

CHARACTERISATION OF RUNAWAY REACTIONS AND USE OF DATA IN SIMULATION PROGRAMS

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Characterisation of runaway reactions is required when safety in the event of a maloperation is to be based on dealing with the consequences of the runaway. Usually tests are carried out in adiabatic reaction calorimeters and often the data obtained are corrected. Kinetic constants calculated from corrected data are used in simulation programs to model the runaway reaction. This paper considers the limitations of the methods used for correcting data and accuracy of the kinetic constants obtained. Simulation programs were developed and used in a parametric analysis to determine the sensitivity of critical values for the simulated reaction with expected variation in the experimentally determined kinetic constants.

Keywords: Phi Factor, Kinetics, Runaway, Simulation

INTRODUCTION

The basis of safety of exothermic reactions is usually based upon prevention and/or venting of the runaway reaction. If the runaway is to be vented, the accurate prediction of the behaviour of the runaway reaction is required. In particular, when assessing the consequences of a runaway reaction, the prediction of the time available to take action, known as the time to maximum rate (TMR), the adiabatic temperature rise and the rate of change of temperature with time at the set pressure of the relief device is required. For this purpose computational models to simulate these process parameters are developed and these simulation programs are used to predict the behaviour of the runaway at the process conditions. Simulation programs are also useful in predicting the change in critical process parameters if the conditions for the reaction change, for example if the starting temperature for the reaction changes. For the simulation models data such as kinetic constants and heat of reaction are required and these physical data are obtained from experiment. Such data when obtained by thermocalorimetric experiments have limitations because of the experimental conditions and therefore require correction. If accurate data are used computational models should predict the behaviour of the reaction, provided the mechanism given for the reaction is correct. In this paper the accuracy of data generated from experiment, the methods used for correcting experimental data and also the effect this has upon data generated from simulation models are considered.

KEY DATA

For the development of a simulation model certain data are of fundamental importance. These data are generated from experimental data usually obtained by adiabatic reaction calorimetry, for example the Phi-Tec. As the experimental data depend upon experimental conditions, the temperature/time data produced in this manner must be corrected before the key data for the

simulation model can be deduced. Temperature/time data obtained from an experiment must be corrected for the effect of the vessel's heat capacity, as the heat generated by the reaction is used to heat both the reactor contents and the container. The temperature/time data measured within the experiment are corrected using the phi factor (ϕ) (first introduced by Townsend and Tou (8)), where ϕ is defined as

$$\phi = \frac{\text{Heat capacity of the sample} + \text{Heat capacity of the test cell}}{\text{Heat capacity of the sample}}$$

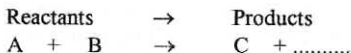
Using the corrected experimental data the equation

$$k_1 = Z \exp\left(-\frac{E}{RT}\right) \quad (1)$$

can be used to calculate the required data, where k_1 is the rate constant, Z the pre-exponential factor, E the activation energy, R the gas constant and T the temperature in Kelvins. From equation 1 it can be seen that when $\ln k_1$ is plotted against $1/T$, Z and $-E/R$ can be deduced from the gradient and intercept of the resulting straight line. Further data required for the model are the heat of reaction and this again can be calculated from the experimentally determined adiabatic temperature rise and the specific heat capacity of the reactants and products. Therefore the fundamental data required for the simulation models are the heat capacity of the components, the phi factor of the system, the heat of reaction and the kinetic constants.

SIMULATION MODELS DEVELOPED

Two simulation models were developed, one using Excel (1) and another using ISIM (5). Both models were based upon the following reaction schemes. For a normal nth order reaction the reaction can be described as



Therefore the rate of consumption of A, r_A , can be defined as

$$r_A = k' c_A^n \quad (2)$$

where c_A is the concentration of component A, k' is the rate constant in $\text{mol}^{n-1}/\text{l}^{n-1}\text{s}$ and

$$c_A = c_{A0} (1 - X) \quad (3)$$

where c_{A0} is the initial concentration of A and X the conversion, then

$$r_A = k' c_{A0}^n (1 - X)^n \quad (4)$$

and

$$r_A = -\frac{dc_A}{dt} = c_{A0} \frac{dX}{dt} \quad (5)$$

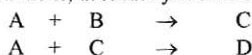
$$\frac{dX}{dt} = k_1 (1-X)^n \quad (6)$$

where k_1 is in units of s^{-1} . The rate of change of consumption of the reactants with time can be deduced from equation 6. From the heat of reaction, ΔH_R , in kJ/kg the rate of change of reaction temperature with time can be found from equation 7.

$$\frac{dT_R}{dt} = \frac{\Delta H_R}{c_{PAV}} \frac{dX}{dt} \quad (7)$$

where c_{PAV} is the half the sum of the specific heat capacity of the reaction mixture at the start of the time interval and at the end of the time interval.

