



Kinetic Study of Catalyzed and Uncatalyzed Esterification Reaction of Acetic acid with Methanol

M.B. Mandake^a, S.V. Anekar^b, S.M. Walke^c

^a Department of Chemical Engineering, Tataysaheb Kore Institute of Engineering and Technology, Waranangar, Kolhapur 416113, India.

^b Department of Chemical Engineering, Tataysaheb Kore Institute of Engineering and Technology, Waranangar, Kolhapur 416113, India.

^c Department of Chemical Engineering, Bharati Vidyapeeth college of Engineering, Navi Mumbai, India.

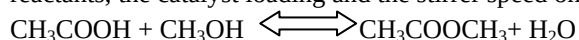
Abstract: The kinetics of esterification of acetic acid with methanol will be investigated extensively for homogenous and heterogeneous catalyzed reactions. The experiments will be carried out in a batch stirred reactor at different temperatures by using ion exchange resin as a catalyst. The concentration – time profile will be observed for different sets of conditions. The effects of temperature, Catalyst loading and feed molar ratios on reaction kinetics will also be studied. The activation energy and equilibrium constants for this reaction will be determined experimentally at different temperatures. The temperature dependency of the constants appearing in the rate expression will also be determined.

Key Words: Esterification, Kinetics, Heterogeneous, Catalyst, Methyl Acetate, Ion exchange resin.

I. Introduction

There is an increasing the inclination of chemical industries toward new processes that should meet requirement such as generation of nearly zero waste chemicals, less energy, and sufficient uses of product chemicals in various application. Hence the esterification is widely employed reaction in the organic process industry. The reaction is carried out between carboxylic acid and alcohol at with or without present of different acid catalyst under such specific conditions. Esters are used as solvents of paints, adhesives and organic media instead of aromatic compounds. Esterification reactions are extremely slow; it requires several days to attain the equilibrium in the absence of a catalyst. To accelerate the reaction rate, catalysts are always employed in liquid phase esterification. Despite the strong catalytic effect, the use of homogenous catalysts, such as Sulphuric acid and p-toluenesulphonic acid suffers from several draw-backs, such as the existence of side reactions, corrosion of the equipment and the need to deal with acidic wastes. Homogenous catalysts may also result in sulphur contamination of the final ester product. In this situation, the use of solid catalysts has received increasing attention in the past years. Many solid-acid catalysts have been used, such as iodine, zeolite-T membrane, ZSM-5, HY zeolite, zeolite beta, acid treated clays, heteropolyacids, copper catalysts, sulphated oxides and zirconia. Ion exchange resins, however, are the most commonly used solid acid catalysts instead of liquid ones.

The goal of this work was to study the esterification kinetics of acetic acid with methanol in the presence of catalyst and in the absence of catalyst. The effect of the reaction temperature, the initial molar ratio of the reactants, the catalyst loading and the stirrer speed on esterification kinetics were studied.



Most reactions catalyzed by ion exchange resins can be classified as either a quasihomogenous or a quasiheterogeneous. The kinetics of this model reaction catalyzed by Amberlyst-15 was described as a quasihomogenous and a quasiheterogeneous model.

II. Experimental

A. Chemical and catalysts

All chemicals and catalysts were procured from firms of repute and used without further purification: Acetic acid (S.D. Fine Chemicals, Mumbai India), Methanol (Merck India), Amberlyst-15 (Rohm and Hass, USA). The physical properties of these resins are reported in Table 1. The macroporous resin was dried at 70°C for 6 hrs in vacuum drier before use. In all the experiment, the dried catalyst was used.

Table 2.1:- Properties of Amberlyst-15 ion exchange resin

Shape	Beads
Average particlesize (mm)	0.5
Internal surface area (m ² /gm)	55
Capacity (meq /gm)	4.7
Cross-linking density (% DVB)	20-25
Porosity (%)	36
Max.operating temperature (°C)	120

B. Reaction Procedure

The reaction was carried out in a 500 ml glass reactor of 7.5 cm I.D. equipped with four equally spaced full baffles and four-bladed turbine impeller. The reaction temperature was maintained by means of a thermostatic water bath in which the reaction assembly was immersed. Reactions were carried out in the presence and in the absence of Amberlyst-15 resin catalyst. The reaction mixtures were allowed to reach the desired temperature and the zero time sample was collected. Agitation speed was then commenced at sufficiently high speed measured with a tachometer. In most of the cases, alcohol was taken in far molar excess over acetic acid to drive the equilibrium away towards the ester formation.

