# KINETIC STUDIES OF ESTERIFICATION OF N-PROPIONIC ACID AND 2-PROPANOL WITH SULPHURIC ACID CATALYST

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**Abstract**

The kinetic studies of esterification of n- propionic acid and 2- propanol were carried out in a stirred and temperature controlled batch reactor. Sulphuric acid was chosen as a homogeneous catalyst in the present esterification reaction. The influence of different variables on rate of reaction such as reactant molar ratios, catalyst concentration and reaction temperature was studied. The molar ratio of acid to alcohol was varied from 0.5 to 1.5, the reaction temperature ranging between 50°C and 70°C and catalyst concentration was from 1.0 to 3.0 weight percent. Box- Behnkem design of experiments was employed in the present study, from which the batch kinetics were evaluated. The reaction rate in terms of acid concentration was found to be second order by employing integral method of analysis. Also, an equation was correlated using non linear regression analysis to predict the reaction rate constant.

*Keywords: Esterification; Homogeneous catalyst; Box- Behnkem design; Acid concentration; Rate constant;*

## 1. Introduction

Iso-propyl propionate esters are the organic chemical compounds derived by reacting n- propionic acid with a hydroxyl compound, 2-propanol. Esters have a pleasant characteristic fruity odour and common in organic chemistry and biological materials. This leads to extensive applications in the fragrance, polymer and flavour industries. The most common homogeneous catalysts are mineral acids such as sulphuric acid, hydrochloric acid, hydrogen iodide and strong organic acids such as formic acid[1].

In the present study, the kinetic experiments of esterification of n-propionic acid and 2- propanol were conducted in a stirred and temperature controlled batch reactor, using homogenous catalyst as sulphuric acid. Isopropyl propionate is the ester formed with the reaction between n-propionic and 2-propanol. The esterification reaction is shown in equation (1).

$$CH_2COOH + (CH_3)_2CHOH \overset{H_2SO_4}{\rightleftharpoons} CH_3CH_2COO(CH_2)_2CH_3 + H_2O \quad \ldots(1)$$

(n-Propionic acid) (2-Propanol) (Iso-Propyl Propionate) (Water)

The reaction was carried out in a batch reactor to obtain the kinetic data for interpretation and design. The effect of different parameters was investigated in the current study and the rate of the reaction was determined using a fractional factorial design known as Box-Behnkem design of experiments. The experimental data on rate constant were correlated as a function of catalyst concentration, mole ratio and temperature[2].

**2. Experimental**

N-propionic acid, 2-propanol, sulphuric acid, sodium hydroxide, oxalic acid and phenopthalein were the chemicals used in this study.

The esterification reaction of n- propionic acid with 2-propanol was carried out in a 500 ml three neck round-bottom flask placed on a magnetic hot plate stirrer, which facilitated constant stirring and heating. The temperature was adjusting using the heating knob. Proper stirring speed was maintained by means of the speed control knob to ensure uniform mixing of reactants and catalyst in the reaction mixture such that there is no vortex formation. A thermocouple was inserted into the reactor through one of the side neck to measure the reaction mixture temperature inside the flask. A reflux condenser was placed vertically at the center neck of the reaction flask to prevent any vapor losses from the reactor[3]. The third side of the neck was closed with glass stopper, used for sample collection at each time interval.

Batch esterification experiments were performed in 500 ml three neck round-bottom flask on a magnetic hot plate stirrer with temperature control (±0.2$^o$C) and stirring speed control (0–1500 rpm). Equimolar quantities of n-propionic acid and 2- propanol were weighed separately in two conical flasks using electric pan balance. The measured quantities of $H_2SO_4$ catalyst was added to the flask containing n-propionic acid. Now, conical flask containing 2- propanol was charged into the reactor at required temperature 60$^o$C. The stirring speed was maintained at 200 rpm. The conical flask with n-propionic acid and catalyst was heated separately at the same temperature. Once the desired temperature was reached, the mixture of acid and catalyst was added to the reaction flask containing 2- propanol which constitutes to a mixture of 1.0 mole ratio (acid to alcohol). At zero time, 2 ml of sample was drawn using pipette into the conical flask containing 20 ml of sodium hydroxide and 20 ml of distilled water. The samples were drawn at regular time intervals and the concentration of unreacted propionic acid was estimated using standard titration analysis. Equilibrium samples were taken after 24 h of