Besides normal nth order reactions, autocatalytic reactions of the form,



often occur in practice and these reactions are also included within this investigation. To include these reactions within the models it is necessary to modify equation 8 to

$$\frac{dX}{dt} = r_1 (1-X)^n (1+PX^m) \quad (8)$$

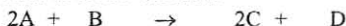
to account for the autocatalytic effect.

After programming these equations into ISIM and Excel the simulation models could be used to calculate the time predicted for the reaction, the adiabatic temperature rise and the maximum value of dT/dt . The results from the ISIM and Excel models were compared. As shown in figure 1 the time predicted for the reaction from ISIM and Excel are not identical, however it is very similar (within $\pm 2\%$). The difference found was due to the different methods of integration used by the two models. In the simpler Excel model the differential equations are integrated numerically over a specified timestep, whereas in the ISIM model Runge-Kutta methods of integration are available and the timestep is therefore optimised.

EXPERIMENTAL DATA

Both models developed require physical data to be input into the model, which are obtained from experimental data. Adiabatic reaction calorimetry is one technique used to obtain the data required. In this work the experimental equipment used was the Phi-Tec reaction calorimeter. The advantage of the Phi-Tec equipment is that it has a very low phi factor of 1.05 when a steel can is used. The temperature vs time data are used to calculate the kinetics for the reaction. The reaction was taken as an nth order reaction and knowing the order of reaction a plot of $\ln k_1$ vs $1/T$, as previously described, enables the kinetics of the reaction to be determined.

The reaction of Methanol with Acetic Anhydride was studied experimentally. This reaction was chosen because kinetics for the reaction have been published by several authors within the literature, see Wright and Rogers (9), Singh (6). Traditionally the reaction is assumed to be a first order reaction therefore initially within this study the reaction was assumed to be a first order reaction. The reaction was assumed to follow the form



The reaction was carried out in the Phi-Tec equipment and from the results obtained the kinetics for the reaction were evaluated.

As seen from figure 2 first order kinetics, where the \ln of the pre-exponential factor was $17.6324s^{-1}$ and the value of E/R was $8611.9K$, could be found from the first set of experimental data which when used in the simulation model produced a good fit compared with the experimental data. The simulation model predicted the time for the reaction to be 4797s with an adiabatic temperature rise of $146.2^{\circ}C$ whereas the experimentally determined reaction time was 4729s with an adiabatic temperature rise of $146.7^{\circ}C$. The first experiment was carried out at a start temperature of $28.8^{\circ}C$. A further experiment was carried using the same reaction, but this time using a different start temperature of $23.5^{\circ}C$. The kinetics derived from the first reaction were used to predict the behaviour of the second experiment, only the start temperature was altered to the new value. The experimental data for the second experiment together with the curve predicted using the kinetics from experiment 1 are also shown in figure 2. Comparing the experimental and predicted results for the second experiment it is seen that the simulation model using the kinetics for the first experiment does not accurately predict the behaviour of the reaction at the new start temperature. The time for the reaction measured experimentally was 7650s whereas the time predicted by the simulation model was 7393s. The adiabatic temperature rise measured experimentally was $147.2^{\circ}C$, whereas that predicted by the simulation model using the heat of reaction from the first experiment was $146.3^{\circ}C$. The difference between the predicted and measured time for reaction was approximately 5 minutes, which in this case is not a significant practical difference. However the inability of the reaction kinetics from the first experiment to predict the behaviour of the second experiment indicates that the proposed mechanism of reaction is incorrect.

