



# Kinetic and Thermodynamic Modeling of Esterification of 2- Propanol and N- Butyric Acid

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## KEYWORDS

Batch kinetics, Butyric acid conversion, Catalyst, Esterification, Rate constant.

## ABSTRACT:

Experiments are conducted to obtain kinetic data of esterification of 2- propanol and n-butyric acid in a stirred and temperature controlled batch reaction vessel. Sulphuric acid is chosen as catalyst in the present study. The effect of different variables on butyric acid conversion is studied in the present work. Molar ratio of reactants (acid to alcohol) is varied from 0.5 to 1.5. Catalyst concentration is changed from 1.0 to 3.0 weight percent. The reaction temperatures chosen are 50°C, 60°C and 70°C. The reaction products are analyzed using TLC, FTIR and NMR techniques in order to know the occurrence of any side reactions. The reaction obeyed second order, and the rate constants are evaluated using integral method of analysis. Correlation equations in terms of operating parameters for the rate constants are obtained by employing least squares regression analysis. The kinetic data are compared with the five thermodynamic models, viz., UNIQUAC, UNIFAC, WILSON, modified UNIFAC and NRTL. The corresponding activity coefficients are estimated using ASPEN Plus software.

## 1. Introduction

Esters are most widely used organic chemical compounds in process and allied industries. Esterification is usually a reversible reaction and the conversion of the reactants can be enhanced by using catalyst addition. Since the presence of catalyst improves the yield of products, both homogeneous and heterogeneous catalysts can be employed.

Although numerous studies are reported on esterification of acetic acid with different alcohols, to the best of the knowledge of the author, the studies available on esterification of 2-propanol with n- butyric acid are scarce.

In the present study, experiments are carried out on esterification of 2-propanol with n- butyric acid in a stirred and temperature controlled batch reactor, using sulphuric acid as a homogeneous catalyst. The effect of

different parameters on reactant conversion and rate constant is investigated in the present study using a full factorial design of experiments. By regression analysis the rate constant is correlated as a function of catalyst concentration, mole ratio and temperature[1]. Analysis of the products was carried out using TLC, FTIR and NMR spectroscopy. Chemical reactions always have a tendency to approach equilibrium. The dynamics towards equilibrium are well related to the chemical reaction of non- ideal reaction mixtures, in which activity coefficient in the rate equation had a significant role[2-10]. In the present study, UNIFAC, UNIQUAC, Wilson, Modified UNIFAC and NRTL models were employed to obtain the activity coefficients of the present system using ASPEN Plus software.

The chemical reaction of the present study is shown in eqn(1). The experimental conditions were shown in the Table 1 for the variables that influence the reaction.

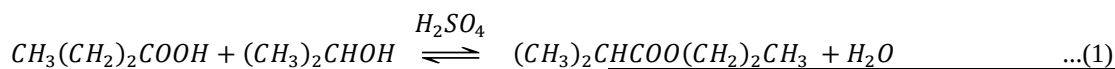


Table 1. The experimental variables with the conditions that influence the reaction.

| S.No | Variable               | Conditions  |
|------|------------------------|-------------|
| 1    | Catalyst concentration | 1, 2, 3 wt% |

|   |             |               |
|---|-------------|---------------|
| 2 | Mole ratio  | 0.5, 1.0, 1.5 |
| 3 | Temperature | 50, 60, 70°C  |



## 2. Materials and methods

N-butyric acid, 2-propanol, sulphuric acid, sodium hydroxide, oxalic acid and phenolphthalein were the chemicals used in this study. The experiments were carried out in 500 ml three neck round-bottom flask placed on a magnetic hot plate stirrer with temperature control ( $\pm 0.2^\circ\text{C}$ ) and stirring speed control (0–1500 rpm). Accurately measured quantities of the butyric acid and 2-propanol were taken separately in two conical flasks. Accurate quantity of sulphuric acid catalyst was added to the flask containing the acid. Now, 2-propanol in the flask was transferred to the reaction vessel and the temperature is increased to the required temperature. The stirring speed was maintained at 200 rpm. The conical flask with carboxylic acid and catalyst mixture was heated separately to the same temperature. Once the desired temperature was reached, the mixture of butyric acid and catalyst was transferred to the reaction flask containing 2-propanol. Thus the resulting mixture of required mole ratio is obtained. At zero time, 2 ml of sample was drawn using pipette into the conical flask containing 20 ml of 1.0 N sodium hydroxide and 20 ml of distilled water. The samples were drawn at regular time intervals and the concentration of unreacted butyric acid was estimated using standard titration analysis. Equilibrium samples were taken corresponding to a reaction time of 24 hours. Several experiments were carried out at temperatures  $50^\circ\text{C}$ ,  $60^\circ\text{C}$  and  $70^\circ\text{C}$ ; the mole ratio of 0.5, 1.0 and 1.5; catalyst concentrations of 1.0, 2.0 and 3.0 weight percent.

