Kinetics of Esterification of Acetic Acid with Methanol in the Presence of Ion Exchange Resin Catalysts

P. E. JagadeeshBabu,* K. Sandesh, and M. B. Saidutta

Department of Chemical Engineering, National Institute of Technology Karnataka, Surathkal, Mangalore, India

ABSTRACT: Esterification kinetics of acetic acid with methanol was studied with solid acid catalyst in an isothermal batch reactor at 333−353 K. Different types of ion exchange catalyst (Indion 130, Indion 190, and Amberlyst 15 wet) were used for the esterification of acetic acid. It was found that Indion 130 was an effective catalyst for acetic acid esterification. The effects of stirrer speed, reaction temperature, initial reactant concentration, and catalyst loading on reaction rate were investigated and optimized. Temperature dependence of the reaction rates and activation energies was determined by an Arrhenius plot. A complete kinetic equation for describing the reaction catalyzed by Indion 130 was developed. This equation can be used in the simulation and design of the catalytic distillation column for the synthesis of methyl acetate.

INTRODUCTION

Esterification of carboxylic acids is an important class of reactions. The kinetics and the equilibrium of different reactions have been investigated throughout the history of physical chemistry, dating back to pioneering efforts of Berthelot and Gilles (1863). Esters can be produced by different methods, on both laboratory and commercial scales. The simplest route to produce esters with high yield is the direct esterification of acids with alcohol in the presence of homogeneous (mineral acid) or heterogeneous catalyst (ion exchange resins).

Methyl acetate is a high volume commodity chemical that is manufactured commercially. Methyl acetate is a colorless liquid, with a mild ester-like odor and it is miscible with many organic solvents. Due to these properties, it is widely used as a solvent in glues, nail polish removers, perfumery, dye manufacture, and chemical reactions and for extractions. It is also used in the manufacture of a variety of polyesters such as photographic film base, cellulose acetate, tenite cellulosic lastics and Estron acetate, and fast-drying paints and for the manufacture of celluloid adhesives from waste film.

In general, methyl acetate is produced using methanol and acetic acid using an acid catalyst. Esterification of acetic acid with menthol is a slow reaction[1] and to accelerate the reaction, acid catalyst is used. Both homogeneous and heterogeneous catalysts have been used for this purpose, where mineral acids are the widely used homogeneous catalysts[1,2] and cation exchange resins in their acid form are the widely used heterogeneous catalyst. The use of a heterogeneous catalyst has the following inherent advantages over homogeneous catalyst: (a) they eliminate the corrosive environment; (b) the catalyst can be easily removed from the reaction mixture by decantation or filtration; (c) the purity of the products is higher because the side reactions can be completely eliminated or are less significant.[3] Salmi et al.[1] studied esterification kinetics of acetic acid with methanol in the presence of hydrogen iodide as a homogeneous acid catalyst in an isothermal batch reactor. From the experiment, Salmi et al., have observed that the catalyst, hydrogen iodide, was esterified by methanol and produced methyl iodide as a byproduct.[1]

Wide varity of solid acid catalysts are available for esterification reactions. Among them, cation ion exchange resins are the most commonly used solid acid catalysts in organic reactions.[4] Ion exchange resins have also been used in esterification[2,3,5,6] and in hydrolysis of methyl acetate.[7,8] Ion exchange resins are the most common heterogeneous catalysts used for esterification reaction and have proven to be more effective for etherification reactions also. Because of their selective adsorption of reactants and swelling nature, these resins not only catalyze the esterification reaction but also affect the equilibrium conversion.[2,9] In heterogeneous catalysis, the forces active at a solid surface can distort or even dissociate an absorbed reactant molecule and affect the rate of reaction.[10]

The synthesis of high purity methyl acetate using batch process is very difficult due to the formation of methyl acetate−methanol and methyl acetate−water azeotropes.[11−13] To achieve high yield, many chemical process industries use reactive distillation (RD) technique. Here the reaction and separation of the product takes place in a single column. Due to the interaction of reaction and distillation in one single apparatus, suitable process control strategies have to be developed and applied, ensuring optimal and safe operation. To model reactive distillation, the reaction kinetics for the particular reaction should be known.[14]

In this present work, esterification of methanol with acetic acid was studied in the presence of Indion 130, Indion 190, and Amberlyst 15-wet. Experiments were conducted to determine the best catalyst for the reaction. The effect of various operating parameters like reaction temperature, reaction time, catalyst loading, molar ratio of the reactants and speed of agitation were studied on the esterification using the selected catalyst.

