

# TO STUDY REACTION KINETICS OF ACETIC ACID – METHANOL SYSTEM AND DETERMINE CONVERSION IN DIFFERENT REACTORS

Karan Rana<sup>1</sup>, Pravin Saidane<sup>2</sup>, Siddharthsinh Parmar<sup>3</sup>, Akshaysinh Magodara<sup>4</sup>

<sup>1,2,3</sup> student, Chemical Engineering, Department of Chemical Engineering,  
Shroff S R Rotary Institute of Chemical Technology. Ankleswar-Valia Road At & Post-Vataria

<sup>4</sup> Assistant Professor, Department of Chemical Engineering,  
Shroff S R Rotary Institute of Chemical Technology. Ankleswar-Valia Road At & Post-Vataria

## ABSTRACT

Chemical reaction is the most important phenomena in chemical engineering and Reaction engineering. The reaction kinetics of acetic acid with methanol presence of homogeneous catalyst or without catalyst both analyzed. Batch esterification of acetic acid was carried out at operating conditions, temperature from 303.15k to 323.15k, methanol to acetic acid molar ratio from 1:1. Reaction is 2nd order reversible reaction having Activation energy for the 27.72 kJ/kmol and 20.18 kJ/kmol for forward and backward reaction respectively. Homogeneous H<sub>2</sub>SO<sub>4</sub> catalyst is used and activation energy for the 17.86 kJ/kmol and 13.61 kJ/kmol for forward and backward reaction respectively. At 323.15k the conversion of acetic acid 0.58 and 0.63(with H<sub>2</sub>SO<sub>4</sub> catalyst).scale up this reaction in continues stirred tank reactor (CSTR) at 323.15k the conversion of acetic acid 0.59 and 0.66(with H<sub>2</sub>SO<sub>4</sub> catalyst).

**Keyword:** - Reaction Kinetics, Activation Energy, Batch Reactor, Sulfuric Acid Catalyst, Continuous Stirred Tank Reactor (CSTR)

## 1. Introduction

Organic esters are widely used in the manufacturing of flavors, pharmaceuticals, plasticizers; and many synthetic routes are available for obtaining esters, which have reviewed by Yadav and Mehta [1] 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. [2] Chemical kinetics is the scientific foundation for the analysis of most chemical processes The prime significance of reaction rate expression is to provide a satisfactory framework for the interpretation and evaluation of experimental data and industrial scale up of the plant. As a general rule, elementary processes involve a transition between two atomic or molecular states separated by a potential barrier. The potential barrier constitutes the activation energy of the process, and determines the rate at which it occurs. When the barrier is low, the thermal energy of the reactants will generally be high enough to surmount the barrier and move over top products, and the reaction will be fast. However, when the barrier is high, only a few reactants will have sufficient energy, and the reaction will be much slower. The presence of a potential barrier to reaction is also the source of the

temperature dependence of reaction rates [3] Esterification is one of the most important reactions in chemical industry; and the relative reaction is usually conducted by using, in general, homogeneous acid catalysts [4].  $\text{CH}_3\text{COOH} + \text{CH}_3\text{OH} \rightleftharpoons \text{CH}_3\text{COOCH}_3 + \text{H}_2\text{O}$ . In order to measure order of reaction and rate constant there are differential, integrated methods are available. The differential method of analysis deals directly with the differential rate equation to be tested, evaluating all terms in the equation including the derivative  $dC/dt$ , and testing the goodness of fit of the equation with experiment. The integral method of analysis always puts a particular rate equation to the test by integrating and comparing the predicted  $C$  versus  $t$  curve with the experimental  $C$  versus  $t$  data. If the fit is unsatisfactory, another rate equation is guessed and tested.[5] The goal of this work was to study the esterification kinetics of acetic acid with methanol in the presence of catalyst and in the absence of catalyst. The effect of the reaction temperature, the initial molar ratio of the reactants, the catalyst loading the esterification kinetics was studied

## 2. Material and Methods

### 2.1 Chemicals

Acetic acid, methanol, sulfuric acid catalyst, phenolphthalein indicator

### 2.2 Experimental procedure

In the experiment, equimolar quantities of methanol and acetic acid charged to the reactor. The sample were withdrawn at regular time and analyzed for acetic acid concentration the reaction is carried out for sufficient time to reach equilibrium conversion. Same procedure carried out at 303.15K, 313.15K and 323.15K without catalyst and with catalyst (sulfuric acid) and find the kinetics of the reaction.



