Esterification of Acetic Acid with Ethanol Catalysed by an Acidic Ion-Exchange Resin*

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Abstract
The esterification of acetic acid with ethyl alcohol catalysed by an acidic ion-exchange resin (Amberlyst-15) was carried out in a batch reactor at temperatures between 323 and 353 K at various starting compositions ranging from stoichiometric regime to the dilute regions. The resultant kinetic model fitted the experimental data well. The activation energy was found to be 104129 kJ.kmol$^{-1}$ for the formation of ethyl acetate. The ethyl acetate production was also carried out in a packed bed reactive distillation column operated in batch and continuous modes. The effects of the variables such as the reflux ratio, vapour rate and feed flow rate on ethyl acetate production were studied experimentally. A packed bed reactive distillation column operated in continuous mode gave the highest ethyl acetate composition, far surpassing the chemical equilibrium at operating conditions.

Key Words: acetic acid, ethanol, esterification, kinetic model

Asidik İyon Değiştirici Reçine Katalizörü Varlığında Etanolün Asetik Asitle Esterifikasyonu

Özet

Anahtar Sözcükler: asetik asit, etil alkol, esterifikasyon, kinetik model

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Introduction

Esters are an important class of chemicals, having applications in a variety of areas such as solvents, plasticizers, pharmaceuticals and intermediates (Kirk and Othmer, 1980; McKetta, 1984; McCraken et al., 1967). Obviously different approaches have been employed to prepare esters, and the traditional homogenous catalysed reactions are less favoured owing to the attendant problems of separation and reuse (Yadav and Metha, 1994; Xu and Chuang, 1996).

In all kinetic studies done with ion-exchange resins as catalysts, acidic ion-exchange gel-type styrene-divinyl benzene (DVB) resins have been used (Gimenez et al., 1987). Research in catalysis by ion-exchange resins is undoubtedly interesting, not only from a purely physicochemical point of view but also in terms of the advantages of these types of catalyst over the conventional ones. Ion exchange resins increase the product yield, keep their activity a long time, and do not pollute. Ion exchange resins separate from reaction media easily and they regenerate easily for reuse (Roy and Bhatia, 1987; Xu and Chuang, 1996; Dassy et al., 1994; Yadav and Metha, 1994; Darge and Thyrion, 1993).

The esterification of acetic acid with ethanol has been widely studied, mainly because of its industrial uses (Arnikar et al., 1970; McKetta, 1984; Gimenez et al., 1987; Savkovic-Stevenovic et al., 1988; Mazotti et al., 1997). The overall reaction between acetic acid and ethyl alcohol over a catalytically active resin is as follows:

\[
\text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH} \xrightarrow{\text{catalyst}} \text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O} \tag{1}
\]

(where A = acetic acid, B = ethanol, E = ethyl acetate, W = water)

A common method of operating equilibrium-limited reactions is to use an excess of one reactant in order to increase the conversion of the limiting reactant. In reactive distillation, the continual separation of products from reactants forces the reaction to surpass the equilibrium conditions.

Reactive distillation is a process where separation of the components of a reaction system is accompanied by a chemical reaction in a column. The combination of a reversible reaction and distillation is a widely used technique to increase the conversion of the reactants to levels above equilibrium conversion. The reactive distillation is becoming more and more popular in chemical industries (Backhaus, 1921; Neumann and Sasson, 1984; Gresser et al., 1987; Sawistowski and Pilavakis, 1988; Savkovic-Stevenovic et al., 1988; Agreda et al., 1990; Doherty and Buzad, 1992).

The objectives of the present study were to determine the heterogeneous kinetic model and test the applicability of the macroporous cation-exchange resin (Amberlyst 15) as a catalyst for the esterification reaction. In the kinetic studies, the variables studied were catalyst concentration, mole ratio of reactants, initial water concentration and reaction temperature. A mechanism based on rate data was proposed and corresponding rate equations were derived. The batch and continuous production of ethyl acetate was also carried out in a packed bed reactive distillation column. The kinetic equations and performance data from distillation columns are to be used in future reactive distillation modeling studies.

Materials and Methods

Chemicals: Acetic acid and ethyl alcohol were supplied by Merck AG. Acetic acid of 99.98% (w/w) purity (Merck) and ethanol aqueous solution with a content of 96% w/w ethanol (Merck) were used as supplied.

