



# KINETIC OF ESTERIFICATION OF ETHYL ALCOHOL BY ACETIC ACID ON A CATALYTIC RESIN

**Erol İNCE**

University of Istanbul, Engineering Faculty, Department of Chemical Engineering, 34850/Avcılar/İstanbul

Geliş Tarihi : 09.07.2001

## ABSTRACT

The conversion kinetics of diluted acetic acid to ethyl acetate by ethanol esterification in a batch reactor in liquid phase with an acidic polymer catalyst (Iewatit series) was studied. The intrinsic rate constants have been correlated with the reaction temperature, concentration of catalyst, initial ratios of reactants and initial water concentrations. The kinetic analysis was restricted to the system at hand in which a liquid and vapor phase are at equilibrium.

**Key Words :** Ethanol, Acetic acid, Esterification and catalytic resin

## ASETİK ASİTİN ETİL ALKOL İLE KATALİTİK REÇİNE KATALİZÖRLÜĞÜNDE ESTERLEŞME KİNETİĞİ

### ÖZET

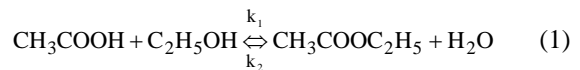
Seyreltik asetik asit çözeltilerinin asidik gruplu polimerik reçine katalizörlüğünde etil alkol ile esterleşme reaksiyonu kesikli bir reaktörde gerçekleştirilmiştir. Reaksiyon kinetiği üzerine sıcaklık, başlangıçtaki reaktanların mol oranları, başlangıçtaki su konsantrasyonu ve katalizör konsantrasyonu etkileri incelenmiştir. Kesikli reaktörde sıvı ve buhar fazlarının hızla dengeye ulaşmasının reaksiyon kinetiğini sınırladığı belirlenmiştir.

**Anahtar Kelimeler :** Etanol, Asetik asit, Esterleşme ve katalitik reçine

### 1. INTRODUCTION

Reactions using acetic acid anhydride as reagent, e.g., acetylations, or as solvent, produce large amounts of aqueous waste acetic acid. The major methods for recovering acetic acid to this day are fractional distillation, azeotropic distillation i.e. the Clarke-Othmer process (Kirk and Othmer, 1980) and solvent extraction using amines or other bases to improve partition coefficients (Neumann and Sasson, 1984). The first objective of this study was to determine the kinetics of esterification reaction and the equilibrium concentration of ethyl acetate in the liquid phase in the presence of a resin with

sulphonic group using a batch reactor. And also it was secondary aim of this study to utilize the intrinsic catalytic kinetics in a reacting distillation column. The esterification reaction of acetic acid with ethanol has been widely studied, mainly because of its industrial interest. There are also a few kinetic studies done with ion-exchange resins as catalysts (Backhaus, 1921; McKetta, 1984; Gimenez et al., 1987; Mazotti et al., 1997). The reaction between ethyl alcohol and acetic acid over a catalytically active synthetic resin is as follows.



A                      B                      E                      W

Where; A = acetic acid, B = alcohol, E = ethyl acetate, W = water

Advances in reacting distillation systems (Neumann and Sasson, 1984; Agreda et al., 1990) enabled the selective separation of ethyl acetate, thus also enabled the reaction to proceed beyond the equilibrium. Therefore, it is necessary to understand and formulate a theoretical catalytic rate equation which deals with the reversibility and the effect of water on the reaction (Savkovic-Stevenovic et al., 1988; Yadav and Metha, 1994; Xu and Chuang, 1996).

## 2. MATERIAL AND METHOD

All the reagents were of synthesis grade and obtained from Merck AG. Acetic acid and ethyl alcohol, respectively was 99.98 % w/w and 96 % w/w and rest being water. Synthetic acidic resin Lewatit (Bayer AG) was used as catalyst. The experimental assembly consisted of a 250 ml reactor fitted with a long reflux condenser to prevent any loss of products

and a thermometer pocket. Aliquots of sample were taken via reflux condenser. A magnetic stirrer was used to stir the reaction mixture. The reaction vessel was placed in a thermostat bath with an electronic temperature regulator ( $\pm 0.10$  K). Experiments were conducted at various molar ratios of acetic acid and ethyl alcohol in the temperature range of 333.15, 343.15, 353.15, 373.15  $\pm 0.10$  K using different catalyst concentrations, as such 1, 10, 20 % ( $\frac{g_{\text{catalyst}}}{g_{\text{acetic acid}}}$ ).