reaction. The experiments were carried out at temperatures between 50°C and 70°C, the mole ratio varied from 0.5 to 1.5 and catalyst concentrations between 1.0 to 3.0 weight percent. The $H_2SO_4$ equivalent titer was estimated by taking equal amounts of distilled water for butyric acid and 2- propanol in a separate conical flask, $H_2SO_4$ was added, samples were titrated against sodium hydroxide with phenolphthalein as indicator and the concentration of $H_2SO_4$ was found.

**3. Results and discussions**

In the present system, esterification of n-propionic acid and 2- propanol with sulphuric acid as catalyst, the effect of different variables like mole ratio of reactants, catalyst concentration and reaction temperature were studied with conversion using Box- Behnkem design of experiments. The mole ratio of acid to alcohol was varied from 0.5 to 1.5, the reaction temperature between 50°C and 70°C and catalyst concentration was varied from 1.0 to 3.0 weight percent.

*3.1.. Effect of catalyst concentration*

The effect of catalyst concentration at different mole ratios and temperatures was investigated to determine conversion with time. Fig.1. shows the conversion of n-propionic acid with time during esterification of the mole ratio of acid to alcohol being 1.5 and temperature being 60°C. It was seen that with increase in the catalyst concentration, the conversion of n-propionic acid also increased.

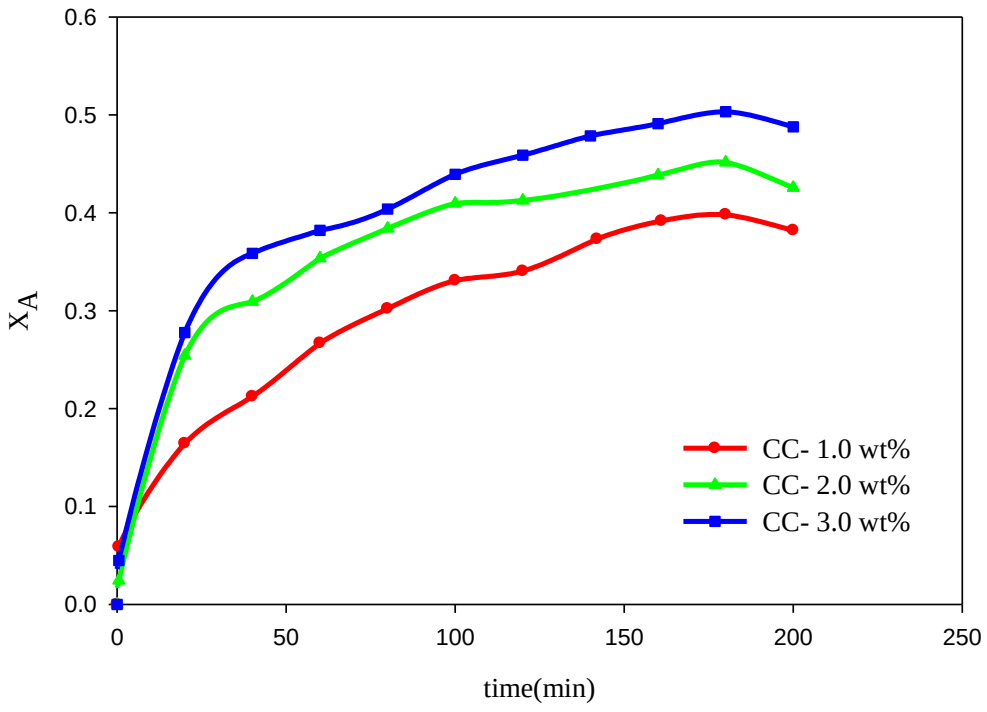


Fig.1. Effect of catalyst concentration on conversion {MR=1.5; T = $60^0$C}

*3.2. Effect of temperature*

The effect of temperature on the conversion of n-propionic acid during its esterification with 2-propanol was studied by conducting the reaction at three different temperatures 50, 60 and 70ºC. The conversion of n-propionic acid with time was plotted for mole ratio 1.5 and catalyst concentrations of 2.0 wt% as shown in Fig.2. The observation made was that the conversion increased with the increase in reaction temperature.