The unreacted carboxylic acid concentration was determined by titration with standard solution of 1.0 N sodium hydroxide against 0.5 N oxalic acid using phenolphthalein indicator. The sulphuric acid catalyst equivalent titer was estimated by taking equal amounts of distilled water for butyric acid and 2-propanol in a separate conical flask and approximate quantity of sulphuric acid catalyst was added. The conversion of the butyric acid in the experiment was determined. The effect of different independent variables such as mole ratio of acid to alcohol, catalyst concentration and temperatures were evaluated using full factorial design of experiments.

## 3. Results and Discussion

### 3.1 Chemical Analysis

The reaction products obtained in the present study were subjected to chemical analysis using TLC, FTIR and NMR methods and ascertained that there are no side reactions and only the anticipated ester is formed.

### 3.2 Effect of operating parameters

The effect of catalyst concentration at different mole ratios and temperatures was investigated and the data was obtained as butyric acid conversion versus time. Fig.1 shows the conversion of butyric acid with time during esterification with the mole ratio of acid to alcohol as 1.0 and temperature being  $60^\circ\text{C}$  respectively. It was seen that with increase in the catalyst concentration, the conversion of butyric acid also increased.

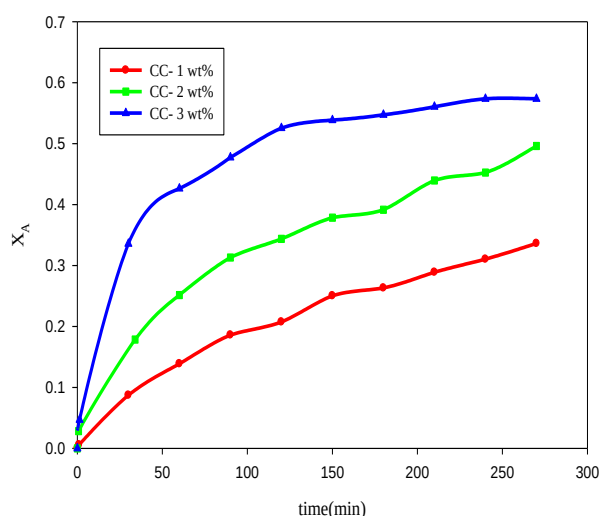


Fig.1. Effect of catalyst concentration on conversion {MR = 1.0; T =  $60^\circ\text{C}$ }

The effect of mole ratio on butyric acid concentration was investigated at different temperatures and catalyst concentrations. The conversion of butyric acid against time was shown in Fig.2 for a catalyst concentration of 3.0 wt% at a temperature of  $70^\circ\text{C}$ . The conversion obtained was maxima in the case of 0.5 mole ratio and got decreased with increasing mole ratio.

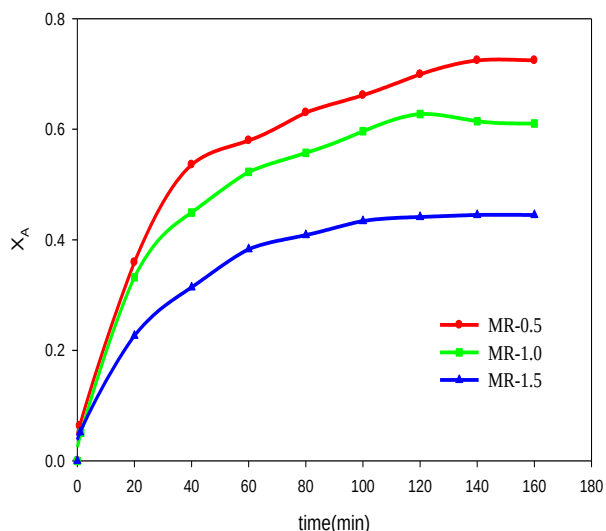


Fig.2. Effect of mole ratio on conversion { $T = 70^{\circ}\text{C}$ ;  $\text{CC} = 3.0 \text{ wt\%}$ }

