



KINETICS OF ESTERIFICATION OF CITRIC ACID WITH BUTANOL USING SULPHURIC ACID

PRATIBHA SINGH, SANJAY P. KABLE^{*a} and PRAKASH V. CHAVAN^{*}

Department of Chemical Engineering, Bharati Vidyapeeth Deemed University,
College of Engineering, PUNE (M.S.) INDIA

^aDepartment of Chemical Engineering Process and Development, National Chemical Laboratory,
PUNE (M.S.) INDIA

ABSTRACT

Reaction kinetics was studied for esterification reaction of citric acid with butanol in the batch isothermal experiments using sulphuric acid as a catalyst. The effect of temperature on the rate of reaction has been studied in the range of 100-140°C. It has been found that the rate of reaction increases with an increase in temperature and optimum temperature was found to be 140°C. At optimum temperature, the conversion of citric acid was found to be 86.8% with corresponding yield of tri-butyl citrate equal to 99.43%. The rate expression has been proposed and kinetic parameters, activation energy and frequency factor, have been determined.

Key words: Kinetics, Esterification, Tri-butyl citrate, Activation energy.

INTRODUCTION

Tri-butyl citrate (TBC) is widely used as a solvent and plasticizer in polymers, food and pharmaceutical industries^{1,2}. Acidic catalysts like sulphuric acid and para-toluene sulphuric acid have been commonly used as a catalyst to synthesis TBC.³ The reaction pathway is as follows:



The formation of mono-butyl citrate and di-butyl citrate is instantaneous.⁴ Therefore, kinetics of esterification of di-butyl citrate with butanol has been studied using sulphuric

* Author for correspondence; E-mail: sp.kamble@ncl.res.in, pvchavan@bvucoep.edu.in

acid as a catalyst. Water, one of the reaction products, has been continuously removed using Dean and Stark apparatus to drive the reaction to forward direction.⁵⁻⁷

EXPERIMENTAL

Materials

Citric acid and butanol were obtained from S. D. Fine, Mumbai and Suma Chemicals Pvt. Ltd., respectively. TBC and sulphuric acid (98% w/w) were obtained from Himedia Laboratories Pvt. Ltd. Analytical grade of toluene and concentrated sulphuric acid (99% w/w) were used for the experiment.

Analysis

An analysis of reaction mixture was carried out using potentiometric titration and Gas Chromatography (GC) using Br-1 column of 30 m length and 0.25 μm diameter. The potentiometric titration with 0.5 M sodium hydroxide analyses unreacted citric acid while GC analyses formed TBC. Oven column temperature was 280°C. GC injector and detector temperature were kept at 300°C with the nitrogen flow rate 25 mL/min, hydrogen flow rate 30 mL/min and air flow rate 300 mL/min.

Procedure

Esterification reactions were performed in a 1 L glass reactor equipped with constant temperature oil bath. The reaction volume was maintained between 350-400 cm^3 . The glass reactor was equipped with temperature and stirrer speed monitoring devices and a sampling port. The schematic is shown in Figure 1.

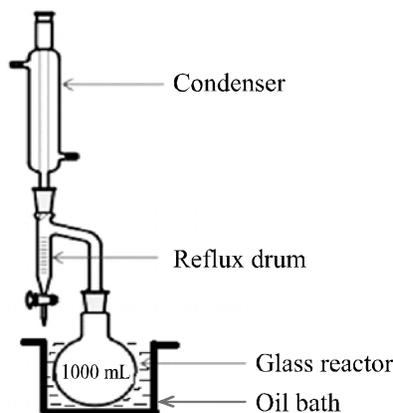
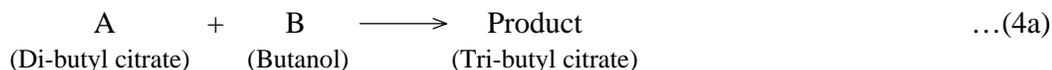


Fig. 1: Experimental setup

The mixture of citric acid and butanol in the mole ratio 1:4 was fed into the reactor and stirred well with the stirrer of speed 350 rpm and oil bath heater was started. After reaching the predetermined reaction temperature, sulphuric acid (1% w/w) was added to reaction mixture. During the reaction, water was continuously removed and butanol was fed back to reactor.

Kinetic model

The reaction between di-butyl citrate and butanol can be assumed as follows:



If the reaction is assumed to be second order, then conversion of tri-butyl citrate can be expressed as –

$$-r_A = -dC_A/dt = k C_A C_B = k C_{A0}^2 (1-X_A) (M - 2X_A) \quad \dots(4b)$$

The integrated form is given as follows:

$$\ln (C_B C_{A0}) / (C_{B0} C_A) = \ln (M - 2X_A) / (M(1 - X_A)) = C_{A0}(M - 2) kt, \quad M > 2 \quad \dots(5)$$

RESULTS AND DISCUSSION

Effect of reaction temperature

The effect of temperature on esterification reaction of citric acid with butanol was studied in the temperature range of 100°C to 140°C with the sulphuric acid loading of 1% (w/w) and an initial mole ratio of citric acid: butanol as 1:4. Fig. 2 shows that experimental

