

Catalytic Hydrolysis of Ethyl Acetate using Cation Exchange Resin (Amberlyst - 15) : A Kinetic Study

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Received: 19 July 2009; Revised: 20 August 2009; Accepted: 22 August 2009

Abstract

The kinetic behavior of the heterogeneous hydrolysis of aqueous ethyl acetate over an acidic cation exchange resin, Amberlyst 15, was investigated. The experiments were carried out in a fixed bed reactor at temperatures from 313.15 to 343.15 K and feed molar ratios θ_{B_0} (water to ethyl acetate) from 62.4 to 265.88. The conversion of ethyl acetate was found to increase with increasing reaction temperature. Gas bubble formation was observed at reaction temperature ≥ 343.15 K. Absence of mass transfer resistance was verified by conducting the experiments at different catalyst loadings (20g, 40g, 64g) under varied feed flow rates (1 to 25 cm³/min). The kinetic data was correlated with pseudo first order model and model parameters were determined using Nelder-Mead algorithm for minimizing the objective function. © 2009 BCREC. All rights reserved.

Keywords: Hydrolysis, Ethyl acetate, Amberlyst-15, Kinetics

1. Introduction

Liquid phase hydrolysis and esterification in which water exists as one of the reactants or products are usually catalyzed by homogenous acids such as H₂SO₄. Sulphuric acid being a homogenous acid poses problems due to corrosion, disposal, and handling. Alternatively, the use of heterogeneous catalyst like Niobic acid [1], ion exchange resin [2,3] and metal oxides [1] have been reported to have overcome these problems. However, catalyst like Niobic acid and metal oxides needs special treatment and performance of these catalysts is sensitive to the pretreatment conditions [1]. Hence, ion-exchange resins are

preferred over homogenous acids due to ease of product separation and catalyst recovery. Apart from their prominence in separation and purification of products, ion exchange resins have been used as catalyst for esterification/hydrolysis reactions [2,3], phenol alkylation and hydration of olefins [4].

The reaction kinetics and chemical equilibrium of the reversible esterification of methanol with acetic acid were investigated by Popken et al. [5], and Han et al.[6]. The reaction was catalyzed both homogeneously by acetic acid itself and heterogeneously by an acidic ion-exchange resin (Amberlyst-15). New phenomenon of in-situ coating by the reactant/product on ion exchange

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resin catalyst, Amberlyst-15, that helps to improve the reaction kinetics of dicyclopentadiene (DCPD) hydration has been reported by Talwalkar et al. [7]. The aza-Michael reactions of amines with unsaturated carbonyl and nitrile compounds have efficiently been carried out at room temperature using Amberlyst-15 as a heterogeneous reusable catalyst. The products were formed in short reaction times and in high yields [8]. The catalyst Amberlyst-15, is commercially available, inexpensive and non-hazardous. It works under heterogenous conditions, can easily be handled and removed by simple filtration [8]. There is growing research using amberlyst-15 catalyst for esterification reactions [5,9-11] but not much work is reported on hydrolysis reaction.

Recovery of ethyl acetate from dilute aqueous process waste streams commonly found in the specialty chemicals and pharmaceutical industry may be handled by pervaporation or hydrolysis. In case of hydrolysis, recovered acetic acid can be reused in the process.

The aim of the present study was to investigate the applicability of the macro porous cation exchange resin (Amberlyst 15 in acid form) for the hydrolysis reaction and to examine the effects of flow rate, temperature, and catalyst loading on the reaction rate.

2. Materials and Methods

2.1. Materials used

Reagent grade Ethyl Acetate (98%) from Qualigens Fine chemicals Ltd and double distilled water have been used in all the experimental runs. Amberlyst-15 supplied by Rohm and Haas was used as catalyst and its relevant characteristics are summarized in Table 1.