EXPERIMENTAL METHODS

Materials. Chemicals used in this present study were procured from different sources. Acetic Acid (glacial 99%) was supplied by

Table 1. Physical Property of Different Cation Exchange Resins

physical property	Indion 130	Indion 190	Amberlyst 15 wet
shape	beads	beads	beads
physical form	opaque, gray colored	opaque, faint dark gray colored	opaque, gray colored
average size (μm)	725	725	700
concentration of acid sites (mequiv/g of dry, min)	4.8	4.7	4.7
apparent bulk density (g cm^{-3})	0.55—0.60		0.98
surface area (m^2/g)	20—24	28—32	53
pore volume (mL/g)	0.38—0.42	0.32—0.38	0.30—0.35
maximum operating temp (°C)	150	150	120
pH range	0—7	0—7	
matrix type	styrene DVB	styrene DVB	styrene DVB
resin type	macroporous strong acidic cation	macroporous strong acidic cation	macroporous strong acidic cation
standard ionic form	H$^+$	H$^+$	H$^+$
functional group	$-SO_3^-$	$-SO_3^-$	$-SO_3^-$

Nice chemical, Cochin, India. Methanol (99%) and methyl acetate (99.8%) were obtained from Merck Limited, Mumbai.

Cation exchange resins such as Indion 190, Indion 130, and Amberlyst 15 wet were used for the initial comparison with respect to acid conversion. All the resins were purchased from Ion exchange India Ltd., Mumbai. Indion 130 has a cross-linked three-dimensional structures of polymeric material obtained by sulfonation of a copolymer of polystyrene and divinylbenzene (DVB). It is an opaque, gray solid spherical bead. The resins used in this study, were dried in the oven at 90—100 °C to remove the moisture content. The main properties of the ion exchange resin used in this work are listed in Table 1.

Equipments. The esterification reaction was performed in a 250 mL three neck round-bottom flask, which was placed in a heating rota mantle. The rota mantle contains a heating knob and the speed control knob. The rota mantle was maintained at constant temperature. The stirring speed was varied from 0 to 200 rpm using the speed control knob. A glass thermometer was inserted into the flask to measure the reactant temperature inside the flask. A spiral condenser was connected to the reaction flask to condense the vapors and recirculate it to the reactor.

Experimental Procedure. Measured quantities of Acetic acid (BP: 118 °C) and methanol (BP: 64.7 °C) were charged into the reactor, and the reactor was kept in the heating mantle, which was coupled with the magnetic stirrer. Once the desired reaction temperature was attained, a known quantity of catalyst was charged into the reactor, and the time was considered as zero reaction time. Reaction was allowed to run for a fixed period of time. After the completion of the fixed period time, a known quantity of the reaction mixture was collected for the further analysis. Because the withdrawn sample did not contain catalyst and the samples were immediately brought to room temperature, the reaction was completely stopped. The samples were stored in a refrigerator to prevent evaporation loss and were analyzed using GC (gas chromatography). The stoichiometry equation of acetic acid with methanol in the presence of ion exchange catalyst is as follows,

