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Research paper

Kinetic Studies for the Esterification Process with Ionic Resin Catalyst: Optimization using Response Surface Methodology

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Abstract

The esterification reaction between acetic acid (AA) and methanol was studied in a batch reactor with solid catalyst. The temperature range applied was 323.15 K to 353.15 K. Experiments with feed mole ratios ranging from 1:1 to 1:4 were conducted. The influence of temperature, catalyst loading, initial reactant mole ratio, and the reaction time on AA conversion has been investigated. To design experiments, central composite method of response surface methodology (RSM) has been used for the esterification process. A regression model is developed for AA conversion. The model correlates the acetic acid conversion and four significant independent variables. The four most significant variables are temperature, mole ratio of reactants, catalyst loading and reaction time. The statistical test shows that the model is well fitted with experimental data. It is observed from present investigation that model is predicting the experimental data at optimum conditions for acetic acid conversion.

Keywords: *Esterification, Kinetics, Solid Ionic Resin Catalyst, Response Surface Method.*

1. Introduction

Methyl acetate produced from an esterification reaction between an acetic acid and methanol is crucial chemical component in applications such as solvent in adhesives, paints, printing inks, delicious odors, nail polish removers [1]. This reaction is sluggish without catalyst even at elevated temperatures [2]. Generally, the rate of reaction can be improved by adding catalyst. The reactions are carried out in presence of different catalysts, either homogeneous or heterogeneous. Furthermore, the heterogeneous catalysts are more superior to homogeneous catalyst, because it will separate form post reaction mixture without adding another separation unit as required for homogeneous catalyst, high selectivity of desired product and less corrosion [1]. Due to these advantages, the ion-exchange catalysts are more preferable [3].

The rates of esterification reaction with both alcoholic as well as non-hydroxylic medium have studied in one of the earlier study [4]. The authors developed kinetic model by the assumption of theory of molecular statistics for this reaction. Ronnback et al. [5] have studied esterification of acetic acid and methanol by using H_2SO_4 catalyst. They observed the formation of by product in the reaction of esterification of acetic acid with methanol. In side reaction, Methanol reacts with the hydrogen iodide catalyst and forms a methyl iodide is one of the by product.

A kinetic equation for esterification reaction proposed by Agreda et al.[6] by using H_2SO_4 as catalyst. The proposed rate equation was nonlinear as function of catalyst concentration. Chakrabarthi and Sharma [7] have presented a comprehensive review on cationic ion-exchange resins for different esterification reactions. A variety of the chemical reactions catalyzed by ion-exchange resins were discussed. Song et al.[8] have described the residue curve maps and the heterogeneous kinetics for the synthesis of methyl acetate. They conducted experiments using a batch reactor and varied temperatures and concentrations of catalyst. Adsorption experiments were done to find the adsorption constants. Popken et al. [2] have investigated the kinetics along with chemical equilibrium for this reaction both without catalyst and with Amberlyst 15.

Kirbaslar et al. [8] have investigated the catalytic esterification of acetic acid with methanol by using Amberlyst 15 as heterogeneous catalyst in the temperature range of 318 K-338 K and at atmospheric pressure. Yu et al.[9] have conducted the experiments for an esterification of AA and methanol as well as methyl acetate hydrolysis in a packed bed reactor in presence of the Amberlyst 15 catalyst. Ehteshami et al.[10] have studied the kinetics and chemical equilibrium for the hydrolysis of the methyl acetate in the batch reactor using Amberlyst 15 catalyst.

An investigation of kinetics of esterification of AA with methanol in liquid state (21-60 ^{0}C) and gas state (100-140 ^{0}C) experiments performed by using catalyst of tungstated zirconia (WZ) [11]. In our earlier work, the kinetics of methyl acetate formation in presence of H_2SO_4 [12] and solid catalysts (Indion 190 and Indion 180) [13-15] was studied.

