

Homogeneous and Heterogeneous Catalyzed Esterification of Acrylic Acid with Ethanol: Reaction Kinetics and Modeling

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ABSTRACT: Kinetics of esterification of acrylic acid with ethanol in the presence of homogeneous (H_2SO_4 , HCl, *p*-TSA, HI) catalysts as well as heterogeneous catalysts (Dowex 50WX, Amberlyst 15) was studied. The effects and performance of these catalysts on the conversion of acrylic acid were evaluated. In the kinetics of homogeneous catalyzed reaction, both concentration and activity-based model were employed. Activity coefficients were predicted by the Universal Functional group Contribution (UNIFAC) method to consider nonideal behavior of the liquid phase. The heterogeneous catalyzed reaction mechanisms were developed using Eley–Rideal theory. The model results were compared with the experimental results and were in good agreement. The temperature dependency of the constants, reaction enthalpy, and entropy, and activation energy were determined. The conversion of acrylic acid was obtained as 63.2%, 61.02%, 53.3%, 21.4%, 34.96%, and 14.84% for H_2SO_4 , *p*-TSA, HCl, HI, Dowex 50WX, and Amberlyst 15, respectively, under process temperature of 70°C, reactant molar ratio of 1:1, and catalyst concentration of 2% (v/v) for homogeneous and 2.17 g for heterogeneous catalyst. These outcomes provide an approach to understand the significant effect of each catalyst on the esterification kinetics of acrylic acid and ethanol. © 2018 Wiley Periodicals, Inc. *Int J Chem Kinet* 50: 370–380, 2018

INTRODUCTION

Esterification is an essential reaction-producing esters in chemical industries. Desired product esters are

widely employed in the application of solvents, plasticizers, sealants, medicinal agents, flavors, and fragrances [1,2]. These reactions are reversible and having low reaction rate, which shows limited conversion. Owing to low and slow reaction rate, suitable catalyst are employed in this reversible reaction. It takes a lot of energy to remove the –OH from the carboxylic acid, so appropriate catalyst and heat are needed to produce the

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necessary energy. Once the $-OH$ has been removed, the hydrogen on the alcohol can be removed and that oxygen can be connected to the carbon. Because the oxygen was already connected to a carbon, it is now connected to a carbon on both sides, and an ester is formed.

Both homogeneous and heterogeneous catalysts are used to increase the reaction rate. A homogeneous catalyst such as sulfuric acid (H_2SO_4), hydrochloric acid (HCl), and para-toluene sulfonic acid (*p*-TSA) acts as a protonating catalyst during the esterification reaction [3,4]. Drawbacks of homogeneous catalyst such as corrosion of equipment, side reactions, and difficult to separation from the product mixture can be resolved by the employment of heterogeneous catalysts. Many researchers have done comparative study of homogeneous and heterogeneous catalysts [4–7]. These literature reports suggest that the homogeneous catalyst favors more conversion of acid or yield of product than a heterogeneous catalyst. But heterogeneous catalysts lead easy recovery of catalyst and more purity of product than the homogeneous catalyst.

Compared to the homogeneous catalyst, the reaction rate in the heterogeneous catalyst will proceed at a slower rate. This is due to the fact that the homogeneous catalyst and reactants have a similar phase and hence the reaction rate is faster [1]. This finding has already been reported by several researchers. Aafaqi et al. [8] reported that the homogeneous catalyst gives better conversion than the heterogeneous catalyst for esterification of palmitic acid with isopropanol. Yalcinyuva et al. [9] reported similar comparative results for esterification of myristic acid with isopropyl alcohol. They concluded that heterogeneous catalysts gave poor conversions due to the diffusion problem of fatty acid into the pores of the catalyst. Henceforth, a lot of reports [2,10,11] suggested that the homogeneous catalyst induces more conversion compared to heterogeneous catalyst.

Generally, for performing the kinetics of the homogeneous catalytic esterification reaction, the power law model is employed [1,12]. To describe the kinetic behavior of heterogeneous catalytic esterification reactions, several kinetic models have been reported. The simplest one is the pseudo-homogeneous (P-H) model, which is similar to the power law model for homogeneous reactions [13–16]. The other widely adopted models are Langmuir–Hinshelwood (L–H) and Eley–Rideal (E–R) models. The P-H model assumes that the surface reaction is the controlling step, and adsorption is negligible for all components. The L–H model is applicable for correlating the kinetic data whenever their occurs the adsorption of the molecules is taking

part in the reaction [14,17–19]. Finally, the E–R model is applied when the reaction between one adsorbed species and one nonadsorbed reactant from the bulk liquid phase is assumed to occur [7,16,20].

The present work investigates the kinetics of esterification of acrylic acid and ethanol catalyzed by various homogeneous and heterogeneous catalysts. The effect of reaction temperature on kinetics of reaction was described. For comparative study of catalysts, four homogeneous catalysts, namely H_2SO_4 , HCl, *p*-TSA, HI, and two heterogeneous catalysts, i.e., Dowex 50WX and Amberlyst 15, are employed. The kinetic studies of both homogeneous and heterogeneous catalyzed esterification reactions were performed. Nowadays, it is essential to study the kinetics and reaction equilibrium of reaction to understand and describe chemical reactions in a better way. Both concentration and activity-based model were considered for homogeneous as well as heterogeneous catalysts. The E–R model was employed to correlate the experimental data of ion-exchange catalysts.