$$CH_3COOH_{(A)} + CH_3OH_{(B)} \leftrightarrow CH_3COOCH_{3(C)} + H_2O_{(D)}$$

$$(1)$$
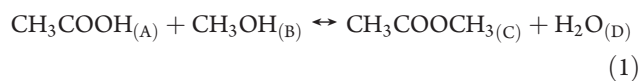
Analysis. The samples were analyzed using gas chromatograph (Thermo Electron Corp.) equipped with a flame ionization detector
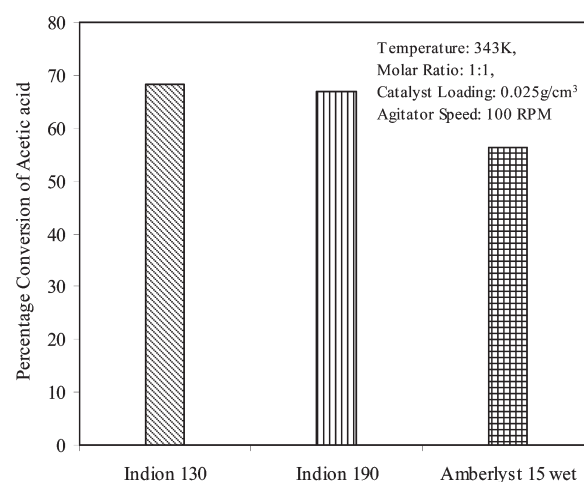

Figure 1. Effect of different catalyst on the conversion of acetic acid.

(FID). Capillary column DB-1701 (30 m × 0.53 mm × 1 μm) was used to analyze the sample. High purity nitrogen gas was used as a carrier gas at a flow rate of 2 mL/min. The oven temperature was programmed at 40 °C for 2 min and then raised from an initial value of 40 to 150 °C at a ramp rate of 10 °C/min. The right inlet and detector temperature were maintained at 250 and 300 °C respectively.

■ RESULTS AND DISCUSSION

Catalyst Selection. Experiments were conducted with different types of solid acid catalyst to assess their efficacy in this reaction. Three types of ion exchange resin, Indion 130, Indion 190, and Amberlyst 15-wet were used for the esterification reaction. Figure 1 shows the efficacy of all the three ion exchange catalyst. From the Figure 1, it was observed that Indion 130 and Indion 190 gave maximum conversion of 68.18% and 66.76%, respectively; where as Amberlyst 15-wet gave a conversion of 56.37%. The reason for the variation in the conversion could be the variation in the concentration of H$^+$ ion on the surface of the catalyst, pore size distribution and also the initial water content in the resin bead.[15] The mequiv/g of dry values for Indion 130 and Indion 190 are higher than that for Amberlyst 15 wet.[10] Both Indion 130 and Indion 190 were found equally effective but mequiv/g of
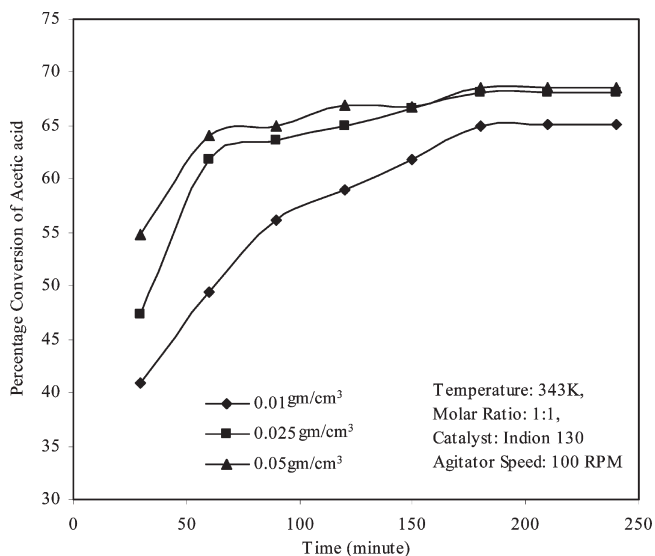
Figure 2. Effect of different catalyst loading on the conversion of acetic acid.
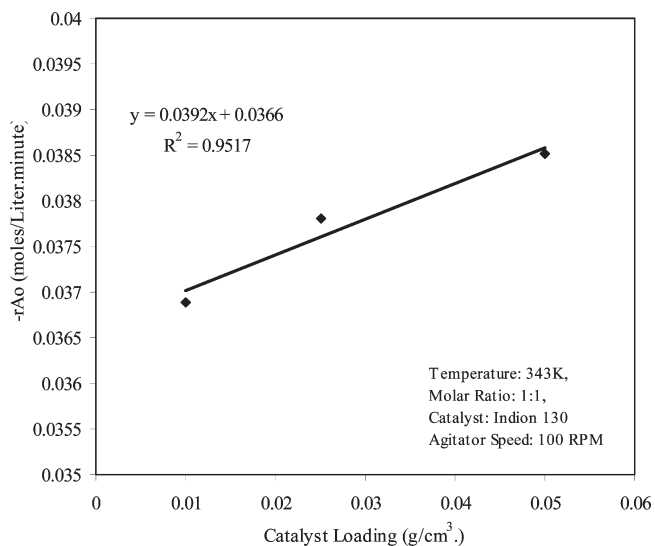

