

USE OF ISOPERIBOLIC REACTION CALORIMETER FOR THE STUDY OF REACTION KINETICS OF ACETIC ANHYDRIDE HYDROLYSIS REACTION: EFFECT OF ACETIC ANHYDRIDE AND WATER RATIO

Rajendra Kumar^{1*}, Anurag Kumar Tiwari²

¹Council of Scientific and Industrial Research – National Chemical Laboratory, Chemical Engineering and Process Development Division, Pune, India – 411008

²Dr B R Ambedkar National Institute of Technology, Department of Chemical Engineering, Jalandhar, Punjab, India – 144011

Reaction kinetics of acetic anhydride hydrolysis reaction is being studied at a fixed reaction temperature and ambient pressure using an isoperibolic reaction calorimeter. Temperature versus time data along with heat and mass balance is used to determine the kinetics parameters i.e. activation energy and Arrhenius coefficient. It has been studied with the varying volumetric ratio of acetic anhydride and water; and kinetics parameters were compared and plotted for each ratio. Such a study has not been done previously to determine the kinetics dependency on varying the acetic anhydride water ratio. As the acetic anhydride hydrolysis reaction is exothermic in nature, the present study will help to decide the safe and suitable operating conditions such as concentration and temperature for conducting this reaction at plant scale. The kinetic data presented can be used further for the mathematical modeling and simulation of such exothermic hydrolysis reactions.

Keywords: acetic anhydride, water, reaction calorimeter, hydrolysis, kinetics

1. INTRODUCTION

Reaction calorimeter is an instrument which is widely used by scientists and engineers in chemical and pharmaceutical process development to measure the amount of thermal energy released or absorbed by a chemical or physical reaction. Reaction calorimeter allows the investigation of chemical processes under process-like conditions, providing a full set of information about the scalability and safety of the process. The information obtained from the reaction calorimeter is essential for the safe transfer of a process from lab scale to plant scale. Basic principles and its use for process development and process safety have been described by many researchers (Singh, 1997). Reaction kinetics of a reaction is an important

* Corresponding author, e-mail: k.rajendra@ncl.res.in

<https://journals.pan.pl/cpe>

Presented at the International Chemical Engineering Conference 2021 (ICHEEC): 100 Glorious Years of Chemical Engineering and Technology, held from September 16–19, 2021 at Dr B. R. Ambedkar National Institute of Technology, Jalandhar, Punjab, India.



© 2022. The Author(s). This is an open-access article distributed under the terms of the Creative Commons Attribution (CC-BY 4.0, <https://creativecommons.org/licenses/by/4.0/>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

information, which is used at various places such as process development, process scale-up, equipment design, mathematical modelling and simulation, etc.

The traditional method to determine the reaction kinetics of a chemical reaction involves the measurement of concentration with respect to time, which requires continuous sampling and analysis. Apart from using the concentration data researchers have used other techniques such as conductivity measurement (Kralj, 2007), pH measurement (Wiseman et al., 2020), various spectroscopic methods such as Raman, IR and NMR (Bell et al., 1998; Haji and Can, 2005; Susanne et al., 2012). Few researchers have used the temperature versus time profile of the reaction to determine the reaction kinetics (Asiedu et al., 2013; Hirota et al., 2010). These alternative techniques do not require sampling and offline analysis, because a suitable in-situ probe or sensor captures the required data such as conductivity, pH, spectra or temperature in real time. Captured information can be used to determine the reaction kinetics by analyzing the raw data and using mathematical equations. These alternative techniques are suitable for the reactions where continuous sampling and offline analysis is difficult due to process conditions.

If the kinetics of the reaction is not fully understood, then while conducting reaction, several serious issues may arise, such as runaway which leads to high amount of pressure and thermal energy liberation resulting into release of environmentally dangerous substances, serious equipment damage, and an explosion. Unfortunately, for most important industrial reactions, there is limited knowledge about their kinetics and thermodynamics. Since several industrially important chemical reactions are moderately highly exothermic such as hydrolysis, acid-base neutralization, esterification, hydrogenation, nitration etc.; it is possible to quantify their kinetics using the thermal data.