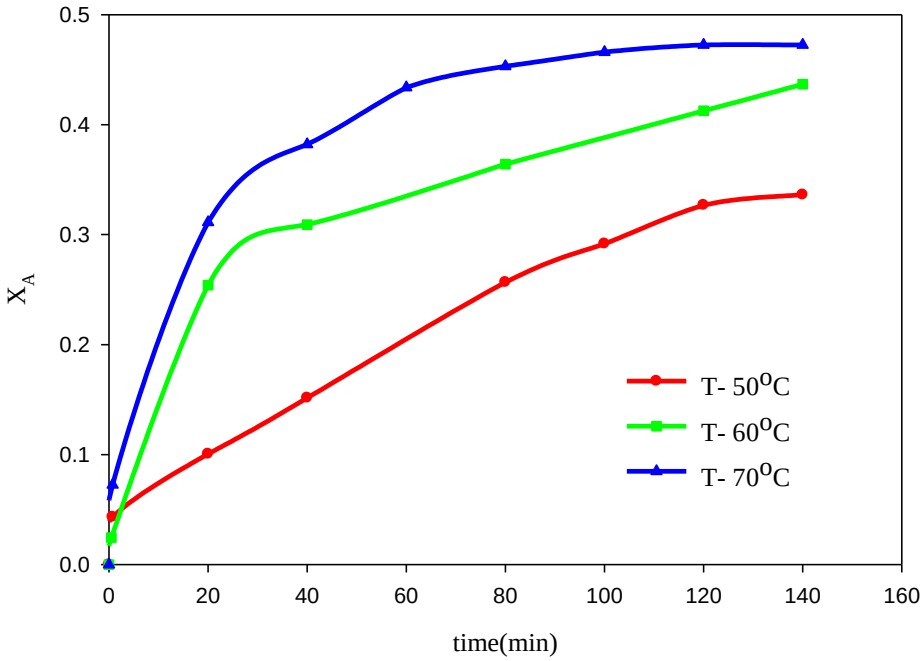


Fig.2. Effect of temperature on conversion {MR=1.5; CC = 2.0 wt%}

*3.3. Effect of mole ratio*

The effect of mole ratio at different temperatures and catalyst concentrations was studied to know the conversion versus time. The conversion of n-propionic acid against time was shown in Fig.3. for a catalyst concentration of 2.0 wt% at a temperature of 70°C.