Catalyst: The acidic ion exchange resin (Amberlyst 15 of Rohm and Haas Co.) was supplied by Sigma AG. It is a macroporous type styrene-DVB (20%) resin. The detailed physical and chemical properties of the catalyst have been given elsewhere by Mazotti et al. (1997) and Tanabe et al. (1989).

Batch reactor: The experimental assembly consisted of a 0.250 dm³ reactor fitted with a long reflux condenser to prevent any loss of products. Aliquots of samples were taken via a reflux condenser. The reaction mixture was magnetically stirred at about 900 rpm. Under these conditions, with the appropriate catalyst particle size ranges, it was experimentally assured that there were no internal or external transport limitations. The reaction vessel was kept in a stirred constant temperature bath, where the
temperature could be controlled within an accuracy of ± 0.2 K by an electronic PID controller.

Procedure: Experiments were carried out at various molar ratios of acetic acid and ethyl alcohol at temperatures of 323, 333, 338, 343, 353 ± 0.2 K and at different catalyst loading: 1.0, 3.0, 5.0, 7.0 and 10.0 g per 100 g acetic acid. Acetic acid and catalyst were charged into the reaction vessel. The volume of the reaction mixture remained almost constant (0.200 dm$^3$) during all experiments. After the desired temperature was reached, ethyl alcohol preheated to the same temperature was quickly poured into the reactor. This moment was taken as the beginning of the reaction. Several samples of approximately 500 microlitres were taken by a cold glass syringe. At the beginning of the experiments, samples were taken every 20 min, but towards the end of the experiments samples were drawn from the reactor every hour, until completion. Repeating three experimental runs under identical conditions checked the reproducibility of the experimental data. The reproducibility was of the order of ± 5% of conversion of the limiting reactant.

Reactive distillation column: The experiments were performed in a glass column with a packing height of 800 mm and a diameter of 45 mm. The height of the column with the reboiler and partial condenser was approximately 2000 mm. Half of the column was filled from the bottom with a mixture of Raschig ceramic rings with an average diameter and length of 6 mm, and 50 g of Amberlyst 15 with an average diameter of 0.7 mm. The upper section of the column was filled with Raschig ceramic rings only. An acetic acid and ethanol mixture (0.500 dm$^3$) was put in the reboiler (Figure 1).

Batch operation procedure: Firstly the column was operated under total reflux conditions for 30 min. Then the valve of the top product line was opened. During batch reactive distillation, top product flow rates were measured periodically (every after 60 min). Samples from the top product were taken every 60 min. The batch operation conditions, initial molar ratios, reflux ratio and vapour flow rates and the composition of top product flow are given in Tables 1 and 2.

Continuous operation procedure: The column was operated under total reflux conditions for 30 min. Then the feed and bottom product pumps were turned on and the valve of the top product line was opened. During continuous reactive distillation, top and bottom product flow rates were periodically measured every 60 min. Samples from the top product for GC analysis were also taken every 60 min. The steady state was achieved within 5-6 hours. The operating conditions at the steady state are listed in Table 3.

![Figure 1. Schematic diagram of reactive distillation column](image)

Analysis: The liquid samples were analysed using a gas chromatograph (Hewlett Packard GC, Model 6890 Series) equipped with two detectors, a thermal conductivity detector (TCD) and a flame ionisation detector (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 micrometers in diameter with 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 the carrier gas.
Table 1. The reflux ratios effect on the top product composition and flow rate versus time for the batch reactive distillation ($n_{Hac} = 1.95$ mole; $n_{EtOH} = 3.9$ mole; $M = 1/2$)

<table>
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<tr>
<th>Run no.</th>
<th>Reflux ratio</th>
<th>t (min)</th>
<th>$W_{EtAc}$ (%)</th>
<th>$W_{EtOH}$ (%)</th>
<th>$W_{Water}$ (%)</th>
<th>Flow rate (g/h)</th>
<th>Top (K)</th>
<th>Bottom (K)</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5</td>
<td>0</td>
<td>66.87</td>
<td>26.76</td>
<td>6.37</td>
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<td>344.5</td>
<td>351.0</td>
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<td></td>
<td>60</td>
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</tr>
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<td>120</td>
<td>66.60</td>
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<td></td>
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<td>65.71</td>
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<td>5.75</td>
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<td>44</td>
<td>344.5</td>
<td>357.0</td>
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Table 2. The vapour velocities effect on the top product composition and flow rate versus time for the batch reactive distillation ($R=2$)