Acetic anhydride hydrolysis is a fast and moderate exothermic reaction which is very popular among all the users of reaction calorimeter. It is most suitable exothermic reaction for the demonstration of reaction calorimetry technique. The kinetics of acetic anhydride hydrolysis can be considered as first order with respect to acetic anhydride as well as with respect to water. It may also be noted that values of kinetics parameters for acetic anhydride hydrolysis are not same from the different studies reported. They dependent on various factors such as the user, type of instruments used, concentration, temperature, stirring speed of the mixing, catalyst, solvent, etc. (Asiedu et al., 2013; Fritzler et al., 2014; Hirota et al., 2010; Kralj, 2007). In this study an isoperibolic reaction calorimeter was used to determine the kinetics of the acetic anhydride hydrolysis reaction. “Isoperibolic” means the reaction mass is kept at a surrounding of constant temperature, and then temperature changes during the reaction are studied using a thermocouple. This technique is useful for very fast reactions and where kinetics information is not available. We have demonstrated activation energy and Arrhenius coefficient determination of acetic anhydride hydrolysis reaction using reaction calorimeter with varying volumetric ratios of acetic anhydride to water. This type of study of reaction kinetics determination of acetic anhydride hydrolysis reaction has not been done with low to high concentration of acetic anhydride in fixed water quantity or varying the acetic anhydride to water ratios as known to the authors.

2. METHODOLOGY

The details of equations and methodologies used for the reaction kinetics determination using the isoperibolic reaction calorimeter have been described in various reported research papers (Asiedu et al., 2013; Fritzler et al., 2014; Garcia et al., 2021; Hirota et al., 2010; Salahudeen et al., 2020). The hydrolysis reaction of acetic anhydride can be represented as



This reaction can be considered as first order with respect to each reagent.

Considering this reaction to be in batch mode and in liquid phase, mass and energy balance equations are given by:

$$N_{A0} \frac{dX_A}{dt} = (-r_A)V \quad (2)$$

$$mC_P \frac{dT_r}{dt} = (-r_A)V(-\Delta H) - UA(T_r - T_j) \quad (3)$$

Here acetic anhydride (A) is considered to be the limiting reactant, N_{A0} is the initial number of moles of acetic anhydride, V is the effective volume of the reactor used for the reaction, dT_r/dt is the rate of change of the temperature of the reaction mass.

For heat balance it is assumed that there is negligible thermal effect due to dosing and stirring and there is negligible heat exchange from the atmosphere.

Here mC_P in Eq. (3) accounts for the total heat capacity of the system; which has two parts, first is $(mC_P)_{\text{reactor}}$ which is for the empty reactor and stirrer, second is $\sum_j m_j C_{pj}$ which is for the chemical components (acetic anhydride, water and acetic acid), j is the number of chemical components in the reactor.

$$mC_P = (mC_P)_{\text{reactor}} + \sum_j m_j C_{pj} \quad (4)$$

The ΔH is the molar heat of the acetic anhydride hydrolysis reaction, it has to be obtained by isothermal reaction calorimeter experiment. ΔH is fixed for the reaction irrespective of concentration and ratio. UA and mC_P can be obtained by doing the calibration of the reaction mass using the calibration heater from reaction calorimeter.

Considering hydrolysis of acetic anhydride as second order kinetics, the rate law of the reaction can be represented as:

$$(-r_A) = kC_A C_W \quad (5)$$

where k is the rate constant, which is temperature-dependent according to the Arrhenius equation:

$$k = k_0 \exp\left(-\frac{E}{RT_r}\right) \quad (6)$$

In Eq. (5), the molar concentrations of acetic anhydride (C_A) and water (C_W) may be written in terms of the conversion of the acetic anhydride as follows:

$$C_A = C_{A0} (1 - X_A) \quad (7)$$

$$C_W = C_{W0} \left(1 - \frac{C_{A0} X_A}{C_{W0}}\right) \quad (8)$$

T_r is the reactor temperature which is measured and recorded in real time using a temperature sensor.

By combining the mass and energy balances and integrating the resulting equation from time $t = 0$ to $t = t$ and assuming that the conversion of acetic anhydride is 100% at the end of the experiment, conversion formula can be obtained. The conversion of acetic anhydride is given by the following relationship:

$$X_{A_i} = X_{A_f} - \frac{(mC_P)(T_f - T_i) + UA \int_0^t (T_r - T_j) dt}{N_{A0}(-\Delta H)} \quad (9)$$

Here X_{A_i} is the conversion at a given point, and X_{A_f} is the final conversion.