Figure 3. Effect of catalyst loading on the reaction.

dry for Indion 130 is slightly higher and that could be the reason for conversion obtained with Indion 130 compared to Indion 190. Indion 130 was chose as ion exchange catalyst for further studies.

Effect of Catalyst Loading. The amount of catalyst plays a major role in the conversion of acid to ester (esterification reaction). In a batch process the interaction of reactant and catalyst will be more at the start of the reaction, and as the product forms the interaction reduces and at this point, the amount of catalyst plays a major role in increasing the overall conversion. In this study, the effect of catalyst loading on the percentage conversion of acetic has been studied with respect to time. Figure 2, shows the effect of catalyst loading over percentage conversion of acetic acid to methyl acetate. From Figure 2, it is observed that the conversion is low for low catalyst loading, and the percentage conversion gradually increased as the catalyst loading increased. It was observed that with an increase in the catalyst loading from 0.01 to 0.05 g/cm^3, the conversion of acetic
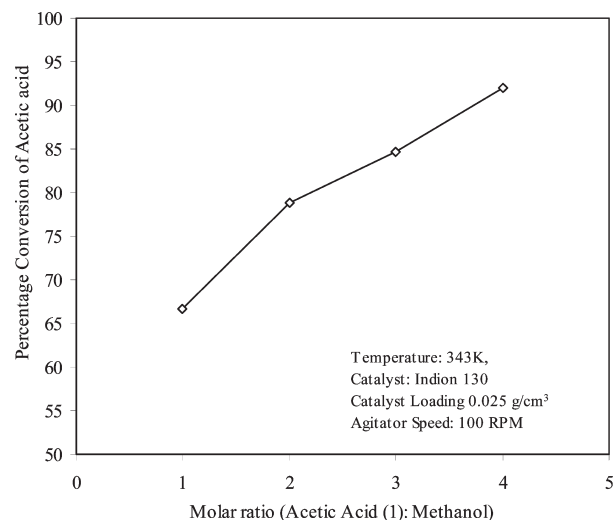

Figure 4. Effect of molar ratio on the conversion of acetic acid.

acid increased from 60 to 70% (at 180 min). The increase in the catalyst loading increases the surface area available for ion exchange and also the availability of H$^+$ ions enhancing conversion.[5,6,15] This behavior can be further confirmed by calculating the initial rate of reaction at different catalyst loading. The initial rate of reaction was calculated as follows[16]

$$-r_{Ao} = \left(\frac{C_{Ao} X_A}{t} \right) \qquad (2)$$

where r_{Ao} is the initial rate of reaction, C_{Ao} is the initial concentration of acetic acid, and X_A is the conversion of acetic acid at time t. The effect of reaction rate on the catalyst loading is shown in Figure 3. From the Figure 3, it is observed that the initial rate of the reaction is directly proportional to catalyst loading. Intersection of this straight line with the y axis gives the uncatalyzed reaction rate at given operating conditions.[16] The mathematical expression relating the initial reaction rate to the catalyst loading can be derived from Figure 3, as follows,[16]

$$-r_{A0} = 0.0366X + 0.0416 \ (g/cm^3) \ mol/(Lmin) \qquad (3)$$

where X is the catalyst loading This equation is valid only at 343 K, 1:1 molar ratio, at which present studies were conducted.