### 2. 1. Procedure

Acetic acid and catalyst resin were charged into the reaction vessel in a predetermined ratio. After the desired temperature was reached, ethyl alcohol was drained into the reactor. This moment was considered as the beginning of the reaction. Several samples of approximately 500 microliters were taken by a micropipet. At the beginning of experiments, samples were taken at frequent intervals but towards the end of the experiments, the samples were drawn off the reactor every 2 hours until completion. The operating conditions of the some selected experimental runs are summarized in Table 1.

Table 1. Operating Conditions of the Batch Experimental Runs

Run	Temp, K	Acetic acid, mol	Ethanol, mol	Water, mol	Resin, g
1	353.15	1	1	0.15	10
2	353.15	1	2	0.23	10
3	353.15	2	1	0.15	10
4	353.15	1	1	0.15	5
5	353.15	1	1	0.15	0.5
6	353.15	1	1	0.33	10
7	353.15	1	1	0.54	10
8	333.15	1	1	0.15	10
9	343.15	1	1	0.15	10
10	373.15	1	1	0.15	10

### 2. 2. Analysis

The liquid samples were analysed using a Gas Chromatograph (Hewlett Packard GC, Model 6890 Series), equipped with two detectors, Thermal Conductivity Detector (TCD) and Flame Ionisation Dedector (FID), installed in series, for the quantitative determination of water, ethanol, ethyl acetate and acetic acid. A 30-m long HP-Innowax column (Polyethylene glycol 320-micrometer

diameter with a 0.5-micrometer film thickness) was used with a temperature programmed analysis. Usually, only the data from TCD were used in data processing while those from FID were used for reference and mass balance calculation only. Nitrogen was used as carrier gas.

## 3. RESULTS AND DISCUSSION

### 3.1. Effect of Initial Reagent Concentrations

The mol ratio of ethyl alcohol to the acetic acid was varied 1 : 2 to 2 : 1 to assess its effect on the rate of reaction and to find the order of reaction at 353.15 K, with a catalyst loading 20 % w/w based on the acetic acid in Figure 1. The maximum conversion is obtained for ( $M = 1/1$ ).

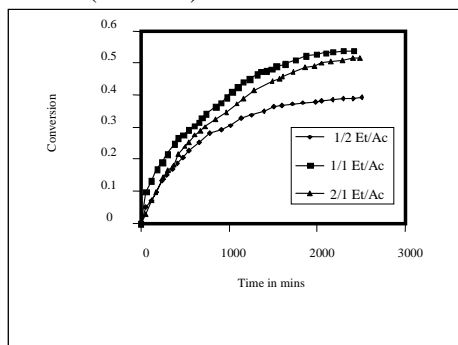


Figure 1. Effect of initial concentrations of ethanol to acetic acid on conversion of acetic acid: Temperature 353.15 K, catalyst loading 20 % (w/w) based on acetic acid;  $M = 1/1$  (-□-) run 1,  $M = 2/1$  (-Δ-) run 2 and  $M = 1/2$  (-◇-) run 3

### 3.2. Effect of the Amount of Catalyst

The catalyst loading was varied over a range of 1-20 % w/w on the basis of the amount of acetic acid. Figure 2 shows the effect of catalyst loading on the conversion of the ethyl acetate. Catalyst concentrations were changed as a percentage of acetic acid at constant temperature. The rate of reaction is directly proportional the catalyst loading because the surface area and hence the total number of active sites increase linearly with it.

