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Optimization of esterification of acrylic acid and ethanol by box-behnken design of response surface methodology

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A Box-Behnken design has been used to study the esterification of acrylic acid and ethanol with sulfuric acid as a catalyst. Effect of reaction temperature, catalyst concentration and initial molar ratio of reactants has been studied. All the three variables significantly influence the conversion of acrylic acid or yield of the product. Esterification reactions are performed in a batch reactor and the reaction sample is analyzed using gas chromatograph. Using Box-Behnken response surface methodology, a quadratic polynomial response equation is developed for conversion of acrylic acid by multiple regression analysis. Statistical design of experiments is carried out to achieve optimum conditions of the reaction.

Keywords: Box-Behnken design, Response surface methodology, Esterification, Anova, Optimization

Acrylic acid as an essential building block in the production of some of our most commonly used industrial and consumer products. Approximately two-thirds of the acrylic acid manufactured is used to produce acrylic esters-methyl acrylate, ethyl acrylate, butyl acrylate and 2 ethylhexyl acrylate which are ingredients in paints, coatings, textiles, adhesives, plastics and many other applications. Acrylic esters are projected to grow by about 3% per year. The acrylic acid esters in the United States and Asia account for the largest consumption of both acrylic acid and acrylate esters in the world, followed by Western Europe and Japan. The largest application for acrylate esters is the production of surface coatings (48%), followed by adhesives and sealants (21%), plastic additives and co-monomers (12%), paper coatings and textiles.

This paper is focused on the ethyl acrylate, which is an important ester obtained by the esterification of acrylic acid with ethanol in the presence of sulphuric acid as catalyst. The esterification is equilibrium limited chemical reaction involves water, an alcohol (ethanol), an organic acid (acrylic acid) and an ester (ethyl acrylate). However, esterification shows limited conversion due to low reaction rate and reversibility[1]. Although the reaction rate and the conversion in esterification reactions can be improved by changing several reaction parameters, including the increase in alcohol-to-acid ratios, the elevation of temperatures and the higher concentration of mineral acids[2].

RSM is a collection of statistical and mathematical techniques useful for developing, improving, and optimizing processes in which a response of interest is influenced by several variables and the objective is to optimize this response. It defines the effect of the independent variables, alone or in combination, on the processes. In addition to analyzing the effects of the independent variables, this experimental methodology generates a mathematical model which describes the chemical or biochemical processes. Application of RSM in chemical industrial processes has been widely studied in the literature[3-7].

Beula and Sai[8] applied statistical design of experiments for optimization of esterification reaction of palmitic acid with ethanol using homogeneous catalyst sulphuric acid. Usually rate of reaction is affected by many factors such reaction temperature, initial mole ratio of reactants, catalyst concentration, type of catalyst and mechanical agitation rate etc. A few work related to the optimization of the esterification by RSM has been reported yet in the literature[9-11].

The objective of the present work is to develop the functional relationship between key variables of esterification reaction (reaction temperature, initial molar ratio of reactant, catalyst concentration) on conversion of acrylic acid or yield of the product. Box–Behnken with response surface method and their applications to the Statistical design of experiments were described to correlate the variables with the output response (conversion of acrylic acid). Optimal operating conditions for esterification of acrylic acid with ethanol catalyzed by sulfuric acid were obtained.

Experimental Section

Materials and methods

Experimental procedure

All the chemicals including ethanol, acrylic acid and sulphuric acid were analytical grade and obtained

from Merck. A batch reactor with a 1000 mL three necked ball glass flask equipped with magnetic stirrer setup was selected for the experiment. Before fed to reactor required amount of acrylic acid and ethanol were preheated up to reaction temperature separately and measured amount of catalyst was added. The reaction temperature was maintained by magnetic stirrer. Sample was taken from one of the access point at regular time intervals and instantly put in a refrigerator in order to avoid any further reaction. The experiments were carried out at 50, 60 and 70°C reaction temperature and catalyst in the range of 1-3% (volume) of reaction mixture with different molar ratio 1:1, 1:2 and 1:3 of reactants.