C. Analysis

For kinetic measurements, samples were withdrawn periodically and analysed by instrumental methods. The product distribution in the sample was determined by Gas Chromatography (GC) on a CHEMITO 7610 gas chromatograph machine (Thermo Fisher Pvt. Ltd, India) equipped with Flame Ionisation Detector. A 3 m long stainless steel column of 0.3175 cm I.D., packed with OV-17 on chromosorb was used for the analysis.

III. Results and discussion

To shift the equilibrium towards the formation of the desired product, excess methanol was used in the reaction. The preliminary experiments were conducted under otherwise similar conditions of reactant concentration (or mole ratio), catalyst loading, speed of agitation, and temperature except the type of catalyst.

Kinetics for Uncatalyzed Reaction:

A. Elimination of mass transfer resistance

Preliminary experiments were carried out to evaluate the influence of the different mass transfer resistances. The batch (solid-liquid and solid-liquid-liquid) reactions were carried out over a wide range of speed of agitation 800-1200 RPM to study the external mass resistance. It was observed that beyond 1000 RPM there was no appreciable change in the rate of the reaction. Hence all the reactions were conducted at 1000 rpm to ensure that there is no resistance to mass transfer at any existing solid-liquid and liquid-liquid interface.

B. Effect of temperature

The study of the effect of the temperature is very important since it is useful to calculate the activation energy of the reaction. The effect of temperature was studied over a temperature range of 308 K to 328 K. The experiments were carried out at three different temperatures i.e. 308K, 318K and 328K with 1:3 molar ratios of acetic acid and methanol, and 1000 rpm speed for uncatalyzed reactions.

Results obtained in the Fig.3.1 indicate that for the limiting component the rate of reaction and conversion are sensitive to a change in temperature. Fractional Conversion of Acetic acid increases with increase in temperature for uncatalyzed reactions.

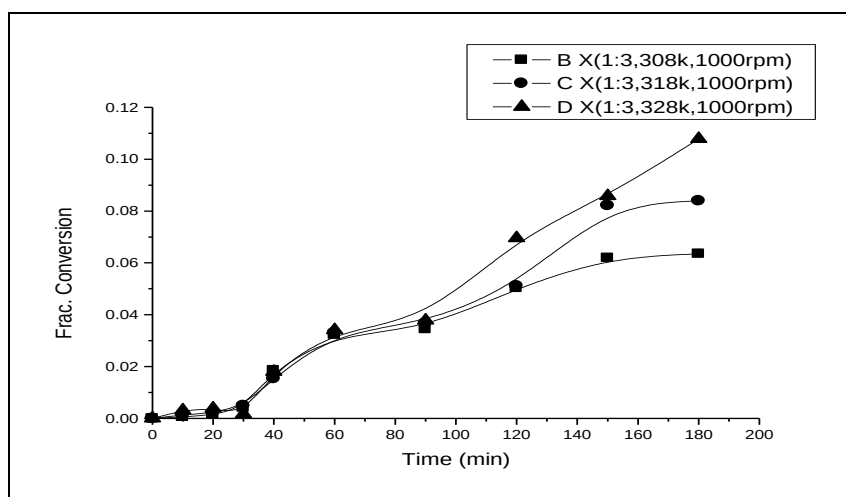


Figure 3.1: Effect of Temperature on Acetic Acid in Uncatalyzed reaction: AA: MeOH mole Ratio = 1:3, rpm=1000

C. Effect of mole ration of reactants

For uncatalyzed reactions the experiments were conducted at different mole ratios like 1:1, 1:2, and 1:2 of acetic acid and methanol at 55°C, 1000 rpm speed. Results obtained in the Fig.3.2 shows the effect of mole ratio of alcohol to acetic acid on the reaction kinetics. As expected the rate and equilibrium conversion of the limiting

reactant increase with increase in mole ratio. It was observed that fractional conversion of acetic acid goes up to high as 14% for the mole ratio of 1:3, 55°C, and 1000 rpm for uncatalyzed reactions.