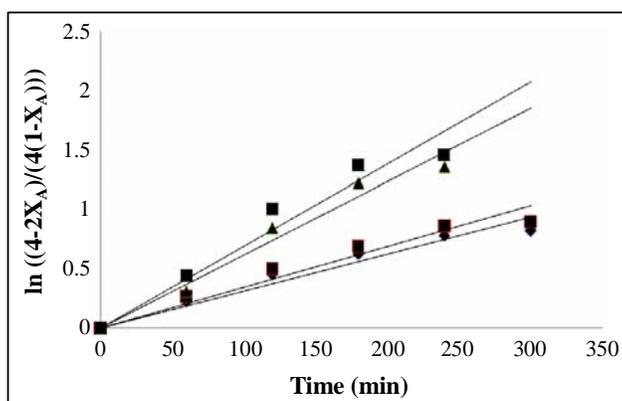


Fig. 2: Second order kinetic plot

data fits to second order bimolecular irreversible reaction kinetics. As the temperature increases the rate of conversion was found to be increased.

Table 1 shows summary of experiments conducted. All the experiments run at constant stirrer speed of 300-350 rpm.

Table 1: Summary of kinetic experiments

S. No.	Mole ratio CA : BtOH	H ₂ SO ₄ Catalyst loading (w/w %)	Oil bath temp. (°C)	Conversion (%)	Yield (%)
1.	1 : 4	1	100	71.9	45.19
2.	1 : 4	1	120	74.5	59.27
3.	1 : 4	1	130	85.2	99.19
4.	1 : 4	1	140	86.8	99.43

The rate constant for a given temperature have been obtained using equation (5). Table 2 shows the results.

Table 2: Second order rate constant

S. No.	Temp. (°C)	k (Lit/mol.min)
1.	100	0.001185
2.	120	0.001299
3.	130	0.002370
4.	140	0.002638

Activation energy and frequency constant

Arrhenius equation has been used to quantify dependence of rate constant on temperature and to determine activation energy of the reaction. Arrhenius equation is given as follows:

$$k = k_0 e^{-E/RT}$$

Rate equation

Figure 3 shows the plot of $\ln kVs 1/T$ where the slope of the line provides value of activation energy (E) and intercept provides the value of frequency factor (k_0), have been

calculated 20.85 KJ/mol and $2.40 \times 10^{-3} \text{ mol}^{-1} \cdot \text{L} \cdot \text{min}^{-1}$, respectively. The final rate expression is as follows:

$$-r_A = 2.40 \times 10^{-3} \times e^{20.84/RT} C_A C_B$$

By putting the concentration value at any time, we get the rate expression for the esterification reaction.

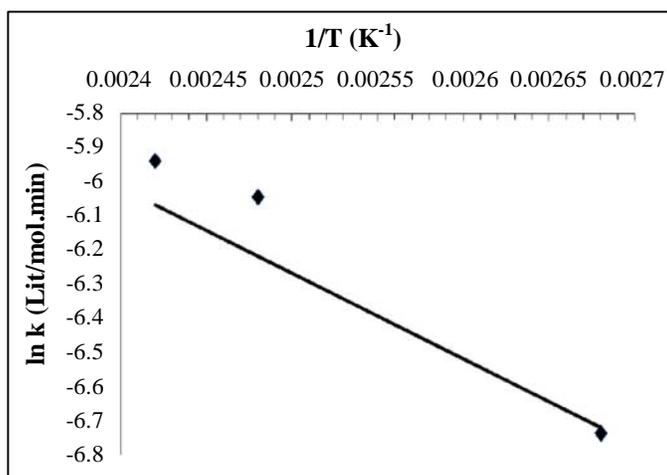


Fig. 3: Temperature dependency of the reaction rate

CONCLUSION

The kinetic parameters, activation energy and frequency factor were estimated to be 20.84 KJ/mol and $2.40 \times 10^{-3} \text{ mol}^{-1} \cdot \text{L} \cdot \text{min}^{-1}$, respectively for the reaction. Hence the rate expression for the reaction is as follows:

$$-r_A = 2.40 \times 10^{-3} \times e^{20.84/RT} C_A C_B$$

REFERENCES

1. N. Ljungberg and B. Wesslem, J. Polym., **44**, 7679-7688 (2003).
2. Y. Lemmouchi, M. Murariu, A. M. D. Santos, A. J. Amass, E. Schacht and P. Dubois, J. Eur. Polym., **45**, 2839-2848 (2009).
3. T. Kawabata, T. Mizugaki, K. Ebitani and K. Kaneda, J. Tetrahedron Lett., **44**, 9205-9208 (2003).

4. J. Xu, J. Jiang, Z. Zuo and J. Li, *J. Process Saf. Environ.*, **88**, 28-30 (2010).
5. A. Kolah, N. Asthana, D. Vu, C. Lira and D. Miller, *J. Ind. Eng. Chem. Res.*, **46**, 3180-3187 (2007).
6. A. A. Backhaus, *U. S. Patent*, **1**, 400, 849 (1921).
7. M. Schmitt, H. Hasse, K. Althaus, H. Schoenmakers, L. Gotze and P. Moritz, *J. Chem. Eng. Proc.*, **43**, 397 (2004).

Revised : 10.06.2014

Accepted : 13.06.2014