

Kinetics of Esterification Reaction using Ion-Exchange Resin Catalyst

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Abstract

The reaction kinetics of esterification between n-butanol and acetic acid on acidic solid catalyst named SERALITE SRC-120 under atmospheric pressure was investigated in this work. Reaction experiments were carried out in a stirred batch reactor at temperature range of 353 to 356 K, under various catalyst loads and various starting reactants feed ratios. The experimental data were fitted to estimate the kinetic parameters for reaction mechanisms. The chemical equilibrium composition was measured and kinetic information was obtained at the same temperature range. The results show that the activation energy of n-butanol esterification reaction was found to be 622.28 KJ/mol. Finally the results of produced reaction mechanisms were compared with Experimental results to validate the reaction mechanism. Then it was conclude that the model results with the regressed kinetic parameters are in excellent agreement with the experimental results.

Keywords: Esterification, Heterogeneous catalyst, n-butyl acetate, Reaction Kinetics, slurry reactor, catalyst loading, ion-exchange resin

I. INTRODUCTION

Esterification reaction is one of the most important industrial reactions. Esters are widely used in chemical industry such as a solvent for plastics, liquors, resins, gums, and coatings. Butyl acetate is commonly synthesized through esterification of acetic acid with n-butanol in the presence of a suitable acid catalyst by reversible and kinetically controlled reaction. Several works have reported the kinetics of the esterification reaction in the presence of ion exchange resin. The kinetics of esterification in the presence of a strong cation exchange resin is studied. The influence of various parameters on reaction rate and proposed the rate equation is analyzed. There is recovery of butyl acetate could be in very high purity. Conventional methods of recovery of 30% acetic acid by reaction with n butanol and isoamyl alcohol in a reactive distillation column using macroporous ion-exchange resin as a catalyst bed. They studied the esterification of acetic acid with n-butanol in the presence of Amberlyst-15. They investigated the influence of various parameters such as temperature, mole ratio, catalyst loading, and particle size and they proposed the rate equation model. [1]. It was noted that, most of the previous studies performed in the literature have focused on the modification of catalysts and only a rather limited number of papers have focused on studying the influence of reaction conditions and the type of catalysts on the activity and selectivity. On the other hand, few studies were focused on production of butyl acetate [1].

The reaction progress is very slow in the absence of acid catalysis. Therefore, both homogeneous and heterogeneous catalysis can be used.

Although homogeneous catalysts such as sulfuric acid, p-toluene sulfuric acid, and hydrochloric acid have a strong catalytic effect, they can cause some issues such as the development of side reactions resulting in a corrosive environment by the discharge of acid-containing waste. . It also results in sulfur contamination of the final product, which is unacceptable. Further, the use of homogeneous catalyst requires neutralization with an alkali, which leads to severe effluent problems on industrial scale. In all kinetic studies done with ion-exchange resins as catalysts, acidic ion-exchange gel-type styrene-divinyl benzene (DVB) resins have been used .Research in catalysis by ion exchange resins is undeniably 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.

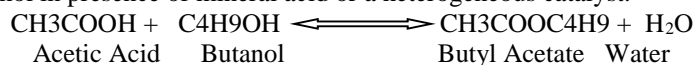
Ion exchange resins separate from reaction media easily and they regenerate easily for reuse. Heterogeneous catalysts such as zeolites, ion-exchange resins, and acidic clay catalysts are gaining importance of high purity of products, because they are easily removed from the reaction mixture and have lower corrosive effects. The solid acid catalysts are non-corrosive, easy to separate from the reaction mixture and a variety of reactor types and configurations can be adopted on industrial scale. They can also be used repeatedly over prolonged period of time without any difficulty in handling and storing. Most reactions catalyzed by ion exchange resins can be classified as either quasi-homogeneous or quasi-heterogeneous.

The kinetics of this model reaction catalyzed by Amberlyst-15 was described in previous investigations with both a quasi-homogeneous and a quasi-heterogeneous model. 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 (RD), the continual

separation of products from reactants forces the reaction to surpass the equilibrium conditions. RD is a process where separation of the components of a reaction system is accompanied by a chemical reaction in a column. [6]

A. Esterification of Acetic Acid with Butanol using SERALITE SRC-120 catalyst

Esterification of carboxylic acids is an important class of reactions, the kinetics and equilibrium of which have been investigated throughout the history of physical chemistry, the dating back to pioneering efforts of Berthelot and Gilles (1863). In 1914 at the beginning of the World War I, amyl acetate in the form of fuel oil acetate was the best known ester solvent. The demand for airplane dope and the corresponding need for cellulose nitrate and cellulose acetate solvents increased rapidly during the war period. The only ester that was developed on a large scale during the war to replace amyl acetate was methyl acetate, thus Esterification of acetic acid with methanol got a boost as an important process. Esters can be produced by different approaches on both laboratory and commercial scales. Among all these, the simplest route to produce esters with high yield is the direct Esterification of acids with alcohol in presence of mineral acid or a heterogeneous catalyst.



