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Kinetic modelling and simulation studies for the esterification process with Amberlyst 16 resin

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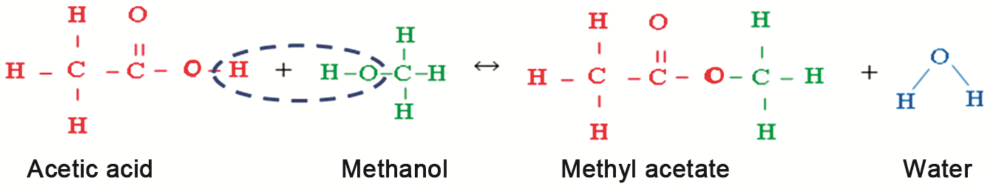
Methyl acetate has been synthesized by the reaction between acetic acid and methanol in an experimental batch reactor. The reaction has been carried out homogeneously without using any catalyst and heterogeneously by using Amberlyst 16 resin catalyst. The reaction is performed using different temperatures in the range of 318.15-333.15 K. The reaction catalyzed by Amberlyst 16 is found faster than the uncatalyzed reaction and the influence of process parameters such as catalyst loading, reaction mixture temperature, initial reactant mole ratio, catalyst size, agitation speed on acetic acid conversion has been investigated experimentally for the catalyzed reaction. Further, pseudo-homogeneous kinetic models have been developed for the catalyzed reaction and the uncatalyzed reaction. The reaction rate expressions of catalyzed reaction and uncatalyzed reaction are used to derive the reaction rate equation influenced by the catalyst alone. This rate equation is useful to examine the influence of catalyst alone in the heterogeneously catalyzed methanol esterification reaction.

Keywords: Esterification, Rate equation, Kinetic model, Amberlyst 16, Diffusion

Methyl acetate is synthesized by the reaction between acetic acid and methanol. It is a commercial product that has many uses such as a solvent for adhesives, oils, paints, perfumery, nail polish removers, and it is also used in printing inks, industrial coatings and dye production. The reaction between acetic acid and methanol is shown schematically in Scheme 1. The ion H^+ from acetic acid combines with OH^- to form water. The remaining species combine to form methyl acetate. This is a liquid phase reversible reaction. The maximum attained conversion of reactants is decided by the equilibrium criterion. In the absence of catalyst, this reaction is very slow and requires longer time to reach steady state. In the presence of catalyst, the reaction attains equilibrium at a faster rate. Usually the catalyst liberates H^+ ions which catalyze the esterification reaction. Catalytic reaction of methyl acetate formation can be carried out as homogeneous catalysis and heterogeneous catalysis. In homogeneous catalysis, the liquid catalysts like HI, HCl, HBr and H_2SO_4 are used as catalysts, whereas in heterogeneous catalysis, many solid catalysts like ion exchange resins, zeolites and acid clay are employed.

Various homogeneous catalytic reactions have been reported in literature for the esterification of acetic acid with methanol. Rolfe and Hinshelwood[1] have investigated the esterification kinetics between acetic acid and methanol by using alcoholic and non-hydroxylic media. The authors proposed the kinetic model based on the assumption of the theory of molecular statistics. Ronnback et al.[2] have studied the esterification of acetic acid with methyl alcohol in presence of hydrogen iodide liquid catalyst in batch reactor in the temperature range of 303-333 K and with the catalyst concentrations of 0.05 wt% to 10 wt%. The protonation of carboxylic acid was considered as rate-initiating step in the reaction mechanism. The authors observed that a side reaction also takes place in addition to the main esterification reaction. In side reaction, methanol is found to react with the hydrogen iodide to form methyl iodide as the by product. Agreda et al.[3] have developed a rate equation for acetic acid with methanol esterification reaction using sulphuric acid as a homogeneous mineral catalyst. The authors proposed the kinetic rate equation as a function of catalyst concentration. Homogeneously catalyzed methanol esterification reaction is found to be slow requiring longer time to reach the equilibrium conversion. Though acetic acid itself may act as a catalyst, its activity is very low due to its weak acidic nature.



Scheme 1 — Esterification reaction between acetic acid and methanol

Heterogeneous catalysis is preferred for methyl acetate formation due to advantages of easy separation of catalyst from the reaction mixture, high selectivity for the formation of the desired product and less corrosion[4]. In heterogeneous catalysis, the forces active at solid surface can distort or even dissociate an absorbed reactant molecule and affect the rate. Various heterogeneous catalytic reactions have been reported in literature for the esterification of acetic acid with methanol. Chakrabarti and Sharma[5] have comprehensively reviewed the use of cationic ion-exchange resins for different esterification reactions. The authors also highlighted some of the industrially important reactions catalyzed by the solid catalysts. Song et al.[6] have studied the heterogeneous kinetics for the production of methyl acetate. The authors carried the experiments at different temperatures and catalyst concentrations in a batch reactor. They conducted adsorption experiments to find the equilibrium adsorption constants. Popken et al.[7] have investigated the reaction kinetics and chemical equilibrium of homogeneously and heterogeneously catalysed acetic acid esterification with methanol. For heterogeneous reaction, Amberlyst 15 was used as the catalyst. Incorporation of adsorption information into the catalyzed kinetic model was found to provide a better fit to the kinetic model. Kirbaslar et al.[8] have studied the catalytic esterification of acetic acid with methanol by using Amberlyst 15 as heterogeneous catalyst in the temperature range of 318-338 K and at atmospheric pressure. Yu et al.[9] have conducted experiments for the esterification of acetic acid with methanol as well as hydrolysis of methyl acetate in a packed bed reactor in the presence of the Amberlyst 15 catalyst. They determined the reaction kinetics under conditions free of both external and internal mass transfer resistances. The estimated kinetics was found to represent the experimental data closely. Ehteshami et al.[10] have studied the kinetics and chemical equilibrium for the hydrolysis of methyl acetate in a batch reactor using Amberlyst 15 catalyst. They observed the temperature variation has considerable influence on the reaction rate, but the effect of the molar ratio of the components in the feed on the reaction rate can be neglected. They found the LLHW model is an appropriate adsorption model for predicting the reaction rate. Liu et al.[11] have performed a comprehensive investigation for the kinetics of esterification of acetic acid with methanol in both the liquid phase and the gas phase by using the homogeneous and heterogeneous catalysts. They used a commercial Nafion/silica nanocomposite catalyst (SAC_13) and H_2SO_4 as catalysts for the esterification reaction. Though several experimental studies and establishment of kinetic models for the esterification reaction involving different catalysts were reported, development of reaction rate expression for the catalyst part of the catalyzed reaction alone has not been much investigated.

