Global Engineering Science and Technology Conference
Dhaka, Paper ID 805

Esterification of Ethanol and Acetic Acid in a Batch Reactor in Presence of Sulfuric Acid Catalyst

Ashraf Ahmed* and Niaz Bahar Chowdhury

Abstract

Chemical reaction is the most important phenomena in chemical engineering and reaction engineering. The main purpose of this study is to understand the rate of the reaction and the kinetics of the reaction to determine the order of the reaction. Esterification reaction was studied for this purpose. The product concentration was determined at equal time interval. The last data was taken at infinite time. Then graphs were plotted from the obtained data to determine the order of the reaction. The order of the reaction was found from the graphs second order irreversible. All the experimental works was conducted in the Reaction Engineering Laboratory of Chemical Engineering Department, Bangladesh University of Engineering and Technology.

Key Words: Esterification, Ethanol, Acetic Acid, Batch Reactor, Sulfuric Acid Catalyst

1. Introduction

The purpose of this study is to determine the order of the reaction and to obtain a valid rate expression by collecting concentration vs. time data at constant temperature. It is related with kinetic study of the Esterification reaction and thus provides an opportunity to get acquainted with the fundamentals of chemical kinetics & the manner in which the rate study has to be performed. It is very important for Chemical engineers to study the kinetic of reaction to describe the reacting systems in terms of macroscopically observed quantities, such as temperature, pressure, etc. Chemical kinetics deals the quantitative study of the rates at which chemical processes occur, the factors on which these rates depends and the molecular actions involved in reaction processes. Reaction constants & reaction orders both are very sensitive to the parameters on which it depends. So, one should be very careful in experimental work as well as in processing data to obtain a valid rate expression.

*Corresponding Author: Ashraf Ahmed, Chemical Engineering Department, BUET, ashche24@gmail.com

2. Literature Review

In this study the order of the acid catalyzed Esterification of ethanol with acetic acid was determined by collecting concentration vs. time data at a constant temperature 80 ^{0} C. starting with a reaction mixture having a molar ratio of ethanol to acetic acid of 7: 4, in presence of sulfuric acid catalyst. It was a homogeneous catalyzed reaction done in a batch reactor. Here both the reactants i.e., ethyl alcohol and acetic acid and catalyst i.e., sulfuric acid were in the same phase i.e., liquid phase. Here, ethanol was chosen as the excess reactant for economic reasons, since ethanol is less expensive of the two. The concentration of the limiting reactant acetic acid in the solution was obtained at different time. Then with the help of this data several graphs were plotted to fit the expression for rate equation. Esters are formed when an organic acid reacts with an alcohol in the presence of concentrated sulfuric acid as the catalyst. Everything is present in a single liquid phase, and so this is an example of homogeneous catalysis. For example, Acetic acid reacts with ethanol to produce ethyl acetate.

$$CH_3COOH + CH_3CH_2OH \xrightleftharpoons{\text{conc } H_2SO_4} CH_3COOCH_2CH_3 + H_2O$$

They proceed slowly in the absence of strong acids, but reach equilibrium within a matter of a few hours when an acid and an alcohol are refluxed with a small amount of concentration sulfuric acid or hydrogen chloride. The inorganic acid serves as a liquid catalyst in this reaction. Since the position of equilibrium controls the amount of the ester formed, the use of excess of either the carboxylic acid or the alcohol increases the yield. Yield of an Esterification reaction can also be increased by removing water from the reaction mixture as it is formed.

3. Methodology

320 ml of Ethanol and 180 ml of Acetic Acid was taken into a conical flask to maintain the molar ratio of Ethanol to Acetic Acid, 7:4. Few drops or 1 ml H_2SO_4 (0.4%w/w) was added to the reaction mixture. The condenser was set with the conical flask containing the reaction mixture. The conical flask was placed on the heater and the heater and stirrer (magnetic stirrer) were turned on. When the reaction temperature was reached to 80°C, 5 cc samples were taken out of the reactor. Sample was diluted with distilled water. The solution was titrated against 2(N) standardized NaOH solution using phenolphthalein as indicator. In this way 5cc sample was taken out after every 10 minutes interval and was titrated. The volumes of NaOH required to titrate the sample were recorded.