The integral part of above equation is calculated for each interval of time using trapezoidal rule:

$$\int_a^b f(x) dx = \frac{\Delta x}{2} [f(x_0) + 2f(x_1) + 2f(x_2) + \dots + 2f(x_n)] \quad (10)$$

Hence, the values of experimental conversion are obtained starting from the time of completion of reaction.

With the known values of mC_P , UA , ΔH and dT_r/dt , the rate of reaction can be determined at each data point experimentally by rearranging the thermal balance as follows:

$$(-r_A) = \frac{(mC_P)_r \frac{dT_r}{dt} + UA (T_r - T_j)}{V(-\Delta H)} \quad (11)$$

Once $(-r_A)$ is determined, the values of the rate constant at each point can be calculated from Eq. (5) as:

$$k = \frac{(-r_A)}{C_A C_W} \quad (12)$$

where C_A and C_W are calculated from Eqs. (7) and (8), respectively.

Finally, the values of the E and $\ln k_0$ are obtained respectively, from the intercept and the slope of the straight line plot of $\ln k$ versus $1/T_r$:

$$\ln k = \ln k_0 - \frac{E}{RT_r} \quad (13)$$

In the result section, the values of $\ln k_0$ will be reported instead of k_0 .

3. EXPERIMENTAL SECTION

Distilled water prepared at NCL lab and high purity Acetic Anhydride from Thomas Baker Mumbai was used for conducting the hydrolysis experiments. A similar model of reaction calorimeter from HEL UK was used (Fig. 1) for conducting the experiments. This reaction calorimeter consists of 1 liter Borosilicate glass reactor and 1 liter SS316 metal reactor in the same unit with interchangeable option. Out of these 2 available reactors, the glass reactor which had vacuumed double jacket for least heat loss into the atmosphere was used for this study. This reaction calorimeter was connected with a high-end Julabo A45 circulator which is used to heat or cool the reaction mass or reactor jacket with temperature range of –40 to 250 °C. A Heidolph made overhead motor and PTFE stirrer was connected with the reactor which is capable to stir the reaction mass at suitable RPM. Separate temperature sensors were connected with the reactor and jacket for the monitoring and recording of the reaction mass temperature (T_r) and jacket temperature (T_j) accurately to two decimal places. The reactor was also integrated with a ProMinent delta pump and Sartorius weighing balance for the controlled addition of reagent into the reactor.

This reaction calorimeter is fully automatic which runs through the WinISO software from the computer. All the process parameters such as temperature, RPM, reactor temperature, jacket temperature, torque, etc. can be monitored and recorded in real time. After the completion of experiments the recorded data is being analyzed by in-build iQ software to determine various parameters such as ΔH , UA , and mC_P . The obtained parameters from the reaction calorimeter, temperature time profile, heat and mass balance equations are used for the reaction kinetics determination.

For ΔH calculation heat flow method of reaction calorimeter was used. UA and mC_P were determined by various calibration experiments using the calibration heater. Calibration experiments were performed



Fig. 1. Reaction calorimeter used for the experiments

before and after addition of acetic anhydride to determine UA and mC_p ; and average value was used for the kinetics calculation for each experiments. Temperature time profiles of all the acetic anhydride hydrolysis experiments were captured at isoperibolic mode of the reaction calorimeter at fixed jacket temperature of 35 °C.

Temperature controlled heat transfer oil was circulated through the jacket of the reactor. The oil temperature was controlled to maintain the desired temperature of the water in the reactor. When both the reactor temperature as well as jacket temperature reached 35 °C, acetic anhydride was added suddenly to the reactor vessel. Stirrer RPM was kept constant at 400 for all the experiments during addition and reaction. The reaction calorimeter constantly measured the T_r , T_j and dT_r/dt after each 2 seconds. As the reaction proceeded, temperature-time profiles for the reaction were obtained. A total of 9 experiments with varying volumetric ratios of acetic anhydride and water; 1:2 (run 1), 1:3 (run 2), 1:4 (run 3), 1:5 (run 4), 1:6 (run 5), 1:7 (run 6), 1:8 (run 7), 1:9 (run 8), 1:10 (run 9) were conducted for this study.