In our earlier work, various studies were carried out for the kinetics of esterification reaction between acetic acid and methanol by using sulphuric acid as liquid catalyst[12] and Indion 190, Indion 180 and Amberlyst 36 as solid catalysts[13-16]. In those works, different kinetic models such as pseudo-homogeneous (PH), Eley-Riedel (ER), Langmuir-Hinshelwood (LH) and Langmuir-Hinshelwood-Hougen-Watson (LHHW) were fitted for the experimental data of the reaction involving Indion 180, Indion 190 and Amberlyst 36 catalysts. Among those fitted kinetic models, the best model was chosen for the catalyzed esterification reaction based on close agreement between the model prediction results and the experimental data. This work considers the development of pseudo-homogeneous kinetic models for methanol esterification reaction that has been carried out without involving any catalyst and with the use of Amberlyst 16 catalyst. Though different kinetic models were established earlier for the catalyzed esterification reaction, it is intuitive to develop a kinetic model for the esterification reaction that considers only the catalyst part of the catalyzed reaction. Thus the main objective of this study is to develop a reaction rate equation for the esterification reaction that accounts only the catalyst part of the heterogeneously catalyzed reaction. The rate equation thus developed can signify the influence of catalyst alone on the reaction rate of heterogeneously catalyzed methanol esterification reaction.

Materials and Methods

Chemicals and catalyst

Methanol and acetic acid with purities of 99% and 99.95% by weight were procured from SD Fine Chemicals Ltd, Mumbai, India. The solid acidic catalyst, namely, Amberlyst 16 wet procured from Rohm & Hass, Mumbai was used for the present reaction system. Before conducting experiments, the wet catalyst was dried at a temperature of 90 ºC in a hot air oven. The physical properties of the Amberlyst 16 catalyst are given in Table 1.

Experimental setup

Esterification reaction was conducted in a half litre volume round-bottom three neck bottle. The reactor was kept in a heating rota mantle which has provision of rotating knobs for adjusting heating as well as stirrer speed. A condenser was connected to the reactor for cooling of vapours. The condensed vapours were returned back and mixed with the reacting mixture. A thermometer was connected to reactor to measure the temperature of reaction mixture.

The desired amount of reactants of acetic acid and methanol were charged to the reactor according stoichiometric ratio. The reaction mixture was heated to the desired temperature. After attaining the desired temperature, the catalyst was added to the reactor contents and the reaction time was noted. Samples were withdrawn every 15 min for first one hour and for each 30 min after one hour. The samples were titrated with standard sodium hydroxide solutions to find acetic acid concentration. The reaction was continued till the attainment of steady state or no change in acetic acid concentration with time was observed.

Table 1— Physical and chemical properties of Amberlyst 16

Physical property	Amberlyst 16wet
Production	Rohm and Hass Company
Appearance and physical state	opaque type beads
Size (µm)	600-800
Bulk density (g cm^{-3})	0.78
Surface area (m^{2} g^{-1})	30
Pore volume (ml g^{-1})	0.20
Max. Operating temperature (ºC)	130
H^{+} capacity (meq g^{-1})	4.8
Matrix	Styrene-DVB
Range of P^{H}	---
Resin type	Macro porous strong acidic cat-ion
Group function	-SO$_{3}^{-}$
Ionic form	H^{+}

Analysis

The acetic acid normality was measured by titration against standard sodium hydroxide solution. A solution of 0.1 N sodium hydroxide was used for titration and phenolphthalein was used as the indicator. The titration was continued until the solution reaches a pink colour. The readings were noted and the concentration of acetic acid was calculated.

Results and Discussion

Experiments were conducted for catalyzed and uncatalyzed methanol esterification reaction under different temperatures, catalyst loading and mole ratios.

Esterification reaction without catalyst

Experiments were conducted for the reaction between acetic acid and methanol without involving any catalyst to find the influence of temperature on the rate of reaction. The experiments were performed using the temperatures in the range of 318.15-333.15 K. The conversion of acetic acid for various reaction temperatures with time is shown in Fig. 1. The symbolic notation in figure shows the conversion of acetic acid for samples drawn at different time points. From the results in figure, the increase in temperature was found to increase the conversion of acetic acid. The reaction has taken relatively longer time to reach the equilibrium conversion. At low temperature

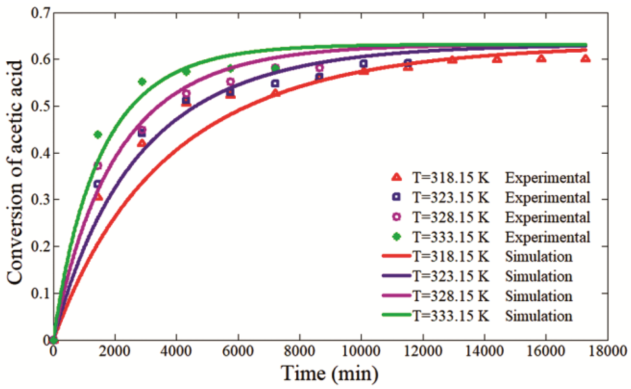


Fig. 1 — Acetic acid conversion for various reaction temperatures in the absence of catalyst.