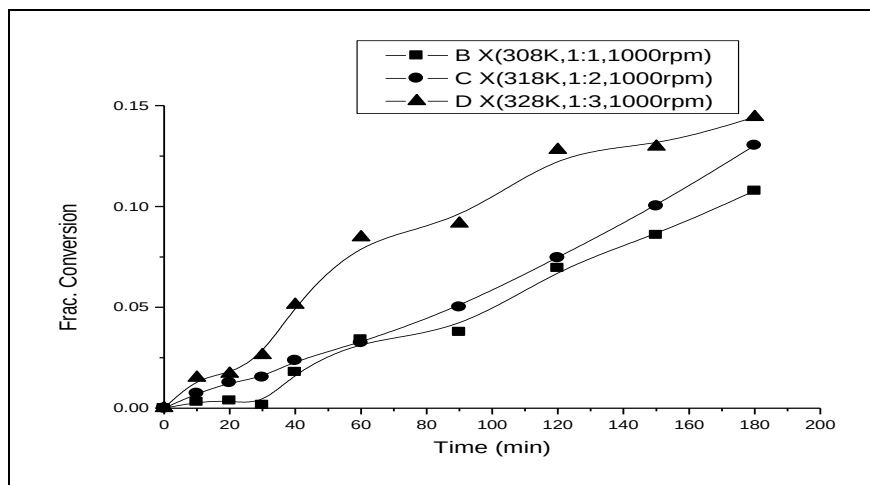


Figure 3.2: Effect of Mole ratio on Acetic Acid in Uncatalyzed reaction: Temperature = 328 K, rpm=1000
Kinetics for Catalyzed Reaction

D. Effect of presence of catalyst

The catalytic activity of the resin was first tested qualitatively through two experiments with different catalytic conditions. In the first one, a non-catalyzed reaction was conducted in a homogeneous liquid phase; in the second, the commercial resin Amberlyst-15 was used. Both the reactions are carried out at 55°C, 1:3 molar ratios of acetic acid and methanol at 1000 rpm speed of agitator. For the reaction with catalyst 10wt% of catalyst dried under vacuum for 8 hrs at 343 K was used. Esterification reaction can take place even in the absence of the catalyst due to the weak acidity of acetic acid itself. However, it was observed that the reaction is extremely slow.

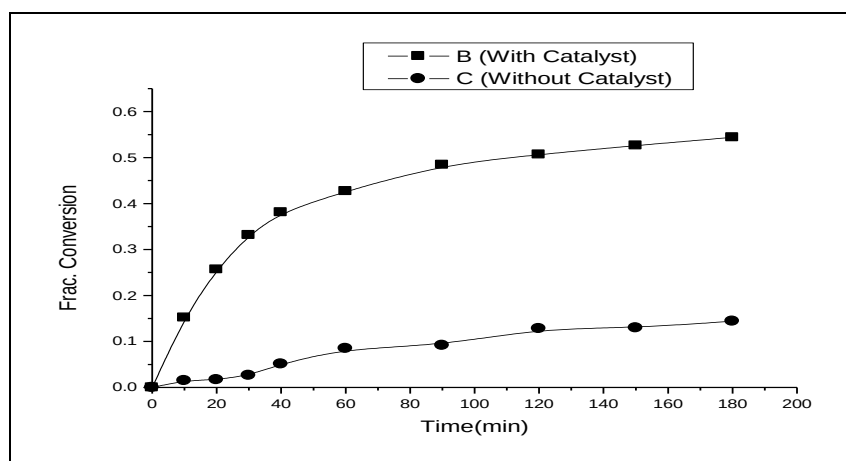


Figure 3.3: Effect of presence of catalyst: Temperature= 328 K, AA: MeOH mole ratio=1:3, rpm= 1000, catalyst loading=10WT%

After about 3 hrs, when the catalyzed processes have already reached equilibrium, the conversion achieved in the non-catalyzed reaction was 14% while in catalyzed reaction it was 54%.