Since the Methanol/Acetic Anhydride reaction is known to show autocatalytic behaviour an autocatalytic model was fitted to the experimental data. As seen in figure 3 the behaviour of the reaction at different starting temperatures could be more accurately predicted using an autocatalytic model. In the first experiment the simulation model predicted the time for the reaction to be 65s slower than was measured by experiment and the adiabatic temperature rise was predicted to be $1^{\circ}C$ higher than it actually was. For the second experiment the same simulation model predicted the reaction to be 67s faster than the reaction actually was and the adiabatic temperature rise was predicted to be the same as that measured by the experiment, showing therefore that the reaction is autocatalytic and not first order as often assumed.

As seen from figures 4 and 5 depending which data are used for determination of kinetics from one experiment affects the value of the pre-exponential factor to a large extent. For example in figure 4 all data up to what was assessed as the end of the reaction was used to fit a straight line to the data. The curve fitting routine gave values of the \ln of the pre-exponential factor as $16.68 s^{-1}$ and a value of E/R of $8253 K$. In figure 5 the end of the reaction was assessed to be ten data points earlier than in the first case. The curve fitting routine gave values of the \ln of the pre-exponential factor of $17.61 s^{-1}$ and a value of E/R of $8598 K$. From this it is seen that there was a 5.6% variation in the \ln of the pre-exponential factor and a 4% difference in the value of E/R . The

difference between the first order kinetics calculated for experiments 1 and 2 and the autocatalytic kinetics are shown in Table 1. The table shows the variability in the value of Z and the value of E/R that can be obtained from experimental results and this variability is considered in the sensitivity analysis and vent sizing below. It has been shown that it is necessary to conduct more than one experiment, preferably using different starting temperatures, when determining the kinetics for a reaction. The kinetics calculated from the first reaction should be used to attempt to predict the behaviour of the second reaction using a simulation model and if this cannot be done to within an acceptable level of accuracy the reaction mechanism should be investigated further.

	$\ln Z \text{ s}^{-1}$	E/R K	P	m
Experiment 1	17.632	8611.2	-	-
Experiment 2	18.033	8750.4	-	-
Singh	17.66	8609.6	-	-
Autocatalytic	17.462	8885	2.65	0.1325

Table 1 - A comparison of kinetics for the Methanol/Acetic Anhydride Reaction

METHODS OF CORRECTING EXPERIMENTAL DATA

As explained previously experimental data cannot be directly used to calculate the time for the reaction and the adiabatic temperature rise. The experimental data must be corrected for the effect of the vessel's heat capacity using the phi factor. There are several methods of correcting for phi available in the literature. The most straightforward is to correct the measured adiabatic temperature rise by

$$(\Delta T_{ad})_{actual} = \phi (\Delta T_{ad})_{measured} \quad (9)$$

and the time for the reaction by

$$t_{actual} = \frac{t_{measured}}{\phi} \quad (10)$$

Alternative methods of correcting for phi given in the literature are the method by Fisher presented in the DIERS project manual (3) and that by Huff (4). The simulation model is corrected for phi by dividing the value of dT/dt by ϕ at each timestep, whereas the Huff and Fisher methods correct the measured temperature as well as the value of dT/dt . Since the method by which the experimental data are corrected could affect the time of reaction and the adiabatic temperature rise, it was decided to compare the methods of correcting for phi with an ideal case to ascertain whether it was preferential to use one of these three methods when correcting experimental data.

Each of the three methods were compared with an ideal case. The ideal case was generated from experimental data by choosing kinetics such that when the simulation model was run with the relevant phi factor the simulation model reproduced exactly the experimental curve. Having exactly matched the experimental data with the simulation curve the simulation model was then run with a phi factor of 1. The temperature/time curve then obtained from the model is the ideal curve against which the other three methods of correcting for phi were compared. In turn each of

the three methods described for correcting for ϕ were used to correct the experimental data such that the $\phi=1$ curve was generated using each method. A comparison with the ideal case for all methods is given in figures 6, 7 and 8. The ϕ factor for the container in this case was 1.38. For the example shown here when the experimental data were measured in a container with a ϕ factor of 1.38, the corrected adiabatic temperature rise when $\phi=1$ was predicted by each of the three methods as 154.9°C whereas the ideal method predicted an adiabatic temperature rise of 152.1°C. Therefore each of the three methods of correcting for ϕ predicts relatively accurately the adiabatic temperature rise when $\phi=1$.

