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Esterification Reaction Kinetics Using Ion Exchange Resin Catalyst by Pseudo-Homogenous and Eley-Ridel Models

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P A P E R   I N F O

A B S T R A C T

This work deals with kinetics and chemical equilibrium studies of esterification reaction of ethanol with acetic acid. The esterification reaction was catalyzed by an acidic ion exchange resin (Amberlyst-15) using a batch stirred tank reactor. The pseudo-homogenous and Eley-Rideal models were successfully fitted with experimental data. At first, Eley-Rideal model was examined for heterogeneous esterification of acetic acid and ethanol. The pseudo-homogenous model was investigated with a power-law model. The apparent reaction order was determined to be (0.88) for Ethanol and (0.92) for acetic acid with a correlation coefficient (R^2) of 0.981 and 0.988, respectively. The reaction order was determined to be 4.1087×10^{-3} $L^{0.8}/(mol^{0.8}.min)$ with R^2 of 0.954. The adsorption constants of acetic acid and ethanol were calculated as 0.023 and 0.044 L/mol, respectively and the lumped reaction constant were determined to be 5×10^{-4} $L^2/g_{cat}.mol.min$. The results of the reaction kinetic study show that the high acetic acid/ethanol molar ratio was favored. The maximum conversion of 70 % was obtained at 70°C for acetic acid/ethanol molar ratio of 4.

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NOMENCLATURE

C_{Ao}	Initial concentration of AcOH	k_e	The overall reaction equilibrium constant
C_{Bo}	Initial concentration of EtOH	m	Weight of catalyst
C_c	The concentration of catalyst	$-r_{Ao}$	Rate of reaction
K	The Pseudo homogenous rate constant or the lumped reaction constant	t	Reaction time
k_A	Adsorption constant of AcOH	ν	Reaction volume
k_B	Adsorption constant of EtOH	X_A	Conversion of AcOH

1. INTRODUCTION

Esters are important organic compounds which are widely used in different industries such as manufacturing of flavours, pharmaceuticals, polymerization polymers, plasticizers, softeners, dispersants, detergents, surfactants, solvents, biodiesel fuels and emulsifiers for food and cosmetics [1,2]. Ethyl

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acetate (EtOAC) is a colourless oxygenated solvent with chemical formula of $CH_3COOC_2H_5$ and molecular weight of 88.10 [3]. Ethyl acetate is the most recognized as a flavouring agent in various commercial products including food industry. Ethyl acetate is a fruity smelling liquid with a brandy note and is the most common ester present in fruits; since this ester has a significant effect on the organoleptic characteristics of distillates. Ethyl acetate can be simply produced by different microorganisms, such as *Kluyveromyces marxianus*, Staphylococcus, *Geotrichum fragans*,

Saccharomyces cerevisiae, Ceratocystis fimbriata, Ceratocysis moniliformis, Pichia anomala, Hanseniaspora guilliermondii 11104, etc. [4]. Ethylacetate has been implemented in several main industrial applications such as surface coating, thinners, flexible packaging, flavours, essences and biodiesel production [3,5].

Esters are reaction products occurring between carboxylic acids and organic alcohols [6]. Different approaches have been employed throughout the years to prepare esters, such as homogenous method, which includes using a mineral acid such as sulphuric or phosphoric acid as the catalyst, and the heterogeneous method which uses acid polymers as the catalyst such as ion exchange resins [7,8]. Use of a heterogeneous catalyst as an attractively alternative to a homogeneous catalyst in esterification reactions allows avoiding the drawbacks of homogeneous catalyst, such as equipment corrosion and side reactions [9]. Also, other properties of heterogeneous catalyst are favoured such as eco-friendly nature, long activity life, non-miscibility with the reaction medium which allows easy separation by filtration or centrifugation and no washing is required as of homogenous catalysts [6,10–12].