(318.15 K), the reaction took almost 12 days to reach the equilibrium. At higher temperatures (333.15 K) it took 3 days to reach the equilibrium. It has been observed that further increase in temperature do not increase the equilibrium conversion and high temperature is also not feasible for industrial production process. Based on the data of the experiments, a kinetic model was developed for the uncatalyzed reaction as discussed in next section.

Esterification reaction with catalyst

The esterification reaction without catalyst takes more time to attain the equilibrium conversion, thus requiring a suitable catalyst to increase the reaction rate. In this work, Amberlyst 16 ion exchange resin was chosen as a catalyst for the methanol esterfication reaction and experiments were conducted at different temperatures, mole ratios of reactants and catalyst concentrations. The data generated from the experiments was used to develop a kinetic model for the heterogeneously catalyzed reaction as discussed in next section.

Effect of reaction parameters on catalyzed reaction

The influence of different parameters such as reaction temperature, catalyst concentration, mole ratio of reactants, external mass transfer and internal mass transfer were studied for the catalyzed reaction.

Reaction temperature

The experimental conversions under various reaction temperatures at fixed catalyst concentration of 0.12 mol H^+ L^{-1} are shown in Fig. 2 with symbolic notation at different sample times. The acetic acid conversion is calculated as:

$$X_A = 1 - \frac{n_A}{n_{A0}} \tag{1}$$

where n_{A0}, n_A, and X_A represent the initial moles, moles at time t, and conversion of acetic acid. From the results in figure, it could be seen that the increase in temperature causes to increase the conversion of acetic acid. This indicates that the reaction rate is enhanced by increasing the temperature.

Catalyst concentration

Experiments were done at fixed temperature and various concentrations of catalyst ranging from 0.048 mol H^+ L^{-1} to 0.24 mol H^+ L^{-1}. The experimental acetic acid conversions obtained at fixed temperature of 323.15 K and different catalyst concentrations of 0.048, 0.12, and 0.24 mol H^+ L^{-1} are shown in Fig. 3 with symbolic representation. From the results in Fig. 3, it can be observed that the increase in catalyst concentration causes to increase the conversion of acetic acid there by indicating the enhancement in reaction rate.

The initial rate of reaction is calculated by

$$-r_{A0} = C_{A0}\left(\frac{dX_A}{dt}\right) \quad \ldots (2)$$

where r_{A0} is the initial rate of reaction, C_{A0} is the initial concentration of reactant and X_A is acetic acid conversion at time of t. The differential term in Eqn 2 represents the rate of change of conversion of acetic acid as a function of time. The initial reaction rates at different catalyst concentrations and at constant temperature were drawn as shown in Fig. 4. From the data in Fig. 4, it can be observed that the increase in catalyst concentration from 0.048 mol H^+ L^{-1} to 0.24 mol H^+ L^{-1} causes to increase the rate of reaction. This shows the proportional relation between the catalyst loading/concentration and reaction rate. A

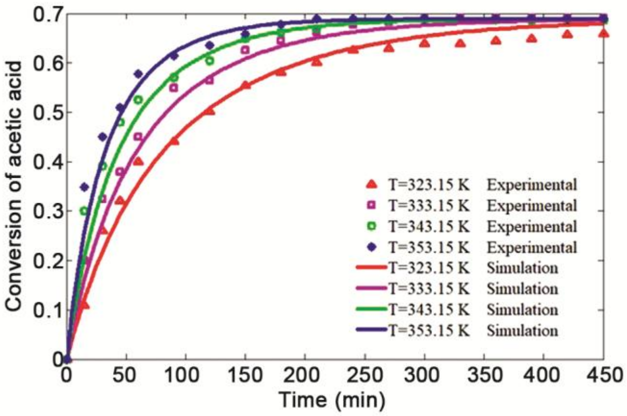


Fig. 2 — Acetic acid conversion for various reaction temperature and at a catalyst concentration of 0.12 mol H^+/L of Amberlyst 16.

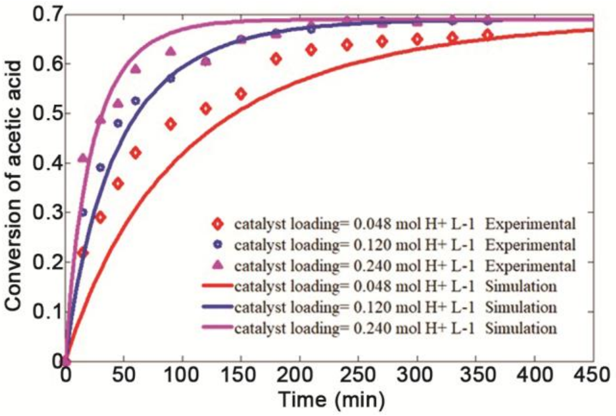


Fig. 3 — Acetic acid conversion for various catalyst concentration of Amberlyst 16 at constant reaction temperature of 343.15 K.