E. Effect of Catalyst Loading

The experiments were conducted with different catalyst loadings i.e. 2.5 wt%, 5 wt% and 10wt% at 55°C, 1:3 molar ratio of acetic acid and methanol and 1000 rpm speed. It was found that with increase in catalyst loading results in an increase in the rate of reaction and fractional conversion of acetic acid because of an increase in number of active sites, which again indicates that mass transfer resistances are absent and the reaction is only

controlled by intrinsic kinetics. At higher catalyst loading the rate of mass transfer is excessively high and therefore there is no more increase in the rate.

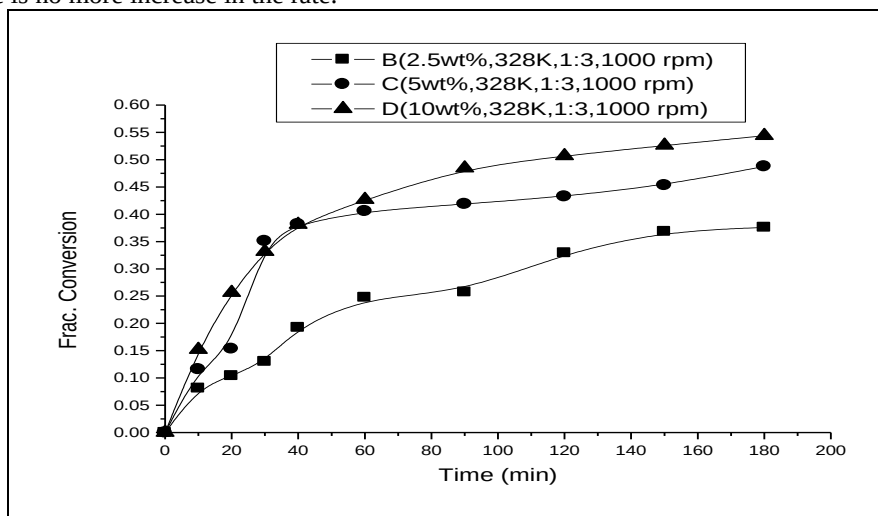


Figure 3.4: Effect of catalyst loading on Acetic Acid: Temperature= 328 K, AA: MeOH mole ratio=1:3, rpm=1000

F. Effect of Temperature

The effect of temperature was studied over a temperature range of 308 K to 328 K. The experiments were carried out at three different temperatures i.e. 308K, 318K and 328K with 1:3 molar ratios of acetic acid and methanol, 10 wt% catalysts, 1000 rpm speed.

Results obtained in the Fig.3.5 indicate that the rate of reaction and conversion are sensitive to a change in temperature. It was seen that Conversion of limiting reactant increases with increase in temperature.

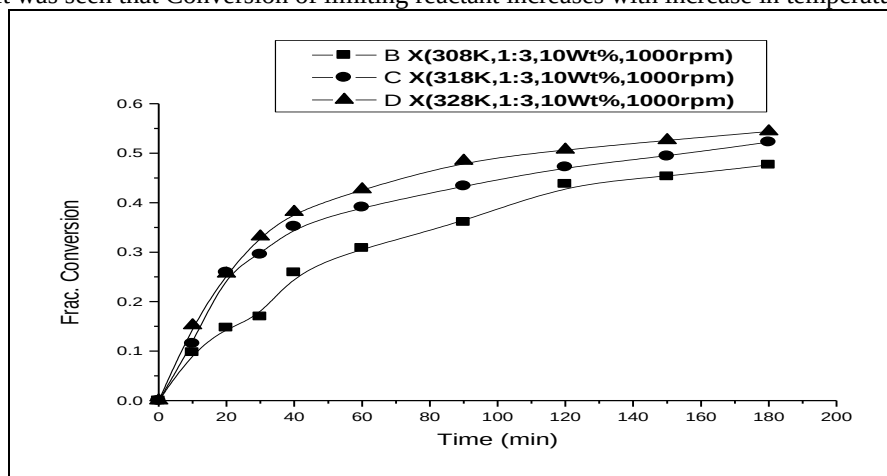


Figure 3.5: Effect of Temperature on Acetic Acid: AA: MeOH mole ratio=1:3, rpm=1000, Catalyst loading= 10 wt%