The difference in each of the three methods is seen when the time for the reaction measured experimentally is corrected for the effect of ϕ . When comparing figures 6 and 7 it is seen that the temperature vs time curve predicted for the reaction when $\phi=1$ by the Fisher method and the usual method of correcting for ϕ does not fit exactly the temperature time curve, but is very close to that expected in the ideal case. However when considering figure 8 it is seen that the Huff method of correcting for the effect of the vessel's heat capacity fitted almost exactly the ideal case. Other experimental data with different ϕ factors when corrected by the three methods for the effect of ϕ confirmed this trend. Therefore these data showed that from the three methods tested the Huff method was the most accurate method of correcting experimental data for the effect of the vessel's heat capacity. The Huff method is more difficult to use than the simple method usually used and the difference in time for reaction is not significant, therefore it is acceptable to continue to use the traditional method for industrial purposes.

SENSITIVITY ANALYSIS

Time to Runaway

As established, certain physical data, such as the pre-exponential factor, activation energy, heat capacity and start temperature for the reaction, are determined from the experimental data for use in the simulation programs. As shown above these data will be subject to experimental error therefore a sensitivity analysis was carried out on all the significant parameters to ascertain whether experimental error will significantly affect the predictions of the model in particular with respect to time available to react to a potential runaway and the adiabatic temperature rise. A sensitivity analysis was carried out on all significant parameters in turn to determine the effect changes in the value of this constant has upon time predicted for the runaway and the adiabatic temperature rise.

Kinetic Constants - Conditions were chosen such that the time for the reaction was 2 hours, 8 hours and 24 hours. These times were chosen as Stoessel (7) suggested that when the time to runaway was 2 hours the reaction would never be carried out industrially without extra safety measures, for example emergency relief venting, if it was greater than 8 hours it could possibly be considered, but when the time to runaway is greater than 24 hours no problems would be foreseen in carrying out the reaction. These conditions were the start temperature, T_0 , was 25 °C, the value of E/R was 9000 K, the value of the specific heat capacity was 2kJ/kg K and the heat of reaction was 286kJ/kgK. The value of the \ln of the pre-exponential factor used was varied to produce the desired time to reaction for each case and is presented in Table 2. For the autocatalytic reaction the value of m used was 1 and the value of P was 3. These values were used as the baseline for the sensitivity analysis. Initially the parameters investigated were the pre-exponential factor and the value of E/R . The effect of a change in the \ln of the pre-exponential factor on the time for the reaction is seen by examining table 2. It is seen, for example for a first order reaction that a 15%

change in the ln of the pre-exponential factor from 16.33 to 18.83 causes the time predicted for the runaway reaction to change from 24 hours to 2 hours.

Parameter	Order 1			Order 2			Autocatalytic		
	2 hrs	8 hrs	24 hrs	2 hrs	8 hrs	24 hrs	2 hrs	8 hrs	24 hrs
$\ln Z \text{ s}^{-1}$	18.83	17.45	16.33	19.02	17.62	16.50	18.60	17.25	16.15

Table 2 - Base conditions used for sensitivity analysis

Having investigated the effect of the ln of the pre-exponential factor the effect of changes in E/R was examined. Taking the baseline conditions for a first order reaction where the time for the reaction was 2 hours, the value of E/R was varied until the time for the reaction was 8 hours and then varied again until the time for the reaction was 24 hours, so that the effect of the change in E/R could be determined. The procedure was repeated for each different set of kinetics, for example for 8 hour kinetics the value of E/R to give a time of reaction of 2 hours and 24 hours was calculated. The results obtained are summarised in table 3.

The results showed that a 8-10% change in the value of E/R caused a change in the time for the reaction from 24 hours to 2 hours. These results show the importance of accurate kinetics for use in simulation models for runaway reactions. A change in the ln of the pre-exponential factor between 10-20% causes the time for the reaction to change from 24 hours to 2 hours. A change in the value of E/R between 8-10% causes the predicted time for the reaction to change from 24 to 2 hours. The small variation in pre-exponential factor or E/R required to change the time for adiabatic calorimetry data are analysed.