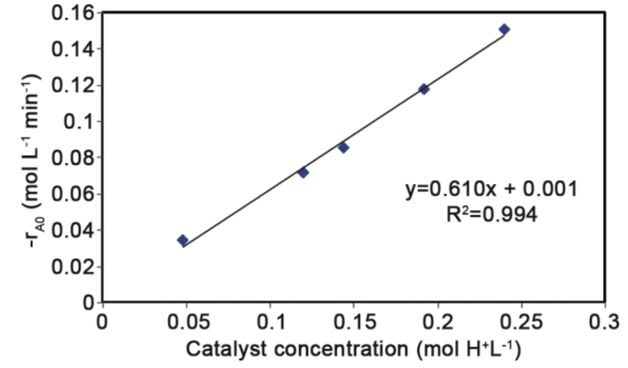


Fig. 4 — Initial reaction rate at different catalyst concentrations at constant temperature.

mathematical expression between reaction rate and catalyst concentration in Fig. 4 is given by

$$-r_{A0} = 0.60 w_C + 0.001 \qquad \ldots (3)$$

where w_C is catalyst concentration in mol H^+ L^{-1}. This equation is valid for the temperature of 323.15 K and mole ratio of 1:1.

Mole ratio of reactants

The effect of molar ratio reactants of acetic acid and methanol (1:1 to 1:4) on the reaction rate at a fixed temperature of 343.15 K and a fixed catalyst concentration of 0.12 mol H^+ L^{-1} is shown in Fig. 5. From the results in Fig. 5, it can be seen that as the mole ratio of acetic acid to methanol increases from 1:1 to 1:4, the conversion of acetic acid increases from 68.7% to 92.4%. This indicates that the supply of methanol in excess amount causes to increase the conversion of acetic acid.

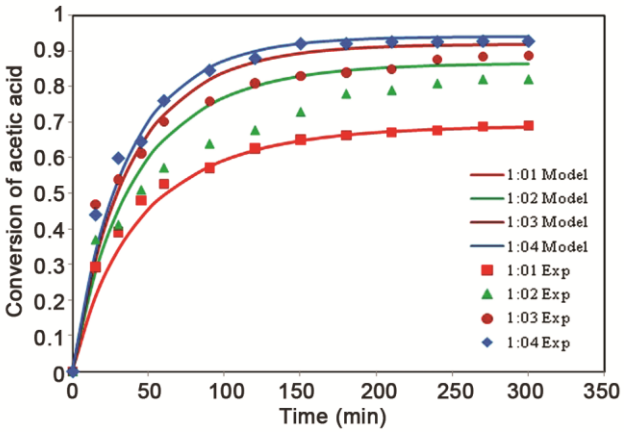


Fig. 5 — Acetic acid conversion for various initial mole ratios of reactants.

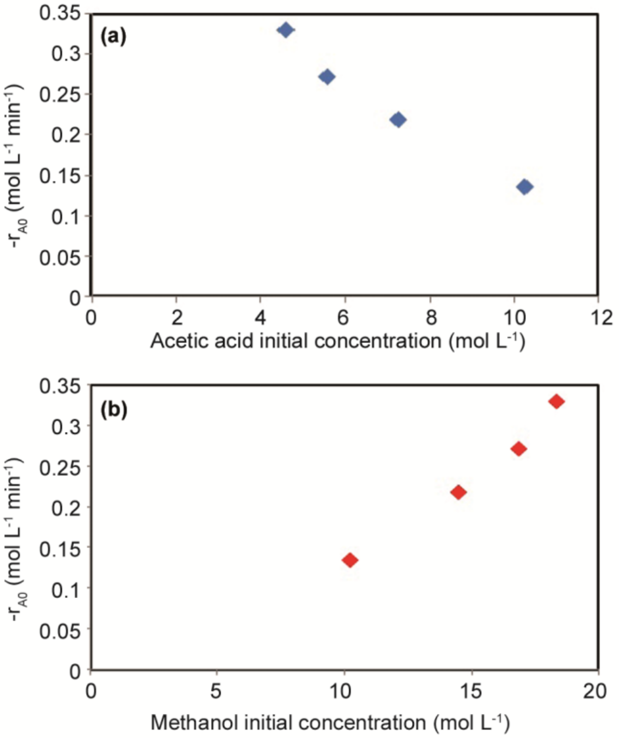


Fig. 6 — (a) Initial reaction rate as function of acetic acid concentration at 333 K and (b) Initial reaction rate as function of methanol concentration at 333 K.

Reactant initial concentration

The effect of the reactant concentration on the reaction rate is determined by varying the concentration of one reactant and keeping other reactant concentration constant at the same operating conditions. The reaction rate vs. initial reactant concentration results in Fig. 6(a) represents the variation of acetic acid concentration when methanol concentration is kept constant as 10.24 mol L^{-1} at a temperature of 333.15 K and a catalyst concentration of 0.12 mol H^+ L^{-1}. The results of Fig. 6(b) represent the variation of methanol concentration when acetic acid concentration is kept constant as 10.24 mol L^{-1} at a temperature of 333.15 K and a catalyst concentration of 0.12 mol H^+ L^{-1}. From these results, it can be observed that the adsorption of the reactants on the catalyst particles are negligible, thus indicating that the reactant molecules are moving through the porous catalyst.