Analytical method

Analysis of the products was carried out by NUCON series gas chromatograph (GC). Acrylic acid, ethanol, ethyl acrylate and water were the only products and no side products were detected.Sample with amount of 1μL was injected in GC for analysis. To obtain correct results, each sample was analyzed two times.The oven temperature was programmed as 180°Cequipped with a TCD detector for the identification of the samples. The carrier gas was hydrogen and a porapak column (id 2mm, od 1/8", length 2 m) with stationary phase was used for separations.Column oven, injection port, and detector temperatures were at 180, 150 and 180°C respectively. The conversion of acrylic acid was determined as follows:

$$\%\ Conversion = \frac{moles\ of\ acrylic\ acid\ reacted}{initial\ moles\ of\ acrylic\ acid} \times 100$$

Experimental design and statistical analysis

Statistical design of experiment is a technique employed to optimize the response surface that is affected by different process parameters and reduce the total number experiments. It is also useful for the modeling of the system response which is influenced by many variables[3,12]. The graphical representation of the response can be plotted either in the three-dimensional space or as contour plots that help visualize the profile of the response surface.

An experimental design for the various parameters used for esterification of acrylic acid with ethyl alcohol over sulfuric acid was built by RSM with MINITAB software. In this study the experimental design was carried out by Box-Behnken Design (BBD), consisting of three independent variables which requiring 15 experimental runs. The independent variables chosen were reaction temperature (X_1), catalyst loading (X_2) and ethanol to acrylic acid molar ratio (X_3). The conversion of acrylic acid (Y) was chosen to be the output or response parameter as a dependent variable. Each variable in the experiment was coded as levels −1, 0 and +1 as shown in Table 1. The Box-Behnken design of the three factors in coded units, uncoded units and corresponding response values are given in Table 2.

The experimental data (Table 3) were analyzed by the response surface methodology (RSM) using a quadratic polynomial model:

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 \quad \ldots (1)$$

where β_0 is intercept, β_1, β_2 and β_3 are the coefficients of linear effect, β_{11}, β_{22} and β_{33} are quadratic coefficients and β_{12}, β_{13} and β_{23} are the coefficients of interaction between the variables. All the experimental data were statistically analyzed by Minitab software. The statistical significance of the developed model was determined by the analysis of variance (ANOVA).

Table 1 — Levels of factors selected for the study

Variable	Levels		
	-1	0	+1
Reaction temperature, °C (X_1)	50	60	70
Initial molar ratio of reactant, ethanol : acrylic acid (X_2)	1	2	3
Catalyst concentration, vol % (X_3)	1	2	3

Table 2—Box-Behnken experiment design

S. No.	Coded unit			Un-coded unit			Conversion of acrylic acid Y
	x_1	x_2	x_3	X_1	X_2	X_3	
1	-1	-1	0	50	1	2	61.20
2	1	-1	0	70	1	2	63.89
3	-1	1	0	50	3	2	75.25
4	1	1	0	70	3	2	79.01
5	-1	0	-1	50	2	1	47.12
6	1	0	-1	70	2	1	52.14
7	-1	0	1	50	2	3	75.54
8	1	0	1	70	2	3	82.00
9	0	-1	-1	60	1	1	43.20
10	0	1	-1	60	3	1	53.16
11	0	-1	1	60	1	3	69.00
12	0	1	1	60	3	3	80.31
13	0	0	0	60	2	2	76.27
14	0	0	0	60	2	2	76.54
15	0	0	0	60	2	2	74.56

Table 3 — Estimated regression coefficient, t and p value of Box-Behnken design using full quadratic model

