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Heterogeneously Catalyzed Esterification Reaction: Experimental and Modeling Using Langmuir- Hinshelwood Approach

Nada S. Ahmedzeki, Maha H. Alhassani and Hayder A. Al-jandeel
Chemical Engineering Department, College of Engineering, University of Baghdad, Baghdad, Iraq

Abstract

The esterification reaction of ethyl alcohol and acetic acid catalyzed by the ion exchange resin, Amberlyst 15, was investigated. The experimental study was implemented in an isothermal batch reactor. Catalyst loading, initial molar ratio, mixing time and temperature as being the most effective parameters, were extensively studied and discussed. A maximum final conversion of 75% was obtained at 70°C, acid to ethyl alcohol mole ratio of 1/2 and 10 g catalyst loading. Kinetic of the reaction was correlated with Langmuir-Hanshelwood model (LHM). The total rate constant and the adsorption equilibrium of water as a function of the temperature was calculated. The activation energies were found to be as 113876.9 and -49474.95 KJ per Kmol of acetic acid for the esterification reaction and the heat of adsorption of water. These results agreed well with the previous published data.

Keywords: Esterification, Langmuir- Hinshelwood, Heterogeneous Catalyzed Reaction

Introduction

Reactions catalyzed by a solid catalyst are having great attention. The ion exchange resins Amberlyst-15 is as an excellent source of strong acid in non-aqueous media. It is a porous sulfonated polystyrene resin that had been explored as a powerful catalyst for various organic transformations and various catalyzed reactions, e.g., esterification, etherification, oxidation, hydration of olefins, condensation, cyclization and electrophilic aromatic substitution [1]. It has many advantages as that it is an inexpensive, non-hazardous solid acid, easily handled, and readily removed at the end of the reaction by simple filtration. An additional advantage is that the catalyst can be regenerated and used several times [2, 3].

Esters are commonly used as solvents, diluents, extract ants, pharmaceuticals, and intermediates [4,5]. Specifically, ethyl acetate primarily used as a solvent for removing pigments for nail varnishes and is responsible for the solvent effect for nail varnish remover. Industrially, it is used for decaffeinate coffee beans and tea leaves and also as an activator hardener. It is present in confectionaries, fruits and is used in perfumes due to its fruity smell [6]. The traditional homogeneous catalytic reaction using liquid acids as the catalyst was the popular method for the preparation of these materials. But the drawback of the reaction like

separation problems and the esterification of the acid catalyst itself producing co-products, made the search for other alternative method inevitable. A great deal of efforts had been concentrated on the development of solid acids to replace the conventional processes.

Heterogeneous Kinetic Models

Esterification reaction catalyzed by an ion- exchange resin can be qualified by using different kinetic models for both the homogeneous and heterogeneous approaches. For high polar reaction, the pseudo-homogeneous model (PHM) can be used because complete swelling in the polymeric catalyst can be assumed, leading to an easy arrival of the reactants to the active sites. Also (PHM) does not pay attention to the sorption effect into the catalyst of different species in the reactant solution [7,8]. The Langmuir-Hinshelwood model (LHM) includes the sorption effect in their kinetic model. The main idea of (LHM) is that all the reactants are adsorbed on the active sites of the catalyst surface before the start of chemical reaction [7]. Delgado et al [7] (2007) suggested an experimental kinetics expression, based on (LHM), assuming that only water is being adsorbed on the catalyst. Sattefield 1980 stated the advantages of (LHM) as:

- The resultant rate equation may be extrapolated more accurately to concentrations beyond the range of experimental measurements used.
- The method takes into account the adsorption and surface (which must occur) in a consistent manner.

The present study is the extension of our previous study on the homogeneously catalyzed esterification reaction [9]. In this study the experimental data of the heterogeneous esterification of acetic acid with ethanol and the hydrolysis of ethyl acetate was correlated using Langmuir-Hinshelwood approach.

Derivation of the Rate Equation

The reaction mechanism as proposed in this study is that the protonated carboxyl group of the acidic resin reacts with alcohol [10]. The ethanol/acetic acid esterification reaction is represented by the following equation:

$$A + B = E + W$$
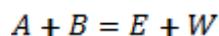
Where, A= AcOH,   B=EtOH, E=EtOAc,   W=H_2O

The derivation of an expression for acetic acid esterification under different experimental condition is based on the following assumption:

1- The reaction mixture was magnetically stirred at about 250 rpm. Under this condition, with the appropriate catalyst particle size range, it was assumed that there was no internal or external transport limitations. This assumption agrees with the work of Patricia et al [11] (2007), who established that external diffusion dose not control the overall reaction rate. While the negligible of internal diffusion agrees with Popken et al [12] (2000) and Patricia et al [11] (2007), who pointed out that intra- particle diffusion resistance is usually negligible for most of the reaction catalyzed by the Amberlyst series resins.