The effect of temperature on the conversion of butyric acid during its esterification with 2-propanol was studied by conducting the reaction at three different temperatures 50, 60 and  $70^{\circ}\text{C}$ . The data presented in Fig.3 correspond to an acid-to-alcohol ratio of 1.0 and a catalyst loading of 3.0 wt%. The conversion increased with increase in temperature.

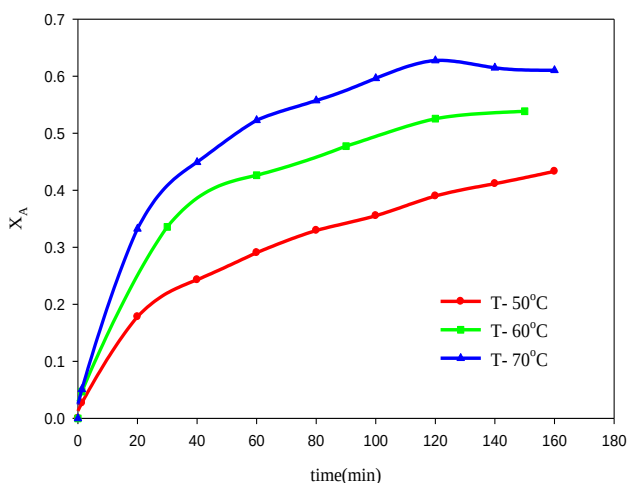


Fig.3. Effect of temperature on conversion { $\text{MR} = 1.0$ ;  $\text{CC} = 3.0 \text{ wt\%}$ }

The esterification reaction usually followed second order kinetics as revealed from previous works[3]. To determine rate constant, for the second order reactions, following integral analysis, the parameters to be taken on ordinate and abscissa are given in Table 2. In the present study also, the data obeyed second order reaction kinetics which is seen from the plots of Figs. 4, 5 and 6.

Table 2. Parameters by integral analysis

| For the condition | Ordinate               | Abcissa | Slope          |
|-------------------|------------------------|---------|----------------|
| $\text{MR}=1$     | $\ln((M-X_A)/(1-X_A))$ | Time    | $C_{A0}(M-1)k$ |
| $\text{MR}\neq 1$ | $1/C_A$                | Time    | $K$            |

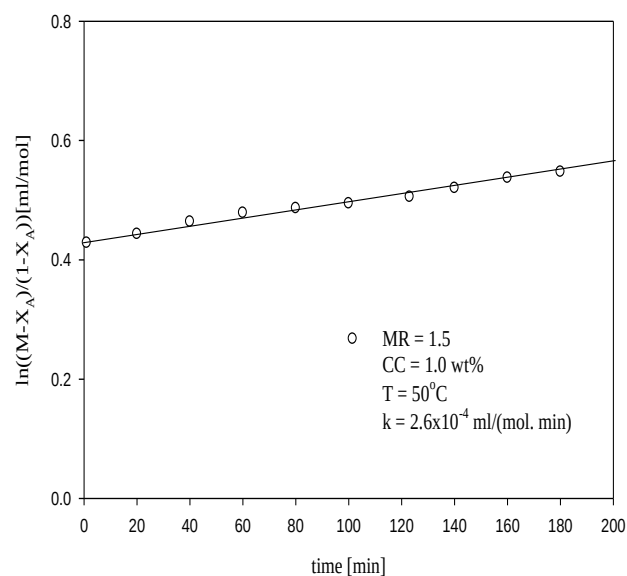


Fig.4. Plot for second order rate constant { $\text{MR} = 1.5$ ;  $\text{CC} = 1.0 \text{ wt\%}$ ;  $T = 50^{\circ}\text{C}$ }