Term	Coefficient in coded term	Coefficient in uncoded term	SE coeff	t value	p value	Significance level (1-p)%
Constant	75.79	-83.7	1.06	71.57	0.000	>99
X1	2.241	2.00	0.648	3.46	0.018	>98
X2	6.305	21.49	0.648	9.72	0.000	>99
X3	13.904	51.09	0.648	21.44	0.000	>99
X11	-1.585	-0.01585	0.955	-1.66	0.158	>84
X22	-4.367	-4.367	0.955	-4.58	0.006	>99
X33	-10.005	-10.005	0.955	-10.48	0.000	>99
X12	0.268	0.0268	0.917	0.29	0.782	>21
X13	0.36	0.036	0.917	0.39	0.711	>28
X23	0.338	0.338	0.917	0.37	0.728	>27

Table 4 — Estimated regression coefficient, t and p value of Box-Behnken design using Linear + Square model

Term	Coefficient in coded term	Coefficient in uncoded term	SE coeff	t value	p value	Significance level (1-p)%
Constant	75.79	-92.6	0.868	87.32	0.000	>99
X1	2.241	2.126	0.532	4.22	0.003	>99
X2	6.305	23.77	0.532	11.86	0.000	>99
X3	13.904	53.92	0.532	26.16	0.000	>99
X11	-1.585	-0.01585	0.782	-2.03	0.077	>92
X22	-4.367	-4.367	0.782	-5.58	0.001	>99
X33	-10.005	-10.005	0.782	-12.79	0.000	>99

Results and Discussions

A three-factor three-coded level Box–Behnken design was used to define the response (conversion of acrylic acid). Reaction temperature (T), initial molar ratio of reactants and catalyst concentration (C_c) were independent variables studied to predict the response (conversion of acrylic acid). Independent variables and their levels for the Box–Behnken design used in this study are shown in Table 1 and the experimental results listed in Table 2.

Model fitting and ANOVA

The second-order response polynomial model representing conversion of acrylic acid (Y) can be expressed as a function of reaction temperature (X_1), initial molar ratio of reactants (X_2) and catalyst concentration (X_3). The relationship between responses (Y) and variables were obtained for coded unit for three reaction parameters as follows:

$$Y = 75.79 + 2.241X_1 + 6.305X_2 + 13.904X_3 - 1.585X_1^2 - 4.367X_2^2 - 10.005X_3^2 + 0.268X_1X_2 + 0.360X_1X_3 + 0.338X_2X_3 \quad \text{... (2)}$$

The significance of each coefficient of Eqn. (2) was evaluated by t-values and p-values of each term[8,11,13] as listed in Table 3. The null hypothesis states that the value of the parameter coefficient is zero, if the t-value for each parameter is greater than the critical t-value, therefore, the null hypothesis is rejected[13]. The p-value was also used to define the significance of these parameters for the response. The smallest p-value of regression coefficient corresponded to the most significant effecton the response. The p-value of greater than 0.05 meant the parameter has no significant effectat the 95.0% confidence interval and can be neglected.

From the Table 3 it is observed that regression analyses of full quadratic model based on t and p values interaction terms have minimum influence on the response. So interaction terms were eliminated and linear + square model was employed for further analysis. The coefficients in coded term and uncoded term, t-value and p-value of the analysis are given in Table 4. Table 4 indicates that fitted model accounted for more than 90% of the variations in the experimental data, which were found to be highly significant.

Based on the data in Table 4 and the quadratic polynomial equation model, the relationship between the conversion and process variables could be represented in both uncoded and coded form as Eqn. (3) and Eqn. (4) respectively.

$$Y = -92.6 + 2.126X_1 + 23.77X_2 + 53.92X_3 - 0.01585X_{11} - 4.367X_{22} - 10.005X_{33} \quad \text{... (3)}$$

$$Y = 75.79 + 2.241X_1 + 6.305X_2 + 13.904X_3 - 1.585X_{11} - 4.367X_{22} - 10.005X_{33} \quad \ldots (4)$$

The validity of the selected model was checked by the statistical analysis of variance (ANOVA).