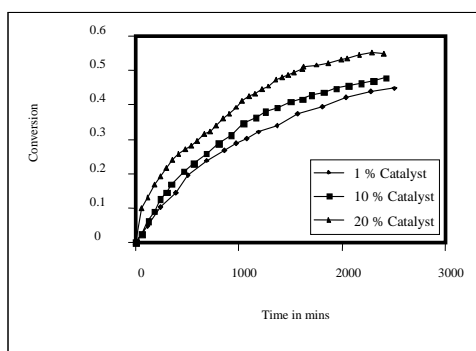


Figure 2. Effect of various catalysts on the conversion of acetic acid ; mol ratio, ethanol : acetic acid ( $M = 1/1$ ); catalyst loading, 1 % (w/w) based on acetic acid, (-◇-) run 5, 10 % (w/w) (-□-) run 4, and 20 % (w/w) (-Δ-) run 1

### 3.3. Effect of Initial Water Concentration

The initial water concentrations were varied and their effects on the rate of reaction were shown in Figure 3. Water concentrations were changed as a percentage of acetic acid at constant temperature at 353.15 K. The rate of reaction is directly proportional the water concentrations because retardation effect of water, adsorbed onto the active surfaces and also due to the thermodynamic equilibrium is inevitable.

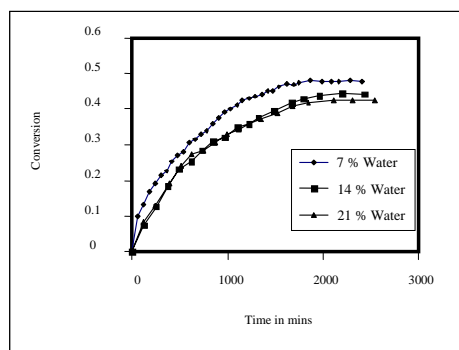


Figure 3. Effect of various water initial concentrations on the conversion of acetic acid ; mol ratio, ethanol : acetic acid ( $M = 1/1$ ); catalyst loading, 20 % (w/w) based on acetic acid, 7 % water (w/w) (-◇-) run 1, 14 % water (w/w) (-□-) run 6, and 21 % water (w/w) (-Δ-) run 7

### 3.4. Effect of Temperature

The effect of temperature on the rate of reaction was studied by conducting the reactions at 333.15, 353.15 and 373.15 K for both cases under otherwise similar conditions. The ester conversion was found to increase with temperature in Figure 4.

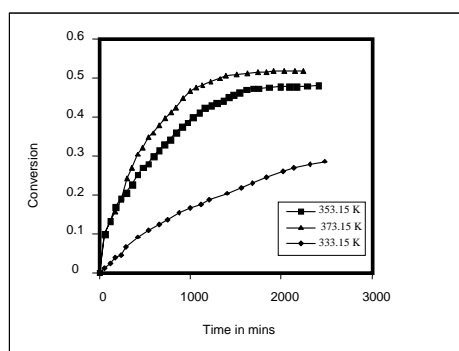


Figure 4. Effect of temperature on conversion of acetic acid; mol ratio ethyl alcohol : acetic acid ( $M = 1/1$ ) catalyst loading 20 % (w/w) based on acetic acid; temperature 353.15 K (-□-) run 1, 373.15 K (-Δ-) run 10 and 333.15 K (-◇-) run 8

### 3. 5. Kinetics of The Reaction

The overall rate of reaction follows a second order kinetics;

$$-\frac{d[C_A]}{dt} = k_1 w [C_A][C_B] \quad (2)$$

For a mol ratio of  $M = [C_{B_0}]/[C_{A_0}] = 1$  Equation (2) can be integrated to give the following equation in terms of the fractional conversion of the acetic acid (Fogler, 1992; Yadav and Metha, 1994).

$$\frac{X_A}{1-X_A} = [C_{A_0}]k_1 w t \quad (3)$$

Where  $X_A$  = fractional conversion of A,

$$X_A = \frac{[C_{A_0}] - [C_A]}{[C_{A_0}]} \quad (4)$$

For the mol ratio of  $M \neq 1$ , the integration of Equation (2) leads to the following;

$$\ln \frac{M - X_A}{M[1 - X_A]} = [C_{A_0}][M - 1]k_1 w t \quad (5)$$

Thus, plots were made of the left hand side versus time for both Equations (3) and (5) to determine the slope of the line from which the values of  $k_1$  were calculated.  $k_1$  is based on the weight of the catalyst having units  $(\text{cm}^3/\text{g}\cdot\text{mol})(\text{cm}^3/\text{g of catalyst})(1/\text{s})$ . The kinetic plots for the reaction between ethyl alcohol and acetic acid: mol ratio, ethyl alcohol: acetic acid ( $M = 1/1$ ); and ethyl alcohol : acetic acid ( $M = 1/2$ ); are shown in Figure 5 and Figure 6, respectively.

