KINETICS OF ESTERIFICATION OF PROPIONIC ACID AND N-PROPANOL

Kusuma Midathana, K.V. Ramesh, G.V.S. Sarma*

Department of Chemical Engineering, Andhra University, Visakhapatnam–530003, India

Abstract

In the current study, an isothermal batch reactor is used to perform the esterification reaction between propionic acid and n-propanol in the presence of sulphuric acid catalyst. The variables are reaction temperatures (50-70°C), molar ratios of reactants (propionic acid/n-propanol = 0.5-1.5) and catalyst loading (1-3wt%). It is found that the conversion increased with temperature and catalyst loading but decreased with the molar ratio of the reactants. Experimental data are used to determine rate constants and activation energy.

Keywords: *Esterification; homogeneous catalyst; kinetics; rate constant.*

1. Introduction

In a wide range of industries, including those in the food, pharmaceutical, cosmetics and chemical sectors, organic esters are significant fine chemicals. These compounds are usually produced by esterifying carboxylic acids with alcohol. These are employed as additives, plasticizers, solvents, and intermediates [1]. Many routes are available for the synthesis of organic esters. The traditional route for preparing esters is by the reaction of the carboxylic acid with alcohol using homogeneous catalysts such as sulfuric acid [2]. Esterification is usually carried out in liquid phase in stirred, temperature-controlled batch reactor. The most common homogeneous and heterogeneous catalysts used in esterification studies are sulphuric and hydrochloric acids, salts of calcium, aluminum, magnesium, etc. Ion-exchange resins in H+ form are also used. The use of sulfuric acid is generally preferred in the industry [3-4]. Esters have the benefit of not accumulating significantly in humans, polluting the environment, posing a minimal chemical risk, offering the highest level of safety during usage, and the majority of them being typically biodegradable for their practical applications.[5]. The U.S. Environmental Protection Agency classifies n-propyl propionate, an easily biodegradable, non-toxic component of industrial solvents, as a non-hazardous air pollutant. The n-propyl propionate has a variety of industrial uses, including the manufacturing of pharmaceuticals and inks, coatings, polymerization processes, and as an ingredient for foods and fragrances.[6].

2. Material and Methods

AR grade propionic acid, n-propanol, sulphuric acid, oxalic acid and LR grade NaOH and phenolphthalein 1% indicator solution were used in this study.

A three-necked, round flat-bottomed flask with a 500 ml capacity was used to carry out the batch esterification reaction between propionic acid and n-propanol using a homogeneous acid catalyst Sulphuric acid. Firstly, accurately measured quantities of propionic acid and n-propanol were taken in two separate conical flasks. Now n-propanol was transferred into the reaction flask which was placed on a magnetic stirrer with a hot plate. A glass condenser was placed at the center neck of the reaction flask for condensing vapors. A thermocouple sensor was inserted into one side neck of the flask for precise temperature control. The temperature was maintained with ±0.2^{o}C. The other side neck was usually closed with a stopper, and it was used whenever the sample was withdrawn. The desired temperature was set by adjusting the heating knob. The stirring speed was maintained at 200 rpm throughout the experiment for uniform mixing of the reaction mixture and to ensure there was no vortex formation by adjusting the speed control knob. Concentrated sulphuric acid in required quantity was taken accurately and added to the conical flask containing propionic acid and heated separately at the same temperature. Once the set temperature was attained, the mixture of acid and catalyst was transferred to the reaction flask to provide a prefixed mole ratio (acid to alcohol) and the reaction time has been monitored ever since.

At time zero, the first sample of about 2ml of the reaction mixture was withdrawn from the reaction flask using a pipette and transferred into the conical flask containing 20 ml of standardized sodium hydroxide and 20 ml of distilled water. At specified intervals, samples were withdrawn and titrated against standard oxalic acid using a phenolphthalein indicator, to evaluate the unreacted propionic acid. The reaction continued until a steady state was attained or there was no longer any change in the concentration of propionic acid over time. When the conversion of propionic acid for at least three consecutive samples was determined to be the same, a steady state was established and confirmed. Thus, the concentration of the unreacted propionic acid versus the time were noted. By examining the reaction sample 24 hours after the reaction began, the experimental equilibrium conversion was estimated. By using the same amounts of distilled water for propionic acid and n-propanol in a separate conical flask, sulphuric acid was added, and samples were titrated against sodium hydroxide with phenolphthalein as an indicator the titre for sulphuric acid equivalent was calculated.