2.2. Experimental Setup

The fluid solid catalytic reaction was carried out in a continuous flow laboratory scale packed bed reactor at atmospheric pressure (Figure 1). A double walled Borosil glass tube (length 70 cm, outer diameter 4.4 cm, inner diameter 2.2 cm) was maintained at constant temperature by circulating water from the constant temperature bath (Julabo F30) through the annulus of the reactor. The temperature was controlled to within ± 0.1 °C. A known amount of fresh/regenerated catalyst in acid form was packed into the reactor supported on a stainless steel mesh. A simple pre-

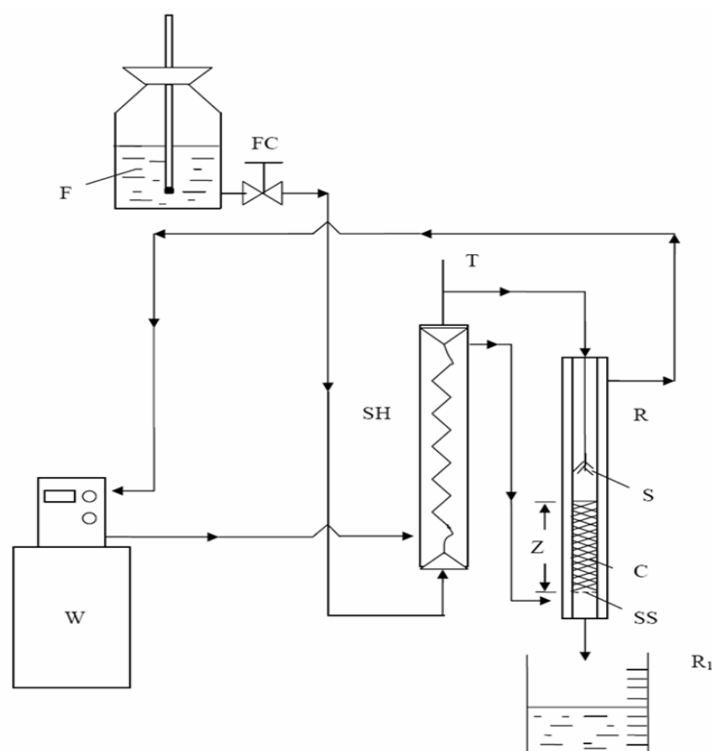
Table 1. Physicochemical properties of Amberlyst-15

Skeleton	Styrene -Divinyl benzene
Type	strong acid
Structure	macro reticular
Functional group	sulfonic (SO ₃ H)
Ionic form	Hydrogen
Cross- linking degree	20 %
Particle size	0.35- 1.2 mm
Internal porosity	0.36
Concentration of acid sites	4.53 m _{equiv} g ⁻¹ . of dry resin
Bulk density	600 kg m ⁻³
Polymer density	1410 kg m ⁻³

treatment was used to convert the catalyst into acid form. At first catalyst was washed with distilled water three to four times and dried at atmospheric conditions. The dried catalyst was soaked in 0.1N hydrochloric acid solution for half an hour. Thereafter the catalyst was separated and dried at ambient conditions for 48 hrs.

2.3. Procedure

The aqueous ethyl acetate solution from the feed tank was first heated to the desired reaction temperature by passing it through a coiled heat exchanger. The feed solution was uniformly dispersed on the top surface of the catalyst bed at the desired flow rate using valve FC (Figure 1). The volumetric flow rate of the feed was periodically calibrated with pure water. The reaction temperature was regulated to within ± 0.1 °C by circulating thermostatic water through the reactor jacket. A precision digital thermometer measured the reactant temperature to an accuracy of ± 0.01 °C. Once a steady state was attained, the product was collected in a sampling flask. The amount of acetic acid in the sample was analyzed with 0.1N standard solution of NaOH. At least five replicated samples were taken under each of the experimental conditions and reproducibility was within $\pm 2\%$. The conversion of ethyl acetate was calculated from the stoichiometry of the reaction. A complete conversion curve was obtained by conducting the experiment with various flow rates. Each set of experiment was carried out using fresh/regenerated catalyst. Experimental runs were carried out at different feed flow rate, reaction temperature, feed solution concentration and



F -Aqueous Ethyl Acetate Feed Tank , FC – Flow Controller , W – Constant Temperature Water Bath , T – Mercury Thermometer , SS – Stainless Steel Sieve , S – Sprayer , R – Packed Bed Reactor , SH – Spiral Heat Exchanger , C – Catalyst Bed , R₁ Receiver , Z – Height of the Catalyst Bed

Figure 1. Experimental setup

catalyst loading. For each run, only one parameter was varied at a time.