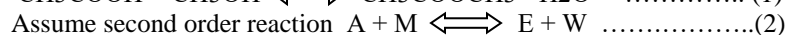
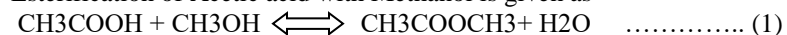
Fig:-2.1 Experimental setup

### 2.3 Analysis

The acetic acid concentration was determined by titration of reaction mixer sample with solution NaOH using phenolphthalein as an indicator.

### 2.4 Kinetic model

Esterification of Acetic acid with Methanol is given as



With the restriction that  $C_{A0} = C_{M0}$  and  $C_{E0} = C_{W0}$

$$-r_A = -dC_A/dt = C_{A0} dX_A/dt = K_1 C_A C_M - K_2 C_E C_W \quad \text{.....(3)}$$

$$= K_1 C_{A0}^2 (1 - X_A)^2 - K_2 (C_{A0} X_M)^2$$

Where A, M, E, and W refer to Acetic Acid, Methanol, Methyl Acetate and Water, respectively.

At the equilibrium,  $-r_A = 0$ . Hence, from the above equations, we find the fractional of A at the equilibrium conditions by

$$K = (C_{Ee} C_{We}) / (C_{Ae} C_{Me}) = X_e^2 / (1 - X_e)^2 \dots\dots\dots(4)$$

And the equilibrium constant by

$$K_e = k_1/k_2 \dots\dots\dots(5)$$

Combining the above three equations, in terms of the equilibrium conversion, we get

$$dC_A/dt = K_1 C_{A0} [(1 - X_A)^2 - (1 - X_e / X_e)^2 X_A^2] \dots\dots\dots(6)$$

With conversions measured in terms of  $X_{Ae}$ , this may be indicated as second-order reversible reaction which, on integration, gives

$$\ln \left[ \frac{X_{Ae} - 2X_{Ae} - 1}{X_{Ae} - X_A} \right] = 2 k_1 (1/X_{Ae} - 1) C_{A0} t$$

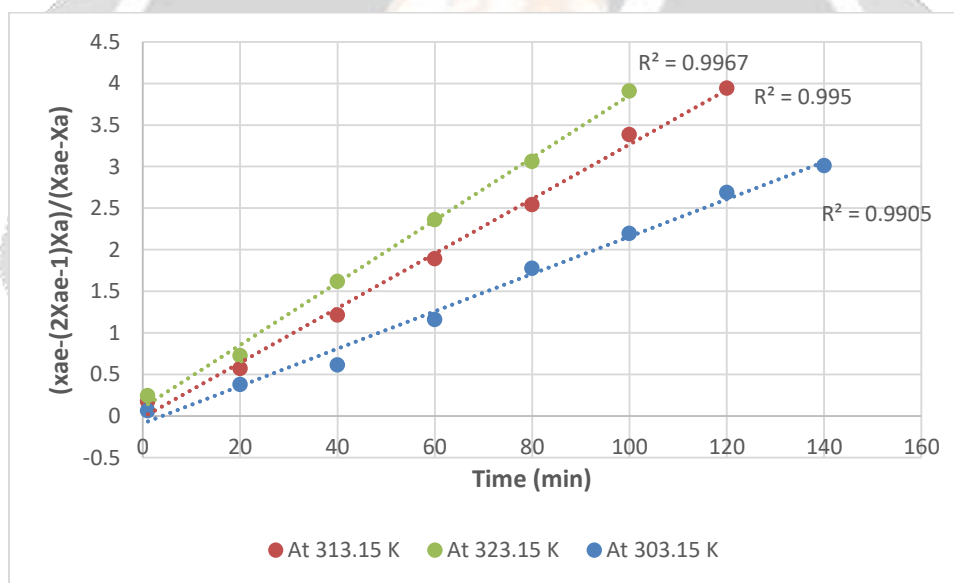


Fig:2.4.1 Typical kinetics plot for the effect of temperature on un-catalyzed reaction at 303.15K & 313.15K & 323.15K