Several kinetic models have been implemented to study the esterification reaction catalysed by ion exchange resins such as Langmuir-Hinshelwood model (LHM), pseudo-homogenous model (PH) and Eley-Rideal (ER) model. The LHM is based on including the sorption effect on the kinetic model through considering that all reactants are adsorbed on the catalyst active sites [13,14]. Complete swelling of the polymeric catalyst which is in contact with a polar solvent was suggested by the pseudo-homogenous model (PH). This suggestion allows an easy access of the reactants to the active sites [15,16]. The PH model does not give a priority to the sorption effect, in contrast to Eley-Rideal (ER) mechanism which includes sorption effect in their kinetic model. The ER model is employed when the reaction starts to occur between the adsorbed and non-adsorbed materials [13]. Since, it is based on the assumption that the molecules adsorbed on the catalyst surface are only some molecules contributed in the reaction [17]. The literature mentioned several contributions in which the kinetic correlations of experimental data using the ER model, such as the esterification of isobutanol alcohol with acetic acid using Amberlyst catalyst, the esterification of octanol alcohol with hexanoic acid on the zeolite BEA and SAC-13 and the esterification reaction of amyl alcohol with acetic acid using acid resin catalysts [1]. In present study, the ER model is first used for the esterification reaction of ethanol alcohol with acetic acid using Amberlyst-15 catalyst.

In this contribution, several experiments were carried out to study the effect of the initial molar ratio of acetic acid (AcOH) to ethanol (EtOH) to produce ethyl acetate (EtOAC) and water (W). The kinetic study of esterification reaction was conducted using both PH and ER models.

2. EXPERIMENTAL WORK

2. 1. Chemicals   The materials used for esterification reaction were ethanol (Sigma-Aldrich, 95%wt) and acetic acid AcOH (Sigma-Aldrich, 99.6%). Amberlyst-15 (a strong acid ion-exchange resin) was used as the catalyst (Sigma-Aldrich). The specifications of Amberlyst-15 are listed in Table 1. The resin was washed with distilled water, overnight dried at 100°C and then stored in a discator.

2. 2. Procedures   The reaction took a place in an isothermal well-stirred batch reactor as previously described by Ahmed Zeki et al. [18]. AcOH and Amberlyst-15 were charged into the reactor to be heated to the desired temperature before conducting the esterification reaction. EtOH was heated individually to the same temperature and then added to the previous reaction mixture. The time of adding EtOH to the reaction mixture was considered as an initial time of reaction (zero time for a run). Samples were periodically taken and analysed by a gas chromatography. The experiments were carried out at 70°C and a constant volume of 500 ml. A catalyst loading weight was of 4 mg, and the initial molar ratio of AcOH to EtOH was ranging of 0.25 to 4.

The analysis was conducted by a gas chromatography (United Technologies Packard) using a SE-30 column, and flame ionisation detector. The initial column temperature was set at 200°C and held for 6 min, and then increased to 325°C at a rate of 1°C/min.

3. RESULTS AND DISCUSSION

The overall reaction between AcOH and EtOH can be represented by the following equation:

$$AcOH + EtOH \leftrightarrow EtOAc + H_2O \tag{1}$$
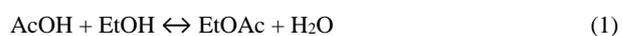
As, symbol (A) was given to AcOH, symbol (B) was given to EtOH, symbol (E) was given to EtOAc and symbol (W) was given to H_2O, the equation will be:

$$A + B = E + W \tag{2}$$
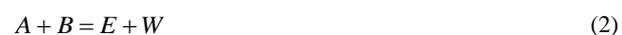
This reaction is reversible and the equilibrium composition is weakly function of temperature [19]. Literature pointed out that the equilibrium constant is slightly influenced by temperature in most esterification reactions due to low heat of reaction.