EXPERIMENTAL

Material and Method

All reactants acrylic acid (99% pure; Loba Chemie, Mumbai, India), ethanol (99% pure; Hayman, Pune, India) and catalysts sulfuric acid (98% pure; Loba Chemie, Mumbai, India), hydrochloric acid (98% pure; Loba Chemie, Mumbai, India), and *p*-toluene sulfonic acid (99% pure; Fisher Scientific) were of analytical grade. Heterogeneous catalysts Amberlyst 15 hydrogen form and Dowex 50WX hydrogen form were obtained from Sigma-Aldrich. No more purification was performed for the experiments. Millipore ultrawater was used for the preparation of aqueous solutions required for product analysis.

The esterification reaction was carried out in a 1000-mL three-necked ball glass flask equipped with a magnetic stirrer (Remi1 RML). The setup is shown in Fig. 1. One of the measured reactant was fed to the reactor and heated up to a desired temperature. Another reactant was heated in a separate flask and transferred to the reactor followed by addition of catalyst. This time was taken as the initial (starting) time of the reaction. In this study, the experiments were performed at 50, 60, and 70°C reaction temperature and the catalyst concentration of 2% (v/v) of reaction mixture with a molar ratio of 1:1 (acrylic acid to ethyl alcohol) of reactants. Samples were collected at regular intervals for 6–7 h and analyzed by a gas chromatograph (GC).

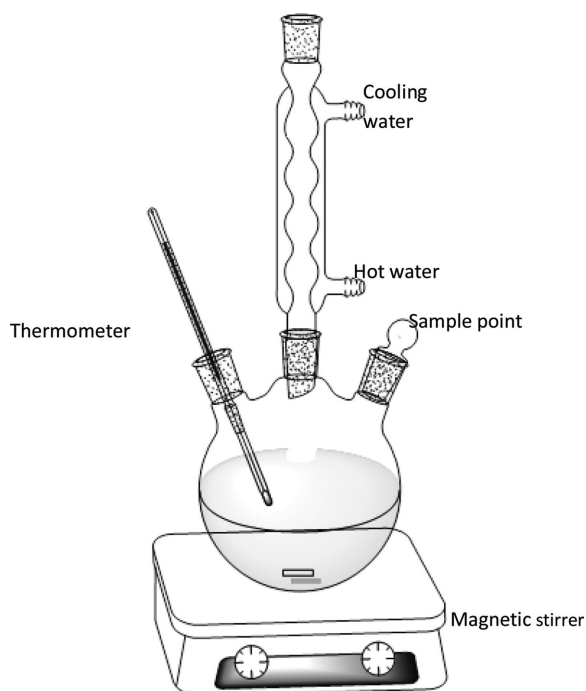


Figure 1 Experimental setup for the esterification process.

GC Analysis

The samples collected from the reactor and the permeate were analyzed by a NUCON series 5700 gas chromatograph equipped with a thermal conductivity detector, a cool glass lined injector, and a pressure programmable software. Separation was carried out on a porapak column (id 2mm, od 1/8", length 2 m). Hydrogen gas taken as a carrier gas with a flow rate of 60 mL/min. The GC was calibrated using a known sample of acrylic acid, ethanol, ethyl acrylate, and water. One microliter of sample was injected into the chromatograph. From the obtained peak area and retention time, the concentration of reactants, products, and permeates were found. The analysis was carried out with the injection chamber temperature at 150°C; the oven and detection chamber temperatures were set at 180°C.

RESULTS AND DISCUSSION

Effect of Different Homogeneous and Heterogeneous Catalyst

The effect of different types of catalysts on the performance of the esterification reaction was studied by using four homogeneous catalysts, e.g., H₂SO₄, HCl, *p*-TSA, and HI, and two heterogeneous catalysts Dowex, e.g., 50WX and Amberlyst 15. The operational con-

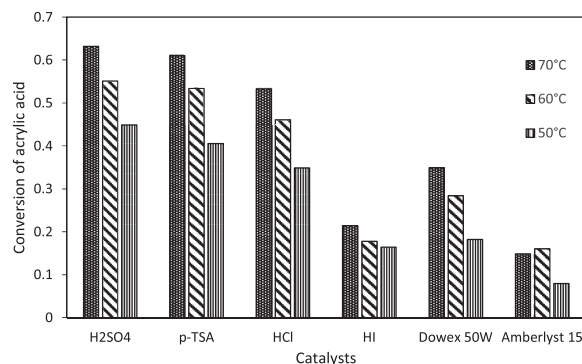


Figure 2 Effect of different catalysts on conversion of acrylic acid at different temperatures ($t = 420$ min).

ditions were kept same for all experiment with same temperature and the molar ratio acrylic acid/ethanol of 1:1. An amount of catalyst of 2% v/v of reaction mixture was considered in case of homogeneous, and the amount of catalyst corresponding to equivalent w/w% of H₂SO₄ was considered in case of the heterogeneous catalyst. Hence the resulted amount of heterogeneous catalyst of 2.17 g was taken.