Esterification reactions are equilibrium processes and must be displaced toward the desired ester by the use of excess of one of the free reactants or by continuous removal of water by azeotropic distillation. Removal of water by chemical or adsorptive binding is also possible in preparative chemistry, while calcium carbide, calcium hydride and calcium and magnesium sulfate have proved successful in industrial application. The rate of ester formation depends on the carboxylic acid and the alcohol used. The lowest members, i.e. methanol and formic acid, react most readily. Primary alcohols react faster than secondary alcohols and the latter react faster than tertiary ones. Within each series, the reaction rate generally decreases with increasing molecular mass. Straight-chain acids react more readily than branched ones; particularly branching in the β -position lowers the rate of esterification. Esterification of aromatic acids, e.g. benzoic acid, is generally slow. Experiments with primary and secondary alcohols have shown that the oxygen in the water formed during acid-catalyzed esterification originates from the acid, not from alcohol. The reactions of tertiary alcohols are more complex and do not proceed clearly via a tertiary carbonium ion. Generally, in industrial processes refluxing the reaction mixture until all the water has been split off facilitates esterification. The water or the esters formed are removed from equilibrium mixture by distillation. The choice of a method to achieve complete esterification depends on the boiling points of alcohols, acids, and esters. With high boiling esters (esters of polyhydric alcohols), the water of reaction may either be removed by evaporation or by means of inert gases. Esterification is usually carried out in a batch or continuous mode depending on the scale of operation. It can also be carried out in the vapor phase by heating a mixture of acid, alcohol, ester, and catalyst to the desired temperature. [3]

II. EXPERIMENTAL

A. Materials

The reactants butanol and acetic acid used were of A.R. grade (99.8%) and were obtained from Fume Chemicals, Kolhapur (Maharashtra, India). The chemicals were used without further purification.

B. Catalyst

The cation exchange resin Saralite 120 SC used as the catalyst before using for experiments, the resin was pretreated using standard procedures. First, the resin was washed with water the catalyst was soaked in distilled water for 15 minutes and then charged into the column. Then, one liter of 0.1 M hydrochloric acid solution and 0.1 M sodium hydroxide solution was passed through the catalyst bed to remove acid soluble and alkali soluble impurities. After acid and alkali treatment each time, the resin was washed with water to ensure complete removal of chloride and sodium ions from the catalyst bed.

Table – 1
Range of operating conditions

Reaction temperature, K	353 K
Catalyst loading, (percentage)	3%, 4%, 5%
Butanol : acetic acid ratio	4:1, 3:1 and 2:1
Particle size, mm	0.458

The esterification of acetic acid with butanol was carried out in a glass reactor of 500 ml volume. The heating mantle is used for heating purpose. The temperature in the reactor was maintained within 80-90°C using a thermometer.