Parameter	Specification
Hydrogen form wet moisture, wt%	48
Appearance (Colour)	Brown-Grey
Appearance (Form), mm	Granules 0.600 - 0.850
Exchange Capacity, meq/ml	1.7
Surface area, m²/g	53
Average pore diameter, °A	300
Total pore volume, ml/g	0.40
Maximum operating temperature, °C	120

Thus in most esterification reactions, increasing temperature leads to increasing conversion until it reaches the same conversion at equilibrium [13]. Due to some limitation, the temperature effect was not studied in the present work. In general, most esterification reactions are conducted under atmospheric pressure because it has no significant effect on the esterification process. However, another researcher studied esterification reaction under vacuum pressure by withdrawing water generated to enhance the forward reaction toward production of more esters and hence increasing conversion in the pervaporation process [20].

This acidic reaction is catalysed by Amberlyst-15, which is an excellent source of acidity (the acidity arising from the presence of acid sites) in a non-aqueous media. It is a porous sulfanated polystyrene resin that has been considered a powerful catalyst for various reactions [21]. The external mass transfer resistance and the inter-particle diffusion were neglected in this reaction making the reaction kinetically controlled. This assumption was based on the fact that the mixing speed of 250 rpm was high enough to eliminate the external mass transfer. Also, it is because the microporosity of the ion exchange catalyst used allows reduction of the resistance to mass transfer and enhancing reactants diffusion. This assumption agree with the work conducted by Ahmed Zeki et al. [14].

3. 1. The Pseudo-Homogenous Model (PH)   The Pseudo-homogenous model (PH) was used to represent the heterogeneous reaction using ion exchange resins. Ahmed Zeki et al. [14] suggested that the homogenous acid catalysed esterification reaction follows a second order kinetics, and first order with respect to each reagent. However, the study of heterogeneous reaction kinetic parameters is complicated because of disproportionate catalyst surface, or what is known as adsorbate interaction.

Apparent kinetics parameters, such as reaction order and rate constant, can be determined using the power-law given in the following equation [22]:

$$-r_A = -\frac{dC_A}{dt} = kC_A{}^n C_B{}^m \tag{3}$$

First, the initial reaction rate has to be calculated at 70°C using the following Equation:

$$-r_A = -\frac{dC_A}{dt} = -C_{Ao}\frac{dX_A}{dt} \tag{4}$$

where, C_{Ao} is the initial concentration of AcOH, and X_A is the conversion of AcOH.

Figures 1(a) and 1(b) show the AcOH conversion versus time (t) at different AcOH/EtOH and EtOH/AcOH molar ratio at 70°C. The initial molar ratio of AcOH/EtOH varied between (0.25-4) for the esterification reaction. The general trend of Figures 1(a) and 1(b) is that the conversion of AcOH increased when the initial AcOH/EtOH molar ratio increased from 1 to 4 with time until the reaction time reached to about 90 min after that they tended to be constant.

In addition, Figures 1(a) and 1(b) show that the equilibrium conversion increases up to 70% for AcOH/EtOH = 4, while the conversion reached to 55% for AcOH/EtOH = 0.25.
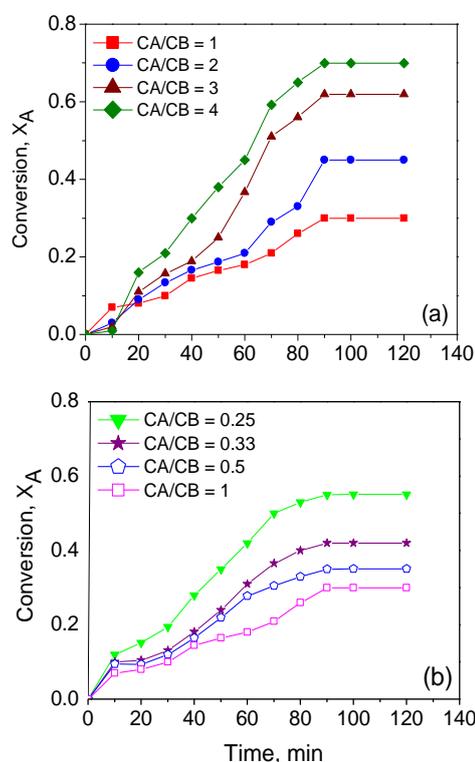