External mass transfer

The influence of mass transfer resistance outside the catalyst particle on reaction rate was studied at an agitation rate of 240-640 rpm and a reaction temperature of 343.15 K. The catalyst concentration of 0.12 mol $H^+ L^{-1}$ with a catalyst size of 725 μm was used for this study. It could be observed that the acetic acid conversion does not show any affect with the change of stirrer speed. This indicates that the mass transfer resistance on reaction rate is negligible. This result agrees with the reported data as well as with the results of our previous studies[5,7,14]. With this observation, further experiments for the esterification reaction were conducted at an agitator speed of 240 rpm. The effect of external mass transfer on acetic acid conversion was also studied theoretically by means of Mears parameter calculated from the following equation:

$$C_M = \frac{r_{A,avg}\rho_b R_c n}{k_c C_{Ab}} \qquad \ldots (4)$$

The notation C_M , $r_{A,average}$, ρ_b, R_c, n, k_c, and C_{Ab} represent the Mears parameter, average reaction rate, catalyst density, catalyst radius, order of reaction, mass transfer coefficient and limiting reactant concentration, respectively. The average reaction rate, $r_{A,avg}$ of limiting reactant in Eqn (4) is found from the following equation:

$$r_{A,avg} = \frac{(n_{A0} - n_A)}{w_C \times t} \qquad \ldots (5)$$

where w_C is the catalyst concentration in mol $H^+ L^{-1}$ and t is time.

The coefficient of mass transfer, k_c in Eqn (4) is calculated from the correlation of Dwivedi-Upadhyay[17] as given by

$$k_c = \frac{2D_{AB}}{d_p} + 0.31 N_{Sc}^{-2/3} + \left[\frac{\Delta\rho\mu_c g}{\rho_c^2}\right] \qquad \ldots (6)$$

where ρ_c, D_{AB}, N_{Sc}, $\Delta\rho$, d_p and μ_c are the catalyst density, diffusivity coefficient of acetic acid in reaction mixture, Schmidt number, difference in densities of solution and catalyst, catalyst average diameter and the viscosity of the reaction solution, respectively. The diffusion coefficient for the mixture in Eqn (6) is calculated by Perkin and Gean Koplis correlation [18] as given by,

$$D_{Am}\mu_m^{0.8} = \sum_{\substack{j=1 \\ j \neq A}}^{n} x_j D_{Aj}\mu_j^{0.8} \qquad \ldots (7)$$

where D_{Am}, D_{Aj}, μ_j, μ_m, and x_j are the diffusion coefficient of A, diffusion coefficient of A in j, viscosity of the j^{th} component, mixture viscosity and mole fraction of j^{th} component, respectively. The diffusion coefficient D_{AB} for binary mixture is calculated from Wilkie-Chang correlation[18] as given by,

$$D_{AB} = \frac{117.3\times10^{-18}(\zeta_B M_B)T^{0.5}}{\mu_B \upsilon_A^{0.8}} \qquad \ldots (8)$$

where ζ_B , M_B, μ_B and υ_A are the association factor, molecular weight, viscosity of component B and υ_A molar volume of component A, respectively. Table 2 gives the Mears parameter values for different temperatures. From these results, it could be observed that the values of Mears parameter are below 0.15 for all the reaction temperatures. This indicates that the mass transfer resistance on reaction could be neglected outside the catalyst [19].

Internal mass transfer

The mass transfer resistance inside the catalyst on reaction rate was investigated by conducting experiments at various catalyst sizes of 425 μm to 925 μm. The catalyst concentration of 0.12 mol $H^+ L^{-1}$, reaction temperature of 343.15 K, agitation rate of 240 rpm and the feed molar ratio of 1:1 were used for the experiments with these catalyst sizes. The experimental results have shown that the conversion of acetic acid is not affected by the catalyst particle sizes, which has also been confirmed by other studies carried out for the reaction[5,7,14]. This confirms that the catalyst particle size has no influence on esterification reaction rate. The effect of internal mass transfer inside the catalyst for the esterification reaction rate was studied by the theoretical calculation of Weisz-Prater parameter according to the following equation:

Table 2 — The criterion of external and internal mass transfer effects at different temperatures

Reaction Temperature (K)	r_{obs} at 60 min	Weiz –Prater Parameter		Mears Parameter	
		D_{eff} ($cm^2 s^{-1}$)	$C_{W\text{-}P}$	k_c ($cm s^{-1}$)	C_M
323.15	9.2×10^{-4}	1.80817×10^{-10}	0.3203	0.585295781	0.0588
333.15	10.43×10^{-4}	2.04396×10^{-10}	0.2834	0.66270459	0.0519
343.15	12.15×10^{-4}	2.29511×10^{-10}	0.2523	0.74453742	0.0462
353.15	13.36×10^{-4}	2.55429×10^{-10}	0.2493	0.829250859	0.0415

$$C_{W-P} = \frac{-r_{A,avg}\,\rho_{cat}\,R_{cat}^{2}}{D_{eff}\,C_{lr}} \qquad \ldots (9)$$

where ρ_{cat}, $r_{A,avg}$, $R_{cat,}$ D_{eff} and C_{lr} are the catalyst density, rate of reaction of A at a given time, catalyst volume to the external surface area ratio, effective diffusivity and acetic acid concentration, respectively. The D_{eff} in Eqn (9) is calculated by the equation:

$$D_{eff} = \varepsilon^{2} D_{lr} \qquad \ldots (10)$$

where D_{lr} is the acetic acid diffusivity at $\boldsymbol{\varepsilon}$=0.2. The limiting reactant or acetic acid diffusion coefficient is calculated by Perkins Geankoplis and Wilkie–Chang correlations [18]. The Weisz-Prater parameters obtained at different temperatures are shown in Table 3. These results show that the values of Weisz-Prater parameters are less than unity. This confirms that the mass transfer inside the catalyst could be neglected for the esterification reaction[18]. With this observation, further experiments for the esterification reaction were conducted at an average catalyst particle size.