2- Since only water adsorbed onto the Amberlyst [12] in considerable amounts, the terms other than water can be neglected. To simplify the derivative of the reaction equation.

3- For the heterogeneously catalyzed reaction, it was founded in the literature that the goodness of fit can be improved by using activities instead of mole fractions [9] , but in

our study mole fractions were used because this study exhibited similar performance with the previous study.

The expression of the reaction rate can be described by Kirbasilar [5] (2000):

$$-r_A = k \frac{C_A C_B}{C_B + C_W k_W} \qquad \ldots(1)$$

Equation (1) can be rewritten in a straight line form as follows:

$$\frac{C_A}{-r_A} = \frac{1}{k} + \frac{k_W C_W}{k C_B} \qquad \ldots(2)$$

Where, k is the total rate constant, and k_w is the adsorption equilibrium constant of water.

The esterification reaction shows a strong non-ideal behavior due to the presence of water and ethyl alcohol which are highly polar compared to the non-polar ethyl acetate. Therefore, this non-ideality of the liquid phase was considered by using activities instead of mole fractions or concentrations [13]. The activity coefficients of the components at constant catalyst loading [14, 15] were calculated using UNIFACAL program. Therefore, Equation (1) becomes:

$$-r_A = k \frac{\alpha_A \alpha_B}{\alpha_B + \alpha_W k_W} \qquad \ldots(3)$$

Where α_i represents the activity of species i which is defined as:

$$\propto_{\square i} = \gamma_i \; x_i \qquad \ldots(4)$$

γ_i is the activity coefficient and x_i is the mole fraction.

Materials and Method
Materials

Acetic acid of analytical grade (99.6%) GCC, and local commercial alcohol 95% were used. The strong acidic ion-exchange resin (Amberlyst15), which supplies from Sigma-Aldrich was used as the catalyst. The specification is given by supplier, listed in Table.1. The resin was washed with distilled water, dried at 100°C over night and stored in a desiccator.

Procedure

The study of the kinetics of esterification reaction was carried out in a thermostatic batch reactor. A volumetric flask of 500ml fitted with a long reflux condenser to prevent any loss. A magnetic stirrer type (Stuart,) was used and the speed of 250 rpm which was high enough to eliminate external mass diffusion [16]. The aqueous AcOH solution and Amberlyst 15 were charged into the reactor and heated to the desired temperature. EtOH was heated separately to the same temperature and was added the reaction mixture. This time accounts for the start of the reaction. Samples were taken every 20 minutes by a syringe and analyzed by Gas Chromatography .Experiments were carried out at temperature range of 40-70°C. Values of temperature higher than this range causes an increase in the rate of the hydrolysis reaction as stated by Ahmedzeki et al [9]., (2010). The acetic acid to ethanol molar ratio of 1/2 to 2 and catalyst loading of 0.5-2g were also studied. The volume of the reaction mixture remained constant during all experiments. The effect of particle size was not studied as it had found in literature that it had negligible effect [17] . Where the macroporous resins consist of gel-type microspheres that form a macroporous polymer structure composing of very small microspheres which are similar in size. This result indicates indeed a mass transfer limitation. These observation agree well with the results reported by Song et al [18] (1998).

Effect of Catalyst Loading

The relation between acetic acid conversion with various catalyst loading is shown in Fig. 1. From this figure, it can be concluded that, the conversion increases with increasing catalyst loading due to an increase in the total number of active catalyst sites.

Table 1, Specification of Amberlyst 15

Test	Specification
Hydrogen form, wet, moisture $\cong$,wt%	48
Appearance (Color)	Brown-Grey
Appearance (Form)	Granules 0.600 to 0.850 mm
Exchange Capacity	1.7 meq/ml
Surface area	53 m^2/g
Average pore diameter	300 $\mathring{A}$
Total pore volume	0.40 ml/g
Max. operating temperature	120°C

Consequently the equilibrium is reached faster with increased catalyst loading. In the absence of mass transfer resistance, the initial rate of reaction is directly proportional to the catalyst loading. This further supports that the controlling mechanism is the surface reaction on the pore wall. At higher catalyst loading the rate of mass transfer is high and these are not significant increase in the rate. A similar trend was reported by Yadav and Thathaga [19] (2002). The maximum conversion approximately 0.75, was obtained for an acetic acid to ethyl alcohol molar ratio of M 1/2 with catalyst loading 10 g and temperature of 70 °C.