Figure 1. Conversion of AcOH versus time for AcOH esterification when (a) AcOH/EtOH molar ratio was 1-4 at 70°C (b) EtOH/AcOH molar ratio was 0.25-1 at 70°C

This is because the reaction is normally catalysed by acid and thus, the reaction favoured increasing of AcOH/EtOH molar ratio. The conversion enhanced and the reaction proceeded in the forward direction when an excess of one of the reactants used. Also, plotting the conversion against times showed a linear relation when the conversion is less than 10%.

By applying a fixed value of C_B in Equation (3), a straight line with a slope of n can be obtained when plotting $\ln r_{A0}$ versus $\ln C_A$.

The linear plot of $\ln r_{A0}$ versus $\ln C_A$ is shown in Figure 2 (a). Also, the value of m can be determined by plotting $\ln r_{A0}$ versus $\ln C_B$ at a fix value of C_A as shown in Figure 2 (b). Therefore, the reaction order of AcOH and EtOH were found as 0.92 and 0.88 with correlation coefficients (R^2) of 0.988 and 0.981, respectively; the results of this study are presented in Table 2. While, the rate constant value was obtained by a linear plot of $-r_{Ao}$ against $C_{Ao}^{0.92}$. $C_{Bo}^{0.88}$ and it was 4.1087×10^{-3} $L^{0.8}/(mol^{0.8}.min)$ with R^2 of 0.9534, see Figure 3.

The initial concentrations of both EtOH and AcOH positively affect on the reaction rate. It is clear that there is an obvious increasing in the reaction rate when a higher molar ratio of AcOH/EtOH was used as the reaction is catalysed by acid.
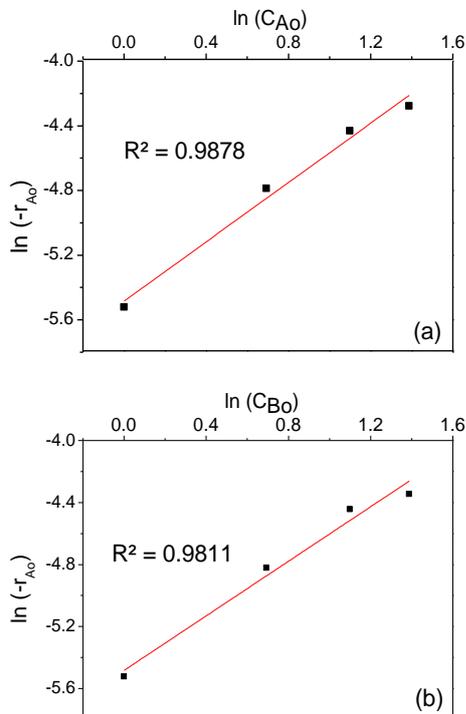
TABLE 2. The initial reaction rate values used to obtain the apparent reaction order of AcOH and EtOH at 70°C

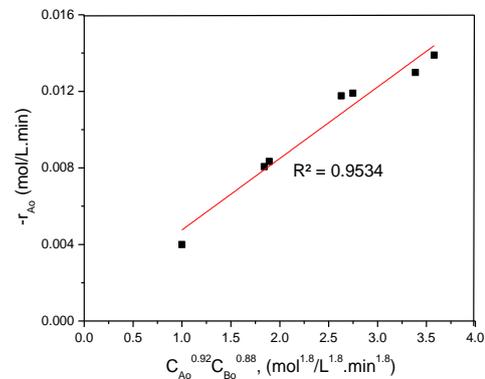| C_{Ao}(mol/l)	C_{Bo}(mol/l)	$-r_{Ao}$ (mol/l.min)x10³
1	1	4±0
2	1	8.330±0.003
3	1	11.904±0.001
4	1	13.889±0.001
1	2	8.0645±0.002
1	3	11.7647±0.001
1	4	12.987±0.002

Figure 2. Determination of the rate constant of at 70°C for Amberlyst -15.