### 3.3. Kinetic Interpretation from batch reactor data

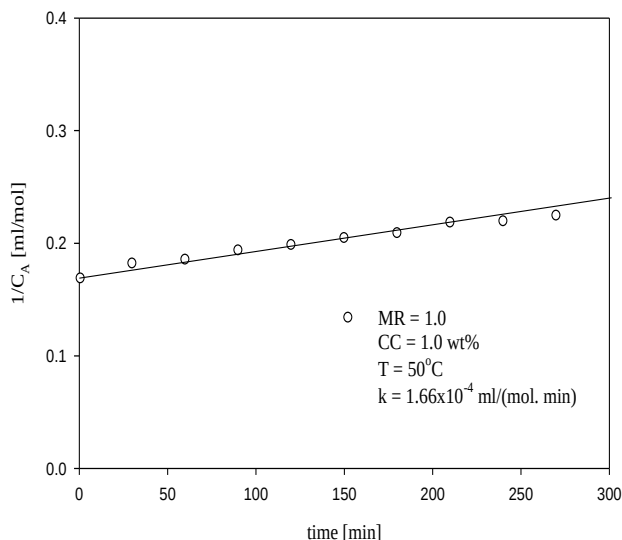


Fig.5. Plot for second order rate constant {MR = 1.0; CC = 1.0 wt%; T = 50°C}

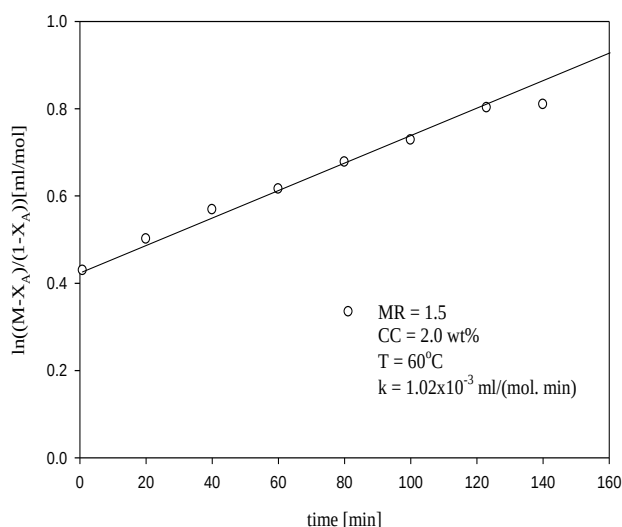


Fig.6. Plot for second order rate constant {MR = 1.5; CC = 2.0 wt%; T = 60°C}

Earlier, investigators analyzed the esterification reactions as a one way reaction. Therefore, in the present study also, the authors analyzed the reaction in similar lines by obtaining rate constant by integral analysis. The data belonging to all 30 such experimental runs were processed in a similar way and then the rate constant data were subjected to regression analysis to obtain following correlation equation.

$$k = 0.3784 \times 10^5 (\text{MR})^{0.2180} (\text{CC})^{1.278} e^{-5826/T} \quad \dots(2)$$

Average deviation = 7.214 percent

Standard deviation = 9.032 percent

A few investigators[2] interpreted the data by considering the esterification reaction as a reversible one. Therefore, an attempt is made by the authors in this direction. The mathematical treatment is provided here under.

In general, a second order reversible can be written as:



For the second- order reversible reaction the rate equation is:

$$-r_A = -\frac{dC_A}{dt} = C_{A0} \frac{dX_A}{dt} = K_1 C_A C_B - K_2 C_C C_D \quad \dots (4)$$

$$-\frac{dC_A}{dt} = C_{A0} \frac{dX_A}{dt} \quad \dots (5)$$

#### Case-1: $C_{A0} = C_{B0}$ , and $C_{C0} = C_{D0} = 0$

$$\ln \left[ \frac{X_{Ae} - (2X_{Ae} - 1)X_A}{(X_{Ae} - X_A)} \right] = 2K_1 \left( \frac{1}{X_{Ae}} - 1 \right) C_{A0} t \quad \dots (6)$$

which is the equation for second order reversible reaction for same initial concentrations of reactants A and B.