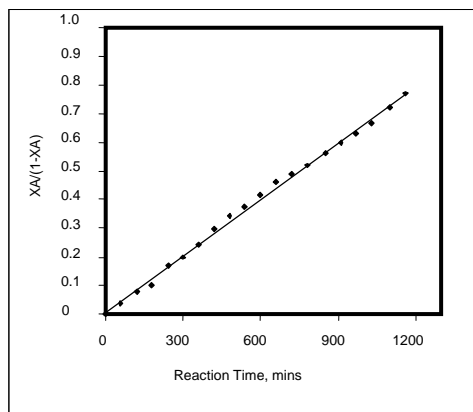


Figure 5. Kinetic plots for the reaction between ethyl alcohol and acetic acid; mol ratio ethyl alcohol : acetic acid temperature 353.15 K, ( $M = 1/1$ , run 1)

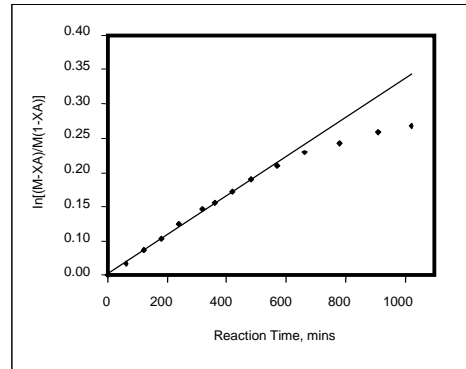


Figure 6. Kinetic plots for the reaction between ethyl alcohol and acetic acid; mol ratio ethyl alcohol : acetic acid temperature 353.15 K, ( $M = 1/2$  run 3)

### 3. 6. Calculation of Experimental Equilibrium Constant

Experimental equilibrium constant of esterification reaction is calculated using the equilibrium conversions determined experimentally and using the equation below;

$$K_{\text{exp}} = \frac{C_{Ee}C_{We}}{C_{Ae}C_{Be}} = \frac{X_{Ae}^2}{[(1 - X_{Ae})(M - X_{Ae})]} \quad (6)$$

The equilibrium constant  $K_{\text{exp}}$  is calculated experimentally and given Table 2. At equilibrium, we have  $K_{\text{exp}} = k_1/k_2$ , where  $k_1$  and  $k_2$  are the rate constants for the forward and backward reactions (Arnika et al., 1970; Yadav and Metha, 1994). The rate constant  $k_1$  at various temperatures now having been determined, it is possible to calculate the corresponding values of  $k_2$  at these temperatures. Since the heat of reaction is nearly zero, the energy of activation of forward and reverse reaction is the same. Arrhenius equation.

$$\ln k_{1,2} = \ln A - \frac{E_A}{R} \left( \frac{1}{T} \right) \quad (7)$$

Where;  $E_A$  : Activation energy,  $A$  : Frequency factor,  $T$  : Temperature (K) and  $R$  : Gas constant ( $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ).

Table 2. The Kinetic Parameters of the Reaction, Mol Ratio, Ethyl Alcohol : Acetic Acid ( $M = 1/1$ ) at 353.15 K

$k_1$ ( $\text{cm}^3/\text{g}\cdot\text{mol})(\text{cm}^3/\text{g of cat.})(1/\text{s})$	$k_2$ ( $\text{cm}^3/\text{g}\cdot\text{mol})(\text{cm}^3/\text{g of cat.})(1/\text{s})$	$K_{\text{exp}}$	$E_A$ (J/mol)	$A$ ( $\text{cm}^3/\text{mol}\cdot\text{s}$ )
---	---	------------------	------------------	--

0.0244	0.0047	3.98	84 878	46 617
--------	--------	------	--------	--------

The parameters of  $E_A$  and  $A$  were determined for the forward reactions from the experiments which were carried out at various temperatures. The data of  $\ln k$  against  $1/T$  were fitted by using linearized Arrhenius equation (7). The activation energy ( $E_A$ ) and frequency factor ( $A$ ) of forward reaction constant ( $k_1$ ) were estimated from Figure 7.