The model ANOVA confirmed the validity of the models. The Fisher variance ratio, the F value is a statistically valid measure to determine how well the factors describe the variation in the mean of data. The F-value indicates that the factors explain adequately the variation in the data about its mean, and the estimated factor effects are real[14]. F value of regression (171.34) is higher than the tabulated value of 3.58 and that of lack of fit (2.28) is less than the tabulated value of 8.94. The ANOVA table (Table 5), which implies that obtained model to predict the response with good accuracy.

Figure 1 shows a comparison between experimental and predicted values of the conversion of acrylic acid, and which indicates that experimental results and predicted values both are in good agreement. The value of R^2 and adjusted R^2 were 0.9922 and 0.9865, which indicated that the obtained model equation could explain 99.22% of the variability.

Effect of process variables on conversion of acrylic acid

Response surfaces can be better understood by contours or/and 3D plots generated from the obtained model to represent the variation of the response with two parameters, holding the other variable constant[4]. The contours and 3D surface plots for response (conversion of acrylic acid) as a function of variables including temperature vs. initial reactants molar ratio, temperature vs. catalyst concentration and initial reactants molar ratio vs. catalyst concentration are shown in Figs. 2-4, respectively. In all of these cases response is plotted against two variables keeping third variable fixed.

Figure 2 describes the comparative effect of reaction temperature vs. initial mole ratio of reactants at catalyst concentration of 2% (vol.). It can be observed that both the variables temperature and mole

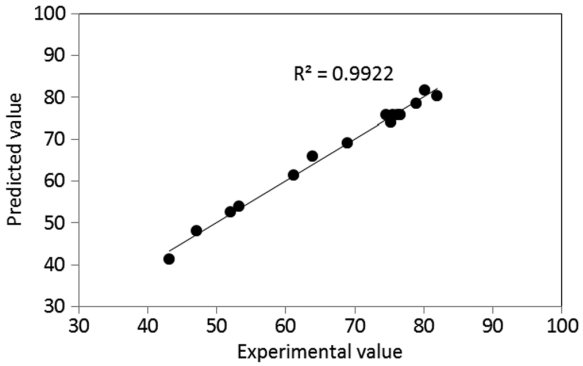

Fig. 1 — The comparison of experimental and predicted values for the conversion of acrylic acid

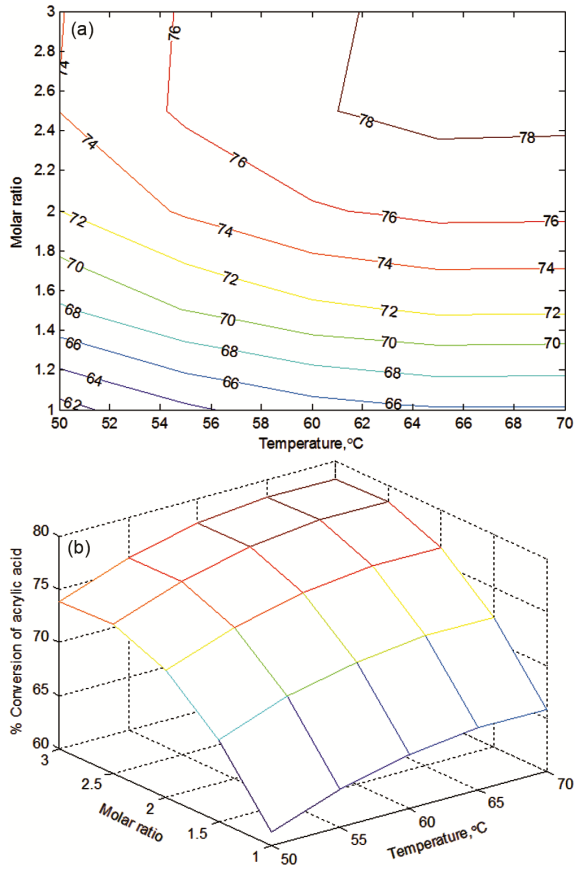

Fig. 2 — Effect of temperature and molar ratio of reactants on conversion of acrylic acid at catalyst concentration of 2%, [a] contour plot [b] surface plot