3. Results and Discussion

The kinetics of hydrolysis of ethyl acetate was studied at temperatures from 313.15 to 343.15 K with four different molar feed ratios ($\theta_{B_0} = 265.88, 130.226, 85.115, 62.4$, where θ_{B_0} is the molar ratio of water to ethyl acetate). All the experiments were carried out with various volumetric flow rates of feed (F) at fixed conditions of reaction temperature and feed composition. The contact time (τ) of the reactants with catalyst is defined as :

$$\tau = W/F \quad (1)$$

A wide range of volumetric flow rates of the

feed was covered in the experiments for which conversion of ethyl acetate (X_A) varied from 0.112 to 0.877. Results of the hydrolysis measurement are tabulated in Table 2. Figure 2 presents the variation of X_A with contact time for the hydrolysis reaction taking place at $\theta_{B_0} = 265.88$, $W = 64$ g, over a temperature range of 313.15 to 343.15 K. It shows that the conversion of ethyl acetate increases with increase in reaction temperature. Figure 3 illustrates the variation in conversion with contact time at 323 K under different feed compositions. At a given contact time, greater conversions are achieved at higher θ_{B_0} .

By visual inspection, gas bubbles were formed at temperature greater than 343.15 K. To investigate the influence of the transport resistance by film diffusion or pore diffusion, experiments were also carried at different catalyst loadings (20 g, 40 g, 64 g). Figure 4 compares the results at 323.15 K and $\theta_{B_0} = 265.88$ with different catalyst loading

Table 2. Range of experimental parameters observed during hydrolysis of aqueous ethyl acetate using Amberlyst-15 as catalyst

S. No.	Reaction Temp., T, K	Molar feed Ratio, θ_{B_0}	Catalyst Weight, W, g	Feed Conc., C_{A_0} , 10^{-3} mol cm^{-3}	Range of Contact Time, τ , g min cm^{-3}	Range of conversion, X_A
1	313.15	265.88	64	0.205	3.333-16.671	0.130- 0.492
2	323.15	265.88	64	0.205	3.152-16.671	0.199-0.657
3	333.15	265.88	64	0.205	2.958- 16.954	0.275- 0.819
4	343.15	265.88	64	0.205	3.133- 13.333	0.385- 0.877
5	313.15	130.23	64	0.410	3.125- 16.671	0.115- 0.450
6	323.15	130.23	64	0.410	3.333-16.671	0.195- 0.601
7	333.15	130.23	64	0.410	2.985- 16.628	0.261-0.760
8	343.15	130.23	64	0.410	3.333-13.333	0.378-0.812
9	313.15	85.12	64	0.614	3.333-16.667	0.112-0.418
10	323.15	85.12	64	0.614	3.333- 14.267	0.112-0.377
11	333.15	85.12	64	0.614	3.333-16.667	0.263-0.701
12	343.15	85.12	64	0.614	2.958-13.333	0.318-0.760
13	313.15	62.40	64	0.820	3.333-16.667	0.109- 0.385
14	323.15	62.40	64	0.820	3.125-16.728	0.156-0.536
15	333.15	62.40	64	0.820	3.136-16.667	0.236-0.659
16	323.15	265.88	64	0.205	3.152-16.671	0.199-0.658
17	323.15	265.88	40	0.205	2.139-17.778	0.124-0.587
18	323.15	265.88	20	0.205	1.053-12.121	0.066-0.525