Agreda, V. H., Partin, L. R. and William, H. 1990.

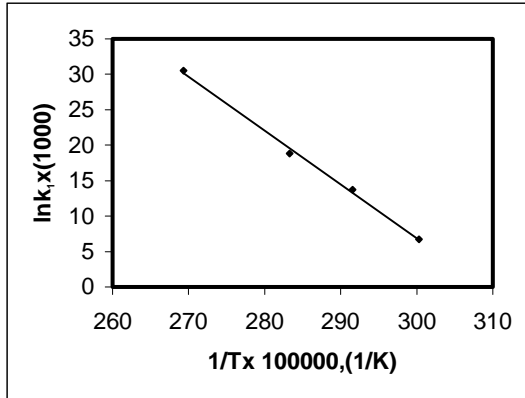


Figure 7. Arrhenius plot: mol ratio, ethyl alcohol : acetic acid ( $M = 1/1$ ), catalyst loading, 20 % (w/w) based on acetic acid

#### 4. CONCLUSIONS

The esterification reaction between ethyl alcohol and acetic acid is studied over a commercial acidic resin. Polymeric acid catalysis in the preparation of ethyl acetate is very effective from the viewpoint of activity, selectivity, reuse and noncorrosiveness in comparison with the homogeneous catalysts. A catalytic rate equation was derived based on a well-known mechanism. Kinetic parameters of the esterification reaction are calculated. These parameters are forward and backward reaction rate constant, experimental equilibrium constant, activation energy and frequency factor of forward reaction rate constant.

#### 5. ACKNOWLEDGEMENT

This work was supported by The Research Fund of University of Istanbul. Project number : 837/190496

#### 6. REFERENCES

High-Purity Methyl Acetate Via Reactive Distillation, Chem. Eng. Prog. 86, 40-46.

Arnikar, H. J., Rao, T. and Bodhe, A. A. 1970. A Gas Chromatographic Study of Kinetics of Uncatalysed Esterification of Acetic Acid by Ethanol, J. of Chromatog., 47, 265-268.

Backhaus, A. A. 1921. Continuous Process for the Manufacture of Esters, U.S.A. Patent, P. Number 1, 400, 849.

Fogler, H. S. 1992. Elements of Chemical Reaction Engineering, Prince-Hall Inc., New Jersey.

Gimenez, J., Costa, J. and Cervera, S. 1987. Vapour-Phase Esterification of Acetic Acid With Ethanol Catalysed by a Macroporous Sulfonated Styrene-Divinylbenzene (20 %) Resin, Ind. Eng. Chem. Res., 26, 198-202.

Kirk, R. E. and Othmer, D. F. 1980. Encyclopedia of Chemical Technology, 9, 291-298, Wiley & Sons. Inc. New York.

Mazotti, M., Neri, B., Gelosa, D., Kruglov, A. and Morbidelli, M. 1997. Kinetics of Liquid-Phase Esterification Catalysed by Acidic Resins, Ind. Eng. Chem. Res., 36, 3-10.

Mc.Ketta, J. J. 1984. Encyclopedia of Chemical Processing and Design, 19, 381-402, Marcel Dekker, Inc., New York.

Neumann, R. and Sasson, Y. 1984. Recovery Of Dilute Acetic Acid by Esterification in Packed Chemorectification Column, Ind. Eng. Chem. Process Des. Dev., 23, 654-659.

Savkovic-Stevenovic, J. B., Misic-Vukovic, M., Slavejkov, A. G., Trisovic, B. Lj. and Boncic-Caricic, G. 1988. Distillation with Reversible Esterification Reaction, J. Serb. Chem. Soc., 53, 323-336.

Xu, Z. P. and Chuang, K. T. 1996. Kinetic of Acetic Acid Esterification over Ion Exchange Catalysts, The Can. J. of Chem. Eng. 74, 493-500.

Yadav, G. D. and Metha, P. H. 1994. Heterogeneous Catalysis in Esterification Reactions: Preparation of Phenethyl Acetate and Cyclohexyl Acetate by Using a Variety of Solid Acidic Catalyst, Ind. Eng. Chem. Res. 33, 2198-2208.