The objectives of present investigation is to establish the relation of acetic acid conversion as a function of operating conditions, and also the optimal operating conditions for the esterification process using a batch reactor in the presence of the Amberlyst 16 wet solid acid catalyst. Central Composite method of Response Surface Methodology is used to design the experimental combinations for data generation. A statistical mathematical model has been developed by using generated data. This model represents the four significant parameters for acetic acid conversion. The Optimum model parameters estimated by the ANOVA analysis.

2. Experiment

2.1. Chemicals

High purity of methanol as well as Acetic acid were supplied by SD Fine Chemicals Ltd. (Mumbai, India).

2.2. Solid Acid Catalyst

Amberlyst 16, which is resin solid catalyst was supplied by Rohm &Hass, Mumbai. Using hot air oven, the solid catalyst was dried at 90^0C to remove the maximum moisture content.

3. Statistical Methods

3.1. Response Surface Methodology

For the production of methyl acetate in terms of acetic acid conversion, RSM is applied and used for the process parameters optimization. The most significant process variables on conversion of AA are determined by using a Central Composite Design (CCD) method [16-18]. The most significant process variables are reaction temperature (X_1), catalyst loading (X_2), mole ratio of AA to methanol (X_3) and reaction time (X_4). The experiments were carried out to determine the ranges of the reaction temperature, catalyst loading, AA/methanol mole ratio, and reaction time [19]. The table 1 shows the operating conditions which are feasible for experimentation.

Table 1: Experimental design of conversion of acetic acid in an isothermal batch reactor.

S.No.	Variable	Low value	High value
1	Reaction temperature (K)	323.15	353.15
2	Catalyst amount (g/ cc)	0.01	0.05
3	AA/methanol mole ratio	1:1	1:4
4	Reaction time	60 min	300 min

In present investigation, the number of parameters (m) is four. The number of experiments is thirty based on (2^m+2m+6) using CCD method. The following Eq. (1) is used for the coded values

$$X_i = \frac{W_i - W_{i0}}{\Delta W_i} \quad (1)$$

Where W_i, X_i, W_{i0} and ΔW_i are real value, the coded value, center point real value and step increment of W of independent variable respectively. Hence the obtained coded values always lie in between -1 and +1.

The relation between response to the variables using linear and quadratic terms is given by Eq. (2)

$$\beta = \alpha_0 + \sum_{j=1}^{k} \alpha_j x_j + \sum_{j=1}^{k} \alpha_{jj} x_j^2 + \sum_{i} \sum_{<j=2}^{k} \alpha_{ij} x_i x_j + e_i \quad (2)$$

β is the response, x_i and x_j are the independent factors, α_0 is the constant coefficient, α_j, α_{jj}, α_{ij} are linear, quadratic and interaction effect coefficients and e_i is the error.

$$R^2 = 1 - \frac{SS_{resid}}{\left(SS_{model} + SS_{resid}\right)} \quad (3)$$

$$R^2_{adj} = 1 - \frac{SS_{resd} \big/ DF_{resid}}{\left(SS_{model} + SS_{resid}\right) \big/ \left(DF_{model} + DF_{resid}\right)} \quad (4)$$

$$\text{Adequate precision} = \frac{Max(\hat{Y}) - Min(\hat{Y})}{\sqrt{\bar{V}\hat{Y}}} \quad (5)$$

$$\bar{V}(\hat{Y}) = \frac{1}{n}\sum_{1}^{n} V((\hat{Y}) = \frac{P\sigma^2}{n} \quad (6)$$

In equation (3) and (4), R^2 and R^2_{adj} values gives the fitting quality of polynomial equation i.e, higher the R^2 values, indicates the better quality of the model. The statistical consequence is checked by using Eq. (5) and Eq. (6) and also by F and P-values[16].

In equation (4), (5) and (6) where, DF, P, SS, σ^2 and n are the degrees of freedom, parameters number, squares sum, the residuals mean square and number of experiments respectively. Design Expert 9.0.3.1 (trail version) is used to study response surface curves for experimental data.