G. Effect of Mole Ratio

The concentration of methanol has an influence on the reaction rate and on the concentration. The experiments were conducted at different mole ratios like 1:1, 1:3, and 1:5 of acetic acid and methanol at 55°C, 10 wt% catalysts, 1000 rpm speed. Results obtained in the Fig. 3.6 shows the effect of mole ratio of alcohol to acetic acid on the reaction kinetics. As expected the rate and equilibrium conversion of the limiting reactant increase with increase in mole ratio. It was observed that fractional conversion of acetic acid goes up to high as 54% for the mole ratio of 1:3, 55°C, and 1000 rpm.

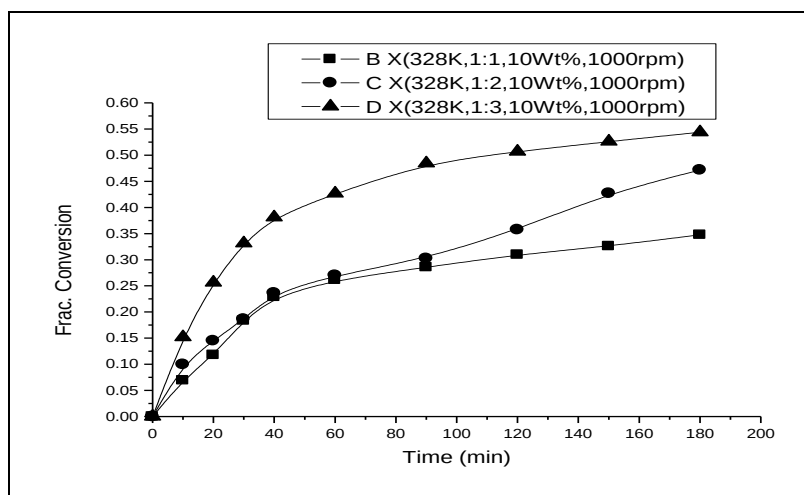


Figure 3.6: Effect of Mole ratio on Acetic Acid: Temperature= 328 K, rpm=1000, catalyst loading= 10 wt%

3.8 Reaction Kinetics

Since the external mass transfer resistance and the intraparticle diffusional resistance were absent, the reaction was kinetically controlled. The catalyst used is a macroporous ion-exchange resin. This is because, in a macroporous resin, the pores are so large ($>400 \text{ \AA}$) that the reactants are able to diffuse into the pores and the products to diffuse out without any resistance. This is the so called pseudo homogeneous model.

a. Kinetic model

Esterification of Acetic acid with Methanol is given as



Esterification reactions are known to be second- order reversible reactions. Therefore, for the bimolecular-type second order reactions.



With the restrictions that $C_{AO} = C_{BO}$ and $C_{EO} = C_{WO}$, the rate can be written as

$$\begin{aligned} -r_A &= -\frac{dC_A}{dt} = C_{AO} \frac{dX_A}{dt} = k_1 C_A C_B - k_2 C_E C_W \\ &= k_1 C_{AO}^2 (1 - X_A)^2 - k_2 (C_{AO} X_A)^2 \end{aligned} \quad (3)$$

Where A, B, E, and W refer to Acetic Acid, Methanol, Methyl Acetate and Water, respectively.

At the equilibrium, $-r_A = 0$. Hence, from the above equations, we find the fractional of A at the equilibrium conditions by

$$K = \frac{C_E C_W}{C_A C_B} = \frac{X_{Ae}^2}{(1 - X_{Ae})^2} \quad (4)$$

And the equilibrium constant by

$$K = \frac{k_1}{k_2} \quad (5)$$

Combining the above three equations, in terms of the equilibrium conversion, we obtain

$$\frac{dX_A}{dt} = k_1 C_{AO} \left[(1 - X_A)^2 - \left(\frac{1 - X_{Ae}}{X_{Ae}} \right)^2 X_A^2 \right] \quad (6)$$

With conversions measured in terms of X_{Ae} , this may be indicated as a pseudo second-order reversible reaction which, on integration, gives

$$\ln \left[\frac{X_{Ae} - X_A}{X_{Ae} - X_{Ae}} \right] = 2k_1 \left(\frac{1}{X_{Ae}} - 1 \right) C_{BO} t \quad (7)$$