C. Experimental Setup and Procedure

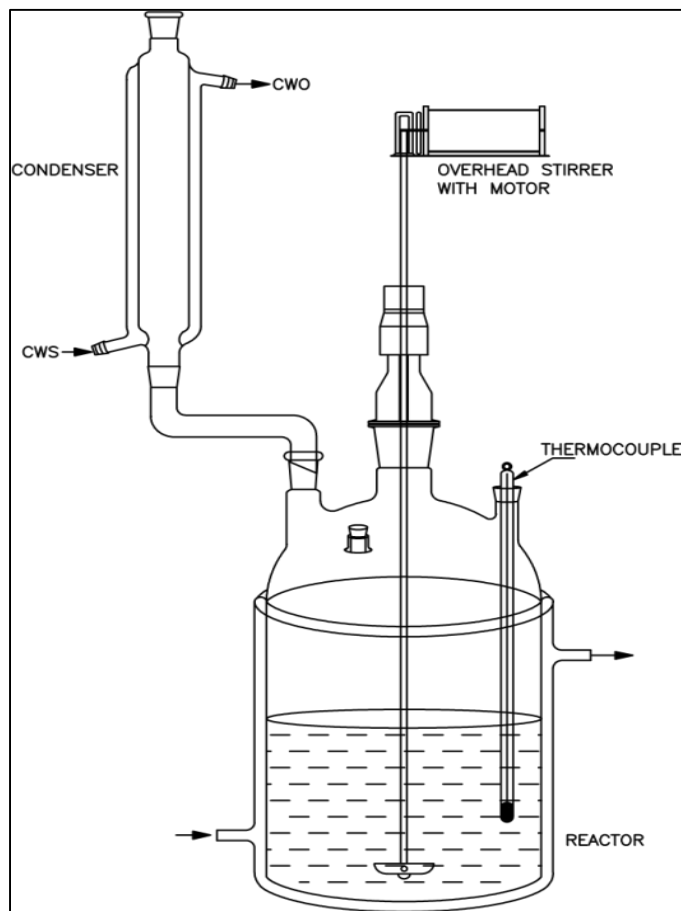


Fig. 1: Experimental setup of a batch slurry reactor for Esterification reaction

In all the experiments, a known amount of butanol was charged to the reactor and heated to the desired temperature. When the temperature remained constant, the required amount of acetic acid was added under constant stirring. It was observed that the temperature fall as a result of this addition was not significant and the temperature equilibrium was reached in a short time. A sample was removed for analysis. This was taken as the starting point of homogeneous (uncatalyzed) reaction. For the catalytic reaction, after attaining the desired temperature, a known quantity of ion exchange resin along with acetic acid was added to the reactor. The moment of resin addition was taken as the starting time of reaction. Samples were withdrawn at regular time intervals for analysis. The volume of sample withdrawn from the reactor during a run was negligible compared with the total volume of the system. [6]

D. Analysis

The analysis of reactants and products was carried out using simple titration with 1N NaOH solution and phenolphthalein as indicator. The end point of reaction is colourless to faint pink.

E. Result and Discussion

Calculation for conversion of acetic acid

(NaOH) vs. (Acetic acid)

$$N_1 V_1 = N_2 V_2$$

$$N_2 = (1 \times 11.1) / 10$$

$$N_2 = C_{A1} = 1.11 \text{ mole/lit}$$

Now conversion is given by

$$X_A = (C_{A0} - C_{A1}) / C_{A0}$$

$$X_A = (2.8070 - 1.11) / 2.8070$$

$$X_A = 0.6046$$

$$\text{Conversion} = 0.6046 \times 100 = 60.46 \%$$

As there is no side reaction present, hence

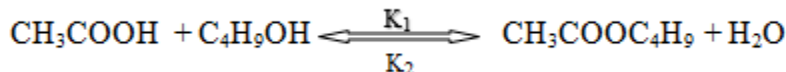
$$\text{Yield} = \text{Conversion} = 60.46 \%$$

Table – 2
Calculation of conversion for different time interval.

Sr. no	Time (hour)	Burette reading (ml)	Concentration (mol/lit)	Conversion XA
1	1	23.5	2.35	0.1628
2	1.5	21.4	2.14	0.2376
3	2	19.6	1.96	0.3017
4	2.5	16.1	1.61	0.4264
5	3	12.1	1.21	0.5689
6	3.5	11.1	1.11	0.6046

III. KINETICS OF ESTERIFICATION REACTION

A relation between the conversion of acetic acid and reaction time is obtained by using Pseudo-homogeneous model. Order of reaction and rate constant is obtained as follows. Rate of esterification reaction can be determined thus:



The rate expression for this reaction is given by:

$$-r_{\text{CH}_3\text{COOH}} = k_1 C_{\text{CH}_3\text{COOH}} \cdot C_{\text{CH}_3(\text{CH}_2)_2\text{CH}_2\text{OH}} - k_2 C_{\text{CH}_3\text{COOC}_4\text{H}_9} \cdot C_{\text{H}_2\text{O}} \quad \dots\dots(1)$$

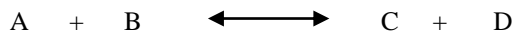
The reaction equilibrium constant is given by

$$K = k_1/k_2$$

The reaction equilibrium constant is calculated from

$$\ln \frac{K}{K^\circ} = \frac{\Delta H_R}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad \text{Where, } K^\circ = \exp\left[\frac{\Delta G_R}{RT_1}\right]$$

Esterification reactions are known to be second order reversible reaction. Therefore, for the bimolecular type second order reaction,



With reaction that,

$$C_{\text{AO}} = C_{\text{BO}} \quad \text{and} \quad C_{\text{CO}} = C_{\text{DO}} = 0$$

The rate expression can be written as,

$$-r_B = -dC_A / dt = C_{\text{AO}} \cdot dX_A / dt = k_1 C_A \cdot C_B - k_2 C_C \cdot C_D \\ = k_1 C_{\text{AO}}^2 (1 - X_A)^2 - k_2 (C_{\text{AO}} X_A)^2 \quad \dots\dots\dots(2)$$