4. RESULTS AND DISCUSSION

A reaction calorimeter was used to determine the kinetic parameters of a reaction using temperature-time profiles. Figure 2 represents the temperature versus time data for different volumetric ratios of acetic anhydride to water. From the temperature time profile, the peak shows the 100% conversion of acetic anhydride to acetic acid. The absolute amount of heat released by the reaction is proportional to the amount of acetic anhydride taken. Hence temperature peak is highest for run 1 and lowest for run 9. Similarly, reaction time also decreases from run 1 to run 9; reaction time is inversely proportional to the amount of acetic anhydride used.

Molar heat of reaction ΔH was determined to be 56.1 kJ/mol, which is in agreement with several other reported values (Asiedu et al., 2013; Fritzler et al., 2014; Hirota et al., 2010). Values of UA and mC_P are dependent on the quantity of reaction mass, hence they are different for all the runs. UA and mC_P were determined separately for each experiments and are represented in Figures 3 and 4. It is observed that UA and mC_P both decreased from run 1 to run 9 as the amount of acetic anhydride decreased with respect to the fixed quantity of water. With the known values of UA , ΔH and mC_P for all the runs, conversions at

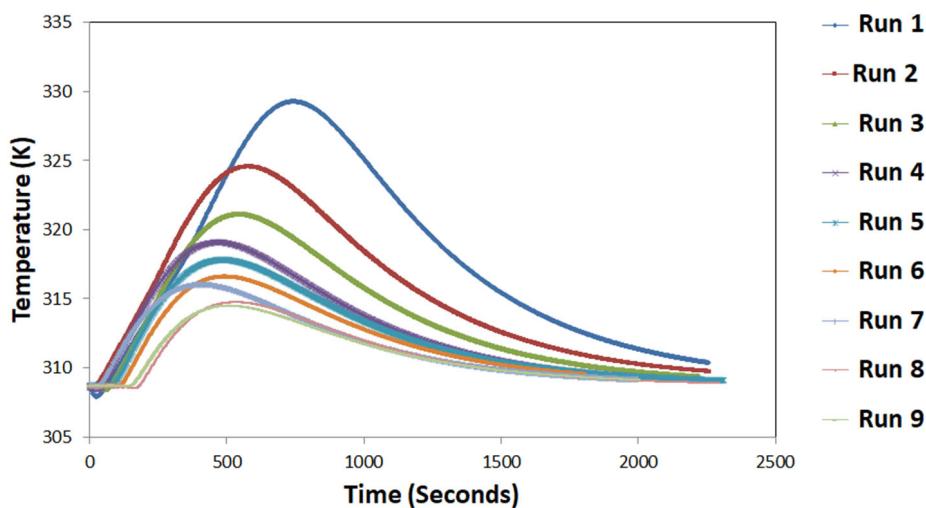


Fig. 2. Temperature-time profile for all the runs

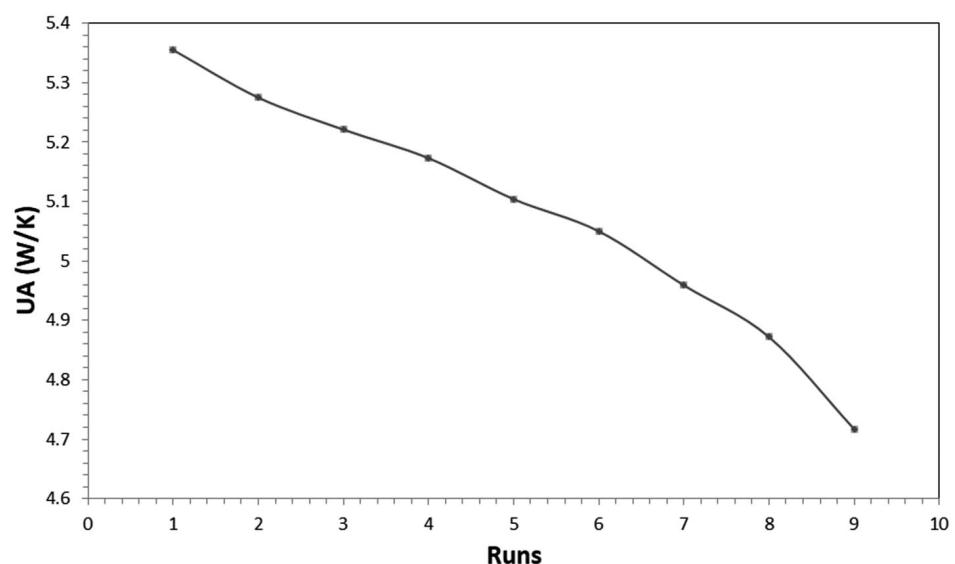
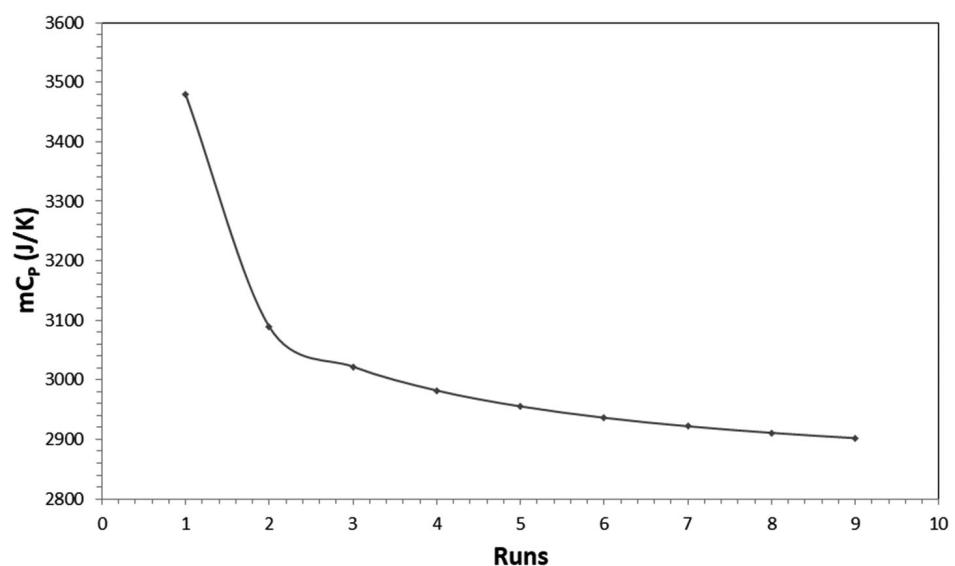


Fig. 3. UA variation for all the runs

Fig. 4. mC_p variation for all the runs

each point were calculated using Eq. (9). It was in reverse manner starting from the last point assuming 100% conversion at the completion of the reaction. Figure 5 depicts conversion-time data for all the runs. Initial conversion of acetic anhydride at the start of the reaction or time $t = 0$ for each run is shown in Fig. 6, it varies from zero to 10% for run 1 to run 9. It indicates that initial conversion is highly dependent on the quantity of acetic anhydride used. Lowest initial conversion for run 1 means that more quantity of reagent makes it difficult to start the reaction.