Effect of Molar Ratio. The molar ratio of acetic acid to methanol was varied from 1:1 to 1:4, while the other operating variables were kept at constant values. Figure 4 shows the effect of molar ratio on the percentage conversion. From Figure 4, it can been seen that the conversion of acetic acid increases with increase in mole ratio. With an increase in mole ratio of acetic acid to methanol from 1:1 to 1:4, the conversion of acetic acid increased from 66 to 91%. From Figure 4, it is clear that the conversion of acid decreases by lowering the alcohol concentration. This is due to the lower alcohol concentration, which in turn shifted the reaction equilibrium toward the reactant side. Increasing the acid to alcohol ratio, more acid reacts, because of excess of alcohol.[15,17] The maximum conversion of acetic acid was obtained for 1:4 mol ratio.

Effect of Agitation. The external mass transfer resistance to the reaction process can be affected by stirrer speed. The effect of external mass transfer on the catalytic efficiency was investigated with and without stirring the reaction mixture. Mixing was done at two different rpm's (100 and 200 rpm). Form the experimental
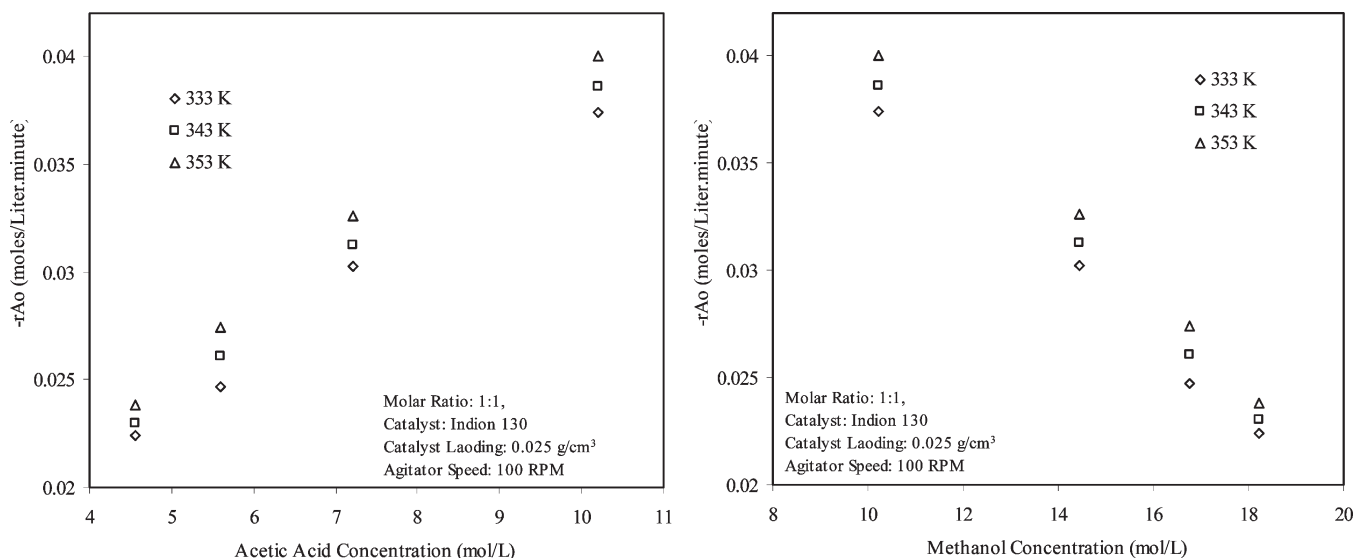
Figure 5. Effect of acetic acid and methanol concentration on the initial reaction rate.

data it is observed that the conversion of acetic acid is unaffected by stirrer speed. This indicates that the external mass transfer resistance is not a rate-controlling step.[15,18] This suggests that the diffusion is not the controlling mechanism in the rate of reaction in ion exchange catalyzed process.[4] Chakrabarti and Sharma[4] have reported that the external diffusion will not control the rate of ion exchange catalyzed process unless the viscosity of the reactant mixture is very high or the speed of the agitation is very low. Further experiments were conducted with 100 rpm.