Reac ⁿ Order	Kinetics	E/R for 2h reac ⁿ time	E/R for 8h reac ⁿ time	E/R for 24h reac ⁿ time
1	2 hour	9000 K	9425 K	9770 K
1	8 hour	8550 K	9000 K	9350 K
1	24 hour	8200 K	8650 K	9000 K
2	2 hour	9000 K	9450 K	9790 K
2	8 hour	8580 K	9000 K	9360 K
2	24 hour	8200 K	8660 K	9000 K
Autocatalytic	2 hour	9000 K	9420 K	9750 K
Autocatalytic	8 hour	8600 K	9000 K	9340 K
Autocatalytic	24 hour	8250 K	8650 K	9000 K

Table 3 - Effect of change in E/R on time for reaction (Highlighted values base case)

Specific Heat Capacity and Heat of Reaction - The effect of using an inaccurate specific heat capacity within the simulation models was determined. For the baseline cases a specific heat capacity of 2 kJ/kgK was used, but in the sensitivity analysis specific heat capacities of $\pm 20\%$ from this value were used for each of the baseline cases. The value of specific heat capacities compared were therefore 1.6, 2.0 and 2.4 kJ/kgK. Over 100°C the heat capacity of a typical organic substance can change by 20% without a change in composition. The results showed that for nth order and autocatalytic reactions a change in the specific heat capacity changed the time predicted for the reaction, but not too such as a large extent as a change in the kinetic constants. Using 2 hour baseline kinetics and specific heat capacities of $2 \pm 20\%$ kJ/kgK the time predicted for the reaction varied between 1.5 and 2.5 hours, similarly using 8 hour baseline kinetics the time predicted for the reaction varied between 6 and 10 hours and for 24 hour baseline kinetics it varied between 18 and 30 hours. The greatest effect of the value of the specific heat capacity used

was seen to be upon the adiabatic temperature rise for the reaction. When the specific heat capacity was 1.6 kJ/kgK the adiabatic temperature rise was calculated as 179°C, for a specific heat capacity of 2.0 kJ/kgK it was 143°C and for a specific heat capacity of 2.4 kJ/kgK it was 119°C. A change in the specific heat capacity of $2\pm 20\%$ can cause therefore a 60°C difference in the value of the adiabatic temperature rise predicted by the model. Therefore an accurate value of the specific heat capacity is required for use within the model.

	Specific Heat Capacity			Heat of Reaction		
	1.6kJ/kgK	2.0kJ/kgK	2.4kJ/kgK	230kJ/kg	286kJ/kg	343kJ/kg
ΔT_{ad}	179°C	143°C	119°C	172°C	143°C	114°C

Table 4 - Prediction of the adiabatic temperature rise with variation in c_p and ΔH_R

A similar investigation was conducted into the value of the heat of reaction used, where the heat of reaction was varied in a range of $\pm 20\%$ from the baseline value. The effect was seen to be similar to that of varying the specific heat capacity, both on the time predicted for the reaction and also the adiabatic temperature rise. Therefore an accurate value of the heat of reaction is also important in obtaining accurate predictions from a simulation model, but the difference in time for the reaction is not significant in terms of time available to react to a runaway situation.

Start Temperature - Simulation models are often used to predict the effect a change in start temperature will have upon the time predicted for the reaction, therefore this was considered within the sensitivity analysis. The start temperature in the baseline cases was 25°C and this was varied by $\pm 10\%$ to 22.5°C and 27.5°C. Evidently such a change in start temperature will not alter significantly the adiabatic temperature rise predicted, however may alter the time predicted for the reaction. The time predicted for the reaction was affected by the start temperature, but again not to the same extent as a change in the kinetic constants. For both nth order and autocatalytic reactions, using 2 hour baseline kinetics the time for the reaction was predicted between 1.6 and 2.6 hours, for 8 hour kinetics the variation was between 6 and 10 hours and for 24 hour baseline kinetics the variation was between 19 and 31 hours. Therefore again the start temperature for the reaction can affect the time available to react to the consequences of a runaway reaction, but the most significant factors have been shown to be the \ln of the pre-exponential factor and the value of E/R .