<table>
<thead>
<tr>
<th>Run no.</th>
<th>Vapour flow rate, (mole/h)</th>
<th>t (min)</th>
<th>$W_{EtAc}$ (%)</th>
<th>$W_{EtOH}$ (%)</th>
<th>$W_{Water}$ (%)</th>
<th>Flow rate (g/h)</th>
<th>Top (K)</th>
<th>Bottom (K)</th>
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<td></td>
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<td>69.00</td>
<td>26.84</td>
<td>4.16</td>
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<td>344.5</td>
<td>354.0</td>
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<td>34.76</td>
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<td>6.70</td>
<td>42</td>
<td>349.5</td>
<td>379.0</td>
</tr>
</tbody>
</table>

Derivation of a catalytic rate equation: In the esterification reaction mechanism used in this study, it was envisaged that a protonated carboxyl group by the acidic resin reacted with alcohol (Fogler, 1992). The reaction mechanism (Goto et al., 1991) can be written as follows:

$$
RCOOH + H^+ \xrightarrow{k_1} RCOOH^+_2 \quad (2)
$$

$$
RCOOH^+_2 + R'OH \xrightarrow{k_2} RCOOR' + H_2O \quad (3)
$$

$$
RCOOR' + H^+ \xrightarrow{k_3} RCOOR' + H_2O \quad (4)
$$

For step one of the mechanism (Equation 2), the following rate equation can be written:

$$
-\frac{dC_A}{dt} = k_1 C_A C_C - k_{-1} C_{AH} \quad (5)
$$

At steady state conditions, the rate of production of intermediates (AH, EH) can be equated to zero. Therefore, rates for AH and EH become as follows:
assumptions can be made. Therefore, by assuming
addition, for the sake of simplification, the following
terms other than water can be neglected. In ad-
(Pöpken et al., 2000) in appreciable amounts, the
duced to Equation (9)

\[ \frac{dC_A}{dt} = k_A C_C - k_{-1} C_{AH} - k_2 C_{AH} C_B + k_{-2} C_{EH} C_W = 0 \]  \hspace{1cm} (6)

\[ \frac{dC_E}{dt} = k_2 C_{AH} C_B - k_{-2} C_{EH} C_W - k_3 C_{EH} + k_{-3} C_{EH} C_C = 0 \]  \hspace{1cm} (7)

Eliminating \( C_{AH} \) from equations 6 and 7 results in the following rate equation:

\[ -\frac{dC_A}{dt} = C_C \left( \frac{k_3 k_2 C_B - k_{-1} k_{-2} C_W}{k_3 k_{-1} + k_2 k_3 C_B + k_{-1} k_{-2} C_W} \right) \]  \hspace{1cm} (8)

Since only water adsorbs onto the Amberlyst
(Pöpken et al., 2000) in appreciable amounts, the
terms other than water can be neglected. In ad-
ition, for the sake of simplification, the following
assumptions can be made. Therefore, by assuming
\( k_3 k_{-1} k_{-3} C_B \langle k_{-1} k_{-2} C_W \) Equation (8) can be re-
duced to Equation (9)

\[ -\frac{dC_A}{dt} = k_K C_C \left( \frac{C_A C_B - C_W C_W}{C_B + C_W K W} \right) \]  \hspace{1cm} (9)

where \( K = \frac{k_3 k_2 k_3}{k_{-1} k_{-2} k_{-3}} \).

Experimental equilibrium constants were calculated
from conversions at equilibrium and were found
to be almost constant over the range of experiments
carried out (4±0.2). This value was in the range of
those found in the literature (Pöpken et al., 2000).

If Equation (9) is rewritten with a new forward rate constant including the concentration term of
solid acid, \( C_C \), then the final equation can be written
as follows:

\[ -\frac{dC_A}{dt} = k \left( \frac{C_A C_B - C_E C_W / K}{C_B + C_W K W} \right) \]  \hspace{1cm} (10)

where \( K = \frac{k_3 k_2 k_3}{k_{-1} k_{-2} k_{-3}} \), \( K_W = \frac{k_{-1} k_{-3}}{k_2 k_3} \).

Blank tests indicate a small quantity of conver-
sions even if no catalysts exist. Then the rate con-
stant without catalyst \( k_B \) should be considered. The
total rate constant can be defined by \( k = k_K C_C + k_B \).