Effect of Reactant Concentration. The effect of initial reaction rate was determined by altering the concentration of the reactant (alcohol and acid individually). The results are shown in Figure 5. The ordinate value for the graph is calculated from eq 2. From the graph it is clear that the initial reaction rate increases as the concentration of acid increases. Increasing concentration of acid initiates the forward reaction.[15] Methanol reacts with excess acid and as a result methanol concentration reduces as time proceeds. This leads to the reduction in the rate of the reaction. This phenomenon seen in Figure 5 can be explained as follows: by increasing the concentration of alcohol in the reactor. For lower concentration of alcohol the rate is high and it reduces as the concentration of the alcohol in the reactor increases. Initially, the acids present in the reactor react with alcohol and form the product. Upon a further increase of the alcohol concentration in the reactor, the acid concentration in the reactor reduces and it will not be available for the reaction and hence the reaction rate decreases.

Effect of Reaction Temperature and Kinetic Model. The effect of temperature on the reaction rate constant was investigated by setting the reaction temperature at 333, 343, and 353 K.[1,10] The molar ratio was kept at 1:1, and catalyst loading was 0.025 g/cm^3, reaction time 180 min. The experimental data showed that the effect of temperature on the conversion of acetic acid is very significant and the conversion of acetic acid increased with increasing reaction temperature.

Catalytic reactions can be classified as heterogeneous and homogeneous reactions. In heterogeneous catalysis the force active at the solid surface distorts or even dissociates an adsorbed reactant molecule to increase the rate of reaction.[18] The ion exchange catalyzed reaction can be classified as quasi homogeneous or as quasi heterogeneous reactions.[18] It has been
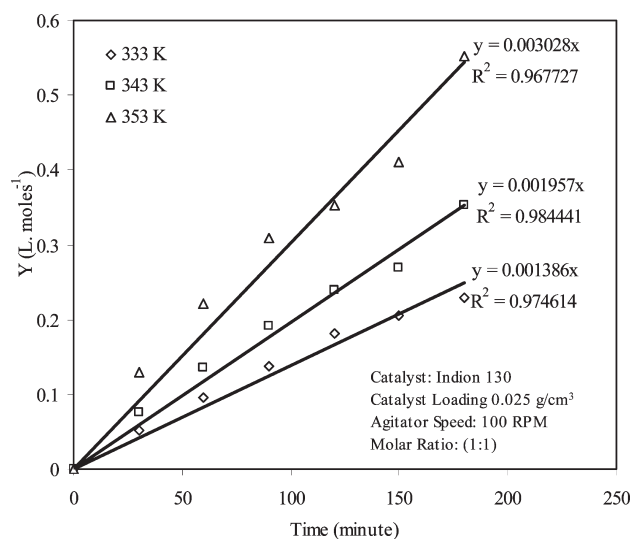

Figure 6. Y vs t of eq 5.

concluded that the kinetic orders of the chemical reaction in both cases are same. The power law model usually used for homogeneous reaction can be deduced from the Langmuir—Hinshelwood model for heterogeneous reaction by assuming that the adsorption is week for all components. By assuming the surface reaction is rate controlling, the Langmuir—Hinshelwood rate equation for the esterification of acetic acid using ion exchange resins as shown in eq 1 can be expressed as follows,[18]

$$\frac{dC_A}{dt} = k_f (C_A C_B - C_C C_D / K) \tag{4}$$

where k_f is the forward rate constant, K is the equilibrium constant, C is the concentration (mol/L), and A, B, C, D represent acid, alcohol, ester, and water respectively.