As evident from Fig. 2, the conversion of acrylic acid increases with an increase in the temperature because of acceleration of the forward reaction. It is due to the fact that high temperature gives rise to more frequent and successful collision having sufficient energy (activation energy) to break the bonds, and hence leads to higher conversion of reactants to ester products [1,21,22]. However, the reaction at too high temperature leads to vaporization of reactants, which in turn decreases the efficiency of the system. Hence, there exists a trade-off between the high reaction rate due to the increased temperature and the decrease of the reaction rate, resulting from the vaporization of reactants. It is therefore essential to determine the optimal reaction temperature or temperature profile for efficient operation of the system considering the production rate as well as the vaporizing rate of reactants [23].

Figures 3–5 show the effect of different homogeneous and heterogeneous catalysts on conversion of acrylic acid at 50, 60, and 70°C, respectively. From the figures, the obtained conversion of acrylic acid with different catalysts is in the following order: H₂SO₄ > *p*-TSA > HCl > Dowex 50W > HI > Amberlyst 15. This trend is maintained at all temperature except 60°C where the conversion is nearly same for *p*-TSA and HCl. At 70°C, the final conversion is 63.2% for H₂SO₄, 61.02% for *p*-TSA, 53.3% for HCl, 21.4% for HI, 34.96% for Dowex 50WX, and 14.84 for Amberlyst 15. As expected, the conversion of acrylic acid is higher for the homogeneous catalyst as compared to

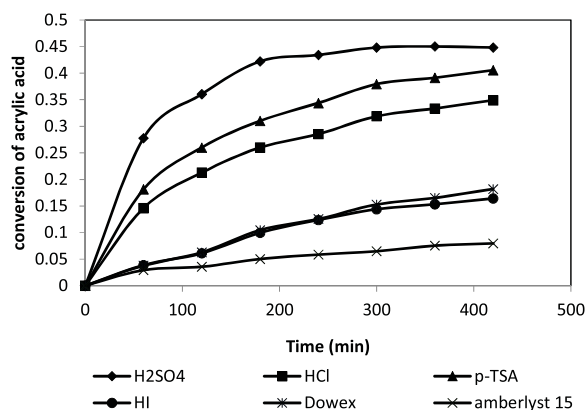


Figure 3 Effects of different catalysts on conversion of acrylic acid for the esterification of acrylic acid and ethanol at 50°C, 1:1 acid/alcohol molar ratio, and catalyst concentration of 2% (v/v) for homogeneous and 2.17 g for the heterogeneous catalysts.

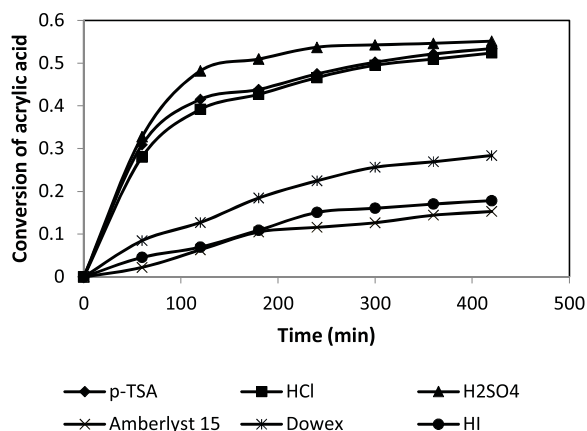


Figure 4 Effects of different catalysts on conversion of acrylic acid for the esterification of acrylic acid and ethanol at 60°C, 1:1 acid/alcohol molar ratio, and catalyst concentration of 2% (v/v) for homogeneous and 2.17 gm for heterogeneous catalysts.

the heterogeneous one. Overall, H_2SO_4 was found to be the best among the all providing higher conversion in the studied conditions. The conversion of acrylic acid changes from 44.92% to 63.2% when temperature is increased from 50 to 70°C. The sulfuric acid is the most efficient homogeneous catalyst for the esterification reaction as it can lend two H^+ ions for each molecule of the acid present. Additionally, H_2SO_4 is stable and liquid in (nearly) the pure form. Moreover, concentrated sulfuric acid is a great dehydrating agent; hence, it will even seize some of the water produced in the reaction. Finally, sulfuric acid is neither a strong oxidant (nitric acid) nor a strong reductant (hydroiodic acid), thus reducing the possibilities for undesired side

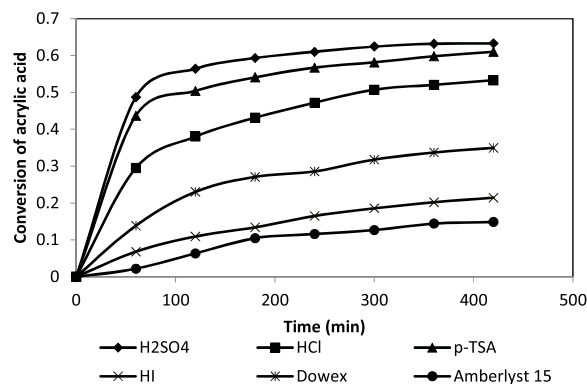


Figure 5 Effects of different catalysts on conversion of acrylic acid for the esterification of acrylic acid and ethanol at 70°C, 1:1 acid/alcohol molar ratio, and catalyst concentration of 2% (v/v) for homogeneous and 2.17 gm for heterogeneous catalysts.