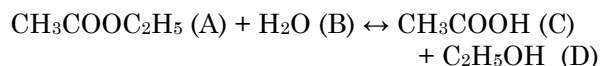
indicating that all experimental points fall on the same curve. Thus the effect of film and pore diffusion appear to be negligible at present experimental conditions [3,13]. Figure 5 illustrates the effect of flow rate on conversion (X_A) at 313 K at $\theta_{B_0}=265.88$. Experiments were carried out using volumetric feed flow rates (F) in the range of 1 to 20 cm^3/min at different molar feed ratios θ_{B_0} . From Figure 5 it is observed that as flow rate increases conversion of ethyl acetate decreases.

Correlation of kinetic data :

The kinetic data were correlated with mass balance equation for ethyl acetate around the entire packed bed reactor by:

$$\left(\frac{W}{FC_{AO}}\right) = \int_0^{X_A} \frac{dX_A}{-r_A} \quad 2$$

The rate expression for $-r_A$ depends on the assumption of the reaction mechanism. The basic reaction stoichiometry involved in hydrolysis of ethyl acetate is :



In the present study, the initial concentration of ethyl acetate (C_{A_0}) was varied from 2 to 8 % (v/v). Since, water being in large excess, a pseudo first order irreversible kinetic model was assumed to represent the data. The rate equation ($-r_A$) for the pseudo-first order formalism is :

$$-r_A = (k_1 C_{B_0}) C_A \quad \text{or} \quad -r_A = k C_A \quad 3$$

Where k is the pseudo first order rate constant based on the weight of the catalyst. Integration of Equation (2) with pseudo first order reaction rate, $-r_A$ (Eq. (3)) yields:

$$\left(\frac{W}{FC_{AO}}\right) = \frac{\ln\left(\frac{1}{(1-X_A)}\right)}{k_0 \exp\left(-\frac{E_0}{RT}\right) \theta_{B_0} C_{A_0}^2} \quad (4)$$

where,

$$\theta_{B_0} = \left(\frac{C_{B_0}}{C_{A_0}}\right) \quad k = k_0 \exp\left(\frac{-E_0}{RT}\right)$$

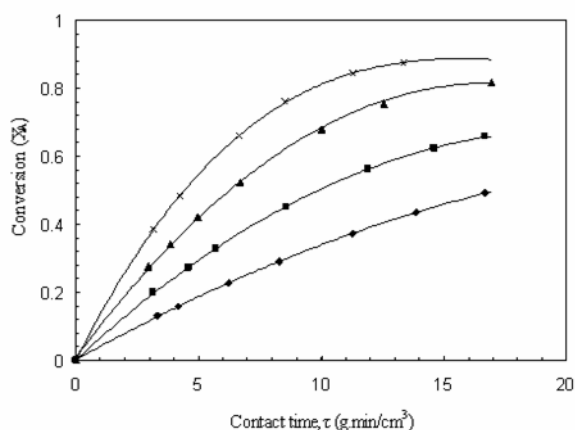


Figure 2. Conversion vs Contact time for $\theta_{BO} = 265.88, W = 64 \text{ g}$; at different temperatures, T: (♦) 313.15 K, (■) 323.15 K, (▲) 333.15 K, (x) 343.15 K.

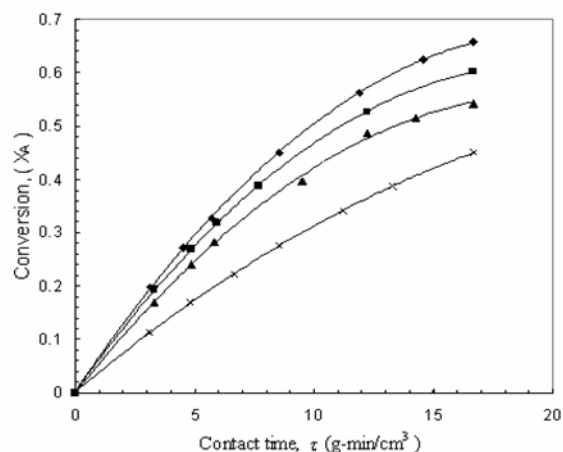


Figure 3. Conversion vs Contact time for $W = 64 \text{ g}$, T = 323.15 K; for different feed ratios, θ_{BO} : (♦) 265.88, (■) 130.226, (▲) 85.115, (x) 62.4