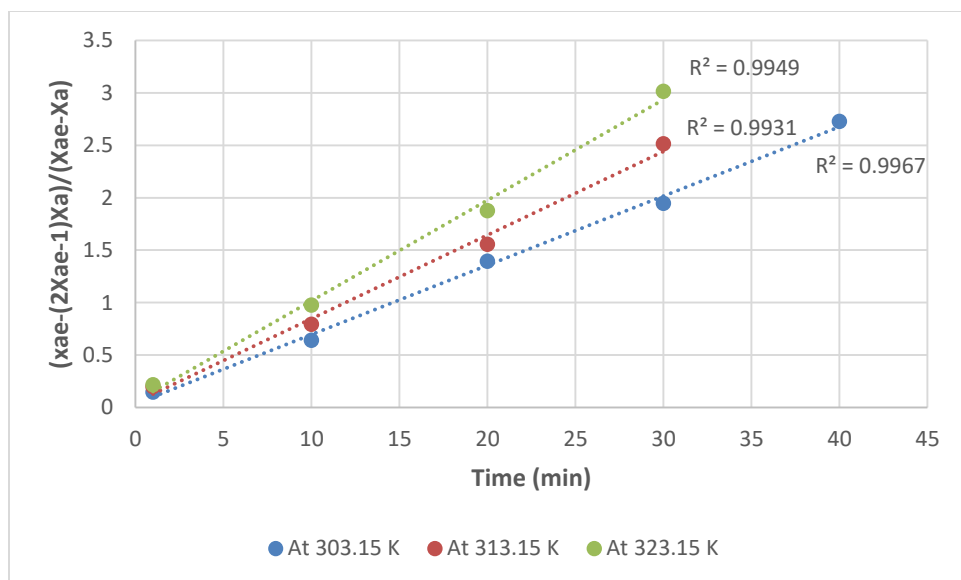


Fig:2.4.2 Typical kinetics plot for the effect of temperature on catalyzed reaction at 303.15K & 313.15K & 323.15K

### 3. Result

Temperature K	K1 $\text{L mol}^{-1} \text{min}^{-1}$	K2 $\text{L mol}^{-1} \text{min}^{-1}$
303.15	0.0557	0.0345
313.15	0.0859	0.0497
323.15	0.1100	0.05656

Table-3.1 reaction rate constant for un - catalyzed reaction

Temperature K	K1 $\text{L mol}^{-1} \text{min}^{-1}$	K2 $\text{L mol}^{-1} \text{min}^{-1}$
303.15	0.1024	0.0408
313.15	0.1303	0.0487
323.15	0.1588	0.0569

Table-3.2 reaction rate constant for catalyzed reaction

### 3.1 Temperature and Reaction Rate:

We can examine the variation of the rate constant with temperature by an Arrhenius' law relationship.

$$K = A \exp(-E/RT)$$

This is conveniently determined by plotting  $\ln K$  versus  $1/T$ .