This result well agrees with the investigation published by Ahmed Zeki et al. [18] and Popked et al. [23].

Applying the values of n, m and k in the power-law represented by Equation (3) leads Equation (5). Equation 5 can be expressed in form of conversion X_A to obtain Equation 6 which will be used to fit the experimental rate of reaction (see Figure 4). The experimental reaction rate and mathematical reaction rate obtained using PH model are listed in Table 3 for C_{A0}/C_{B0} molar ratio of (1 to 4) and Table 4 for C_{A0}/C_{B0} molar ratio of (0.25 to 1), respectively. The values of conversion applied on Equation (6) were the same as values on which the experimental results were obtained.

$$-r_A = 4.108 \times 10^{-3} C_A^{0.95} C_B^{0.88} \tag{5}$$

$$-r_A = 4.108 \times 10^{-3} C_{A0}^2 (1 - X_A)^{0.92} (n - X_A)^{0.88} \tag{6}$$

where; n = C_{B0}/C_{A0} is molar ratio.

Figure 4 shows that the theoretical rate of reaction obtained by power-law was close to the experimental rate of reaction. However, it shows an obvious divergence for C_{A0}/C_{B0} molar ratio of 3 and 4.
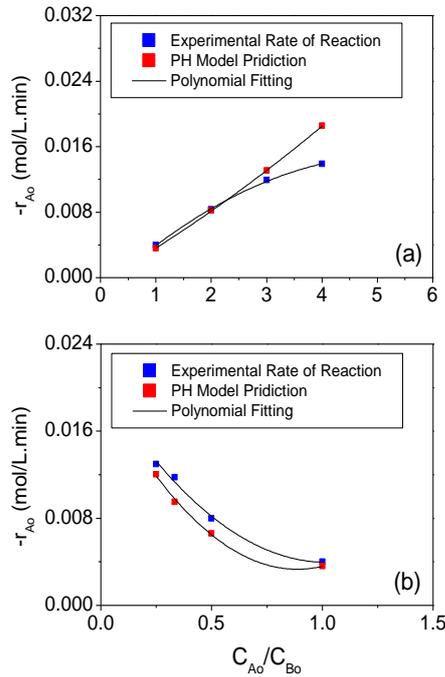

Figure 1. Determination of the apparent reaction order (a) of A at constant C_B at 70°C for Amberlyst -15, (b) of B at constant C_A at 70°C for Amberlyst -15

Figure 3. Fitting of experimental results of the esterification reaction to the PH model at (a) $C_{Ao}/C_{Bo} = 1\text{-}4$, (b) $C_{Ao}/C_{Bo} = 0.25\text{-}1$.

TABLE 3. Experimental reaction rate and mathematical reaction rate obtained using PH model for C_{A0}/C_{B0} molar ratio of (1 to 4)

C_{Ao}(M)	C_{Bo}(M)	Experimental r_{Ao} (M/min)x10³	Mathematical r_{Ao} (M/min)x10³
1	1	4±0	3.6
2	1	8.330±0.003	8.22
3	1	11.904±0.001	13.07
4	1	13.889±0.001	18.55

TABLE 4. Experimental reaction rate and mathematical reaction rate obtained using PH model for C_{A0}/C_{B0} molar ratio of (0.25 to 1)

C_{Ao}(M)	C_{Bo}(M)	Experimental r_{Ao} (M/min)x10³	Mathematical r_{Ao} (M/min)x10³
1	1	4±0	3.6
1	2	8.0645±0.002	6.61
1	3	11.7647±0.001	9.52
1	4	12.987±0.002	12.04

This can be attributed to the presence of (C_{Ao}^2) term in Equation (6) and thus, increasing the initial acetic acid concentration increases the initial rate of reaction.