The kinetic model

The experimental results in Fig. 1 and Fig. 3 show that the esterification reaction occurs faster in the presence of catalyst. It has been observed that the catalyst concentration is more influential on the reaction rate than the temperature. The experimental data generated based on the catalyst concentration of 0.12 mol H^{+} L^{-1} and a catalyst size of 725 μm at different temperatures was used to develop a kinetic model for the catalyzed reaction. On considering the influence of catalyst on reaction rate, a second order reaction was considered for the catalyzed reaction as expressed by

$$A + B + C_{cat} \overset{k_1}{\underset{k_2}{\longleftrightarrow}} C + D + C_{cat} \qquad \ldots (11)$$

However, this reaction also consists of the uncatalyzed reaction part as given by

$$A + B \overset{k_1}{\underset{k_2}{\longleftrightarrow}} C + D \qquad \ldots (12)$$

Table 3 — The forward reaction rate constant ($k_{1,\,obs}$) at various temperatures for the catalyst concentration of 0.12 mol H^{+} L^{-1}

Temperature (K)	$k_{1,obs}$ (L mol^{-1} min^{-1})
323.15	0.0008
333.15	0.0014
343.15	0.001662
353.15	0.002086

The rate equation for the catalyzed reaction can be expressed as

$$-r_A = k_{1,obs}\left[C_A C_B - \frac{C_C C_D}{K_e}\right] \qquad \ldots (13)$$

The catalyzed rate equation in Eqn (13) is rearranged in terms of reactant conversion as

$$-r_A = C_{A0}\frac{dX_A}{dt} = k_{1,obs}C_{A0}^{2}\left[(1-X_A)(M-X_A) - \frac{X_A^{2}}{K_e}\right] \qquad \ldots (14)$$

where M= C_{B0}/C_{A0}.

Eqn. (14) is integrated and expressed in linear form as

$$\ln\left[\frac{(1+M+\eta_2-2\eta_1 X_A)(1+M-\eta_2)}{(1+M-\eta_2-2\eta_1 X_A)(1+M+\eta_2)}\right] = \eta_2 k_{1,obs} C_{A0} t \qquad \ldots (15)$$

where

$$\eta_1 = 1 - \frac{1}{K_e} \qquad \ldots (16)$$

$$\eta_2 = \left[(M+1)^2 - 4\eta_1 M\right]^{0.5} \qquad \ldots (17)$$

Eqn (15) is used to calculate the forward reaction rate constant, $k_{1,obs}$.

The equilibrium constant, K_e values at different temperatures were determined from the equilibrium conversions, X_{Ae} as given by

$$K_e = \frac{X_{Ae}^{2}}{(1-X_{Ae})^{2}} \qquad \ldots (18)$$

The heat of reaction was obtained from van’t Hoff equation as given by

$$\ln K_e = \frac{-\Delta H_R}{RT} + \frac{\Delta S_R}{R} \qquad \ldots (19)$$

The heat of reaction is calculated from Eqn. (19) by plotting *ln(K_e) versus 1/T* as shown in Fig. 7. The heat of reaction is found to be 4.7 kJ mol^{-1} which confirms the reaction as endothermic. The catalyzed reaction rate constant in Eqn (13) can be expressed as a function of temperature by the Arrhenius equation as

$$k_{1,obs} = k_{0,obs}\exp\left(\frac{-E_{1,obs}}{RT}\right) \qquad \ldots (20)$$

where $k_{0,obs}$ is the forward reaction frequency factor, $E_{1,obs}$ is forward reaction activation energy, T is the temperature and R is the gas constant.

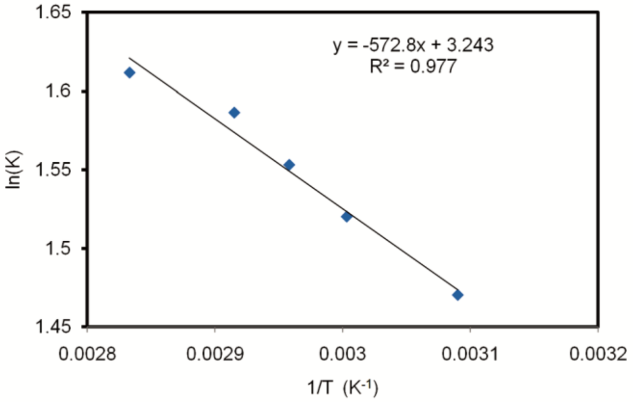


Fig. 7 — Temperature dependency of the equilibrium constant.

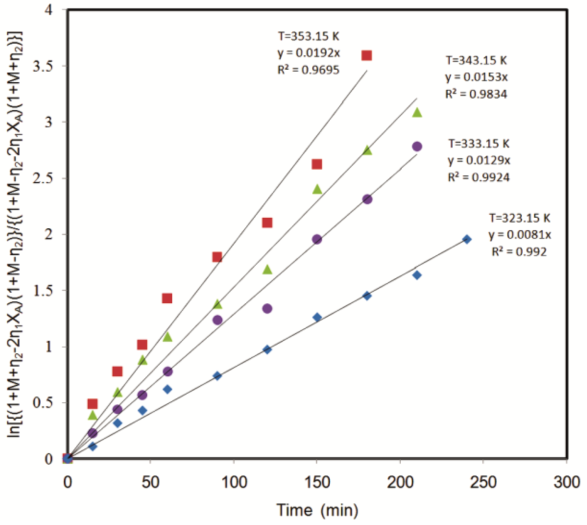


Fig. 8 — Adopting Eqn (15) for calculation of reaction rate constants at different temperature.