According to full factorial design of experiments, the reaction process parameters such as temperature, molar ratio, and catalyst concentration were varied. The experiments were performed at temperatures between 50°C and 70°C, the different initial molar ratio of propionic acid to n-butanol was in the range of 0.5-1.5, and catalyst zoncentrations varied from 1.0 to 3.0 wt%.

3. Results and Discussion

At various mole ratios and temperatures, the effect of the catalyst concentration on the conversion of propionic acid with time was examined. Fig. 1 depicts the conversion of propionic acid with time during esterification with catalyst concentrations of 1.0, 2.0 and 3.0wt%. The acid to alcohol mole ratio was 1.5, and the temperature was 60°C. The plots clear that conversion rises when catalyst concentration is raised.

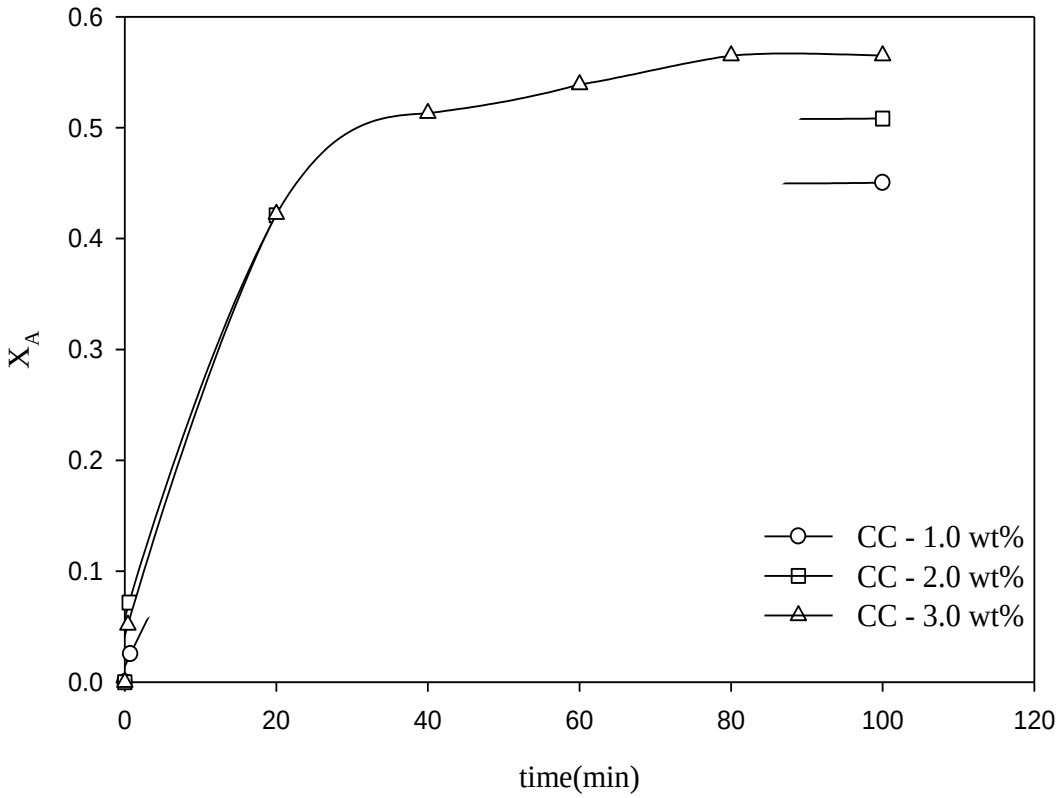

Fig.1. Effect of catalyst concentration on conversion { M.R = 1.5; T = 60^{o}C }

By carrying out the reaction at three different temperatures, viz., 50, 60, and 70^{o}C, the effect of temperature on the rate of propionic acid esterification with n-propanol was investigated. The findings shown in Fig.2 are for the reaction with an acid-to-alcohol ratio of 1.5 and a catalyst loading of 2.0 wt%. The plots showed that the

conversion increased with increase in temperature.