Fig. 1, Effect of contact time on the acetic acid conversion of various catalyst loading , molar ratio of acetic acid to ethanol M 1/2 and temperature 70°C

Effect of Initial Reactant Molar Ratio

The effect of the molar ratio of the reactants on the conversion of acetic acid is shown in Fig.2. From this figure, it can be observed that as the mole ratio decreases, the conversion of acetic acid increases. As stated earlier, to shift the equilibrium towards the formation of the desired product, excess acetic acid was used to drive the equilibrium away toward ester formation [5,9]. The maximum conversion, approximately (0.68), was obtained for mole ratio of M=1/2 with catalyst loading of 5 g and temperature of 70 °C.

Fig. 2, Effect of molar ratio of acetic acid to ethanol on conversion of acetic acid (temperature 70°C, catalyst loading of 5 g)

Effect of Temperature

The effect of temperature is very important in order to calculate the activation energy of the reaction as shown in Fig. 3. The conversion of esterification increases with increasing

reaction temperature within the range 40-70°C, when temperature increase up to 50°C, the rate of hydrolysis reaction is higher than esterfication rate [20] . In general, in esterification reaction, the equilibrium constant is a weak function of the temperature due to the small value of heat of reaction and for this reason the conversion was nearly low in the range of temperature considered in this work. These observations agree well with the results reported by (Patricia et al[11]., 2007).
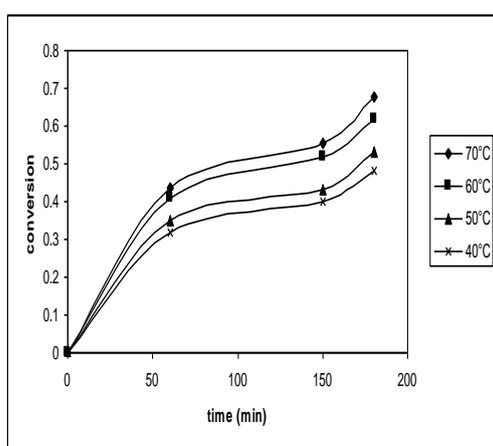
Fig. 3, Effect of temperature on the conversion of acetic acid (M=1/2, Catalyst loading of 5 g)

Kinetic Modeling

The kinetic data of the esterification was correlated with LHM, as shown in equation (2). According to the differential method, the rate of reaction can be found by finding of line tangent to the curve which represents the relationship between acetic acid concentration and time as shown in Fig.4. at any temperature and at any given point. It enable the simultaneous determination of k,kw from slope and intercept of plot $\ln\dfrac{CA}{-rA}$ and $\ln\dfrac{CW}{CB}$ as shown in Fig. 5,6,7 and 8 . The value of k, kw at various temperature are tabulated in table (2).
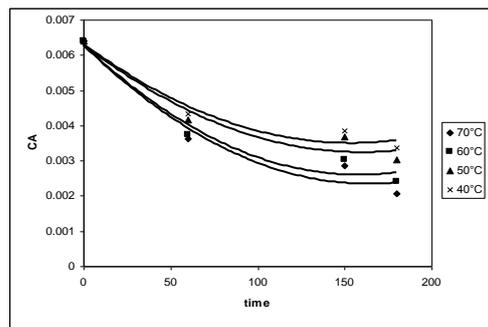
Fig. 4, Experimental full line concentration of acetic acid of 40-70°C, M=1/2, Catalyst loading of 5 g
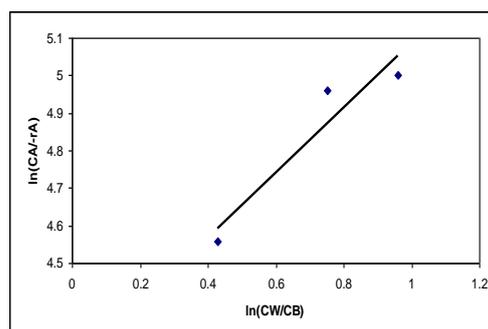
Fig. 5, Experimental reciprocal rate equation plot at 70°C, M=1/2, Catalyst loading of 5 g
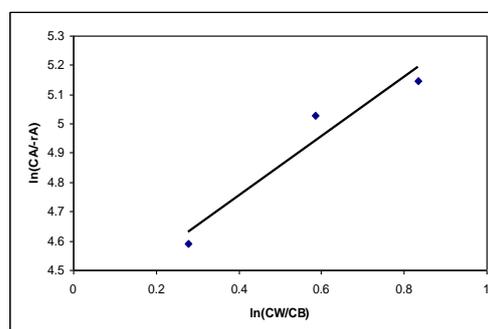
Fig. 6, Experimental reciprocal rate equation plot obtained of acetic acid at 60°C, M=1/2, Catalyst loading of 5 g
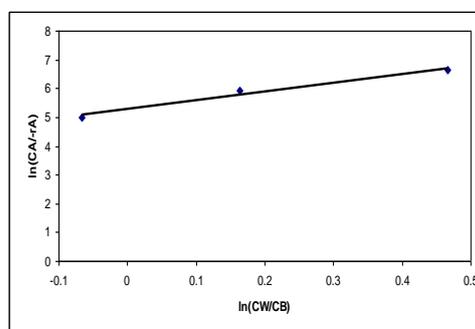
Fig. 7, Experimental reciprocal rate equation plot at 50°C, M=1/2, Catalyst loading of 5 g
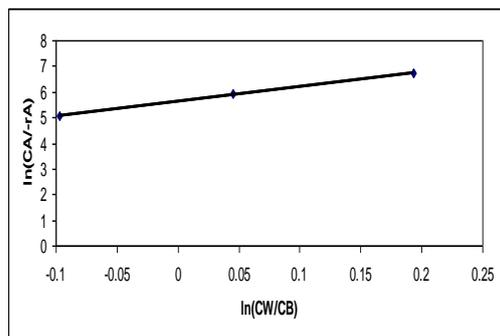
Fig. 8, Experimental reciprocal rate equation plot at 40°C ,M=1/2, Catalyst loading of 5 g