3. 2. The Eley-Rideal Model (ER)
The kinetic data for the esterification reaction was correlated with the ER model represented by Equation (7) because the reaction occurred between the adsorbed EtOH and AcOH in the bulk of the catalyst [24].

$$-r_A = \frac{k\dfrac{m}{v}C_A C_B - \dfrac{C_E C_W}{k_e}}{1 + k_A C_A + k_B C_B} \tag{7}$$

where, k is the forward reaction rate or it so called as the lumped constant, k_e is the overall reaction equilibrium constant, k_A, k_B are the adsorption constants of AcOH and EtOH respectively, m is the amount of catalyst used and v is the volume of reaction. To determine the parameters of Equation (7), the second part of nominator can be considered as zero, i.e. $\dfrac{C_E C_W}{k} = 0$ for the initial rate when conversion < 10% as the hydrolysis reaction is not started yet. Thus, Equation (7) can be rewritten as following:

$$-r_A = \frac{k\dfrac{m}{v}C_A C_B}{1 + k_A C_A + k_B C_B} \tag{8}$$

A mathematical model was developed to estimate the esterification rate using Equation 8 and the initial rate of reaction r_{A0} at different initial reactant concentrations. Equation (8) can be rearranged to obtain:

$$\frac{1}{-r_{A0}} = \frac{k_B}{k\dfrac{m}{v}C_{A0}} + \frac{1 + k_A C_{A0}}{k\dfrac{m}{v}C_{A0}}\left(\frac{1}{C_{B0}}\right) \tag{9}$$

$$\frac{1}{-r_{A0}} = \frac{k_A}{k\dfrac{m}{v}C_{B0}} + \frac{1 + k_B C_{B0}}{k\dfrac{m}{v}C_{B0}}\left(\frac{1}{C_{A0}}\right) \tag{10}$$

The value of C_{A0} applied in Equation (9) and (10) was fixed to 1 mol/l. A straight line with a slope/intercept ratio = $[1 + (1\ \text{mol/l})\ k_A]/k_B$ of Equation 9 was obtained from a linear plot of $\dfrac{1}{-r_{A0}}$ versus $\dfrac{1}{C_{B0}}$ (shown in Figure 5 (a)). Also, a slope/intercept ratio of Equation (10) is $[1 + (1\ \text{mol/l})k_B]/k_A$ can be obtained from the linear plot of $\dfrac{1}{-r_{A0}}$ versus $\dfrac{1}{C_{A0}}$ at constant C_{B0} of 1 mol/l (see Figure 5 (b)).

The values of k_A and k_B were found to be 0.0228 l/mol and 0.0443 l/mol with correlation coefficients of 0.9955 and 0.9946, respectively. The PH model results were used to elucidate the results obtained using ER model in term of a comparison between EtOH and AcOH showed that EtOH has larger adsorption equilibrium which is to some extent, in consistence with its lower apparent reaction order (see Equation (5)).

This indicates more EtOH covering the catalyst acid sites.