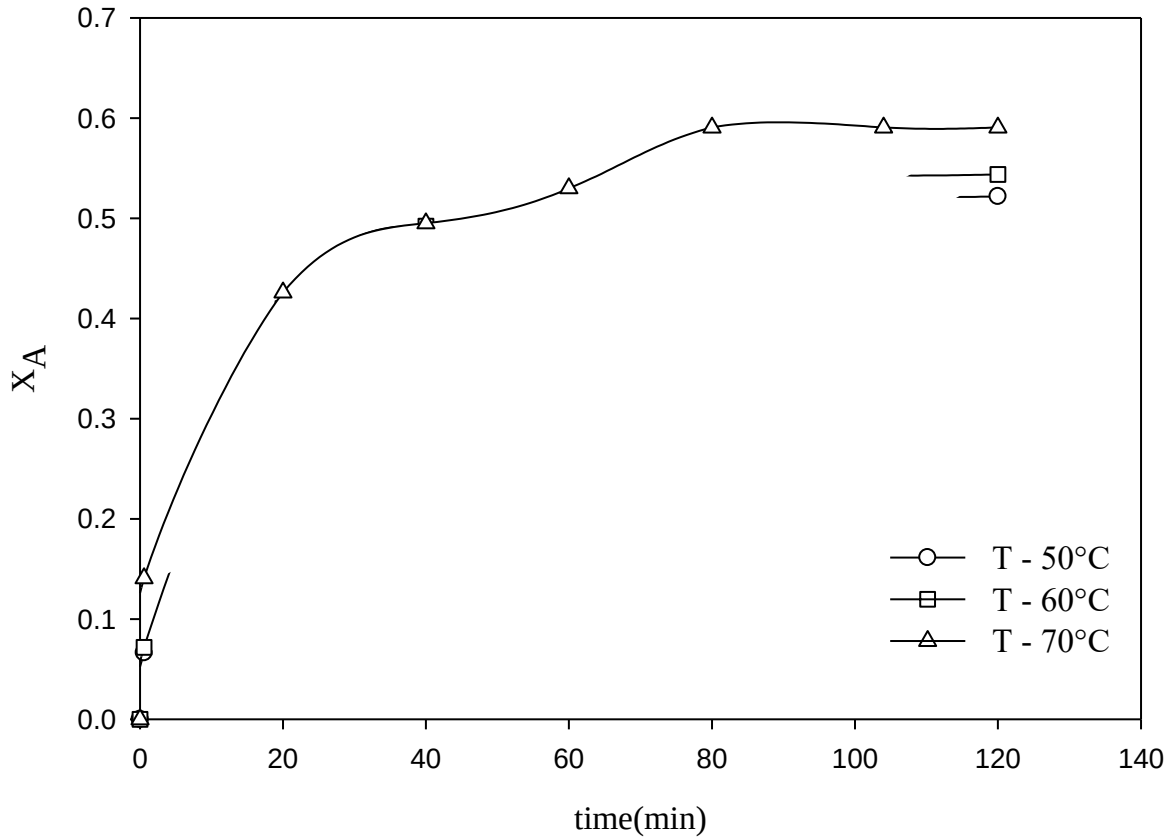

Fig.2. Effect of temperatures on conversion { M.R = 1.5; C.C = 2.0 wt% }

Fig.3 depicts the conversion of propionic acid with time at 70°C, 2.0 wt% catalyst concentration, and for mole ratios of 0.5, 1.0 and 1.5. It shows that a 0.5 mole ratio resulted in a higher conversion rate (77.16%) than for 1.0 or 1.5. The results indicated that when the mole ratio increased, the conversion of propionic acid got decreased.