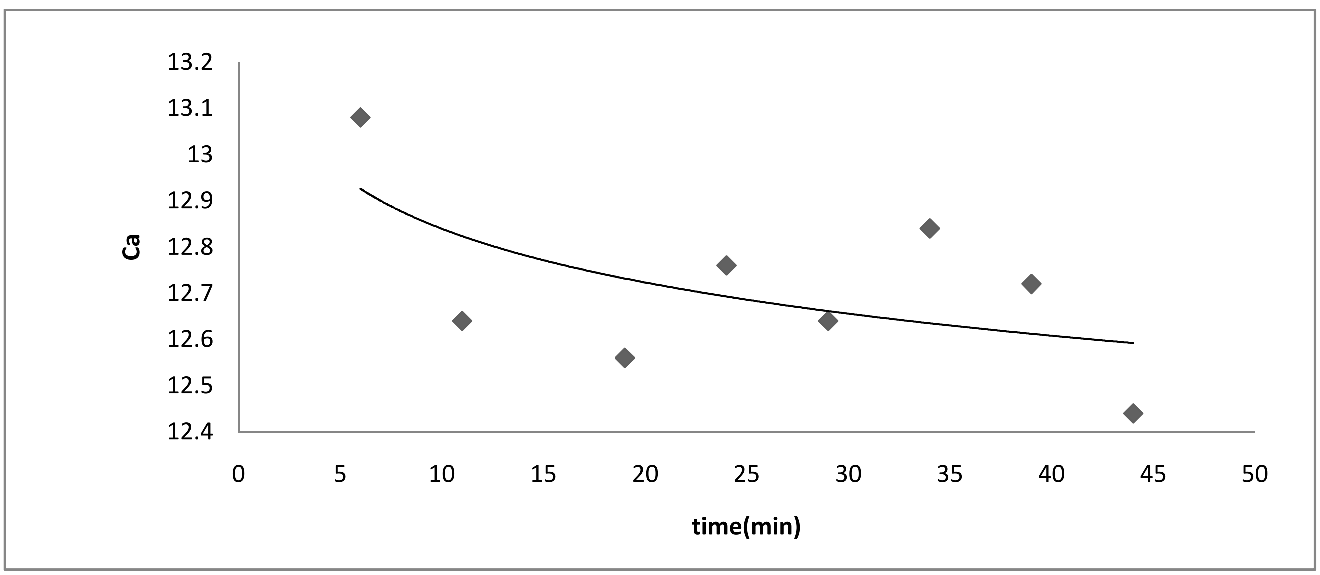
4. Result and Discussion

In this experiment the order of the acid catalyzed Esterification of ethanol with acetic acid was determined by collecting concentration vs. time data at a constant temperature 80 ^{0} C. It was a homogeneous catalyzed reaction done in a batch reactor. Here the reactants i.e., ethyl alcohol and acetic acid and catalyst i.e., sulfuric acid were in the same phase i.e., liquid phase. The concentration of the limiting reactant acetic acid in the solution was been determined at different time. Then with the help of this data several graphs were plotted to fit the expression for rate equation. Here C_A means concentration of Acetic acid after t time. C_{Ae} means concentration of Acetic acid at equilibrium. C_E means concentration of Ethanol after t time. C_{Ee} means concentration of ethanol at equilibrium. L is a complex parameter in case of second order reversible reaction.

4.1 Change of concentration with time

Plot of C_A vs. time indicated that the concentration C_A was decreased continuously with time and the rate was highest at zero time and rate was continuously decreasing with time which was clear from the decreasing slope of the graph with time.

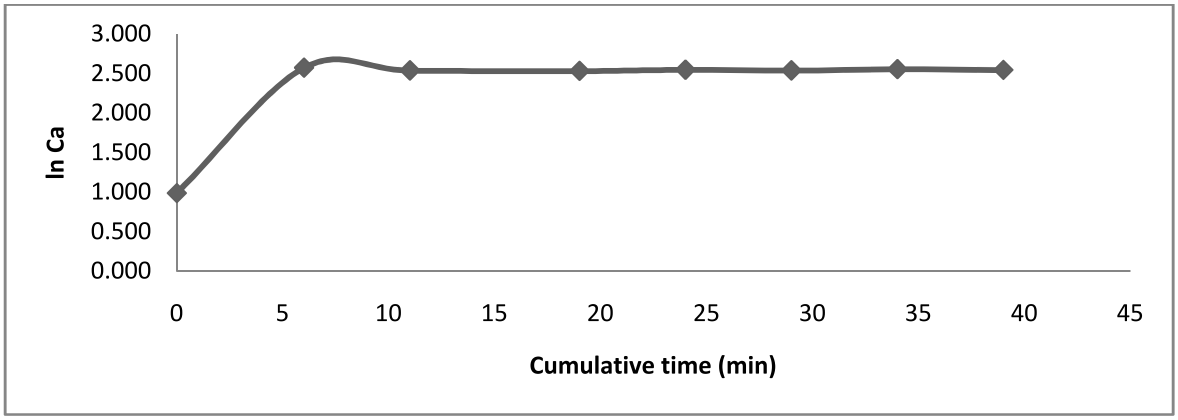
Figure 1: Change of concentration with time



4.2 First order reversible reaction

Graph for first order reversible reaction was plotted. It was an $\ln C_A$ vs. cumulative time was plotted. The graph found didn't match to the one for first order reversible reaction which is a straight line of negative slope. In this case the experimental data fitted for first order reversible reaction shows a complex behavior and it can be certainly said that this Esterification reaction is not following the kinetics of first order reversible reaction.