By applying the adsorption constant and the initial concentration of both EtOH and AcOH as displayed in Table 2, catalyst weight of 4 g and reaction volume of 500 ml on ER model represented by Equation (8), the lumped reaction constant (k) was obtained as 5×10^{-4} $l^2/g_{cat}.mol.min$ with R^2 of 0.9513 at 70°C (see Figure 6).
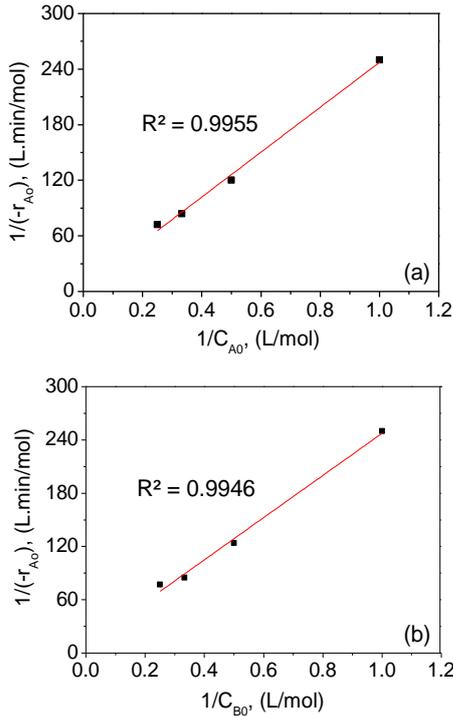

Figure 4. Determination of the adsorption constant for (a) acetic acid at 70°C, (b) for ethanol at 70°C
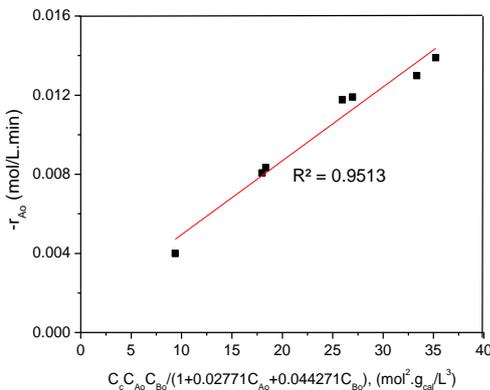

Figure 5. Determination of the lumped reaction constant at 70°C

Thus, the kinetic model can be written as following:

$$-rA = \frac{5 \times 10^{-4} C_c C_A C_B}{1 + 0.022771 C_A + 0.044271 C_B} \tag{11}$$

where; C_c is the concentration of catalyst which equals to m/v. Equation (11) can be expressed in term of X_A as following:

$$-rA = \frac{5 \times 10^{-4} C_c C_{A0}^2 (n - X_A)(1 - X_A)}{1 + C_{A0}[0.022771(1 - X_A) + 0.044271(n - X_A)]} \tag{12}$$

where; $n = C_{B0}/C_{A0}$ is molar ratio.

The applicability of this model to the experimental results was studied at the same values of conversion on which the experimental results were obtained; see Tables 5 and 6.

Figure 7 shows that the kinetic model was best fit to the experimental results of the rate of reaction calculated at different AcOH/EtOH molar ratio of 0.25-4.

Since, the values of the experimental rate of reaction were very close to the values of the rate of reaction obtained from the mathematical model given by Equation (12). Also, these results show that the rate of reaction increased when AcOH/EtOH increased; while the rate decreased with increasing AcOH/EtOH ratio. Thus, these results confirm that the reaction is catalysed by acid and using an excess of acetic acid to ethanol is favoured for this reaction and confirm the results obtained by PH kinetic model.

TABLE 5. Experimental reaction rate and mathematical reaction rate obtained using ER model for C_{A0}/C_{B0} molar ratio of (1 to 4)

$C_{Ao}(M)$	$C_{Bo}(M)$	Experimental r_{Ao} (M/min)x10^3	Mathematical r_{Ao} (M/min)x10^3
1	1	4±0	3.26
2	1	8.330±0.003	6.73
3	1	11.904±0.001	10
4	1	13.889±0.001	13.46

TABLE 6. Experimental reaction rate and mathematical reaction rate obtained using ER model for C_{A0}/C_{B0} molar ratio of (0.25 to 1)