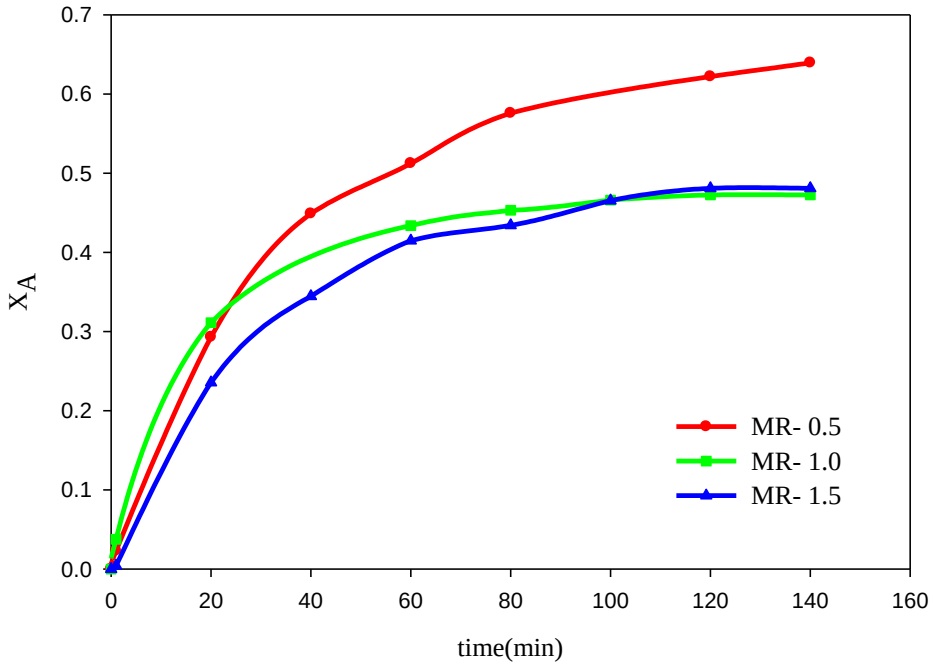


Fig.3. Effect of mole ratio on conversion {T = $70^0$C; CC= 2.0 wt%}

*3.4 Interpretation from batch reactor kinetics*

Using integral method of analysis[4], the reaction rate in terms of acid concentration was found to be second order from the plots of $1/C_A$ versus time as shown in Fig.4. The rate constant k, can be obtained from the slope of the plots of this figure. Likewise k values were obtained for all experimental sets and, these rate constants were correlated as a function of mole ratio, catalyst concentration and temperature, using least square regression analysis yielding the following equation(2).

$$k = 3592(MR)^{-0.9358}(CC)^{0.8724}e^{-5182/T} \quad (2)$$

The average and standard deviations for this equation were found to be 8.65 percent and 11.88 percent respectively. Fig.5.showed the comparison of experimental and calculated k values.