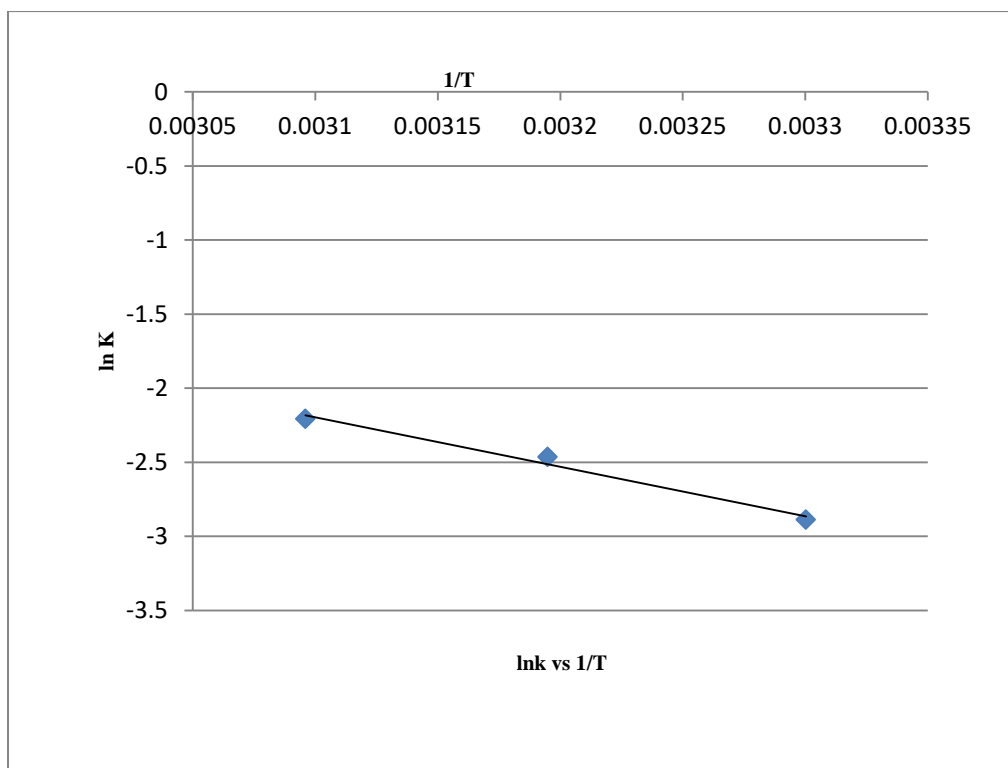


Fig:3.1 un- catalyzed forward reaction activation energy

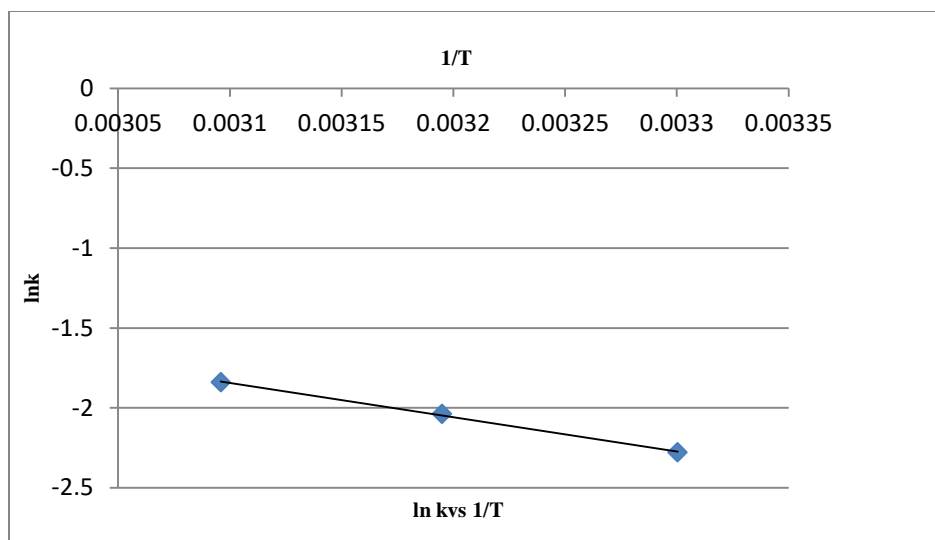


Fig: 3.2 catalyzed forward reaction activation energy

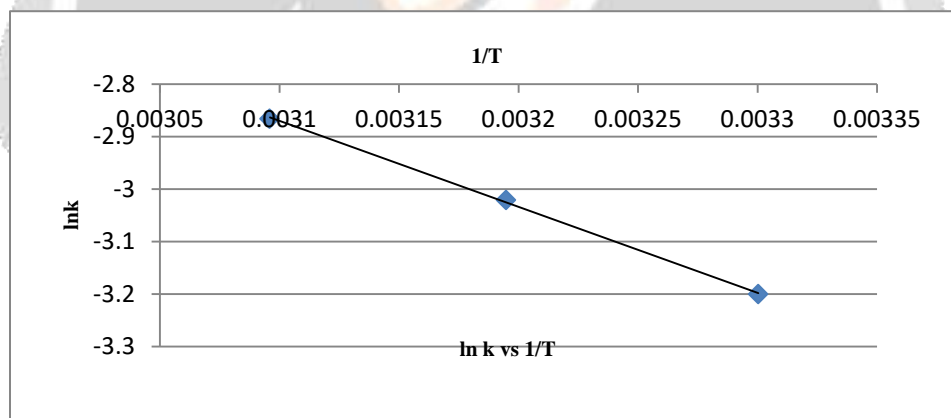


Fig: 3.3 catalyzed backward reaction activation energy

#### 4. CONCLUSIONS

The esterification reaction between methanol and acetic acid is conducted in reactor with sulfuric acid as a catalyst. The experiment result shows that as the temperature increases the reaction rate increases. Reaction is 2nd order reversible reaction having Activation energy for the 27.72 kJ/kmol and 20.18 kJ/kmol for forward and backward reaction respectively. Using Homogeneous  $H_2SO_4$  catalyst activation energy for the 17.86 kJ/kmol and 13.61 kJ/kmol for forward and backward reaction respectively.

## 5. ACKNOWLEDGEMENT

It is great pleasure and privilege to have an opportunity to take this work entitled "To study reaction kinetics of Acetic acid – methanol system and determine conversion in different reactors". We would like to express our deepness of gratitude to our project work guide Mr. AKSHAYSINH MAGODARA (Asst. Prof. C.E Dept.), for his inspiring guidance and invaluable suggestions that he had given throughout the project work. We would like to express our deep sense of gratitude to all faculty members of the department of chemical engineering. At this junction, it is appropriate to express our gratitude to the people who have been with us throughout & have helped us to successfully accomplish this work. Last but not least, we are grateful to our family & friends to provide us support & guidance mentally as well as financially to finish & submit our work successfully. Errors and deficiencies are likely to be there; therefore we apologize for the same in advance.