3.2. Experimental Set Up

The esterification reaction was conducted in a 500 ml batch reactor. The reaction was carried out using rota mantle, in which the heating as well as stirrer speed were controlled by adjusting the knobs. The speed of stirrer was maintained between 240rpm-640rpm. The reactor is connected with condenser to condense the vapours. Simultaneously, the heating is increased slowly to adjust the desired temperature. A thermometer was used to measure temperature of mixture.

3.2.1. Experimental procedure & Analysis

One mole of AA (acetic acid) and one mole of methanol were added in a batch reactor. The reaction mixture is heated to a desired temperature then added the catalyst. Immediately the reaction time is noted. Samples are collected from reaction mixture for uniform time interval and concentration of acetic acid was measured using standard NaOH solution using phenolphthalein as the indicator. The reaction is carried out up to steady state, where there is no change in acetic acid concentration.

4. Experimental Results

4.1. Effect of Reaction Temperature

Fig.1 shows the plot of AA conversion as a function of time at various temperatures and the catalyst concentration of 0.025 g cc^{-1}. If the temperature enhanced to 5-10^0C there is an incremental change in the reaction rate as well as the conversion of the acid. So the reaction can be controlled by temperature as observed in the figure 1.

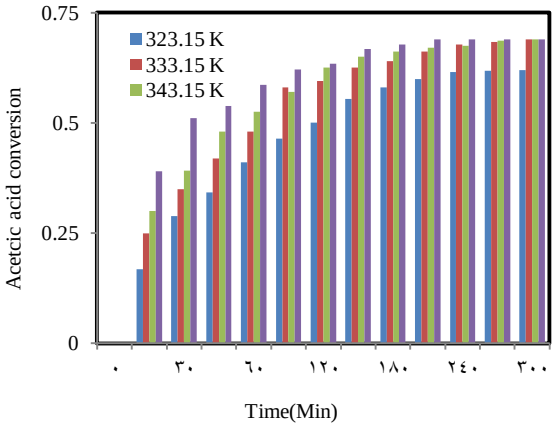


Fig. 1: AA conversion vs temperatures for 0.025 g/cc loading.

4.2. Effect of Catalyst Loading

To understand the effect of catalyst loading on conversation of acetic acid, catalyst concentration is varied from 0.01 g cc^{-1} to 0.05 g cc^{-1} as shown in Figure 2. It is clear that, as the Amberlyst 16 loading increases reaction rate increases due to high catalyst surface availability which increases the conversion of acetic acid.

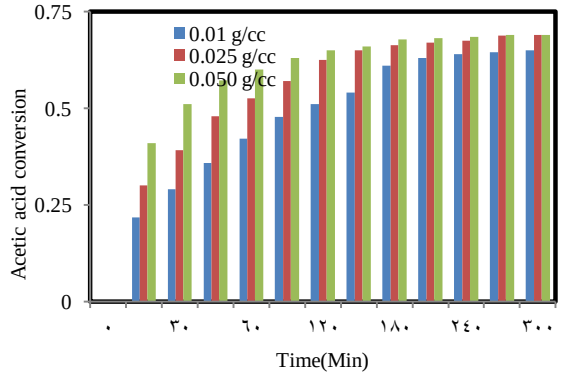


Fig. 2 AA conversion for 0.01- 0.05 g/cc catalyst loadings and T= 343.15 K.

4.3. Effect of AA to Methanol Mole Ratio

The initial AA to methanol mole ratio increased from 1:1 to 1:4. Figure 3 shows effect of initial molar ratio on conversion of AA as a function of time. From Figure 3, it can be concluded that the conversion of AA increases with increase in mole ratio. When the mole ratio increasing from 1:1 to 1:4, the conversion of AA increases from 68.8% to 92.7%.

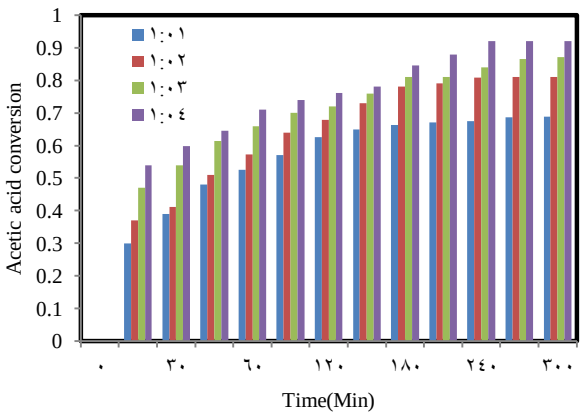


Fig. 3 Conversion of acetic acid at various initial mole ratios of acetic acid and methanol.