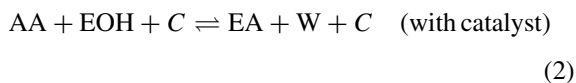
reactions [12]. On the other hand, HCl is a gas and needs to be dissolved in water to use in the liquid state. The problem with this is that water is a product of the esterification reaction, and more water increases the rate of the reverse reaction thereby decreasing the yield of the product ester. Besides, we have also used *p*-TSA, which shows good catalytic activity due to the presence of sulfonic acid groups, and subsequently causes less acidity and less side reactions. Lastly, we have considered the HI catalyst. HI shows very less conversion as compared to other homogeneous catalysts. It may be because of occurrence of side reaction, which leads to formation of ethyl iodide. Ronnback et al. [24] also revealed that in the esterification of acetic acid with methanol in the presence of HI, a side reaction appeared in which HI reacted with methanol forms methyl iodide. The reaction was assumed to be the nucleophilic, whereas the rate-determining step in the hydrogen iodide esterification was supposed to be the substitution of the iodide to protonated methanol. Hydrogen iodide and acetic acid act as proton donors in the mechanism.

There are some drawbacks of homogeneous catalyst such as corrosive nature and existence of possible side reactions. The use of heterogeneous catalyst such as Dowex 50W and Amberlyst 15 may improve the conversion, but due to the diffusion problem of acid into the pores of the catalyst heterogeneous catalysts provided poor conversions [25]. Besides, the poor conversion may be due to unavailability of some acid sites on the catalyst for reaction or reduced activity because of resin swelling or hydrophilicity. Moreover, restricted conformation of intermediate complexes adsorbed on acid sites of the heterogeneous catalyst (as opposed to unrestricted movement in solution in the presence

of the homogeneous catalyst) can also be a factor for reduced conversion [26]. It can be observed from Figs. 3–5 that the performance of Dowex 50Wx8–100 is better than Amberlyst 15 for promoting the reaction. Ali et al. [1] and Sert et al. [27] have also shown higher conversions in the presence of Dowex compared to Amberlyst for propionic acid with 1-propanol and acrylic acid with *n*-butanol, respectively. In industries, generally the concentrated H₂SO₄ catalyst is used for the esterification reaction due to the reason that it is more efficient and economical than other catalysts.

Kinetics of the Homogeneous Esterification Reaction

The kinetic model of esterification of acrylic acid (AA) with ethyl alcohol (EOH) to produce ethyl acrylate (EA) and water (W) can be presented as an elementary second-order reversible reaction, first-order with respect to each reagent [28,29] and is represented as:



The rate expression for the second-order reversible reaction is written as

$$-r_i = k_1 C_{\text{AA}} C_{\text{EOH}} - k_{-1} C_{\text{EA}} C_{\text{W}} \quad (3)$$

Equation (3) can be rewritten as considering a concentration term of catalyst, C_C :

$$-r_i = \frac{-dC_i}{dt} = k_1 C_{\text{AA}} C_{\text{EOH}} C_C - k_{-1} C_{\text{EA}} C_{\text{W}} C_C \quad (4)$$

where C_{AA} , C_{EOH} , C_{EA} , C_{W} , and C_C represent the concentration (mol/L) of acrylic acid, ethanol, ethyl acrylate, water, and catalyst, respectively. k_1 and k_{-1} are the forward and backward reaction rate constants, and t is the reaction time.

Equation (4) can be written as

$$-r_i = \frac{-dC_i}{dt} = k_1 C_C \left(C_{\text{AA}} C_{\text{EOH}} - \frac{C_{\text{EA}} C_{\text{W}}}{K_{\text{eq}}} \right) \quad (5)$$

The equilibrium constant, K_{eq} , can be calculated from the equilibrium conversion (X_{Ac}) of the mixture

(equimolar concentration), which is given as

$$K_{\text{eq}} = \frac{k_1}{k_{-1}} = \frac{C_{\text{EA}} C_{\text{W}}}{C_{\text{AA}} C_{\text{EOH}}} = \frac{X_{\text{Ac}}^2}{(1 - X_{\text{Ac}})^2} \quad (6)$$

Equation (6) can be rearranged in terms of conversion of acrylic acid

$$C_{\text{AA}0} \frac{dx_A}{dt} = k_1 C_C C_{\text{AA}0}^2 \left[(1 - X_A)^2 - \frac{X_A^2}{K_{\text{eq}}} \right] \quad (7)$$

$$\int_0^{x_A} \frac{dX_A}{(1 - X_A)^2 - \frac{X_A^2}{K_{\text{eq}}}} = k_1 C_C C_{\text{AA}0} t \quad (8)$$

where

$$X_A = 1 - \frac{C_{\text{AA}}}{C_{\text{AA}0}} \quad (9)$$

X_A and $C_{\text{AA}0}$ are the conversion and initial concentration of acrylic acid. Equation (9) was solved in MATLAB by applying the experimental data in the temperature range of 50–70°C. A plot of the left-hand side of Eq. (9) against reaction time, t along with the fitted linear curve is given in Fig. 6. The reaction temperature was varied from 50 to 70°C. The forward reaction rate constant, k_1 , was obtained from the slope of straight lines shown in Fig. 6, and the values of the backward reaction rate constant, k_{-1} , was calculated from the K_{eq} relation.