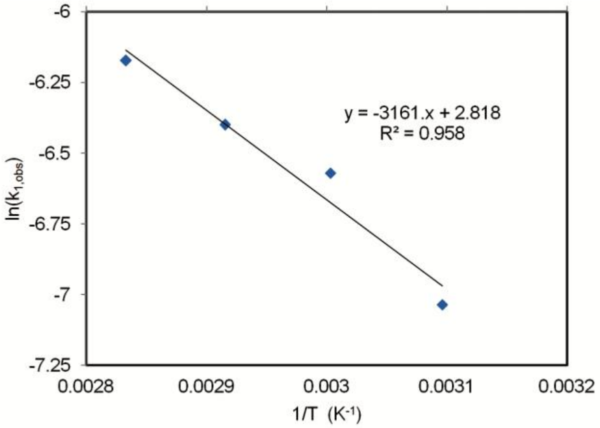


Fig. 9 — Forward reaction rate constant ($k_{1,obs}$) as function of the temperature.

To obtain the values of $k_{1,obs}$ at different temperatures, LHS of Eqn (15) as ordinate and t as abscissa are plotted as shown in Fig. 8. The value of $k_{1,obs}$ for each temperature is obtained from the slope of the straight line in Fig. 8. The R^2 values of the fitted equations in Fig. 8 are found to be more than 0.95, which indicate better fit of the equation to the experimental data. The forward reaction rate constants, $k_{1,obs}$ thus obtained from the experimental data of catalyst concentration of 0.12 mol H^+ L^{-1} and a catalyst size of 725 μm are shown in Table 3. The Arrhenius diagram for the relationship between the forward reaction rate constant and the temperature was shown in Fig. 9. From this figure, it can be observed that the reaction rate constant increases with the increase of temperature at fixed catalyst concentration. The temperature dependent reaction rate, $k_{0,obs}$ and forward activation energy, $E_{1,obs}$ were found from Fig. 9. The fitted forward reaction rate constant expression and activation energy for the catalyzed reaction were given by

$$k_{1,obs} = \exp\left[2.819 - \frac{3161.3}{T}\right] \qquad \dots (21)$$

and 26.3 kJ mol^{-1}

The reaction rate constant $k_{1,obs}$ in catalyzed rate equation in Eqn (14) is a combination of catalyst part of reaction rate constant, k_1^1 and uncatalyzed part of reaction rate constant, k_1.

$$k_{1,obs} = k_1 + k_1^1 \qquad \dots (22)$$

The reaction rate constant of the uncatalyzed reaction as a function of temperature is expressed by the Arrhenius equation as

$$k_1 = k_0 \exp\left(\frac{-E_0}{RT}\right) \qquad \dots (23)$$

The forward reaction rate constants, k_1 for the uncatalyzed reaction at different temperatures were obtained by fitting the experimental data in Fig. 1 to Eqn (15) where $k_{1,obs}$ was replaced by k_1. The reaction rate constants thus obtained for the uncatalyzed reaction are given in Table 4. The Arrhenius plot for the relationship between the forward reaction rate constant and the temperature of the uncatalyzed reaction was shown in Fig. 10. From this figure, the temperature dependent reaction rate constant k_0, and activation energy, E_0 for uncatalysed esterification were found. Thus, the fitted forward reaction rate constant expression and the activation energy for the uncatalyzed reaction were given by

Table 4 — The forward reaction rate constant (k_1) at various temperatures for uncatalysed reaction

Temperature (K)	k_1 (L mol^{-1} min^{-1})
323.15	2.11412×10^{-5}
333.15	3.84804×10^{-5}
343.15	6.76369×10^{-5}
353.15	11.5146×10^{-5}

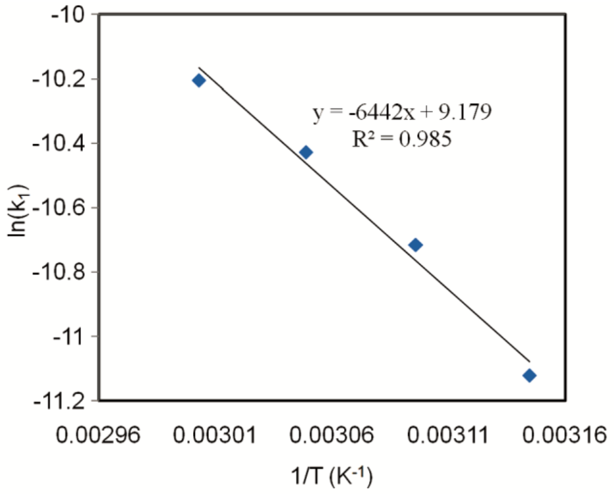


Fig. 10 — Reaction rate constant as function of the reaction temperature for uncatalyzed reaction.

$$k_1 = \exp\left[9.1796 - \frac{6442}{T}\right] \text{and } 53.2 \text{ kJ mol}^{-1}$$

According to Eqn (22), the forward reaction rate constant, $k_{1,obs}$ of the catalyzed rate equation and the forward reaction rate constant, k_1 of the uncatalyzed rate equation evaluated for the temperatures given in Table 3 and Table 4 provide the forward reaction rate constant $k_1^{\,1}$ of catalyst part of the reaction rate constant alone. These results were shown in Table 5. The reaction rate constant of the catalyst part of the reaction alone can be expressed by the Arrhenius equation as

$$k_1^{\,1} = k_c \exp\left(\frac{-E_c}{RT}\right) \qquad \ldots (24)$$

The Arrhenius plot for the relationship between the forward reaction rate constant and the temperature data of Table 5 can be drawn for the catalyst part of the reaction rate constant alone as shown in Fig.10. From this figure, the temperature dependent reaction rate constant $k_{c,}$ and activation energy, E_c for the catalyst part of the reaction alone can be found. Thus the fitted Arrhenius equation for the catalyst part of the reaction alone and the activation energy is given by