Table 5 — ANOVA results for percentage conversion

Source	Degree of freedom	Sum of squares	Mean squares	F value	P value
Regression	6	2323.57	387.26	171.34	0.000
Linear	3	1904.72	634.91	280.92	0.000
Square	3	418.84	139.61	61.77	0.000
Error	8	18.08	2.26		
Lack of fit	6	15.78	2.63	2.28	0.336
Pure error	2	2.31	1.15		
Total	14	2341.65			

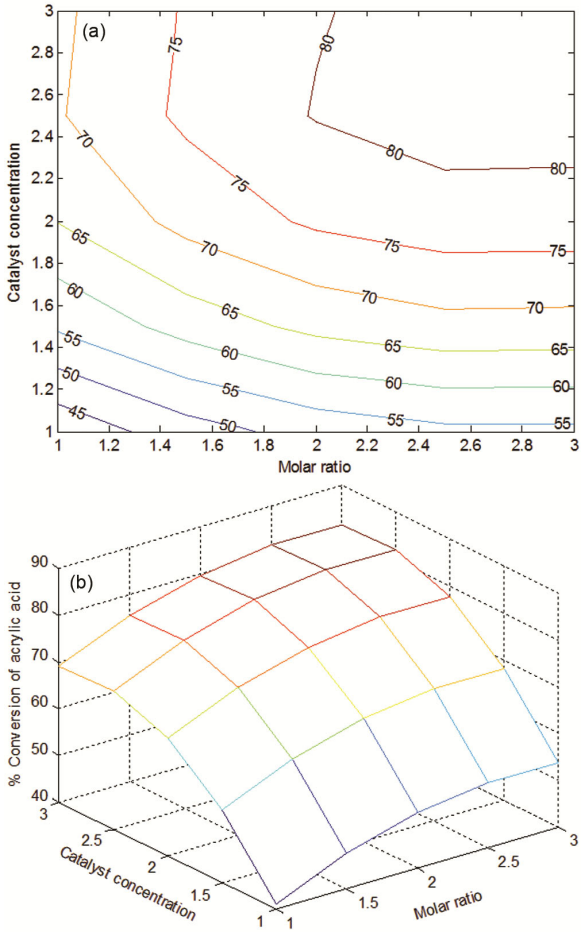

Fig. 3 — Effect of molar ratio of reactantsand catalyst concentration on conversion of acrylic acid at reaction temperature of 60°C, [a] contour plot [b] surface plot

ratio of reactants have significant role in the enhancement of the conversion of acrylic acid. According to Beula and Sai[8] closer contour lines requires the less amount of variables and wide gap between contour lines indicates the demand of the high quantity of variables for enhancement in response. In this study for accomplishment of 74-80% conversion, high temperature and mole ratio are required because there are wide gaps between contour lines.

The variations of the conversion rate of acrylic acid with the molar ratio of ethanol to acrylic acid and catalyst concentration at reaction temperature 60°C were depicted as shown in Fig. 3. Figure 4 shows how temperature and amount of catalyst concentration affect the conversion of acrylic acid at molar ratio of 2 by contour plot and surface plot. It is observed that high amount of catalyst and high reaction temperature favored high conversion rates of acrylic acid.