The temperature dependency of the rate constants, k_1 and k_{-1} , was determined from the Arrhenius expression and is given as

$$k_1 = k_0 \exp\left(\frac{E_1}{RT}\right) \quad (10)$$

$$k_{-1} = k_{-0} \exp\left(\frac{E_{-1}}{RT}\right) \quad (11)$$

where R is a gas constant (8.31 J/mol.K). Table I presents the activation energies of forward and backward reactions for different catalysts used in the present system. The obtained values of E_1 from the literature are 52.3 ± 1.9 kJ/mol for acrylic acid with 2-ethylhexan-1-ol, 40.7 kJ/mol for palmitic acid with isopropanol, and 42.07 kJ/mol for propionic acid with benzyl alcohol [8,30,31]. The difference in results could be because of the different system and catalyst employed in the present study.

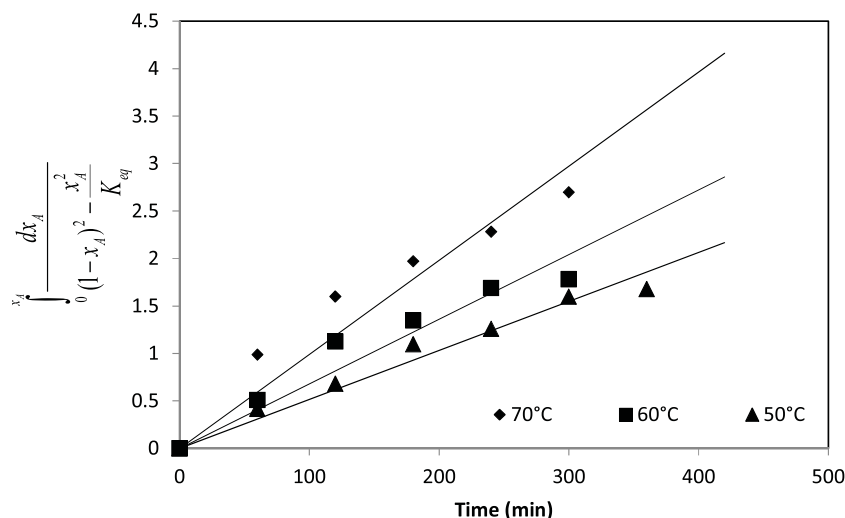


Figure 6 Plot of the left-hand side of Eq. (9) against reaction time t (catalyst used: H_2SO_4).

Table I Kinetic Parameters of Present System (Acrylic Acid + Ethanol) for Different Catalysts

Catalyst	E_1 (kJ/mol)	E_{-1} (kJ/mol)	ΔH (kJ/mol)	ΔS (kJ/mol·K)
H_2SO_4	35.04	36.89	71.94	0.22
p -TSA	42.92	36.18	79.11	0.24
HCl	36.87	38.25	75.12	0.224
HI	23.75	12.28	36.03	0.884

The Van't Hoff equation is employed for the prediction of the nature of reaction endothermic or exothermic by using experimentally determined equilibrium constant (K_{eq}):

$$\ln k_{eq} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (12)$$

Reaction enthalpies for ΔH and entropy ΔS were obtained for various catalyzed reactions and are shown in Table I. The positive value of reaction enthalpy shows that the reaction is endothermic. These values are in a good agreement with the literature findings of 70.1–74.6 kJ/mol for acrylic acid with 2-ethylhexan-1-ol, 69.03 kJ/mol for acrylic acid with n -butanol, and 69–75 kJ/mol for acrylic acid with 2-ethylhexyl alcohol [30,32,33].

To study the nonideality associated with the reaction mixture, we need to consider the activity coefficients along with the molar concentration or mole fractions to show the departure from the ideal case [34]. Real mixtures involve the activity term of the component instead of their concentration term for the calculation of thermodynamic equilibrium constant [30]. Commonly

phase models such as Universal Functional group Contribution (UNIFAC), Universal QUAsi Chemical (UNIQUAC), and non random two liquid model (NRTL) models are used to describe a nonideal factor.

The activity model accounts for the nonideal thermodynamic behavior of the reaction mixtures. It can be developed from the concentration-based model by defining the activity as

$$a_i = \gamma_i x_i = \gamma_i C_i / C_i \quad (13)$$

where, γ_i , C_i , and x_i represent the activity coefficient, concentration, and mole fraction of each component. The activity coefficients in the reaction mixture were calculated by using the UNIFAC method.