Table 5 — The forward reaction rate constant ($k_1^{\,1}$) at various temperatures

Temperature (K)	$k_1^{\,1}$ (L^2 mol^{-2} min^{-1})
323.15	0.00649049
333.15	0.011345997
343.15	0.013286359
353.15	0.016423781

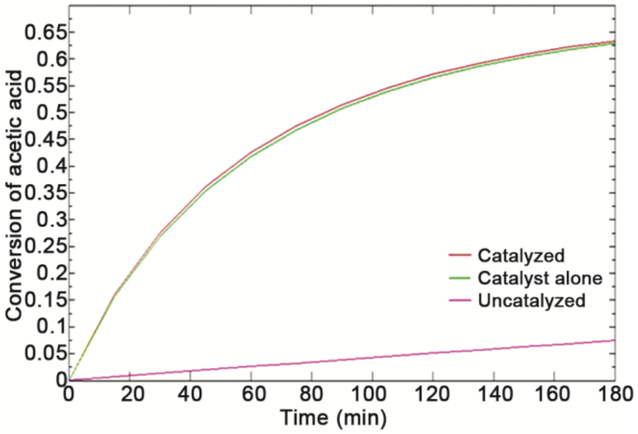


Fig. 11 — Comparison of predictive performance of catalyzed, uncatalyzed and catalyst alone reaction rate equations at 333.15 K temperature and catalyst concentration of 0.12 mol H$^+$ L^{-1}.

$$k_1^1 = \exp\left[5.517 - \frac{3377.5}{T}\right] \text{and } 28.0 \text{ kJ mol}^{-1}.$$

The reaction rate equation based on reaction rate constant, Eqn (25) can be used to compute the reactant conversions based on catalyst alone. The reactant conversions predicted by the rate model of catalyst part alone were compared with those of catalyzed and uncatalyzed model predictions as shown in Fig. 11. These results have shown that the reaction rate of catalyst alone contributes profoundly for the methanol esterification reaction. The reaction rate equation of catalyst part alone can be used to study how different parameters of the esterification reaction can influence the rate of reaction. This equation is useful in the design of esterification reactor where the influence of catalyst alone can be explored on the rate of reaction. It is also useful in the design of reactive distillation where the amount of catalyst plays a crucial role. The kinetic parameters obtained for the esterification acetic acid with methanol under different catalysts of literature results as well as the present results is given in Table S1.

Analysis of results

Methyl acetate has been synthesized by the reaction between acetic acid and methanol in an experimental batch reactor. The reaction was carried out homogeneously without using any catalyst and heterogeneously by using Amberlyst 16 resin catalyst. The reaction was performed using different temperatures in the range of 318.15-333.15 K. Pseudo-homogeneous kinetic models were developed for the catalysed reaction and the uncatalyzed reaction. The reaction rate of uncatalyzed reaction was found slower and the model predictions of this reaction were compared with the experimental results as shown Fig. 11. For the uncatalyzed reaction, the model predictions were found closer to the experimental data.

The influence of catalyst loading, reaction mixture temperature, initial reactant mole ratio, catalyst size and agitation speed were investigated for the catalyzed esterification reaction. The catalyzed reaction was found much faster than the uncatalyzed reaction. The model predictions were compared with the experimental results for the effect different process parameters as shown in Figs, 2, 3 and 5. The model prediction results were found in good agreement with the experimental data for all the cases. The heat of reaction evaluated from van’t Hoff equation has shown the catalyzed reaction to be endothermic.The reaction rate constant expressions were developed for the catalyzed and uncatalyzed esterification reactions as given by Eqn (21) and (24). These expressions were used to derive the equation for the catalyst part of rate constant alone as given in Eqn (25). This reaction rate equation of catalyst part is useful for the design of catalytic reactor/reactive distillation column for the esterification process.

Conclusions

The esterification of acetic acid with methanol by using Amberlyst 16 wet in a well mixed batch reactor was studied under different conditions of the catalyst loading, stirrer speed, Amberlyst catalyst size, temperature and feed mole ratio. From the experimental results, it was observed that the reaction is kinetically controlled instead of diffusion controlled. The parameters such as equilibrium constant, forward and backward reaction rate constants were found from the experimental data by fitting it to a second order differential equation. The influence of temperature on equilibrium constant was found by the van’t Hoff relation. The heat of reaction for the esterification reaction was found to be 4.7 kJ mol^{-1}. Kinetic models were developed for the esterification reaction without using any catalyst and in the presence of Amberlyst 16 catalyst. The developed kinetic models were able to predict the experimental data well. Further, the rate expressions of catalysed and uncatalyzed reactions were used to develop a rate expression for the catalyst part of the reaction alone. This rate expression can be used to find the influence of the catalyst alone on the rate of reaction in heterogeneous catalyzed methanol esterification. This reaction rate equation is useful for the design of catalytic reactor/reactive distillation column for the esterification process.

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Supplementary Data

Supplementary Data associated with this article are available in the electronic form http://nopr.niscair.res.in/jinfo/ijca/IJCA_59A(10)1494-1503_SupplData.pdf.

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