Temperature and Reaction Rate:

We can examine the variation of the rate constant with temperature by an Arrhenius' law relationship.

$$k_1 = k_1^0 \exp\left(\frac{-E_A}{RT}\right) \quad (8)$$

This is conveniently determined by plotting $\ln k_1$ versus $1/T$.

b. Kinetics for Catalyzed Reaction

The experimental data collected at temperatures of 308 K, 318K and 328K at molar ratios of acetic acid to methanol of 1:1 and at a stirring speed of 1000 rpm were used to plot the left-hand side (LHS) of Eq. (7) versus time to get a straight line passing through the origin, thus suggesting that the model developed is adequate to represent the system.

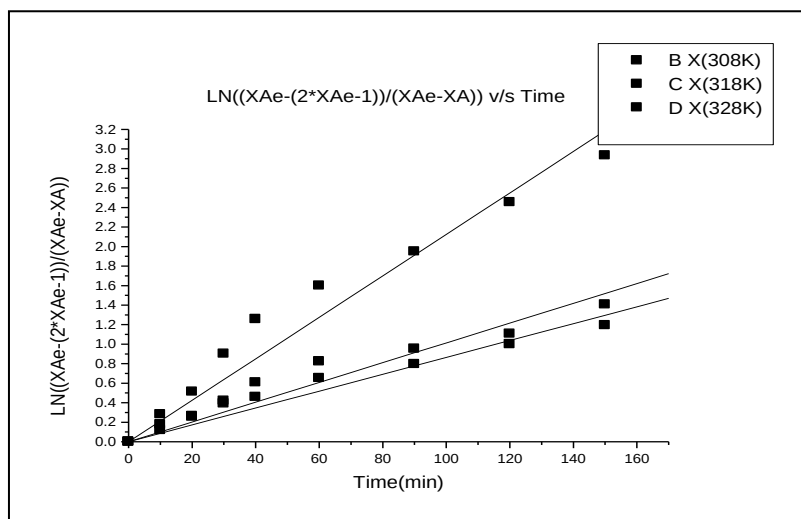


Figure 3.7: Typical kinetic plots for the effect of temperature on Catalyzed Reaction.
Catalyst loading = 10wt%, speed of agitation = 1000 rpm, mole ratio of acetic acid to methanol = 1:1
The optimized values of the heterogeneous reaction rate constants are presented in Table 3.1

Table 3.1: Reaction rate constants for heterogeneous catalyzed esterification

Temp., K	K_1 $L.mol^{-1}.min^{-1}$	K_2 $L.mol^{-1}.min^{-1}$
308	0.060013	0.807277
318	0.081278	0.901893
328	0.147012	1.25339

c. Kinetics for Un-Catalyzed Reaction

For the kinetic study of the uncatalyzed esterification reaction, the experiments are carried out at 308K, 318K, and 328K at molar ratios of acetic acid to methanol of 1:1 and at a stirring speed of 1000 rpm respectively.

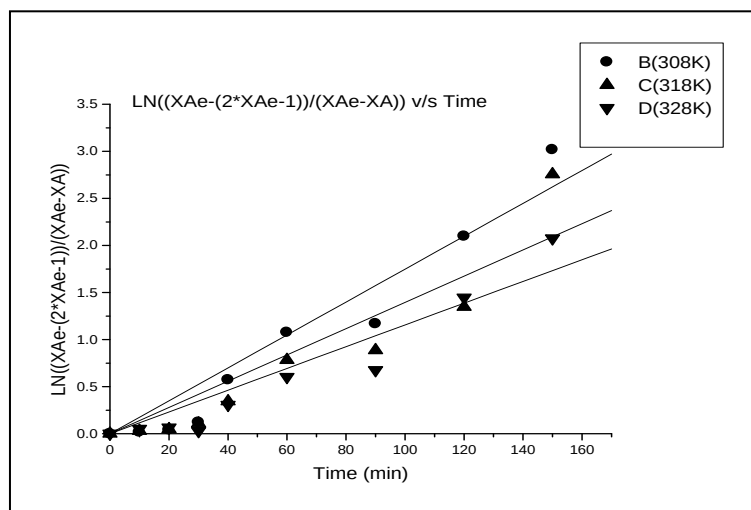


Figure 3.8: Typical kinetic plots for the effect of temperature on Un-catalyzed reaction. Speed of agitation = 1000 rpm, mole ratio of acetic acid to methanol = 1:1