Equation 4 is a familiar power law model for homogeneous reaction. The above equation is purely based on the assumption that the reaction is quasi-homogeneous reaction as long as the adsorption is weak for all components. In the absence of both

Table 2. Rate Constant for Different Reaction Temperatures

reaction temp, K	k_f lit./mol min	k_b lit./mol min	K	ln K	ΔG_o
333	0.001386	0.0002767	5.0096756	1.6113712	4461.181
343	0.001957	0.0003001	6.5209793	1.8750246	5347.0113
353	0.003028	0.0003268	9.2645564	2.226196	6533.5335
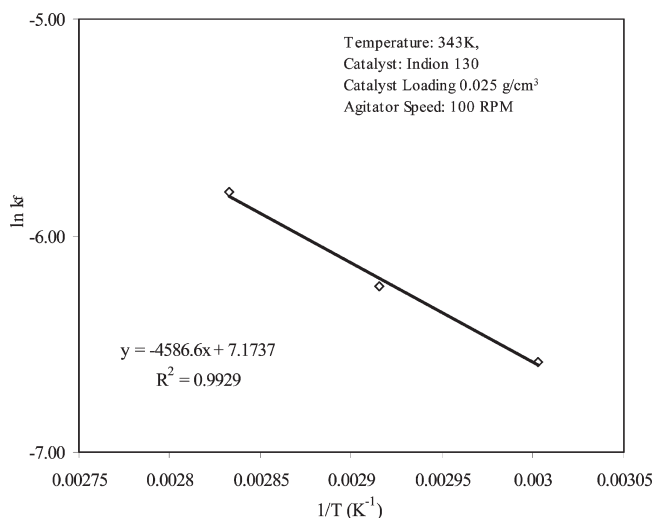
Figure 7. Arrhenius plot for finding the activation energy and the pre-exponential factor.

Figure 8. van't Hoff plot for finding the heat of reaction.

internal and external diffusion resistance to the mass transfer of both reactant and product to the ion exchange resin the intrinsic kinetics can be determined from the experimental data. The equilibrium constant K can be calculated from the equilibrium concentration of all compounds. The forward rate constant k_f can be calculated by integrating and simplifying the above equation (eq 4), which yields

$$\frac{1}{\sqrt{B^2 - 4AC}} \ln \left[\frac{(B + \sqrt{B^2 - 4AC})C_C + 2C}{(B - \sqrt{B^2 - 4AC})C_C + 2C} \right] \equiv Y = k_f t \tag{5}$$

where $A = (1 - 1/K)$, $B = -a - b - d/k$, and $C = ab$, where a, b, d, are the initial concentration of methanol, acetic acid, and water, respectively. The left-hand side of eq 5 is equated with a single variable Y, which has unit of liter per mole.

The kinetic equation (eq 4) representing the esterification of acetic acid is valid, if the Y in eq 5 is linearly related with time t. Figure 6 shows the relationship between Y and t at different temperatures. From the figure, it is observed that Y is linearly related with time through the origin, irrespective of the reaction temperature. The forward rate constant k_f was determined from the slope of the line. The different k_f values with respect to the reaction temperature are tabulated in Table 2. From the k_f values it was found that the rate constant increases with the increase in the reaction temperature. The backward reaction rate constant k_b was calculated using equilibrium constant K and k_f. The linear behavior between the Y and time t through origin shows that the reaction of eq 1 catalyzed by Indion 130 is quasi-homogeneous and eq 4 can be used to describe the kinetics of the reaction.