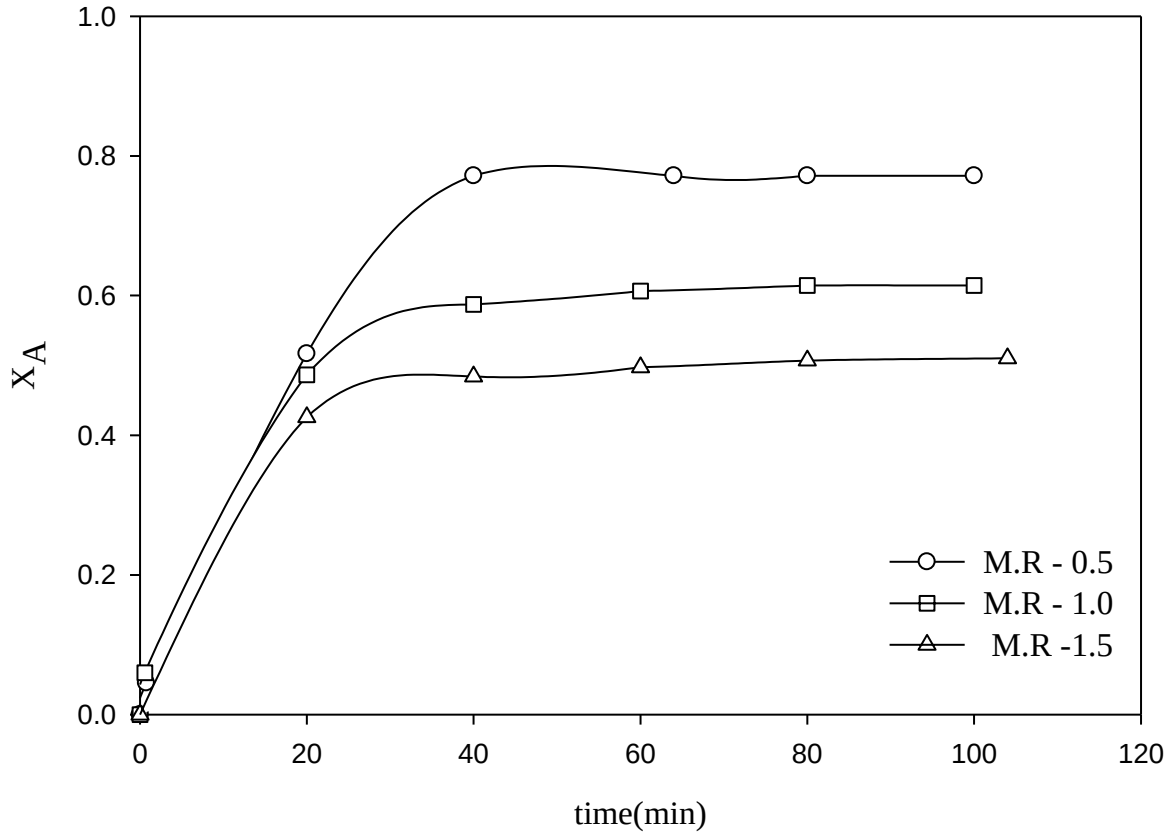

Fig.3. Effect of mole ratio on conversion { T = 70°C; C.C = 2.0 wt% }

The esterification reaction usually followed second order kinetics as revealed from previous works [7]. In the present study also, the data obeyed second order reaction kinetics which is seen from the plots of Figs.4. and 5. The rate constant is obtained by following integral analysis. So that, the second order rate constant 'k' can be calculated from the plots of $1/C_A$

vs. time. The points are joined by a straight line and the slope of this line gives rate constant 'k'.

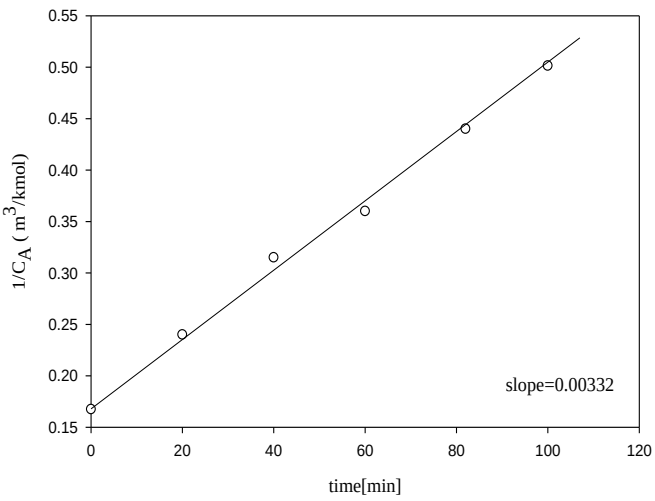

Fig.4. Plot for second order rate constant k
For {MR = 1.0; T = 70°C; CC = 3 wt%}