The optimized values of the Un-catalyzed reaction rate constants are presented in Table 3.2

Table 3.2: Reaction rate constants for Un-catalyzed Esterification

Temp., K	K_3 L.mol ⁻¹ .min ⁻¹	K_4 L.mol ⁻¹ .min ⁻¹
308	0.015088	2.723251
318	0.020076	3.4285
328	0.024358	3.707542

The optimized values of the activation energies for Un-catalyzed and Catalyzed reactions are presented in Table 3.3

Table 3.3: Activation Energies for Un-catalyzed and Catalyzed Esterification Reactions

Type of Reaction	Un-Catalyzed Reaction		Catalyzed Reaction	
	Forward	Backward	Forward	Backward
E KJ/mol	20.12	12.95	37.626	18.473

IV. Conclusion

The esterification reaction of acetic acid with methanol was successfully carried out over Amberlyst-15 as cationic exchange resin as a catalyst and in the absence of catalyst also in stirred batch reactor. The effect of temperature, molar ratios, and catalyst loading on the overall rate of reaction as well as concentration-time profiles were investigated. For catalyzed reaction various experiments were carried out in the temperature range of 308-328K and it has been observed that at 328K conversion was maximum, also catalyst loading varied from 2.5 to 10 wt% and at 10 wt% catalyst loading conversion becomes maximum, similarly if molar ratios varied from 1:1 to 1:3 it has been observed that at molar ratio of 1:3 conversion achieved was maximum. For Uncatalyzed reactions also conversion achieved was maximum at 323K, 1:3 mole ratio. A stirrer speed ≥ 800 rpm was found sufficient for eliminating external diffusion. Internal diffusion was negligible under the employed esterification reaction conditions. The conversion of acid increased with increasing temperature and catalyst loading and initial amount of alcohol. The conversion achieved in the non-catalyzed reaction was 14% while in catalyzed reaction it was 54%. To develop the model, reactions are carried out in the temperature ranging between 308 and 328K and molar feed ratio of 1:1. This reaction was intrinsically controlled. A pseudo homogenous kinetic model was employed to fit the experimental data. The activation energies for Un-catalysed forward and backward reactions were evaluated as 20.12 KJ/mol and 12.95 KJ/mol, for the heterogeneous forward and backward reactions were evaluated as 37.626 KJ/mol and 18.473 KJ/mol.

V. Nomenclature

- C_A - Concentration of acetic acid mol/lit
- C_B - Concentration of methanol mol/lit
- C_E - Concentration of ester mol/lit
- C_W - Concentration of water mol/lit
- C_{AO} - Concentration of acetic acid at $t=0$, mol/lit
- C_{BO} - Concentration of methanol at $t=0$, mol/lit
- E - Activation energy KJ/mol
- K_1 - Rate constant for the heterogeneous forward reaction, lit/mol min
- K_2 - Rate constant for the heterogeneous backward reaction, lit/mol min
- K_3 - Rate constant for the uncatalyzed forward reaction, lit/mol min
- K_4 - Rate constant for the uncatalyzed backward reaction, lit/mol min
- k_c - Equilibrium constant
- r_A - Initial rate mol/lit min
- R - Real gas constant
- T - Reaction temperature, K
- X_A - Fractional conversion of acetic acid
- X_B - Fractional conversion of methanol
- X_{Ae} - Fractional conversion of acetic acid at equilibrium

VI. References

- Ronnback, R., Salmi, T., Vuori, A., Haario, H., Lehtonen, J., Development of a Kinetic model for the esterification of acetic acid with methanol in the presence of a homogenous acid catalyst, *Chemical Engineering Science*, **1997**, 52, 3369-3381.
- Yijun Liu., Edger Lotero., James G. Goodwin., A comparison of the esterification of acetic acid with methanol using heterogeneous versus homogenous acid catalysis, *Journal of Catalysis*, 2006, 242, 278-286.