The kinetic data was fitted to Equation (4) using least square regression technique (Nelder - Mead algorithm) and the model parameters, E_0 and k_0 were evaluated. The total number of data points used in parameter estimation were 108. The results of the data correlation yielded the following:

- Activation Energy $E_0 = 41140 \text{ J/mole}^{-1}$
- Arrhenius pre-exponential factor $k_0 = 5.247 \times 10^6 \text{ cm}^6 \text{ g}^{-1} \text{ mole}^{-1} \text{ min}^{-1}$
- a correlation coefficient $R^2 = 0.99$.

Using these model parameters, parity between

observed (experimental) values of $\left(\frac{W}{FC_{AO}} \right)$ and the values based on pseudo first order kinetic model (Equation (4)) is shown in Figure 6. The model explains the present experimental data to within $\pm 10\%$ with MRQE value of 0.033. Based on pseudo first order model , rate constant,

$$k = \frac{F}{W \theta_{Bo} C_{Ao}} \ln \left(\frac{1}{1 - X_A} \right)$$

at various temperatures were obtained at different feed concentration and are tabulated in Table 3. From this table, constant values of rate constant are observed, within the accuracy of experimental data; for different feed concentrations at all temperatures.

4. Conclusions

The kinetic behavior of the hydrolysis of ethyl acetate in presence of large excess of water over Amberlyst-15 (in acid form) has been studied experimentally over reaction temperature from 313.15 to 343.15 K and molar ratios of feed (θ_{BO}) from 62.4 to 265.88. Under the investigated conditions, the absence of mass transfer resistance was verified experimentally. Pseudo first order kinetic model has been applied to correlate the kinetic data of the liquid solid reaction. The hydrolysis reaction is well represented by:

$$-r_A = 5.247 \times 10^6 \exp \left(-\frac{41140}{RT} \right) \theta_{BO} C_{AO}^2 (1 - X_A)$$

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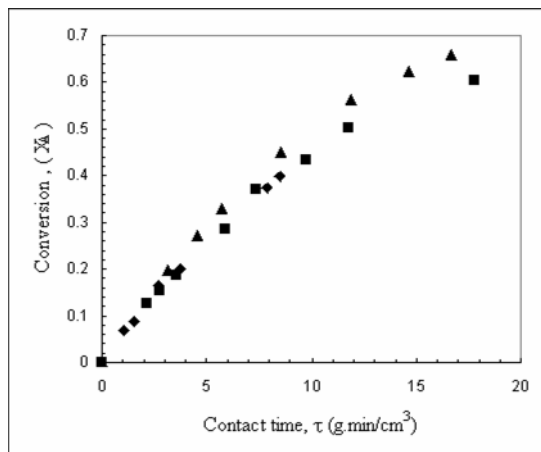


Figure 4. Conversion of ethyl acetate under different catalyst loading at 323.15 K and $\theta_{B0} = 265.88$: (\blacklozenge) 20 g, (\blacksquare) 40 g, (\blacktriangle) 64 g.