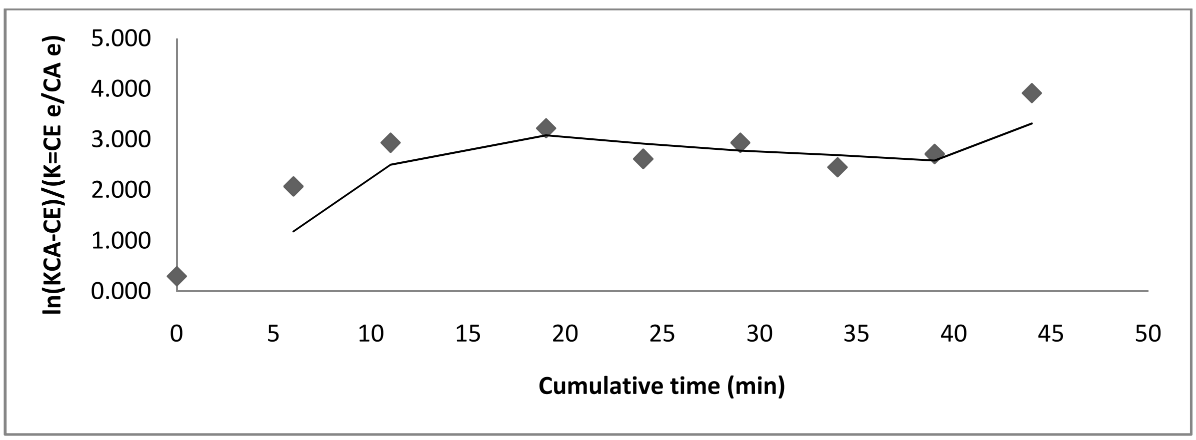
Figure 2: Graph for first order reversible reaction



4.3 First order irreversible reaction

Graph for the first order irreversible reaction was plotted which didn't match the correct one also. From the literature we know that the graph should show a nature of straight

Figure 3: Graph for first order irreversible reaction.

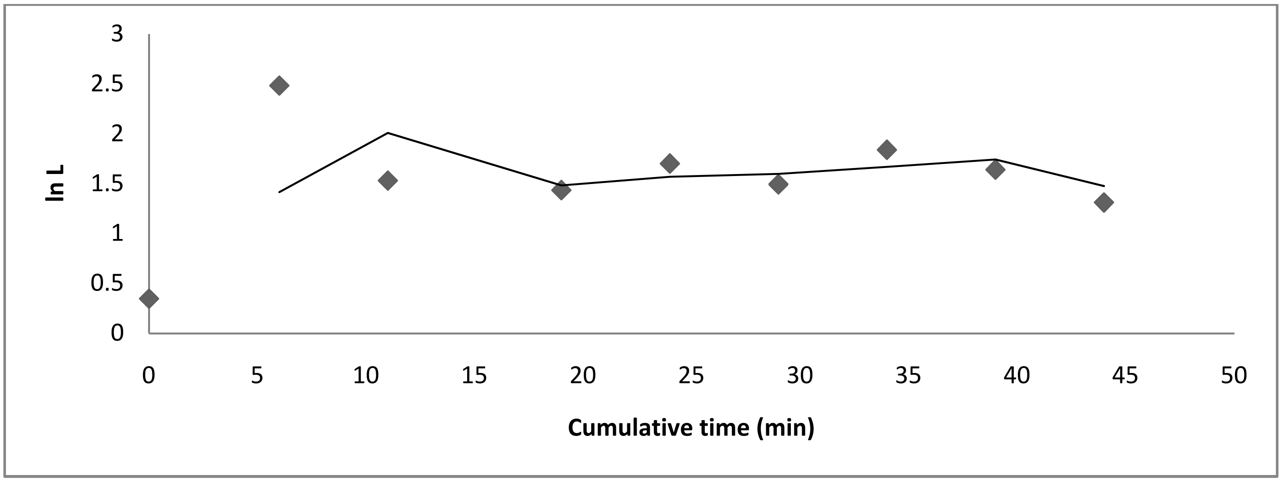


line having negative slope, just like first order reversible reaction. But this graph also shows a non linear and complex behavior which is a complete miss match of the original theoretical curve.