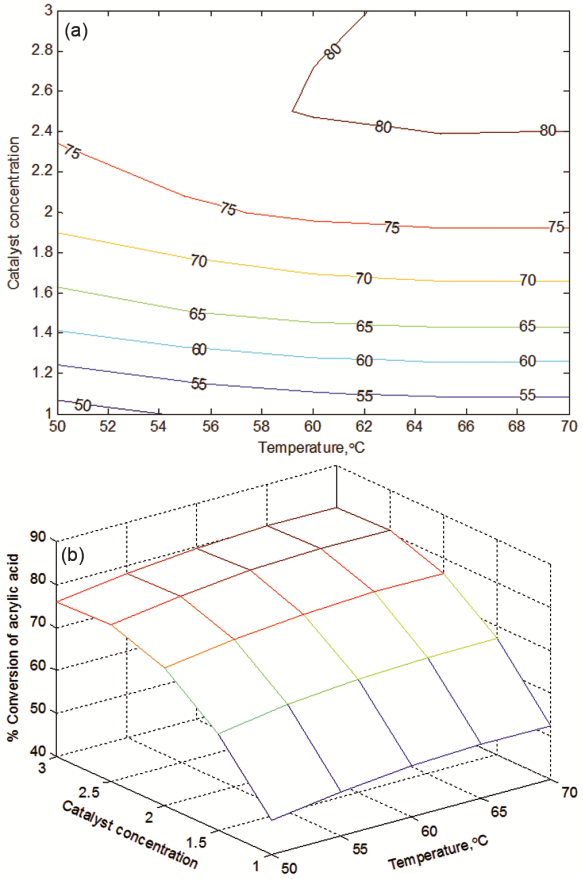

Fig. 4 — Effect of temperature and catalyst concentration on conversion of acrylic acid at initial mole ratio of reactants of 2, [a] contour plot [b] surface plot

Optimization of process parameters for esterification

It is well known that all the response surfaces have the maximum points.The optimum values of the selected variables were obtained using the response optimizer tool of Minitab software. The predicted optimal values to give maximum conversion of acrylic acid were a temperature of 66.97°C, ethanol to acrylic acid molar ratio of 2.7172 and catalyst concentration of 2.697 vol%. Under these optimum conditions the predicted maximum conversion 83.68%. To verify the model expectations, the optimum response variables were also determined by Monte-Carlo optimization technique, according to the following equations[8]:

$$\left[\frac{\partial Y}{\partial X_1}\right]_{X_2X_3} = 0 \quad \ldots (5)$$

$$\left[\frac{\partial Y}{\partial X_2}\right]_{X_3X_1} = 0 \quad \ldots (6)$$

Table 6 — Optimum values of parameters for maximum response

Parameter	Monte-Carlo optimization	Response optimizer
Reaction temperature (°C)	67.07	66.9697
Initial molar ratio (alcohol:acid)	2.7215	2.7172
Catalyst concentration (vol%)	2.6946	2.6970

$$\left[\frac{\partial Y}{\partial X_3}\right]_{X_1X_3} = 0 \quad \ldots (7)$$

Non-linear Eqn. (3) was solved using the above technique produces theoptimal values of the variable for maximum conversion, which is given in Table 6. It is noticed that optimum values of variables obtained from the response optimizer which is in close agreement with Monte –Carlo method.

Conclusion

In this study, the three-level three-factorial Box–Behnken experimental design has been applied. Application of response surface methodology and Box–Behnken design from the point of view esterification reaction is explained. Variables of model investigated in this study are reaction temperature (X_1), ethanol to acrylic acid molar ratio (X_2) and catalyst concentration (X_3) for conversion of acrylic acid. The mathematical model equations are derived for response (conversion of acrylic acid) using setsof experimental data and a software package (MINITAB).The effects of the variables on response (conversion of acrylic acid) are represented in as the contour plot and 3D response surface graphs. The predicted values of the process variables for achieving maximum conversion obtained by response surface optimizer and the results are in good agreement with the Monte-Carlo technique. Response surface methodology and Box–Behnken design can be effectively employed for modeling of chemical reaction system and it is an efficient way to obtain the optimum conditions of parameters in a short duration and with the least number of experiments.

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