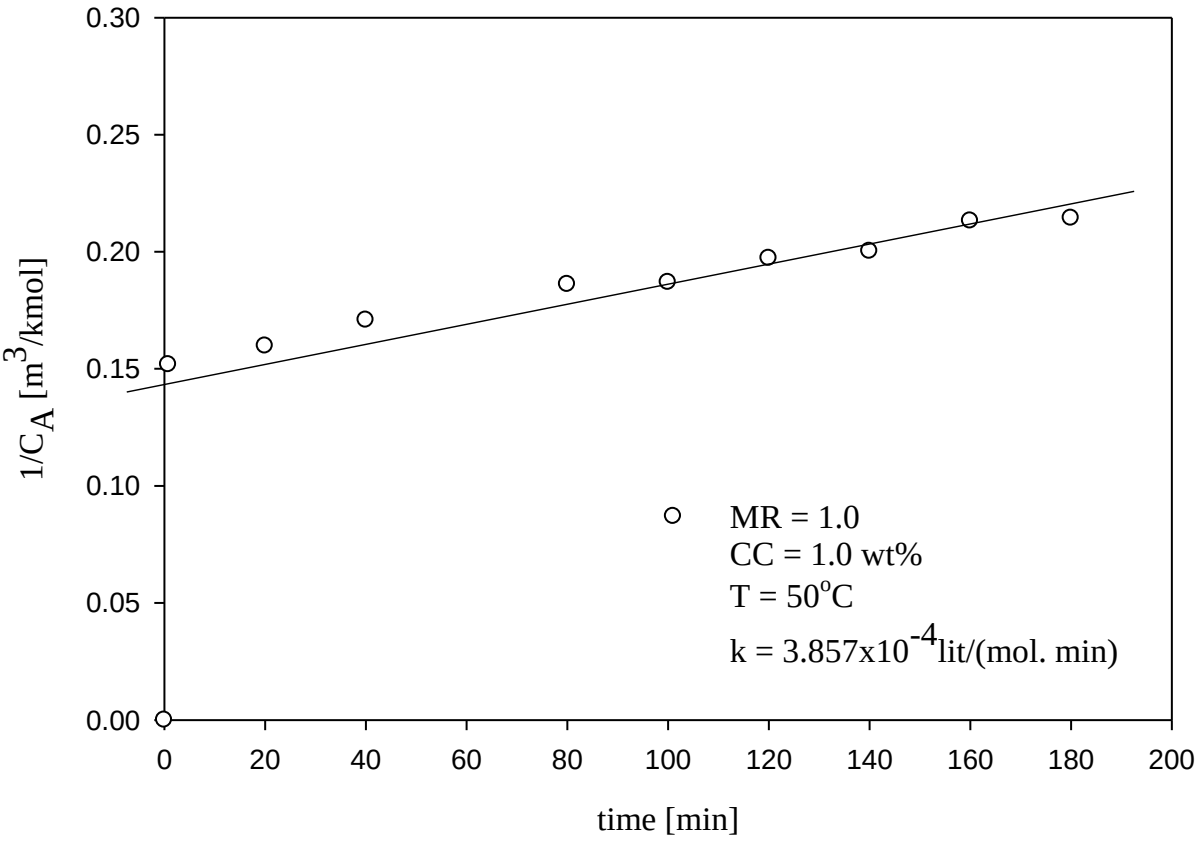


Fig.4. Plot for second order rate constant {M.R = 1.0; C.C = 1.0 wt%; T = 50°C}

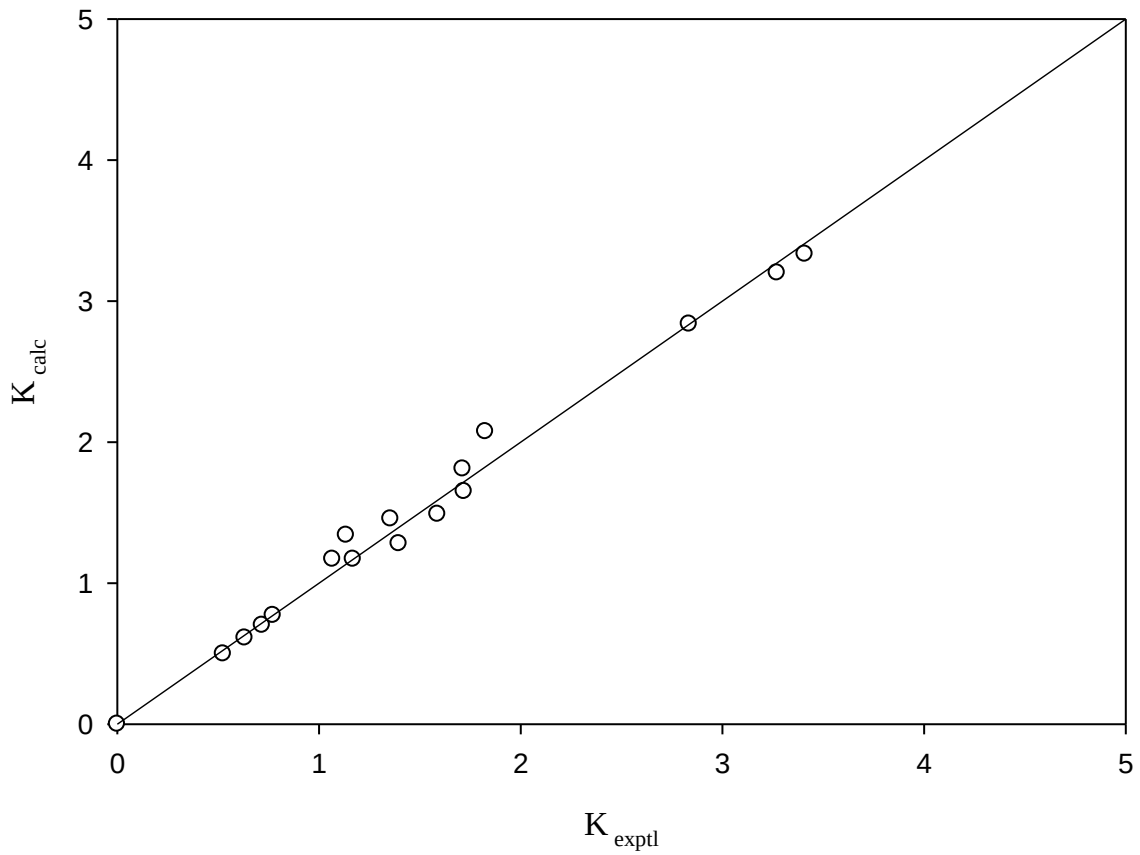


Fig.5. Comparison of experimental k values with value of k calculated values of k according to eqn (2)

## 4. Conclusions

The kinetics of esterification of n-propionic acid and 2- propanol with sulphuric acid as catalyst were studied in this paper. The different variables like mole ratio of reactants, catalyst concentration and the reaction temperature enhanced the conversion of n-propionic acid. The order of this reaction was found to be second order. The reaction rate constant followed Arrhenius law.

## 5. References

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