Vent Sizing

Evidently changes in physical parameters used within the simulation model will affect not only the time to maximum rate and the adiabatic temperature rise, but also the self heat rate at the set pressure of the relief device. Therefore it was decided to investigate the change in self-heat rate with change in physical data to determine whether the vent size chosen is still adequate despite changes or inaccuracies in the physical data input into the model. Within this investigation it is assumed vent sizes are available in standard pipe diameters and that the size of the reactor being investigated is 10m³. As pressure is not included within the models developed the self-heat rate was determined by choosing a relief temperature of 60°C. In order to demonstrate the effect in practical terms rather than just in dT/dt the formula given by Fauske (2),

$$\frac{A_v}{m_o} = 1.5 \times 10^{-3} \frac{(dT/dt)_s}{p_s} \quad (11)$$

where m_o is the mass of reactant in kg, p_s the set pressure in psia, A_v the vent area in m^2 and $(dT/dt)_s$ the self heat rate in $^{\circ}C/min$ at the set pressure of the relief device, was used to give an indication of the vent area required.

In the first instance the pre-exponential factor was considered. It was seen for all types of reaction that if the vent diameter is calculated assuming 24 hours time to runaway, the vent diameter would be approximately four times too small (i.e. 1 inch compared with 4 inches) if the pre-exponential factor was such that the time for reaction was only two hours. Again considering the values of E/R the vent sizes are inadequate if the kinetics are such that the time for reaction is shorter than that expected. For example for a 2nd order reaction with the baseline kinetics of a 2 hour reaction, the vent diameter required when the time for reaction is 24 hours is one half of that required when the time for reaction is in fact two hours, i.e. for a two hour reaction the vent diameter would be 2 inches compared with 4 inches if the time for reaction was 24 hours.

The change in self-heat rate at $60^{\circ}C$ with change in specific heat capacity, heat of reaction and start temperature was considered under exactly the same conditions as those described in the section about time to runaway i.e with a variation of $\pm 10\%$ or $\pm 20\%$. The change in self-heat rate for the conditions investigated was not seen to be large enough that the vent diameter calculated based on one set of conditions would be different owing to small variations or inaccuracies in the specific heat capacity ($\pm 20\%$), start temperature ($\pm 10\%$) or heat of reaction ($\pm 20\%$). Therefore this investigation has shown that accurate values of the ln of the pre-exponential factor and E/R for a reaction are required for calculation of a sufficient vent diameter to relieve the runaway reaction. If the vent size is based upon inaccurate kinetics it is possible that the diameter of vent chosen could be much too small.

DISCUSSION AND CONCLUSIONS

The paper has described how two computational models have been developed to describe the behaviour of runaway reactions. The physical data required for the model are obtained from experiment and it was shown that having calculated the kinetics it is necessary to check them by comparing the simulated data using these kinetics with the experimental data measured. It was also shown that to ensure that the proposed mechanism for the reaction, and therefore the kinetics, are correct it is necessary to conduct more than one experiment using different starting temperatures for a particular reaction. The kinetics obtained from the first experiment should then be used in a simulation model and the predictions of the simulation model should then be checked against the experimental data obtained from the second experiment. If the behaviour of the second experiment cannot be accurately predicted from the kinetics from the first reaction, further investigation is required into the mechanism of the reaction.

Three methods of correcting experimental data for phi were compared - the method usually used industrially, the Fisher method and the Huff method. Whilst the Huff method was seen to be the most accurate the difference in data between the methods was so small that it is acceptable to use the commonly used method as it is simpler to use compared with the Huff method.

Finally the sensitivity of the predictions of simulation models to the physical data input was investigated. From the parameters investigated - pre-exponential factor, E/R, heat of reaction, specific heat capacity and start temperature - it was shown that a 15% change in the ln of the pre-exponential factor was sufficient to cause a significant change in the time predicted for the reaction, when all other variables remained constant. If the value of E/R was altered by 10% with all other values constant, the time predicted for the reaction would also change significantly. Individually changes in the pre-exponential factor or E/R are sufficient to cause a significant change in the time predicted for the reaction. However when the kinetics calculated from the different experiments are used in the simulation models to predict the time for reaction the difference in predicted time for reaction using the different kinetics was not significant (20 minutes difference for the example studied). Therefore when the value of the ln of the pre-exponential factor and the value of E/R are calculated simultaneously, the constants obtained should predict the behaviour of the reaction to a sufficiently accurate extent. In any case the constants obtained should be placed in a simulation model and checked to show they reproduce the experimental data. However, from the data obtained so far, it was shown that as the value of the ln of the pre-exponential factor obtained from an experiment changes so too does the value of E/R and the two changes compensate for each other such that the difference in the predictions of the model using the different kinetics is not significant. Whilst it is very important to obtain kinetics as accurately as possible, the reaction studied in this research has shown that the differences in the time predicted for the reaction using kinetics obtained from different experiments, when the mechanism for the reaction is correct, are not sufficient to affect the decision as to whether a reaction is safe to operate or not.

