘Production of Activated Carbon from Luscar Char: Experimental and Modeling Studies’’. *MicroporMesopor. Mater*:85:219 – 225.
36. Anupam, K., S. Dutta, C. Bhattacharjee, and S. Datta (2011) ‘‘Adsorption Removal of Chromium (VI) from Aqueous Solution over Powdered Activated Carbon: Optimization through Response Surface Methodology. *Jornal of Hazard.Mater*:173:135 – 143.
37. Igbokwe P. K, Ugonabo V. I, Iwegbu N. A, Akachukwu P. C, Olisa C. J, (2008). 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*, 345 – 348.
38. Olebunne F. L; Igbokwe P. K; Onyelucheya O. E; Osoka E. C and Ekeke I. C. (2011). ‘‘Mechanistic modeling of clay-catalysed liquid-phase esterification of acetic acid’’.*Journal of Emerging Trends in Engineering and Applied Sciences*, 2, 4: 631- 635.
39. Panesar, P.S. (2008). ‘‘Application of Response Surface Methodology in the Permeabilisation of Yeast Cells for Lactose Hydrolysis’’.*Biochem. Eng. J*. 39:91 – 96.
40. Ahmad, A.A. and B.H. Hameed(2010) ‘‘Effect of Preparation Conditions of Activated Carbon from Bamboo Waste for Real Textile Waste Water’’,*Journal of Hazard Mater*:173:487 – 493.
41. Onu Chijioke Elijah, Igbokwe P.K, Nwabanne J.T, Nwanjinka O.C, Ohale P.E. Evaluation of Optimization techniques in predicting optimum moisture content reduction in drying potatoe slices. *Artificial intelligence in Agriculture*, 2020;4;39-47.
Available: <http://doi.org/10.1016/j.aia.2020.04.001>
42. Onu C.E, Nwabanne JT, Ohale P.E, Asadu CO. Comparative analysis of RSM, ANN and ANFIS and the mechanistic modelling 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>.