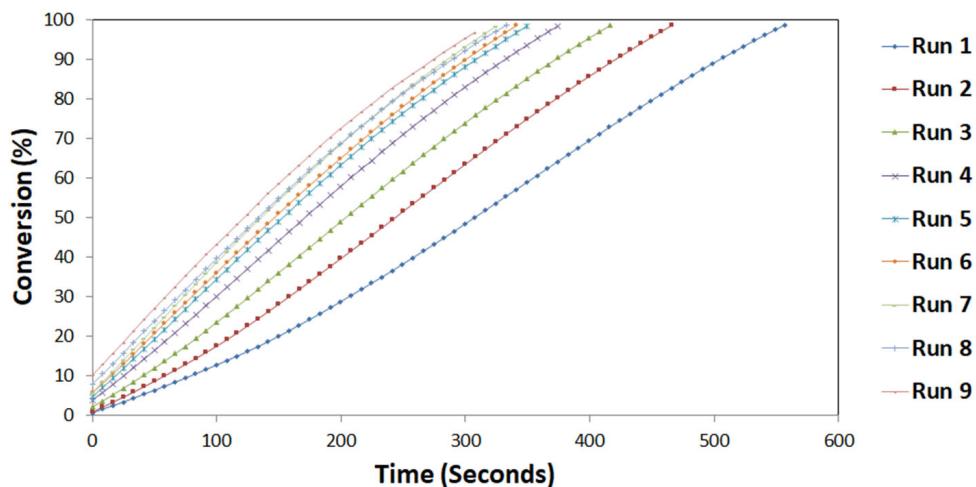


Fig. 5. Conversion-time data for all the runs

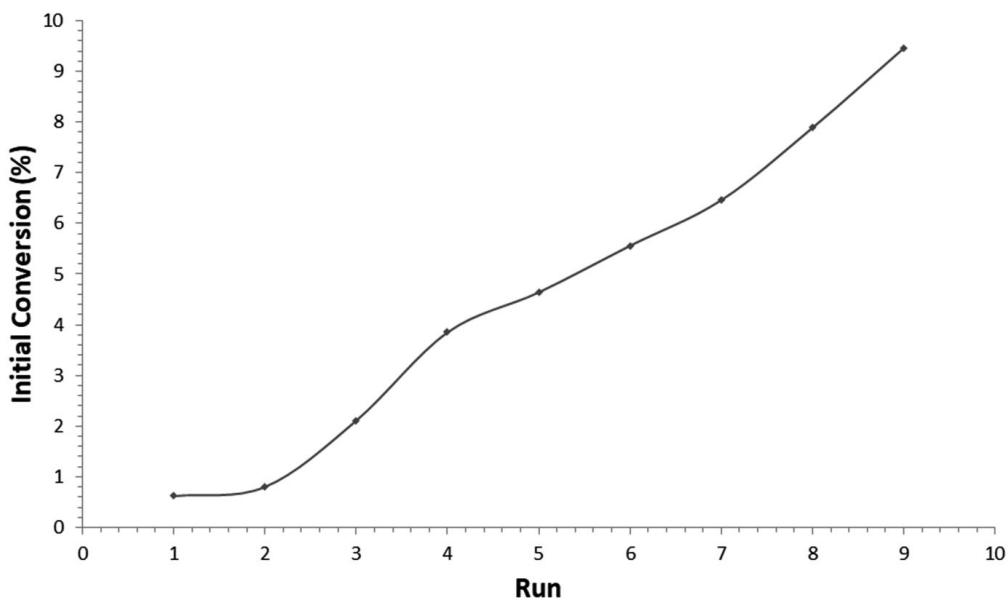


Fig. 6. Initial conversion for all the runs

Figure 7 shows the plots between $\ln k$ vs. $1/T_r$. By fitting these curves into a straight line, slope and intercept values are used to determine the reaction kinetics parameters E and $\ln k_0$. The values of E and $\ln k_0$ obtained are plotted in Figure 8 and Figure 9 against each run. It is observed that activation energy and $\ln k_0$ are almost constant while decreasing the acetic anhydride concentration with respect to fixed quantity of water. It depicts that the activation energy which is the minimum energy required by the acetic anhydride and water system for the hydrolysis and formation of acetic acid does not change while change in the reagent concentration. It is quite expected that it should not change, as activation energy is an independent value and does not depend on parameters such as concentration, temperature, etc; it can only change if we use a catalyst in the reaction.