Further, the forward rate constant k_f listed in Table 2 is used to calculate the pre-exponential factor k_o and activation energy E
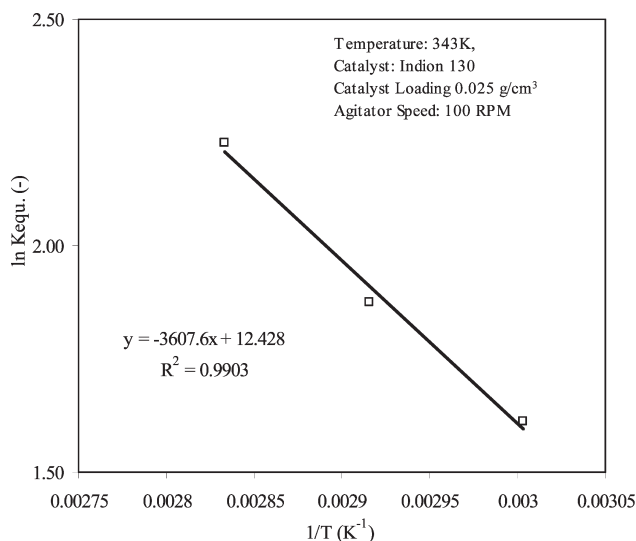
using Arrhenius relation. Figure 7 shows the Arrhenius plot, between $\ln(k_f)$ and $1/T$, which gave a straight line. This indicates that the internal diffusion resistance is not significant.[18] The activation energy was calculated from the slope of the line and the pre-exponential factor was calculated using the intercept. The activation energy and pre-exponential factor were found to be 38.13 kJ/mol and 130.467 (—), respectively. The higher value of activation energy further indicates that surface reaction is the rate controlling step.

The heat of a reaction is calculated by van't Hoff equation as shown below,[19,20] where the van't Hoff equation provides information about the temperature dependence of the equilibrium constant.

$$\Delta G^\circ = -RT \ln K \tag{6}$$

$$\ln K = \left(\frac{-\Delta H^\circ}{RT} \right) + \left(\frac{\Delta S^\circ}{R} \right) \tag{7}$$

The reaction enthalpy (heat of a reaction, ΔH°) and reaction entropy (ΔS°) were obtained from eq 7 by plotting ln K vs $1/T$. The slope of the straight line gives $(-\Delta H^\circ/R)$ and the intercept on the ordinate gives $(\Delta S^\circ/R)$. Figure 8 shows the relation between ln K and $1/T$. The negative slope indicates that the reaction is an endothermic reaction. On the basis of LeChatelier's principle, the increase in the temperature shifts the system in the forward direction to alleviate the stress of additional heat. The shift in the forward direction leads to an increase in product (esters) and a decrease in the reactant (acid), which increases the equilibrium constant as predicted by van't Hoff equation. This was further confirmed by comparing the forward activation energy (38.13 kJ/mol) with the backward activation energy (8.3 kJ/mol), which is less than the forward reaction. The ΔG° values for different

temperatures are listed in Table 2. From Figure 8 the heat of reaction ($\Delta H°$) and reaction entropy were found to be 29.99 kJ/mol and 103.33 kJ/(mol K) respectively.

■ CONCLUSIONS

The kinetic study of esterification of acetic acid with methanol was studied by using different solid acid catalysts, Indion-130, Indion-190, and Amberlyst-15 Wet, in a batch reactor. Among the heterogeneous catalysts the order of catalytic activity was found to be Indion-130 > Indion-190 > Amberlyst-15 Wet. Indion-130 was used for further experiments.

The effect of various parameters, such as reaction temperature, reaction time, catalyst loading, molar ratio, and speed of mixing were studied. Catalyst loading 0.025 g/cm^3 gave better acetic acid conversion. The acetic acid conversion increased with an increase in temperature, which confirmed that the reaction is intrinsically kinetically controlled. The rate constant for different reaction temperature was found using eq 5. The activation energy was found using Arrhenius plot and it found to be 38.13 kJ/mol. The thermodynamic properties $\Delta H°$ and $\Delta S°$ were evaluated using Van't Hoff plot and found that the reaction is endothermic. The rate equation for the esterification of acetic acid with methanol was developed.

■ AUTHOR INFORMATION

Corresponding Author

*Phone: +91 9632896086. Fax: 0824-2474057. E-mail: dr.jagadeesh@yahoo.co.in, jagadeesh_78@nitk.ac.in.

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