4.4 Second order reversible reaction

A graph for second order reversible reaction (lnL vs. time) didn't yield a straight line. But theoretically the graph should be a straight which passes through the origin. In this case the experimental curve shows a complex behavior and hence not satisfies the theoretical curve. So it was not a second order reversible reaction.

Figure 4: Graph for Second order reversible reaction



4.5 Second order irreversible reaction

ln C_E/C_A vs. time was plotted, which was a straight line. And theoretically it should be a straight line having positive intercept. So the reaction kinetics was followed by a second order irreversible reaction. The values obtained from this experiment were, intercept K = 0.0002, order, n = 2, from the plot it was seen that the some observed points were out of the straight line. This deviation may be for the reason that the temperature was not steady throughout the experiment. The reaction temperature was maintained at 80^0 C because it is the optimum reaction temperature for maximum yield with desirable reaction rate and better product quality.

Figure 5: Graph for Second order irreversible reaction

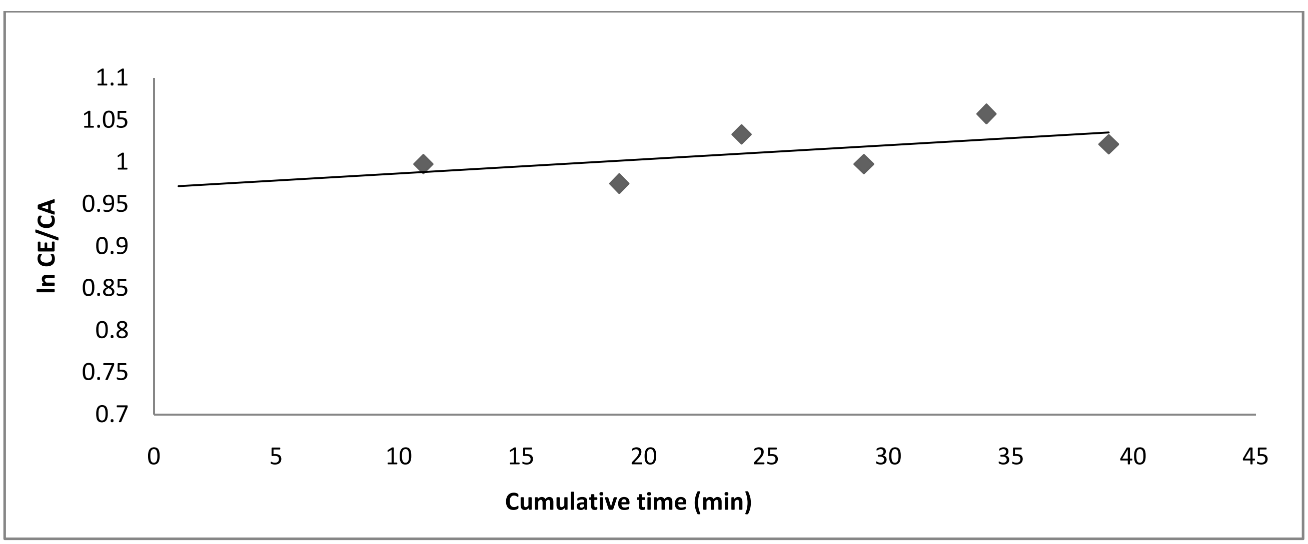


Table 01: Results of Esterification rate calculation

Type of Reaction	Values of rate constants & intercepts
Second order irreversible of Type II n = 2	K = 0.0002 liter/mol.min & Intercept $\ln(C_{Eo}/ C_{Ao}) = 0.969$

Therefore, the final rate expression: $\ln(C_E/ C_A) = 0.0002t + 0.969$

5. Conclusion

The reaction rate expression is very important information for the reaction engineering purposes. The prime significance of reaction rate expression is that they provide a satisfactory framework for the interpretation and evaluation of experimental kinetic data and industrial scale setup of the plant. This study demonstrated the way, how a chemical engineer should interpret laboratory scale kinetic data in terms of kinetic rate functions. Esterification reaction is chosen to perform this study because this reaction has significant importance and most basic form of ester production reaction. Hence an idea about determination of reaction kinetics is obtained through this study

Acknowledgement

The supports from the Department of Chemical Engineering, Bangladesh University of Engineering and Technology are gratefully acknowledged.

6. References

[1] Charles G. Hill, JR., “AN INTRODUCTION TO CHEMICAL ENGINEERING KINETICS & REACTOR DESIGN”, John Wiley & sons, New York, P. 28-29, 127-130, 1977