5. Regression Model and Analysis

The conversion of AA (response) is correlated with the four independent parameters with polynomial Eq. (2). The best model fit for the acetic acid conversion (Y) is given in Eq. (7)

$$Y= 0.88+0.047\times X_1+0.018\times X_2-0.027\times X_3+0.046\times X_4-0.016\times X_1X_2-0.019\times X_1X_3-0.019\times X_1X_4 -0.0067\times X_2X_3-0.0069\times X_2X_4-0.017\times X_3X_4-0.0095\times X_1^2+0.030\times X_2^2-0.094\times X_3^2-0.013\times X_4^2 \quad (7)$$

X_1 is reaction temperature, X_2 is catalyst loading, X_3 is AA/ methanol mole ratio and X_4 is reaction time. ANOVA analysis of this model is given in Table 2. The accuracy of the model verified with experimental results by using F and P - values in addition to lack of fit [20]. From the ANOVA analysis shown in table 2, for higher F – value represents that present model (quadratic) is well fitted and also individual parameter interaction also verified. Smaller P-value implies that smaller the risk of falsely rejecting of model.

From table it can be seen that terms are linear i.e., reaction temperature, acetic acid/methanol ratio, reaction time and catalyst amount have large effect on the acetic acid conversion because of large F-values. If the probability value is less than 0.0001, indicates that there is only 0.01% chance. The quadratic terms of mole ratio have high F value and very low p-value as given in table 2. Thus the effect of the mole ratio on the acetic acid conversion is strong. The significant binary terms given as in between the reaction temperature and mole ratio(X_1X_3), reaction temperature and reaction time(X_1X_4), mole ratio and reaction time (X_3X_4) gives interaction of these binary variables. Null value of lack of fit indicates in significant relative to pure error [21]. The model fitting is evaluated by the regression equation and coefficient of determination and it found to be satisfactory.

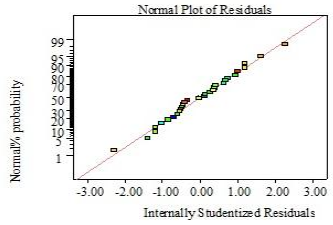
The residuals distribution analyzed for evaluating the accuracy of the model by determining the normal distribution. The deviations of residual values between the actual and predicted values are expected to follow the normal distribution when experimental errors are random [24]. The residuals have normalized as a function of standard deviations and fitting of normal distribution function with studentized residuals. Figure 4a shows the studentized residual predicted by the normal distribution as a function of the experimental studentized residual. Plotted values falls under a straight line which gives an information of studentized residuals follows exactly normal distribution. If, the studentized residuals and the normal distributions are not linear, then the curve forms a S shape [25].

The studentized residuals values are plotted against the predicted acetic acid conversion is shown in Figure 4 b. The plotted values are random scatter may indicates that changing in original phenomena is not agreement with the response value [25]. If the plot is funnel shape, then the variation in the original values is follows a linear relation with the mean value of response. The high values of random scatter of the residuals shows the model is good.

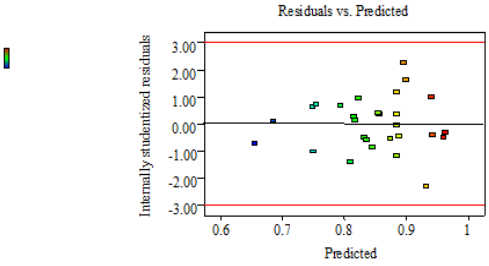
Actual values estimated from the experimental data and the predicted acetic acid conversions obtained from equation (8) are plotted as shown in figure 4c. R^2 indicates the amount of deviation to mean value as given by model. The adjusted R^2 value as given in Eq. (4) is not increase with the increase in model parameters. The difference between R^2 values of actual and adjusted is large, the insignificant terms involved into the model [17,18]. R^2 and adjusted R^2 values for the present model are 0.9782 and 0.958 respectively and both are good agreement which indicates that the model does not have the insignificant terms.