LITERATURE

- (1) Ennis, T., Dynamic Simulation of Batch Reactors Using Spreadsheets (Private Communication)
- (2) Fauske, H.K., Generalized Vent Sizing Nomograph for Runaway Chemical Reactions, *Int/Operations Prog.*, 3(4), 213, October 1984b
- (3) Fisher et al, Emergency Relief System Design using DIERS Technology, *A.I.Chem.E.*, 1992
- (4) Huff, J.E., Emergency Venting Requirements, *Plant/Operations Progress*, 1(4), 211, October 1992
- (5) Ingham, J., Dunn, I.J., Heinzle, E., Prenosil, J.E., *Chemical Engineering Dynamics, Modelling with PC Simulation*, VCH GmbH, 1994
- (6) Singh, J., PHI-TEC - Enhanced vent sizing calorimeter application and comparison with existing devices, *International Symposium on Runaway Reactions*, March 7-9, 313, 1989
- (7) Stoessel, F., A Systematic Approach of the Assessment of Thermal Safety of Chemical Processes, *Chemical Engineering Progress*, 4, 1993.
- (8) Townsend, D.I., Tou, J.C., Thermal Hazard Evaluation by an accelerating rate calorimeter, *Thermochimica acta*, 37, 1-30, 1980
- (9) Wright, T.K., Rogers, R.L., Adiabatic Dewar Calorimeter, *I.Chem.E Symp. Series*, No 97, 121-132, 1986

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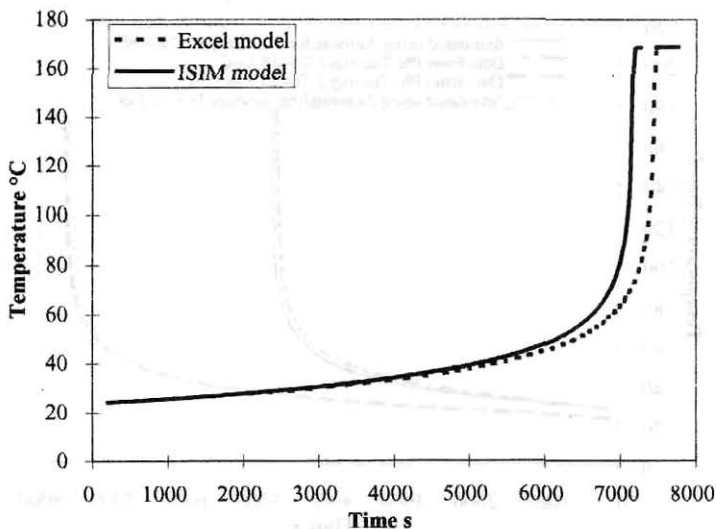


Figure 1 - A Comparison between the ISIM and Excel Models

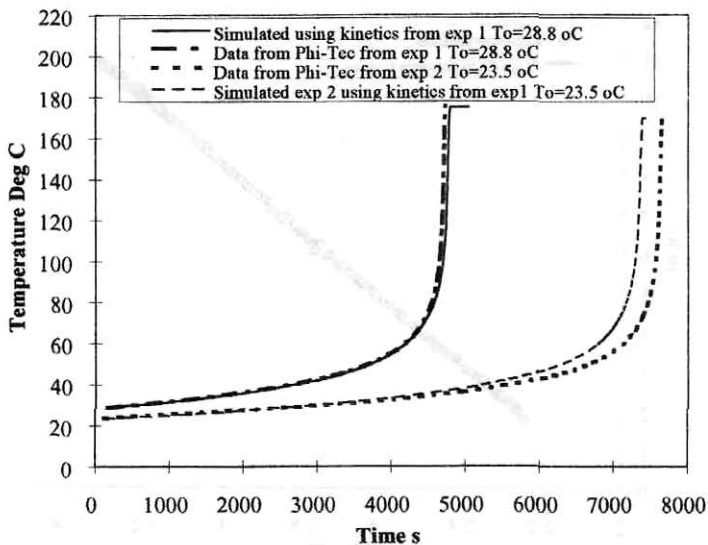


Figure 2 - Simulation of the Methanol/Acetic Anhydride reaction assuming first order kinetics