Where,

- A = Acetic acid
- B = Butyl alcohol
- C = Butyl Acetate
- D = Water

At the equilibrium, $-r_A = 0$

Hence the above equation, we determine the fractional conversion of A at equilibrium condition by following equation:

$$K = C_{\text{Ce}} \cdot C_{\text{De}} / C_{\text{Ae}} \cdot C_{\text{Be}} = X_{\text{Ae}}^2 / (1 - X_{\text{Ae}})^2 \quad \dots\dots\dots(3)$$

The equilibrium constant is given by as,

$$K = k_1 / k_2$$

Combining equation (1), (2) and (3) in term the equilibrium conversion, we obtain,

$$-dX_A / dt = k_1 C_{\text{AO}} [(1 - X_A)^2 - (1 - 1/X_{\text{Ae}}) \cdot X_A^2]$$

With conversion measured in term of X_{Ae} , this may be indicated as a Pseudo second order reversible reaction, which on integration gives, [4]

$$\ln [X_{\text{Ae}} - (2 X_{\text{Ae}} - 1) X_e] / X_{\text{Ae}} - X_a = 2k_1 [1/X_{\text{Ae}} - 1] C_{\text{AO}} t$$

Forward and backward reaction rate constant of the esterification reaction between butanol and acetic acid (catalyzed by serralite catalyst) were determined. Values are calculated as

$$\Delta G^0 = -RT \ln (K_1) \\ K_1 = 0.9998$$

The equilibrium constant at optimum temperature of 83⁰C can be calculated by using Vant Hoff equation

$$\ln \left(\frac{K_2}{K_1} \right) = - \frac{\Delta H_T}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \\ K_2 = 1.0036$$

Following fig2 a plot for concentration vs. time shows that the acetic acid concentration decreases due to formation of butyl acetate product. Acetic acid is consumed by butanol and hence its concentration reduces. Finally line on the graph will be constant due to completion of reaction.

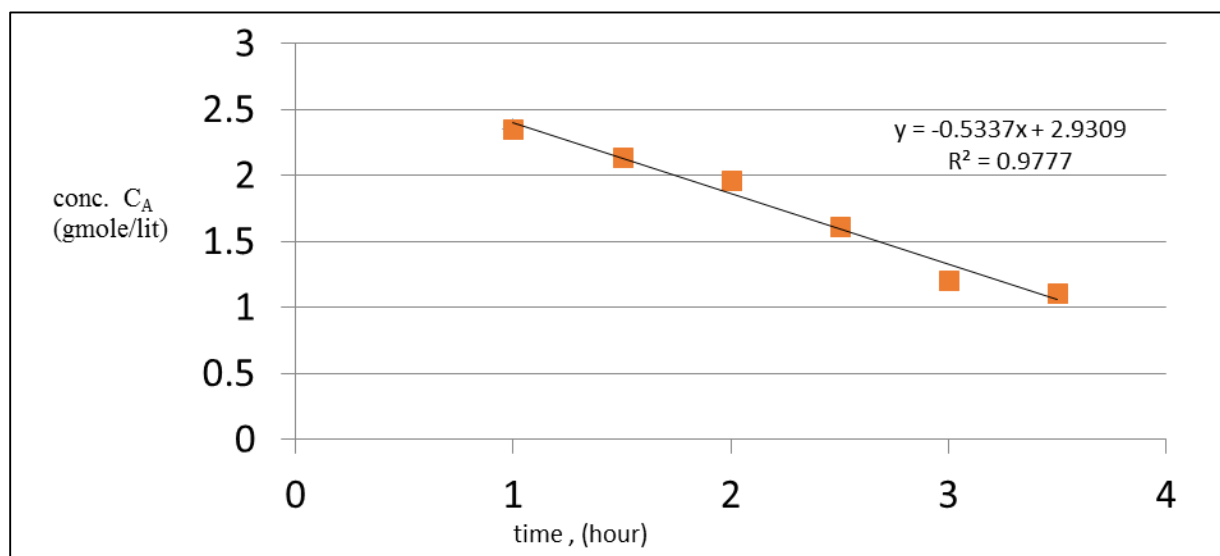


Fig. 2: Plot for Concentration vs. Time

IV. CONCLUSIONS

Earlier studies of the esterification reaction between butyl alcohol and acetic acid considered it to be second order for both the forward and reverse reactions. In this study, the forward and reverse orders of reaction were found to be K_1 and K_2 , respectively. The relationships representing the effect of temperature and catalyst concentration on the reaction-rate have also been developed. The esterification reaction between butanol and acetic acid performed over an acidic ion exchange resin Saralite SRC 120. The interaction between the solid catalyst and the reactants will consider in the model. The rate constant and conversion increases with increasing the temperature of the reaction at a certain mole ratio of reactants. The use of excess reactants on the conversion is studied. Higher the amount of alcohol higher the conversion will obtain.

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