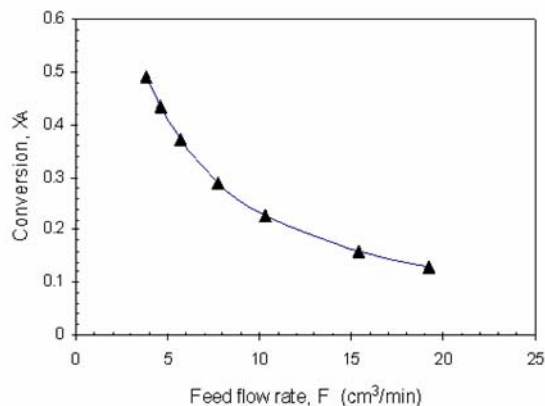


Figure 5. Conversion of ethyl acetate under different feed flow rates at 313.15 K and $\theta_{B0} = 265.88$

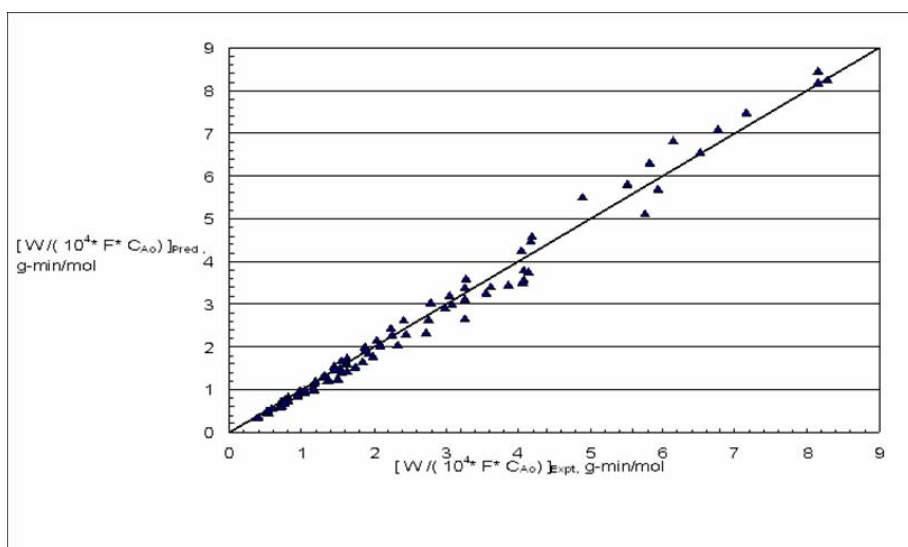


Figure 6. Parity between observed and predicted values of $\left(\frac{W}{F C_{AO}} \right)$

Table 3. Values of rate constant k , at different reaction temperatures, for various initial feed concentrations.

Temperature (K)	Observed Rate Constant, k , $\text{cm}^6 \text{g}^{-1} \text{mol}^{-1} \text{min}^{-1}$			
	2% Feed	4% Feed	6% Feed	8% Feed
313.15	0.760	0.705	0.652	0.634
323.15	1.262	1.170	1.085	0.999
333.15	2.013	1.825	1.639	1.525
343.15	2.948	2.719	2.343	(Bubble formation)

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Nomenclature

A	Ethyl acetate
B	Water
C	Acetic acid
C _{A0}	Inlet concentration of ethyl acetate, mol cm ⁻³
C _A	Concentration of ethyl acetate in exit stream of the reactor, mol cm ⁻³
D	Ethyl alcohol
E ₀	Activation energy, J mol ⁻¹
F	Volumetric flow rate of the feed, cm ³ min ⁻¹
F _A	F * C _{A0} , Molar feed rate of ethyl acetate, mol min ⁻¹
k ₀	Arrhenius pre-exponential factor, cm ⁶ g ⁻¹ mol ⁻¹ min ⁻¹
MRQE	Mean relative quadratic error

$$= \sqrt{\frac{\sum \left(\frac{\text{exp} - \text{pred}}{\text{exp}} \right)^2}{N - 1}}$$

where N is total number of data points

R	Gas law constant, J mol ⁻¹ K ⁻¹
R ²	Correlation coefficient
-r _A	Rate of reaction,
T	Reaction Temperature, K
W	Catalyst loading, g
X _A	Fractional conversion of ethyl acetate
θ _{B0}	Molar ratio of the feed (water to ethyl acetate)
τ	Contact time, g min cm ⁻³