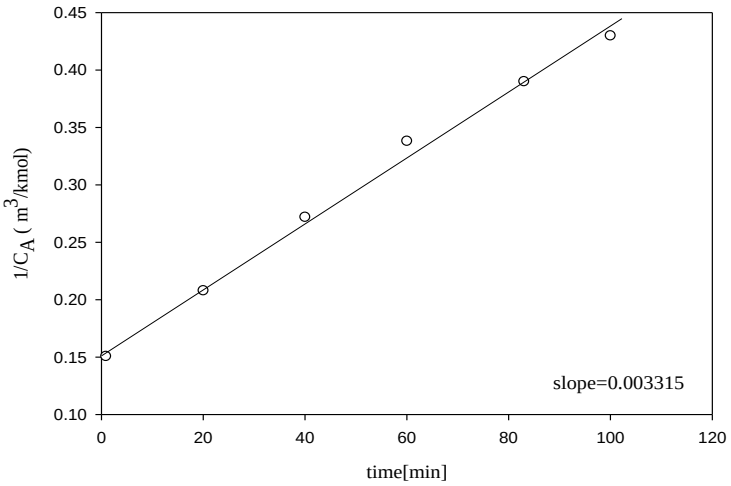

Fig.5. Plot for second order rate constant k
For {MR = 1.0; T = 70°C; CC = 1 wt%}

The data belonging to all the experimental runs were processed in a similar way and then the rate constant data were subjected to regression analysis to obtain the following correlation equation.

$$k = 1.334\, MR^{-1.176} CC^{-0.0865} e^{-2111/T} \quad \ldots (1)$$

Average deviation = 6.098 percent

Standard deviation = 9.477 percent

Fig.6 gives a comparison of calculated and experimental values of rate constant k.

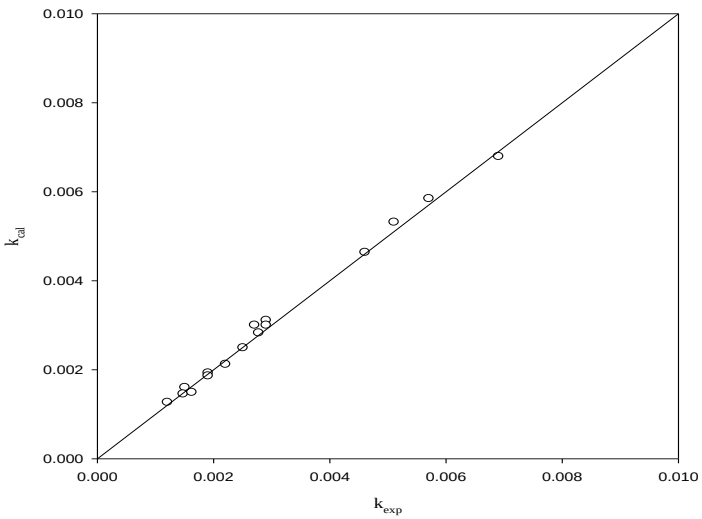

Fig.6. Comparison of experimental and calculated values of k

5. Conclusions

This esterification reaction followed second order. The conversion was found to increase with increasing catalyst concentration. The conversion was observed to decrease with increasing mole ratio. The conversion increased with increase in temperature. The reaction rate constant followed Arrhenius law as far as the temperature effect is concerned.

References

[1] Hamerski, F., Dusi, G. G., Fernandes dos Santos, J. T., da Silva, V. R., Pedersen Voll, F. A., & Corazza, M. L. (2020). Esterification reaction kinetics of acetic acid and n-pentanol catalyzed by sulfated zirconia. International Journal of Chemical Kinetics, 52(8), 499-512.

[2] Dange, P. N., & Rathod, V. K. (2017). Equilibrium and thermodynamic parameters for heterogeneous esterification of butyric acid with methanol under microwave irradiation. Resource-Efficient Technologies, 3(1), 64-70.

[3] Rao, T. K., Kumar, D. S., Vijay, M., & Ramesh, K. V. (2020). Kinetics of Esterification of Propionic Acid and Cyclohexanol.

[4] Ramesh, K. V., & Rao K.V. (2009). Kinetic Studies of Esterification Using Response Surface Methodology (System: Iso-Propanol-Formic Acid). *The Icfai University Journal of Chemistry*, *2*(1), 18-35.

[5] Kastratović, V. R., Radulović, M. M., & Kastratović, K. K. (2022). Esterification of propanoic acid in the presence of a homogeneous catalyst. *Kragujevac Journal of Science*, (44), 45-55.

[6] Nogueira, I. B., Faria, R. P., Requião, R., Koivisto, H., Martins, M. A., Rodrigues, A. E., & Ribeiro, A. M. (2018). Chromatographic studies of n-Propyl Propionate: Adsorption equilibrium, modelling and uncertainties determination. *Computers & Chemical Engineering*, *119*, 371-382.

[7] Otera, J., & Nishikido, J. (2010). Esterification, 2/e, Wiley-VCH, Weinheim, Germany.