In order to determine the parameters of equa-
tion (10), the second part of the nominator can be
equated to zero \( (C_E C_W / K = 0) \) for initial rates.
Then Equation (10a) can be rewritten in the lin-
erised form (Equation 10b) as follows:

\[ r_A = k \left( \frac{C_A C_B}{C_B + C_W K W} \right) \]  \hspace{1cm} (10a)

\[ 1 \left( \frac{1}{r_A} = \frac{1}{k C_A} + \frac{K_W C_W}{k C_A C_B} \right) \]  \hspace{1cm} (10b)

Now by using this linearised form, \( k \) and \( K_W \) were
calculated from experimental results by multiple lin-
ear regression software. \( K_W \) is the adsorption equi-
librium constant of water.

**Results and Discussion**

The esterification reaction of acetic acid with
ethyl alcohol was studied in a batch reactor in the
presence of an acidic ion exchange resin catalyst.
The changes in ethyl acetate and acetic acid concen-
trations that took place in the batch reactor during
the reaction are shown in Figure 2. The effects of
catalyst loading, reactant molar ratios, initial water concentration and temperature on the reaction rate were investigated. By conducting three runs in succession we tested the reusability of the catalyst (Amberlyst 15). There was a small decline in the catalytic activity (5% decrease in conversion), within the repeatability limits of experiments.

The effect of catalyst loading on the conversion of the acetic acid is shown in Figure 3. The increase in the rate with catalyst loading agrees well with the description of the proton mechanism herein and the mechanism proposed by Tsvetkova and Kovenev (1967). Fresh resin was used for each new run.

The mole ratio of acetic acid to ethyl alcohol was varied between 1:2 and 4:1. The effect of the molar ratio of reactants on the conversion of acetic acid is shown in Figure 4. The maximum conversion, approximately 0.75, was obtained for an acetic acid to ethyl alcohol molar ratio of M=1/2 with a catalyst loading of 5.4 g of a 100 g of acetic acid and at a temperature of 353 K.

The initial water concentrations were varied and their effects on the rate of reaction are shown in Figure 5. Water concentrations were varied as a percentage of acetic acid at a constant temperature of 353 K. The rate of reaction, was inversely proportional to the water concentrations because of the retarding effect of adsorbed water on the active surfaces and also due to the thermodynamic equilibrium. The inhibiting effect was quite evident in the reaction, as shown in Figure 5.
The effect of temperature on the rate of reaction was studied by conducting the reactions at 323, 333, 338, 343 and 353 K, the molar ratio of acetic acid and ethyl alcohol being M=1/1 with a catalyst loading of 5.4 g. The acetic acid conversion was found to increase with increasing temperature, as shown in Figure 6.

![Figure 6](image)

**Figure 6.** Effect of temperature on the conversion of acetic acid; (M=1/1; catalyst loading 5.4 g).

The equilibrium constant was found to be approximately $K_{eq} = 4.0 \pm 0.2$ at 353 K. Furthermore, this equilibrium constant was virtually unchanged over range of operating conditions studied here. For the heterogeneously catalysed reaction, it was stated in the literature that the goodness of fit can be improved by using activities instead of mole fractions (Popken et al., 2000), but in our study mole fractions were used and thus the kinetic model with the fitted parameters can be written as follows:

$$r_A = - \frac{dC_A}{dt} = 2.6 \times 10^{14} e^{\left(-\frac{104129}{RT}\right)} \left(\frac{C_A C_B - C_E CW}{C_B + 3.7CW}\right)$$

(11)

The parameters of the Arrhenius equations and activation energy and frequency factor were determined for the forward reaction from experiments carried out at different temperatures. The data of $\ln k$ against $1/T$ were fitted by linear regression and the result of this procedure was plotted in Figure 7. The activation energy was found to be 104129 kJ.kmol$^{-1}$ and corresponding forward frequency factor was $2.6 \times 10^{14}$ (m$^3$)kmol$^{-2}$s$^{-1}$.

![Figure 7](image)

**Figure 7.** Arrhenius plot of forward rates constant for the esterification reaction.

When the kinetic model was fitted to all experimental data, i.e. experiments with different temperatures and molar ratios of ethyl alcohol and acetic acid, the result was good and the goodness of representation is shown in Figure 8. The equilibrium constant was assumed to be independent of temperature and, for the generated values ($r_{theoretical}$) used in Figure 8, a value of 4 for $K$ was used.

![Figure 8](image)

**Figure 8.** Plot showing the goodness of model predictions.

**Batch reactive distillation:** In runs 1, 2 and 3, the reflux ratio was varied from 0.5 to 4. The reflux ratio (R) had a very significant effect on the performance of the distillation column in batch mode. As the reflux ratio increased from 0.5 to 4 the weight percentage of ethyl acetate of distillate increased from...
65.71 to 72.16% (w/w) after 180 minutes of operation but the top product’s flow rate decreased from 69 to 44 g per hour after 180 minutes of operation.