#### Case-2: $C_{A0} \neq C_{B0}$ and $C_{C0} = C_{D0} = 0$

$$\ln \left[ \frac{[MX_{Ae} + X_A(M - (M+1)X_{Ae})]}{M(X_{Ae} - X_A)} \right] = K_1 C_{A0} t \left[ \frac{2M}{X_{Ae}} - (M+1) \right] \quad \dots (7)$$

which is the equation for second order reversible reaction for different initial concentrations of reactants A and B. However, Beula and Sai[2] presented the following equation for the same case.

$$-\ln \left[ \frac{\{2X_A[(M+1)X_{Ae} - M] - [(M+1)X_{Ae}^2 - X_{Ae}Z]\} \{(M+1)X_{Ae}^2 + X_{Ae}Z\}}{\{2X_A[(M+1)X_{Ae} - M] - [(M+1)X_{Ae}^2 + X_{Ae}Z]\} \{(M+1)X_{Ae}^2 - X_{Ae}Z\}} \right] = \frac{K_1 Z C_{A0} t}{X_{Ae}} \quad \dots(8)$$

Where

$$Z = \sqrt{[(M+1)^2 X_{Ae}^2 - 4M(MX_{Ae} + X_{Ae} - M)]} \quad \dots(9)$$



Now this equation (8) can be reduced to the equation derived in the present study, i.e., equation (7).

$$\ln \frac{\{MX_{Ae} + X_A[M - (M+1)X_{Ae}]\}}{\{M(X_A - X_{Ae})\}} = \left[ \frac{2M}{X_{Ae}} - (M+1) \right] K_1 C_{A0} t \quad \dots (10)$$

Equation (10) is the simplified form of equation (8) which was employed in the present esterification studies and interpreted the kinetics of the given second order reaction.

$$Y = \ln \frac{\{MX_{Ae} + X_A[M - (M+1)X_{Ae}]\}}{\{M(X_A - X_{Ae})\}} \quad \dots (11)$$

From the equation (10) and (11), the graphs were plotted for Y vs t for different catalyst concentrations, temperatures and mole ratio for the present system.

From the plots of Y vs t rate constant for the forward reaction  $k_1$  is obtained. These graphs were shown in Figs. 7, 8 and 9 respectively.