The chemical activities instead of concentrations can be used in the reaction rate equation:

$$-r_i = k_1 a_{AA} a_{EOH} - k_{-1} a_{EA} a_W \quad (14)$$

K_{eq} is an equilibrium constant, which can be calculated from the equilibrium molar concentration of components $(C_i)_{eq}$ as given in the equation below

$$K_{eq} = \frac{k_1}{k_{-1}} = \frac{(a_{EA})_{eq} (a_W)_{eq}}{(a_{AA})_{eq} (a_{EOH})_{eq}} = \frac{(C_{EA})_{eq} (C_W)_{eq} \gamma_{EA} \gamma_W}{(C_{AA})_{eq} (C_{EOH})_{eq} \gamma_{AA} \gamma_{EOH}} = K_c K_\gamma \quad (15)$$

Based on the equilibrium conversion or concentration, the activities are computed and using Eq. (16) into

Table II Activity Coefficients of Components in the Equilibrium State of the Reaction at Different Temperatures

Component	50°C	60°C	70°C
Ethanol	1.275	1.269	1.264
Acrylic acid	0.794	0.802	0.810
Ethyl acrylate	1.480	1.476	1.471
Water	2.247	2.229	2.212

Eq. (15), the kinetic rate equation becomes

$$\begin{aligned}
 -r_1 &= k_1 \frac{\gamma_{AA}\gamma_{EOH}}{C_t^2} C_{AA} C_{EOH} \\
 &- k_{-1} \frac{\gamma_{EA}\gamma_W}{C_t^2} C_{EA} C_W \quad (16)
 \end{aligned}$$

In this work, it is assumed that the reaction volume is constant and also observed that the product between the activity coefficients of both reactants and both products do not vary significantly, so the rate constants of forward and backward of Eq. (17) can be grouped as

$$-r_1 = k_{1,act} C_{AA} C_{EOH} - k_{-1,act} C_{EA} C_W \quad (17)$$

where

$$K_{eq} = \frac{k_{1,act}}{k_{-1,act}}$$

The forward rate parameter $k_{1,act}$ is related to the temperature through an Arrhenius relation

$$K_{1,act} = k_{0,act} \exp\left(-\frac{E}{RT}\right) \quad (18)$$

In present work, the UNIFAC model was considered to determine the activity coefficients. The coefficients are directly determined from Aspen Plus software. Truong et al. [35] also used same interface (Aspen Plus) for the determination of activity coefficient by the NRTL model for the same reaction system. The obtained activity coefficients and experimental equilibrium mole fractions of components in the selected temperature range of 50–70°C are presented in Table II.

Comparison of Experimental and Model Predicted Results

The numerical integration of Eq. (9) for each component namely acrylic acid, ethanol, ethyl acetate, and water, which was required during each iterative step in the nonlinear regression, was accomplished by the

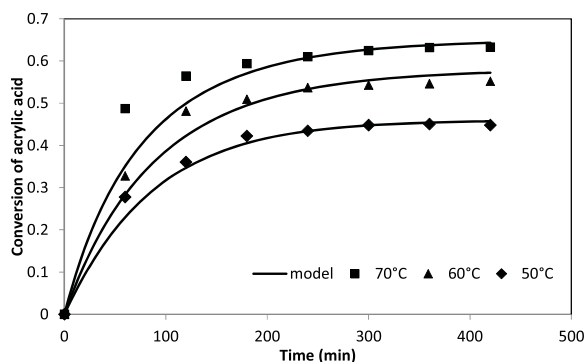


Figure 7 Comparison of acrylic acid conversion between experimental data and simulation results using the concentration-based model with estimated parameters at 2% H_2SO_4 catalyst and 1:1 acrylic acid to the ethanol molar ratio (symbols represent experimental data, and solid lines represent concentration-based model results).

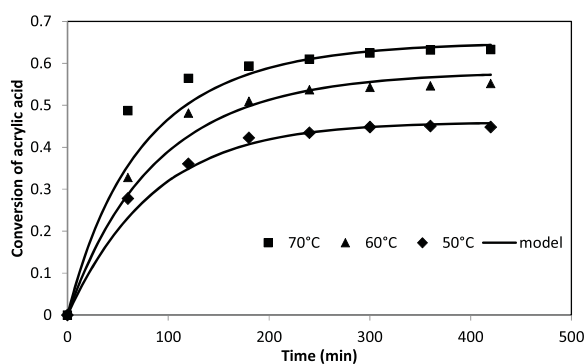


Figure 8 Comparison of acrylic acid conversion between experimental data and simulation results using the activity-based UNIFAC model with estimated parameters at 2% H_2SO_4 catalyst and 1:1 acrylic acid to the ethanol molar ratio (symbols represent experimental data, and dotted lines represent the activity-based model results).

ODE solver, ode15s implemented in the MATLAB. The simulated values of conversion of acrylic acid mentioned in the kinetic modeling section were compared to that obtained experimentally. Figure 7 shows a plot between simulated and experimental values of conversion. It can be seen from the figure that the model (Eq. (9)) predicted and experimental values are in good agreement.

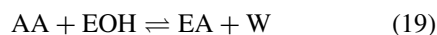
The experimental results and the activity-based model predicted values were plotted for acrylic acid conversion at different reaction temperatures as shown in Fig. 8. The model values match reasonably well with experimental values. It can be observed that beyond 200 min, the activity-based model prediction matches well with the experimental data. The sum of squared error is 0.033 for the concentration-based model

and 0.030 for the activity-based model. Hence, the UNIFAC model predicts the experimental data slightly better than the concentration-based model. In the present system, the obtained value of error is less, which proves the accuracy of the UNIFAC model for estimating the activity coefficients of the components.