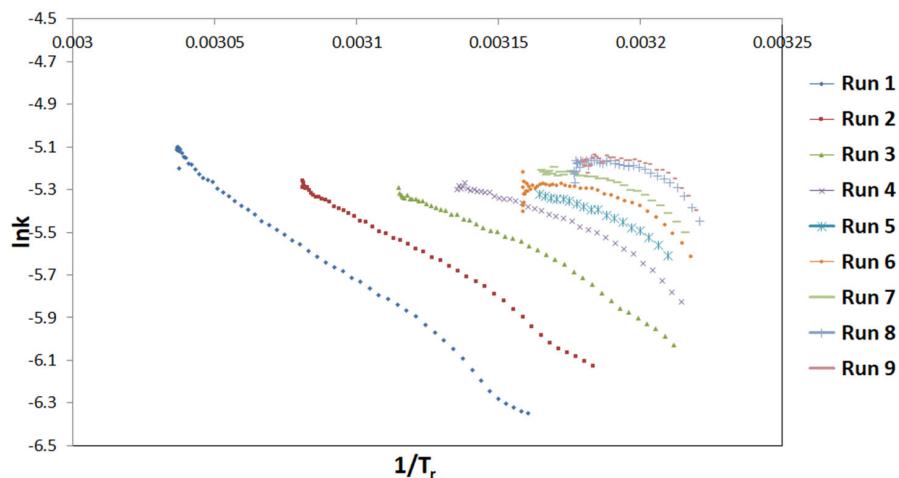
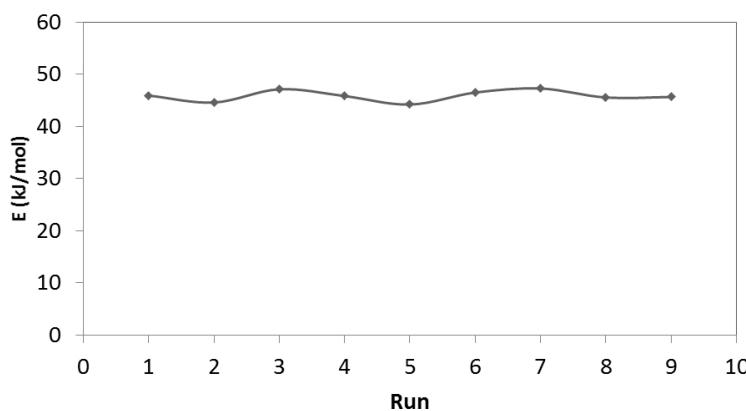
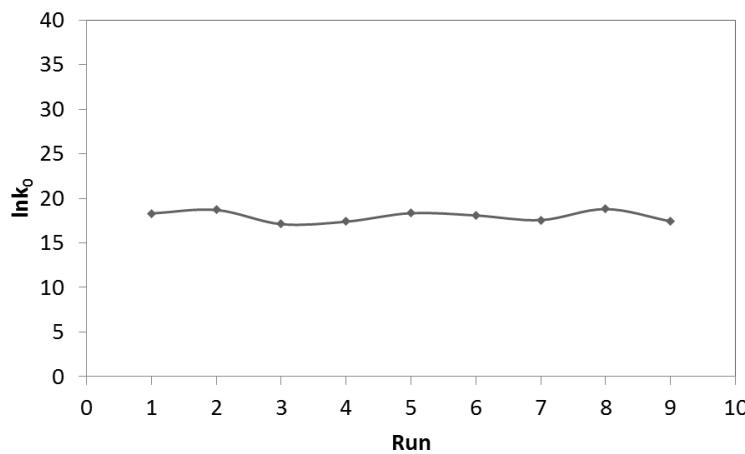
Fig. 7. $\ln k$ vs. $1/T_r$ for all the runs

Fig. 8. Activation energy for all the runs

Fig. 9. $\ln k_0$ for all the runs

5. CONCLUSIONS

This work shows the effect on reaction kinetics of acetic anhydride hydrolysis reaction by varying the ratio of acetic anhydride to water using isoperibolic reaction calorimeter at a fixed temperature of 35 °C. Here temperature time data from the experiments were used for the kinetics determination. The values of ΔH

were fixed for all the experiments, and UA and mC_P were determined separately for each reaction. Kinetics parameters E and $\ln k_0$ were determined for each ratio. It was found that E and $\ln k_0$ does not change with respect to the quantity of acetic anhydride used with the fixed quantity of water. The values of E and $\ln k_0$ were found to be almost constant while acetic anhydride concentration was maximum and then it gradually decreases to minimum from run 1 to run 9. Data also shows that temperature peak was highest for run 1 and lowest for run 9. Complete reaction conversion took maximum time for run 1 and minimum for run 9. The study also indicates that the amount of absolute heat generated is dependent on the amount of acetic anhydride used, however molar heat is independent of amount used. The presented data and study may be helpful to design the acetic anhydride hydrolysis reaction system in a safe and easy to handle manner. It will also be helpful to decide the safe concentration and temperature limits as per the available cooling capacity for the production of acetic acid using acetic anhydride hydrolysis process.

Authors would like to thank Ravi Pohankar, intern student from MANIT Bhopal and Vaibhavi Zanzad, intern student from VIT Pune for helping to conduct the experiments and data analysis.