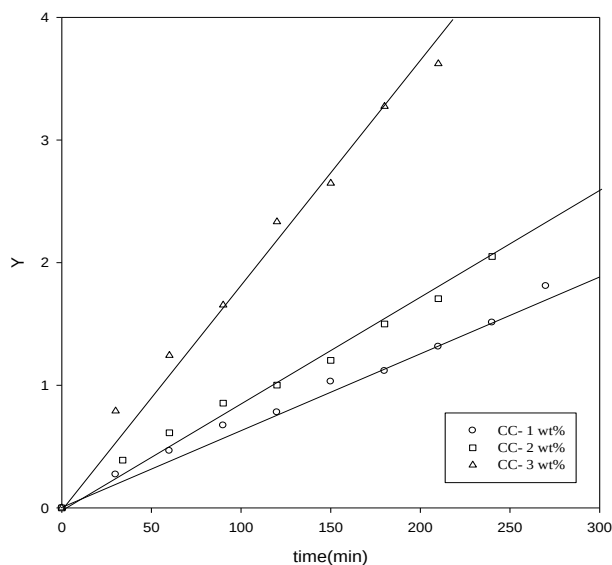


Fig. 7. Test of the rate equation {MR=1.0; T=60°C}

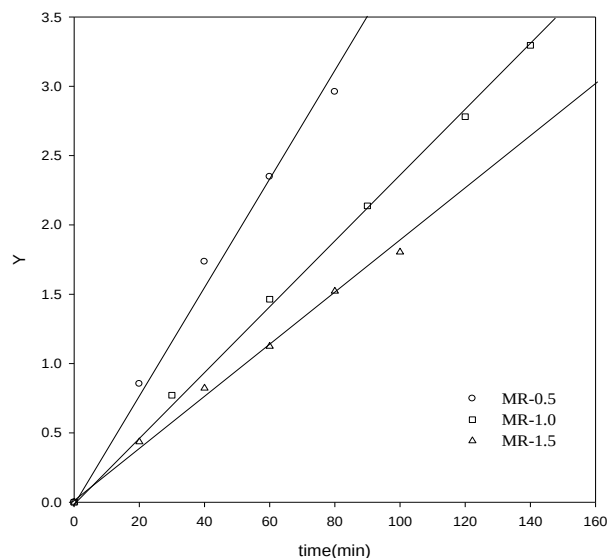


Fig. 8. Test of the rate equation {CC=1.0 wt%; T=70°C}

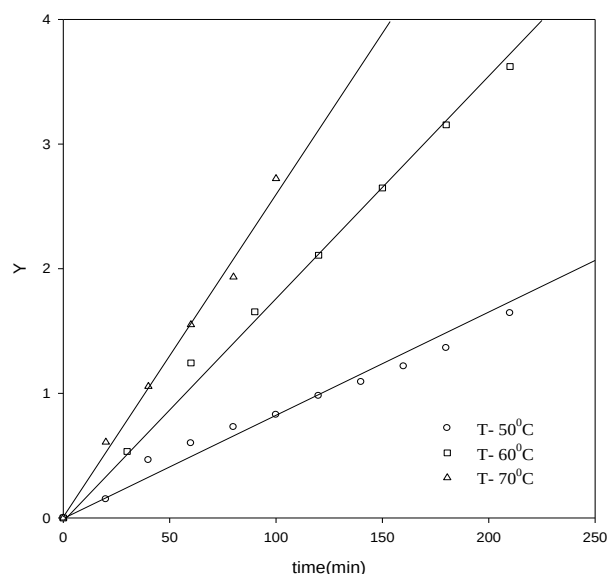


Fig. 9. Test of the rate equation {MR=1.0; CC=3.0 wt%}

From  $k_1$ , the rate constant for backward reaction  $k_2$  is obtained using the following equations.

$$\text{For case-I: } k_2 = \frac{k_1(1-X_{Ae})^2}{X_{Ae}^2} \quad \dots (12)$$

$$\text{For case-II: } k_2 = \frac{k_1(1-X_{Ae})(M-X_{Ae})}{X_{Ae}^2} \quad \dots (13)$$



By regression analysis, the correlation equation obtained for  $k_1$  and  $k_2$  are

$$k_1 = 0.05536(MR)^{0.8861}(CC)^{0.5385}e^{49.59/T} \quad \dots (14)$$

Average deviation = 8.792 percent

Standard deviation = 10.64 percent

$$k_2 = 357.6(MR)^{0.5987}(CC)^{-0.44}e^{-2914/T} \quad \dots (15)$$

Average deviation = 5.456 percent

Standard deviation = 7.131 percent

### 3.4. Thermodynamic modeling:

The thermodynamic equilibrium constant can be written as

$$K_E = \left( \frac{x_C x_D}{x_A x_B} \right) \left( \frac{\gamma_C \gamma_D}{\gamma_A \gamma_B} \right) \quad \dots (16)$$

It can be expressed as

$$K_E = \left( \frac{C_C C_D}{C_A C_B} \right) \left( \frac{\gamma_C \gamma_D}{\gamma_A \gamma_B} \right) \quad \dots (17)$$

$$\text{or } K_E = K_C K_\gamma \quad \dots (18)$$

Here  $K_E$  = thermodynamic equilibrium rate constant

$$= \frac{k_1}{k_2}$$

$$K_C = \text{concentration based rate constant} = \frac{C_C C_D}{C_A C_B}$$

$$K_\gamma = \text{activity coefficient based rate constant} = \frac{\gamma_C \gamma_D}{\gamma_A \gamma_B}$$

Activity coefficient values for each case were computed using ASPEN Plus software. The comparison of experimental data and the data obtained from the activity coefficient models such as UNIQUAC, UNIFAC, Wilson, Modified UNIFAC and NRTL were plotted and shown in Figs. 10, 11 and 12 for different experimental conditions.