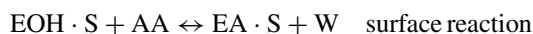
Kinetics of the Heterogeneous Esterification Reaction

The heterogeneous reaction mechanism experimentally performed can be modeled by the E-R model, which is the reaction on the basis of the assumption that one of the adsorbed reactants is reacting with another in the bulk fluid [1]. In this work, it was assumed the reaction between adsorbed ethyl alcohol on acid sites of the catalyst and acrylic acid in the bulk solution, as proposed by Santos et al. [36]. However, ethyl acrylate molecules adsorbed were neglected and adsorption of water by resin has an inhibiting effect on the reaction mechanism [28]. Thus in the present work the adsorption/desorption of water on this ion-exchange resin (solid) was considered.

The esterification reaction of acrylic acid (AA) with ethyl alcohol (EOH) for producing ethyl acrylate (EA) and water (W) in the presence of ion-exchange resin (Dowex 50WX and Amberlyst 15) catalyst is given as follows:



The reaction mechanism can be given as following steps [36]:



where S represents solid site of catalyst. Depending on this mechanism, the reaction rate expression can be given by

$$-r_i = -\frac{dC_i}{dt} = \frac{k_1(m/V)(C_{\text{AA}}C_{\text{EOH}} - (C_{\text{EA}}C_{\text{W}}/K_e))}{1 + K_{\text{EOH}}C_{\text{EOH}} + K_{\text{W}}C_{\text{W}}} \quad (20)$$

where k_1 is the forward reaction rate constant, m is the quantity of dry resin, V the volume of the reaction mixture, K_e the equilibrium constant of the reaction, K_{EOH} and K_{W} the adsorption equilibrium constants. Considering chemical activities instead of concentrations, the reaction rate equation for a nonideal mixture can be written as

$$-r_i = -\frac{da_i}{dt} = \frac{k_1(m/V)(a_{\text{AA}}a_{\text{EOH}} - (a_{\text{EA}}a_{\text{W}}/K_e))}{1 + K_{\text{EOH}}a_{\text{EOH}} + K_{\text{W}}a_{\text{W}}} \quad (21)$$

The model equations described for all the components consists of nonlinear differential equations and are solved by an ODE solver, ode45 in MATLAB, to obtain the concentration profile of reactants and product. The set of kinetic parameters were estimated by a nonlinear optimization subroutine *fmincon* from MATLAB. The objective function of the optimization problem is

$$\phi = \sum_{i=1}^{NC} (C_i^{\text{cal}} - C_i^{\text{exp}})^2 \quad (22)$$

For a nonideal mixture

$$\phi = \sum_{i=1}^{Na} (a_i^{\text{cal}} - a_i^{\text{exp}})^2 \quad (23)$$

where C_i^{cal} and C_i^{exp} are calculated and experimental values of acrylic acid concentration of each experimental point "i," respectively. NC is the number of experimental data points for the concentration of acrylic acid. Similarly, a_i^{cal} and a_i^{exp} are calculated and experimental values of acrylic acid activities of each experimental point "i," respectively. Na is the number of experimental data points for activity of acrylic acid. The kinetic parameters are obtained by solving the model equation based on the successive guess values of the kinetic parameters. The resulting values are given in Table III.

As mentioned previously for the homogeneous system, reaction enthalpy for Dowex and Amberlyst 15 is evaluated as 38.85 and 45.70 kJ/mol, respectively. The positive value of reaction enthalpy shows that the reaction is endothermic. Activation energy of the forward reaction for Dowex and Amberlyst 15 was calculated as 31.04 and 35.52 kJ/mol, respectively.

Comparison of Experimental and Model-Predicted Results

A comparative plot between experimental and model values of conversion of acrylic acid using

Table III Values of Kinetic Parameters at Different Temperatures

Catalyst	T (°C)	k_1 ($\text{m}^3 \text{mol}^{-1} \text{min}^{-1}$)		K_e		K_{EOH} ($(\text{m}^3)^2 \text{mol}^{-1} \text{min}^{-1}$)		K_{W} ($(\text{m}^3)^2 \text{mol}^{-1} \text{min}^{-1}$)	
		Concentration	Activity	Concentration	Activity	Concentration	Activity	Concentration	Activity
		Model	Model	Model	Model	Model	Model	Model	Model
Amberlyst 15	50	0.0040	0.0330	0.0700	0.0007	0.0060	0.0053	0.0258	0.0258
	60	0.0079	0.0285	0.1110	0.0011	0.0010	0.0009	0.0301	0.0301
	70	0.0086	0.0589	0.1890	0.0019	0.0020	0.0009	0.0502	0.0499
Dowrex 50WX	50	0.0264	0.0502	0.0900	0.0090	0.0007	0.0007	0.0266	0.0266
	60	0.0374	0.0800	0.1155	0.0116	0.0009	0.0009	0.0557	0.0557
	70	0.0518	0.1870	0.2100	0.0210	0.0036	0.0013	0.0564	0.5640

Rate constants of channels 29, 30, 36, 37, and 43 were calculated with VTST, otherwise with CTST.