The outlier plot for the data of AA conversion is sown in figure 4 d. If the larger the residuals value, then an outlier diagram shows residual magnitude for every run. When threshold value is 3 standard variations are employed so that maximum residuals are lie in between ±3.0%. if outlier values are beyond the above limit

may gives the error in both experimental and model. From the graph, it observed that no outlier beyond the limits.



(a)



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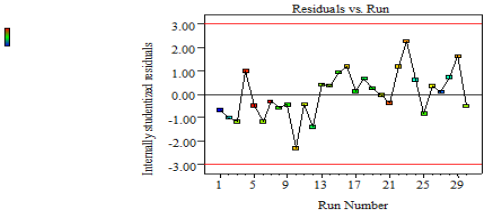
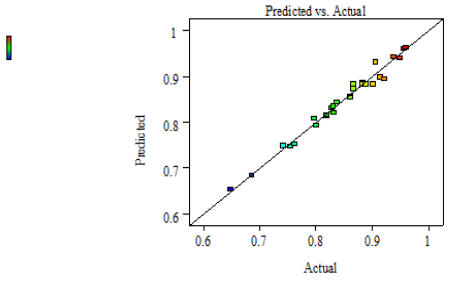


(c)



(d)

Fig. 4: a) Normal percentage of probability as a function of studentized residual , b) studentized residuals as function of predicted response c) actual values versus predicted values d) t plot for outlier.

5.1. Effect of the Parameters on Acetic Acid Conversion

The analysis of statistics to experimental data is revealed that reaction temperature, molar ratio of acetic acid to methanol, catalyst loading and reaction time are the most influencing parameters which have greatest impact on the acetic acid conversion in the batch reactor. As shown in Table 2, temperature, acetic acid/methanol ratio, catalyst loading or amount and reaction time have high F-value along with small P-value gives the most influencing parameters on acetic acid conversion.

The mole ratio has positive influence on AA conversion as shown in table 2, because the low P value (<0.0001) and the high F-value (63.14), indicates its significant effect on the AA conversion. Reaction temperature is the next important parameter which have significant effect on the AA conversion, since it has higher F-value (219.56) and low P-value (< 0.0001), indicates that dependent variable influenced by temperature very high. The effect of other two variables that is the time and mole ratio. It is clear from Table-2; F-values are 152.56 and 50.41 and P-values are less than 0.0001.

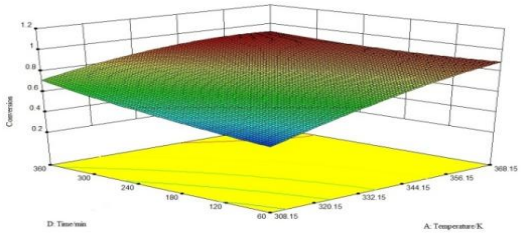


Fig.5: The effect of reaction temperature and reaction time on AA conversion for acetic acid/methanol mole ratio of unity and catalyst amount of 0.025 g/cc.

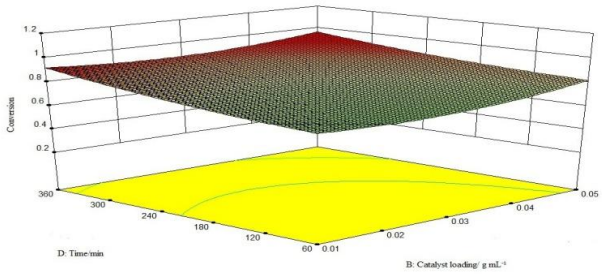


Fig.6: The effect of the catalyst amount and reaction time on AA conversion for acetic acid/methanol mole ratio of unity and T= 343.15 K.