Table 2, The value of rate constant for esterfication and adsorption equilibrium constant for H_2O

T (°C)	K(s^{-1})	Kw
40	0.0003	0.074
50	0.0051	0.01538
60	0.0129	0.013014
70	0.01468	0.012716

The constant of Arrhenius equation, activation energy and frequency factor were determined from experiments, carried out at different temperature. The data of lnk, ln(kw) against 1/T were fitted by linear regression as shown in Fig.9 and 10 respectively. The activation energies were found to be 113876.9 and -49474.95 kJ. $kmol^{-1}$ for esterification reaction and the heat of adsorption for water. While the frequency factor of both reactions were $5.9*10^{15}$ and $2.7*10^{-10}$ respectively.

Applying the Arrhenius equation to the value obtained from experiments, the temperature dependency of the constant were found to be:

$$\ln k = 36.316 - \frac{113876.9}{RT} \qquad \dots(5)$$

$$\ln kw = -22.034 + \frac{49747.95}{RT} \qquad \dots(6)$$

The kinetic model with the fitted parameters can be written as follows:

$$-rA = -\frac{dC_A}{dt} = \frac{5.9*10^{15}e^{\frac{-113876.9}{RT}}C_A C_B}{C_B + 2.7*10^{-10}e^{\frac{4947495}{RT}}C_W}$$
$$\dots(7)$$
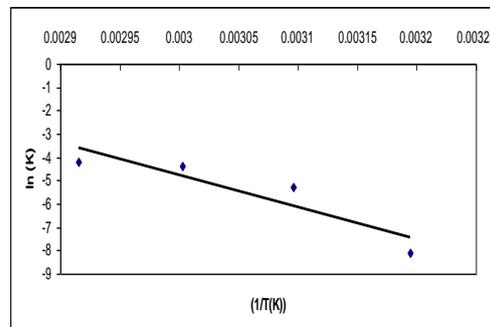
Fig. 9, Arrhenius plot for esterification reaction of forward rate
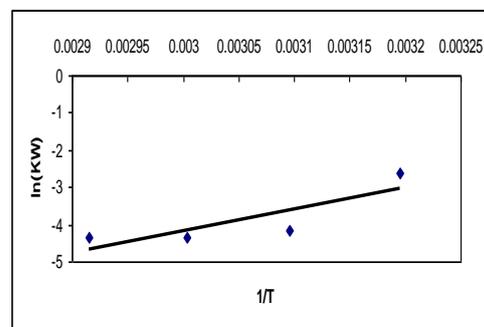
Fig. 10, Arrhenius plot of adsorption for H_2O

Conclusion

From the present study, it was concluded that:

1- The strong acidic resin can be used as a catalyst for the esterification of ethyl alcohol and acetic acid. The modification of this reaction as being switched from homogeneously catalyzed to heterogeneously catalyzed, may offer an easier way for the separation as compared with the conventional process.

2- Conversion of our case study reaction was found to increase with increasing catalyst loading, reaction time, temperature up to 70°C and with decreasing acetic acid to ethyl alcohol mole ratio. Maximum conversion of 75% was obtained using 5g of catalyst, mole ratio of

0.5 at a temperature of 70°C and after three hours.

3- Results represent surface reaction control or mass transfer is not controlling. Micro kinetics investigations as simulated by (LHM) revealed the applicability of this model to the experimental data. Aactivation energies were found to be 113876.9 and -49474.95kJ/mol for the esterification reaction and for the heat of adsorption of water respectively.

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