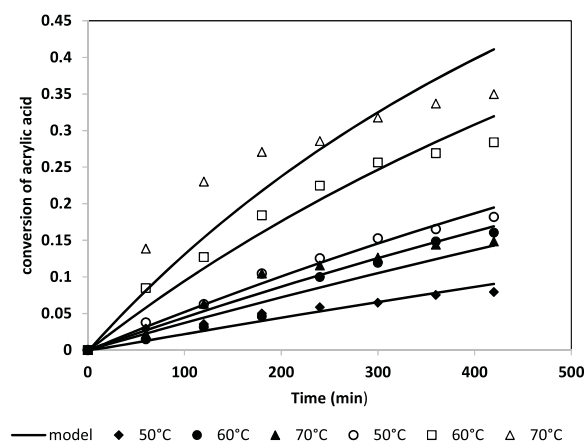


Figure 9 Comparison of acrylic acid conversion between experimental data and simulation results using the concentration-based model with estimated parameters at 2.17 g of catalyst and 1:1 acrylic acid to the ethanol molar ratio (symbols represent experimental data, and solid lines represent model results; the filled symbol represents Amberlyst 15, and the hollow symbol represents Dowex 50WX).

heterogeneous catalysts is presented in Figs. 9 and 10. Figures explain the precision of the model for predicting conversion of acrylic acid and well agreed with the conversion obtained experimentally for both catalysts Dowex 50WX and Amberlyst 15. The sum of squared error for Dowex 50WX and Amberlyst 15 is 0.017 and 0.00314, respectively, for the activity-based model and 0.021 and 0.005, respectively, for the concentration-based model, respectively. In the present system, the obtained value of error is less, which proves the accuracy of the UNIFAC model for estimating the activity coefficients of the components.

The sensitivity of the model prediction (or more precisely final conversion of acrylic acid) to changes in

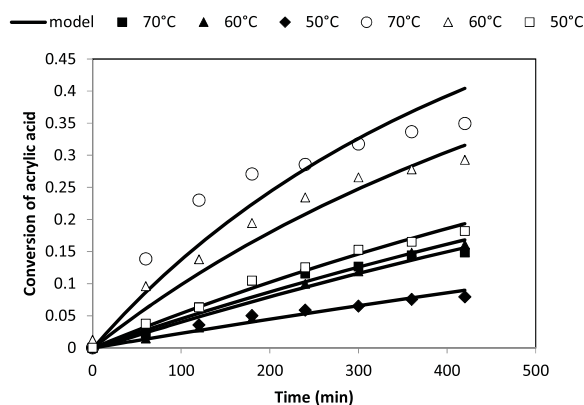


Figure 10 Comparison of acrylic acid conversion between experimental data and simulation results using the activity-based UNIFAC model with estimated parameters at 2.17 g of catalyst and 1:1 acrylic acid to the ethanol molar ratio (symbols represent experimental data, and solid lines represent model results; the filled symbol represents Amberlyst 15, and the hollow symbol represents Dowex 50WX).

values of the kinetic parameters (k_1 , K_e , K_{EOH} , K_{W}) was also performed. To perform the sensitivity analysis, we considered the kinetic parameters obtained for Dowex 50WX case (reaction temperature = 60°C) using the UNIFAC model. The values of the parameters were varied in the range of $\pm 50\%$ of the estimated value. One parameter was varied at a time to realize its effect on system performance. The most sensitive parameter was found to be k_1 , and comparatively the most insensitive parameters were K_{EOH} and K_{W} . The final conversion of the acrylic acid was changed by nearly 8.5% when the value of k_1 was changed by 10% of its base value, whereas even a 50% change of the K_e value changes the conversion by only 0.15%.

CONCLUSIONS

Esterification of acrylic acid with ethanol was studied using different homogeneous (H_2SO_4 , HCl , p -TSA, HI) and heterogeneous (Dowex 50WX, Amberlyst 15) catalysts. It was found that the homogeneous catalyst has the higher activity and gives higher conversion than the heterogeneous catalyst. The kinetics of the homogeneous catalyzed esterification of acrylic acid with ethanol was described by a power law rate expression and heterogeneous catalyzed esterification reaction was explained by the E–R mechanism. Kinetic parameters such as reaction rate constants, equilibrium constants, and activation energy of the heterogeneous model were estimated by a nonlinear optimization technique in MATLAB. Activation energy of the forward reaction for H_2SO_4 , HCl , p -TSA, HI , Dowex, and Amberlyst 15 was calculated as 35.04, 36.87, 42.92, 23.75, 31.04, and 35.52 kJ/mol, respectively. The simulated (model) values were found to be in good agreement with the experimental values.

NOMENCLATURE

a	Activity of components
C_{AA}	Concentration of acrylic acid, mol/m ³
C_{AA0}	Initial concentration of acrylic acid, mol/m ³
C_C	Concentration of catalyst, mol/m ³
C_{EA}	Concentration of ethyl acrylate, mol/m ³
C_{EOH}	Concentration of ethyl alcohol, mol/m ³
C_W	Concentration of water, mol/m ³
E_a	Activation energy, J/mol
k_1	Forward reaction rate constant, (m ³) ² /kmol ² ·min
k_{-1}	Backward reaction rate constant, (m ³) ² /kmol ² ·min
K_{eq}	Equilibrium constant
R	Rate constant, 8.314 J/mol K
t	Reaction time, min
T	Reaction temperature, °C
X_{AA}	Conversion of acrylic acid
X_{Ae}	Equilibrium conversion of acrylic acid
ΔH	Reaction enthalpy, J/mol
ΔS	Reaction entropy, J/mol K
γ	Activity coefficient of components

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