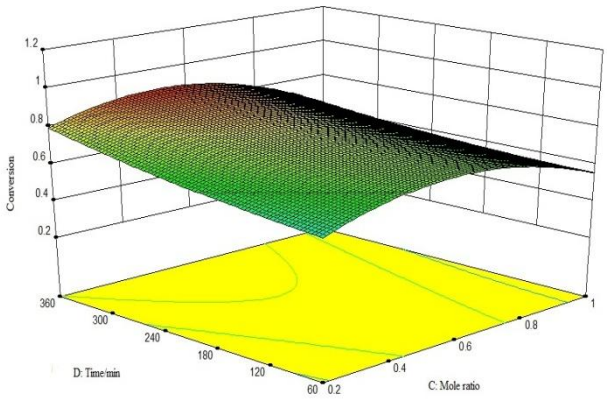


Fig. 7: The effect of the mole ratio and reaction time on acetic acid conversion for acetic acid to catalyst amount of 0.025 g/cc and T= 343.15 K.

The RSM plot for the acetic acid conversion as shown in Fig. 5 by varying reaction temperature and time keeping other conditions constant at namely: catalyst amount 0.025 g cc^{-1} and molar ratio of acetic acid to methanol 1:4. The maximum acetic acid conversion, 92.6%, is obtained at a reaction temperature of 338.15 K, and the reaction time of 240 min. Maximum conversion of acid by experiment is 92.1% , which closest to the predicted value. Figure 6 shows response surface curve for acid conversion by changing the catalyst amount and time. The experimental conditions are the reaction temperature of 338.15 K and mole ratio of 1:4. The predicted highest conversion of acetic acid is about 92.2%. Figure 7 shows response curve for acetic acid conversion by the mole ratio and time. The experimental

conditions are: the reaction temperature is 338.15 K and catalyst amount 0.025 g cc^{-1}. The predicted highest acid conversion is about 92.13%.

6. Conclusion

The reaction of esterification process between acetic acid with methanol using Amberlyst 16 wet in a well mixed batch reactor has been studied under the conditions of the temperature of 323.15 K- 353.15 K and catalyst amount of 0.01 g cc^{-1} to 0.05 g cc^{-1} at feed mole ratios ranging from 1:1 to 1:4. Central composite design of RSM method has applied for optimization of experimental variables. From that optimized parameters a linear equation as unction these parameters have developed for acetic acid conversion. The four most significant variables are temperature, mole ratio, catalyst loading and reaction time. By the statistical tests, it is found that model represents the experimental data very good. The model and experimental data are good agreement.

Table 2: ANOVA analysis

	Sum of		Mean	F	p-value	
Source	Squares	df	Square	Value	Prob > F	
Model	0.16	14	0.012	48.07	< 0.0001	significant
A-temperature	0.053	1	0.053	219.56	< 0.0001	
B-catalyst amount	5.989E-003	1	5.989E-003	24.60	0.0002	
C-mole ratio	0.012	1	0.012	50.41	< 0.0001	
D-time	0.037	1	0.037	152.56	< 0.0001	
AB	4.106E-003	1	4.106E-003	16.86	0.0009	
AC	5.912E-003	1	5.912E-003	24.28	0.0002	
AD	5.574E-003	1	5.574E-003	22.89	0.0002	
BC	5.908E-004	1	5.908E-004	2.43	0.1402	
BD	7.833E-004	1	7.833E-004	3.22	0.0931	
CD	4.661E-003	1	4.661E-003	19.14	0.0005	
A^2	2.564E-003	1	2.564E-003	10.53	0.0054	
B^2	2.142E-003	1	2.142E-003	8.80	0.0096	
C^2	0.015	1	0.015	63.14	< 0.0001	
D^2	3.144E-004	1	3.144E-004	1.29	0.2737	
Residual	3.652E-003	15	2.435E-004			
Lack of Fit	2.398E-003	10	2.398E-004	0.96	0.5575	not significant
Pure Error	1.255E-003	5	2.510E-004			
Cor Total	0.17	29				

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