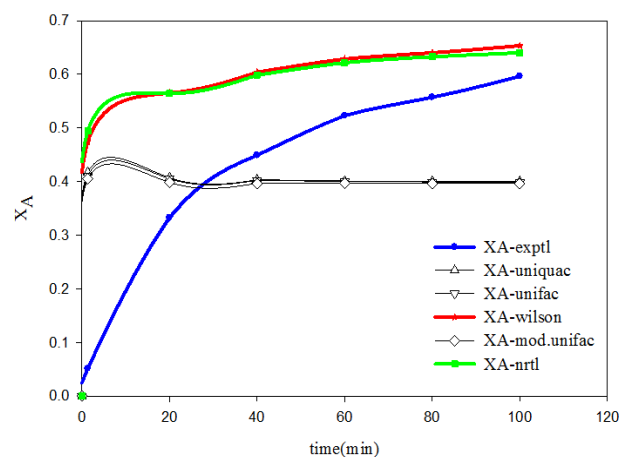


Fig.10. Concentration-based model fit {MR = 1.0; T = 70°C; CC = 3.0 wt%}

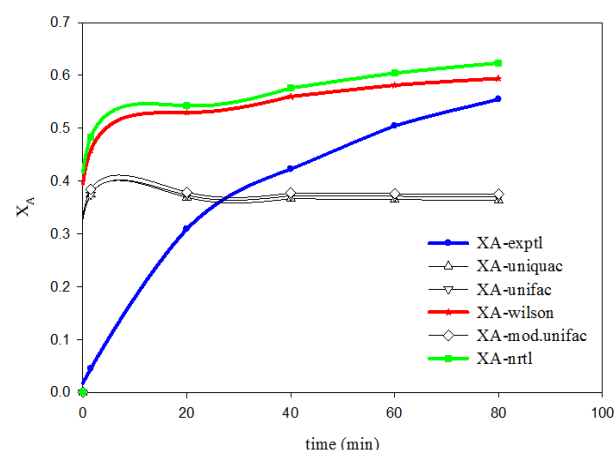


Fig.11. Concentration-based model fit {MR = 0.5; T = 60°C; CC = 3.0 wt%}

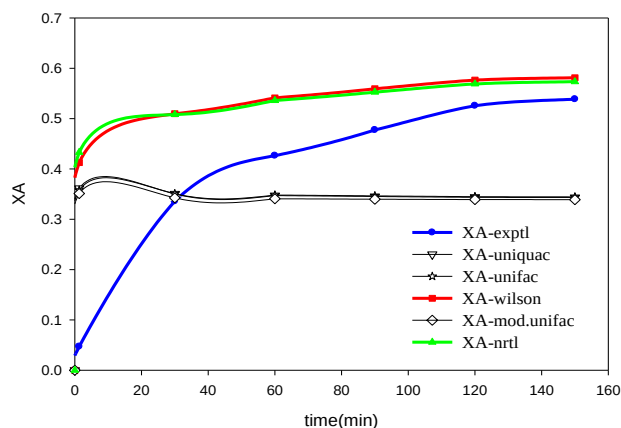


Fig.12. Concentration-based model fit {MR = 1.0; T = 60°C; CC = 3.0 wt%}



A close inspection of the plots of these figures reveals that, in all the cases the predicted model conversion was either more or less than the actual experimental conversion. Further, the Wilson and NRTL models yielded better prediction compared to other models. This indicates that there are no successful models available for the prediction of esterification reaction and hence one has to depend on experiment for accurate data.

#### 4. Conclusion

Within the range of our study, there are no side reactions. This is evident from analyses made from TLC, FTIR and NMR spectroscopy. The conversion decreased with an increase in mole ratio for all the reactions employed in the present study. With increase in catalyst concentration, the conversion also increased. With the increase in temperature the conversion increased. From the interpretation of batch kinetics, the rate constants  $k$ ,  $k_1$  and  $k_2$  for single irreversible reaction and reversible reaction for the three chosen systems were calculated. The correlation equations using regression analysis, in terms of operating parameters for  $k$ ,  $k_1$  and  $k_2$  were obtained. The five thermodynamic models, UNIQUAC, UNIFAC, WILSON, Modified UNIFAC and NRTL were developed and the corresponding activity coefficients were evaluated using ASPEN Plus software. Further, the Wilson and NRTL models yielded better prediction compared to the other models.

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