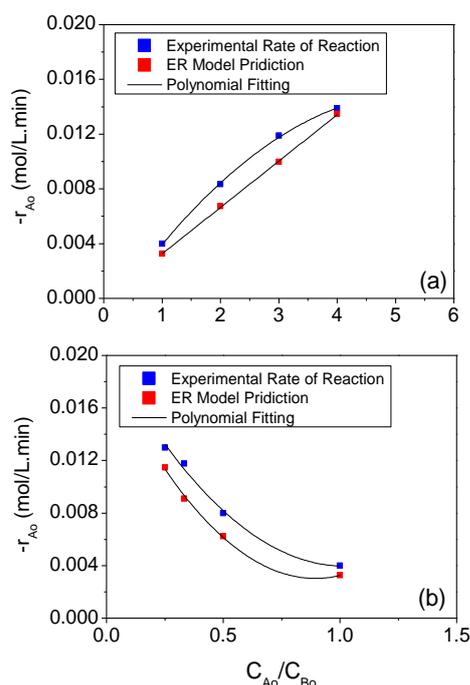| $C_{Ao}(M)$	$C_{Bo}(M)$	Experimental r_{Ao} (M/min)x10^3	Mathematical r_{Ao} (M/min)x10^3
1	1	4±0	3.26
1	2	8.0645±0.002	6.25
1	3	11.7647±0.001	9.1
1	4	12.987±0.002	11.48

Figure 6. Fitting of experimental results of the esterification reaction to the ER model at (a) C_{Ao}/C_{Bo} = 1-4, (b) C_{Ao}/C_{Bo} = 0.25-1

4. CONCLUSIONS

The reaction kinetics of AcOH and EtOH chemical esterification which is heterogeneous catalysed has been investigated. The pseudo-homogenous model and Elay-Ridel model were used to study the reaction kinetics and fit to the experimental results.

The apparent reaction orders were obtained to be 0.88 for EtOH and 0.92 for AcOH with a reaction order of 4.11×10^{-3} $l^{0.8}/(mol^{0.8}.min)$. The reaction appeared to be established between the molecules of adsorbed EtOH and AcOH through the bulk phase, which was confirmed by Elay-Ridel model. Increasing the equilibrium conversion can be obtained by increasing AcOH as the reaction is catalysed by acid. Both PH and ER models showed very good matching to the experimental kinetic data. As this study was conducted at conversion of 10%, it is recommended to conduct it for all range of conversion including equilibrium conversion for the forward and backward reactions.

5. ACKNOWLEDGEMENT

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Esterification Reaction Kinetics Using Ion Exchange Resin Catalyst by Pseudo-Homogenous and Eley-Ridel Models

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چکیده

این کار با مطالعات تعادل سینتیک و شیمیایی واکنش استریابی اتانول با اسید استیک انجام می شود. واکنش استرینگ توسط یک رزین مبادله یونی اسیدی (Amberlyst-15) در یک مخزن مخزن دسته ای مخلوط شد. مدل شبه همگن و مدل Eley-Rideal با نتایج تجربی سازگار است. در این مطالعه ابتدا مدل Eley-Rideal برای استرینگ ناهمگن اسید استیک و اتانول مورد استفاده قرار گرفت. مدل شبه همگن با مدل قدرت قانون مورد بررسی قرار گرفت. منظور واکنش ظاهری (0.88) برای اتانول و (0.92) برای اسید استیک با ضریب همبستگی (R2) 0.99811 و 0.9878 تعیین شد؛ و سفارش واکنش به (mol0.8min4.1087) / L0.8 x10-3) با R2 0.9534 تعیین شد. ثابت بار جذب اسید استیک و اتانول به ترتیب به 0222771 و 044271 لیتر مولار محاسبه شد و ثابت بودن واکنش لومپد به میزان 5 × 10−4 gcat.mol.min / L2 تعیین شد. نتایج مطالعه کینتیک واکنش نشان می دهد که نسبت مولی استیک اسید / اتانول بالا مورد توجه قرار گرفته است. حداکثر تبدیل 70٪ در دمای 70 درجه سانتی گراد برای نسبت مولی استیک اسید / اتانول 4 به دست آمد.

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