## 6. REFERENCES

1. Abbas S. M., "Kinetic study and modeling of oleic acid esterification with ethanol in presence of water", Thesis, University of Baghdad, 2013.
2. Venket Reddy Goli, Kinetics of esterification of methanol and acetic acid with mineral homogeneous catalyst, Chinese journal of chemical engineering. 23(2015) 100-105
3. Levenspiel O., a handbook of "Chemical reaction engineering", published by John Wiley and Sons, third edition, pp.14- 72, 1999.
4. Fogler, H.S. (1992) Elements of Chemical Reaction Engineering 2nd ed., Prentice Hall PTR, Upper Saddle River, NJ – ISBN 013263534 – SEL/EMS TP157.F65 1992
5. S.K. Ismail, H.Z. Tergioğlu, U. Dramur, Catalytic esterification methyl alcohol with acetic acid, Chin. J. Chem. Eng. 9 (1) (2001) 90–96.
6. R. Ronnback, T. Sami, A. Vuori, H. Haario, J. Lehtonen, A. Sundqvist, E. Tirronen, Development of a kinetic model for the esterification of acetic acid with methanol in presence of homogenous catalyst, Chem. Eng. Sci. 52 (1997) 3369–3381.
7. Yijun Liu., Edger Lotero., James G. Goodwin., A comparison of the esterification of acetic acid with methanol using heterogeneous versus homogenous acid catalysis, Journal of Catalysis, 2006, 242, 278-286.
8. Ronnback.R, Salmi. T, Vuori. A, Haario H., Lehtonen J., Development of a Kinetic model for the esterification of acetic acid with methanol in the presence of a homogenous acid catalyst, Chemical Engineering Science, 1997, 52, 3369-3381.
9. Asharaf Ahmed and Niaz Bahar chaowdhury, Esterification reaction in batch reactor presence of sulphuric acid catalyst
10. Hanh H.D., Dong N., Okitsu K., Nishimur R., Maeda Y., "Biodiesel production by esterification of oleic acid with short-chain alcohols under ultrasonic irradiation condition", Renewable Energy, Vol.34, pp.780–783, 2008.