3. Xu Z.P., Chuang K.T., Effect of internal diffusion on heterogeneous catalytic esterification of acetic acid, Chemical Engineering Science, 1997,52(17), 3011.
4. Delgado P., Sanz M.T., Beltran S., Kinetic study for esterification of lactic acid with ethanol and hydrolysis of ethyl lactate using an ion exchange resin catalyst, Chemical Engineering Journal, **2007**,126, 111-118.
5. Kirbaslar, Baykal, Dramur, Esterification of acetic acid with ethanol catalyzed by an acidic ion exchange resin, Turk J Engg Environmental Science, **2001**, 25, 569- 577.
6. Izci A., Hosgun H.L., Kinetics of Synthesis of Isobutanol Propionate over Amberlyst-15, **2007**, 31, 493-499.
7. Sami Ali, Alia T., Merchant S., Taher A., Kinetics of the esterification reaction of propionic acid with 1-propanol over Dowex 50Wx8-400, 2001, 124-130.
8. Altioikka M., Elif Odes., Reaction kinetics of the catalytic esterification of acrylic acid with propylene glycol, Applied Catalysis A: General, 2009,362, 115-120.
9. Animesk Chakrabarti, M.M. Sharma, Cyclohexanol from cyclohexene via cyclohexyl acetate: catalysis by ion- exchange resin and acid-treated clay, Reactive Polymers, 1992, 18, 107-115.
10. A.A.Patwaedhan, M.M. Sharma, Esterification of carboxylic acids with olefins using cation exchange resins as catalysts, Reactive Polymers, 1990, 13, 161-176.
11. M. Ehteshami, N. Rahimi, A.A.Eftekhari, m.J. Nasr, Kinetic study of catalytic hydrolysis reaction of methyl acetate to acetic acid and methanol. Iranian Journal of Science and Technology, 30, **2006**.
12. Peters, T.A.; Benes N.E.; Holmen, A.; Keurentjes, J.T.F., Comparison of commercial Solid acid catalysts for the esterification of acetic acid with butanol, Applied Catalysis A: General, **2006**, 297; 182–188.
13. Das, J., Parida, K.M., Heteropoly acid intercalated Zn/Al HTlc as efficient catalyst For esterification of acetic acid using *n*-butanol, Journal of Molecular Catalysis A: Chemical, **2007**, 264; 248–254.
14. Yadav, G.D.; Thathagar, M.B., Esterification of maleic acid with ethanol over Cation exchange resin catalysts, Reactive & Functional Polymers, **2002**, 52; 99–110.
15. Wu, K.C.; Chen, Y.W., An efficient two-phase reaction of ethyl acetate production in modified ZSM-5 zeolites, Applied Catalysis A: General, **2004**, 257; 33–42.
16. Lilja, J.; Aumo J.; Salmi T.; Yu M.D. , Arvela P. M., Sundell M., Ekman K., Peltonen R., Vainio H., Kinetics of esterification of propanoic acid with methanol over a fibrous polymer supported sulphonic acid catalyst Applied Catalysis A: General, **2002**, 228, 253–267.
17. Yu, W.; Hidajat, K.; Ray, A. K., Determination of adsorption and kinetic parameters for methyl acetate esterification and hydrolysis reaction catalyzed by Amberlyst 15, Applied Catalysis A: General **2004**, 260; 191–205.
18. Chen X., Xu Z., Okuhara T., Liquid phase esterification of acrylic acid with 1-butanol catalyzed by solid acid catalysts, Applied Catalysis A: General, **1999**, 180; 261-269.
19. DuPont P., Lefebvre F., Esterification of propanoic acid by butanol and 2-ethylhexanol catalyzed by heteropolyacids pure or supported on carbon, Journal of Molecular Catalysis A: Chemical, 1996, 114, 299-307.
20. DuPont P., Vedrine J.C., Paumard E., Hecquet G., Lefebvre F., Heteropolyacids Supported on activated carbon as catalysts for the esterification of acrylic acid by butanol, Applied Catalysis A: General, **1995**, 129; 217-227.