Other changes such as top and bottom temperature and other component changes are shown in Table 1.

In runs 4, 5 and 6, the effect of the vapour flow rate was examined and the overall results are given in Table 2. As the vapour flow rate increased from 2.71 to 4.02 moles per hour, the top product flow rate decreased from 63 to 42 g per hour after 180 minutes of operation and, in addition to this decrease, the ethyl acetate content of the top product decreased significantly from 62.49 to 26.30% (w/w) after 180 minutes of operation.

Continuous reactive distillation: Figure 1 is a schematic diagram showing the feed points and arrangements of continuous distillation column. It must be noted that ethyl alcohol and acetic acid were fed to the column from two different points. The reaction occurred in the stripping section (from the reboiler to the feed point) of the column. Above this feed point, water was extracted with acetic acid in the extractive distillation section below the acetic acid feed. Acetic acid and ethyl acetate were separated above the acetic acid feed point in the rectification section. Thus, concentrated ethyl acetate and unreacted ethanol were collected as a top product of the column and water was withdrawn from the reboiler.

In runs 7, 8 and 9, the effects of the reflux ratio on the continuous reactive distillation were examined. The reflux ratio was increased from 1 to 4. As the reflux ratio increased from 1 to 4, the ethyl acetate content of the top product increased from 68.60 to 78.99% (w/w) but the molar flow rate decreased from 0.73 to 0.49 moles per hour. Steady state operating conditions and changes in the followed variables are shown in Table 3.

In runs 10, 11, 12 and 13, the effect of feed flow rate on the continuous distillation column performance was examined. When the molar feed flow rate increased from 0.48 to 2.49 moles per hour, the top product and bottom product flow rates increased correspondingly but the ethyl acetate concentration in the top product decreased from 72.14 to 64.17% (w/w).

Comparison of the batch reactor equilibrium concentration and top product concentrations in reactive distillation operated in batch and continuous modes shows that the highest product (ethyl acetate) concentration was achieved in continuous reactive distillation. In both cases of reactive distillations the top product ethyl acetate composition was much higher than the batch reactor equilibrium conversions and thus by driving off the ethyl acetate by distillation, thermodynamic equilibrium conditions were surpassed in both modes of operation of the distillation columns.

Conclusions

The esterification reaction between ethanol and acetic acid was studied over an acidic ion exchange resin (Amberlyst 15). Reliable kinetic data and a model covering a wide range of operating conditions were presented with the parameters. The interaction between the solid catalyst and the reactants were considered in the model. The resulting model and parameters estimated can easily be incorporated in the simulation of reactive distillation columns. The present investigation also showed that the combination of an esterification reaction with distillation in a reactive distillation column either in batch or continuous mode leads to a large increase in the purity of ethyl acetate in the distillate. A continuous reactive distillation column gave the highest ethyl acetate concentration achieved, which is far better than corresponding thermodynamic equilibrium concentrations.

Acknowledgement

The authors thank to Doç. Dr. İsmail BOZ in the preparation of manuscript.

Nomenclature

\[ [C_A] \] = Concentration of A in bulk liquid phase, mole/dm³
\[ [C_C] \] = Concentration of catalyst’s protium, mole/dm³
\[ [C_{AH}] \] = Concentration of adsorbed A, mole/dm³
\[ [C_{AE}] \] = Concentration of adsorbed A, mole/dm³
\[ [C_{Ac}] \] = Equilibrium concentration of A in bulk liquid phase, mole/dm³
\[ [C_B] = \text{Concentration of B in bulk liquid phase, mole/dm}^3 \]
\[ [C_E] = \text{Concentration of E in bulk liquid phase, mole/dm}^3 \]
\[ [C_W] = \text{Concentration of W in bulk liquid phase, mole/dm}^3 \]
\[ k_1 = \text{Forward rate constant} \]
\[ k_{-1} = \text{Backward rate constant} \]
\[ K = \text{Equilibrium constant} \]
\[ M = \text{Mole ratio of acetic acid to ethanol} \]
\[ R = \text{Gas constant (J.mole}^{-1}\text{K}^{-1}) \]
\[ T = \text{Temperature (K)} \]
\[ t = \text{Time (min)} \]
\[ X_A = \text{Fractional conversion of A} \]

References