SYMBOLS

C_A	concentration of acetic anhydride, mol/l
C_W	concentration of water, mol/l
mC_P	total heat capacity of reactor and components, J/K
E	activation energy, kJ/mol
k	specific reaction rate constant, l/mol s
k_0	arrhenius coefficient, l/mol s
N_{A0}	initial moles of acetic anhydride, mol
N_{W0}	initial moles of water, mol
R	ideal gas constant, J/(mol·K)
$(-r_A)$	rate of disappearance of acetic anhydride, mol/(l·s)
T_j	jacket temperature, K
T_r	reactor temperature, K
UA	product of heat transfer coefficient and used reactor area, J/K
V	volume of reacting fluid, l
X_A	conversion of acetic anhydride
ΔH	molar heat of hydrolysis of acetic anhydride, kJ/mol

REFERENCES

- Asiedu N., Hildebrandt D., Glasser D., 2013. Kinetic modeling of the hydrolysis of acetic anhydride at higher temperatures using adiabatic batch reactor (thermos-flask). *J. Chem. Eng. Process Technol.*, 4, 176. DOI: [10.4172/2157-7048.1000176](https://doi.org/10.4172/2157-7048.1000176).
- Bell W.C., Booksh K.S., Myrick M.L., 1998. Monitoring anhydride and acid conversion in supercritical/hydrothermal water by in situ fiber-optic Raman spectroscopy. *Anal. Chem.*, 70, 332–339. DOI: [10.1021/ac9707141](https://doi.org/10.1021/ac9707141).
- Fritzler B.C., Dharmavaram S., Hartrim R.T., Diffendall G.F., 2014. Acetic anhydride hydrolysis at high acetic anhydride to water ratios. *Int. J. Chem. Kinet.*, 46, 151–160. DOI: [10.1002/kin.20838](https://doi.org/10.1002/kin.20838).
- Garcia J.M., Bernardino I.R.B., Calasans V., Giudici R., 2021. Kinetics of the hydrolysis of acetic anhydride using reaction calorimetry: effects of strong acid catalyst and salts. *Chem. Eng. Res. Des.*, 166, 29–39. DOI: [10.1016/j.cherd.2020.11.024](https://doi.org/10.1016/j.cherd.2020.11.024).

Haji S., Can E., 2005. Kinetics of hydrolysis of acetic anhydride by in-situ FTIR spectroscopy. An experiment for the undergraduate laboratory. *Chem. Eng. Educ.*, 39, 1, Winter 2005.

Hirota W.H., Rodrigues R.B., Sayer C., Giudici R., 2010. Hydrolysis of Acetic anhydride: Non-adiabatic calorimetric determination of kinetics and heat exchange. *Chem. Eng. Sci.*, 65, 3849–3858. DOI: [10.1016/j.ces.2010.03.028](https://doi.org/10.1016/j.ces.2010.03.028).

Kralj A.K., 2007. Checking the kinetics of acetic acid production by measuring the conductivity. *J. Ind. Eng. Chem.*, 13(4), 631–636.

Salahudeen N., Rasheed A.A., 2020. Kinetics and thermodynamics of hydrolysis of crystal violet at ambient and below ambient temperatures. *Sci. Rep.*, 10, 21929. DOI: [10.1038/s41598-020-78937-4](https://doi.org/10.1038/s41598-020-78937-4).

Singh J., 1997. Reaction calorimetry for process development: Recent advances. *Process Saf. Prog.*, 16, 43–49. DOI: [10.1002/prs.680160113](https://doi.org/10.1002/prs.680160113).

Susanne F., Smith D.S., Codina A., 2012. Kinetic understanding using NMR reaction profiling. *Org. Process Res. Dev.*, 16, 61–64. DOI: [10.1021/op200202k](https://doi.org/10.1021/op200202k).

Wiseman F.L., Scott D.W., Tamine J., O'Connell R., Smarra A., Olowoyo S., 2020. Analyses of reaction rate data for the simple hydrolysis of acetic anhydride in the acetonitrile/water and acetone/water cosolvent systems using recently developed thermodynamic rate equations. *Int. J. Chem. Kinet.*, 52, 52–60. DOI: <https://doi.org/10.1002/kin.21329>.

Received 16 February 2022

Received in revised form 22 March 2022

Accepted 6 April 2022