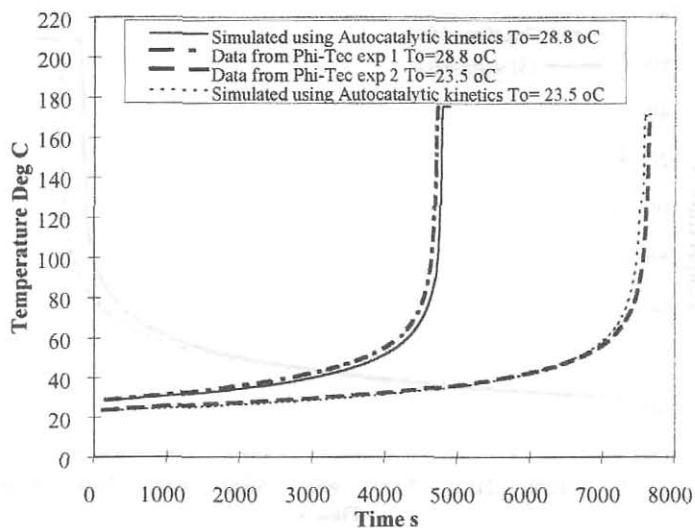


Figure 3 - Methano/Acetic Anhydride reaction assuming autocatalytic kinetics

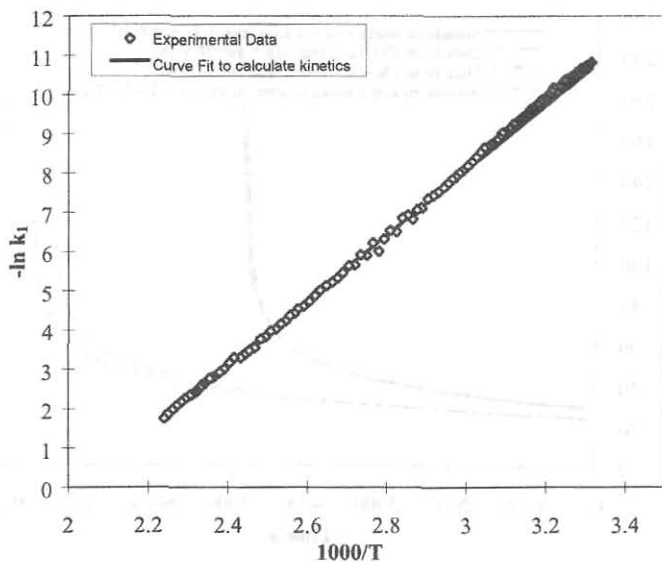


Figure 4 - Kinetics calculated using every data point

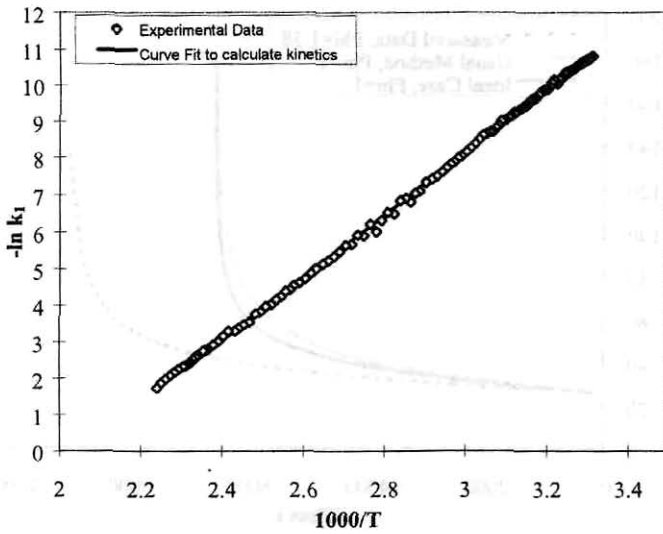


Figure 5 - Kinetics calculated using 10 fewer data points

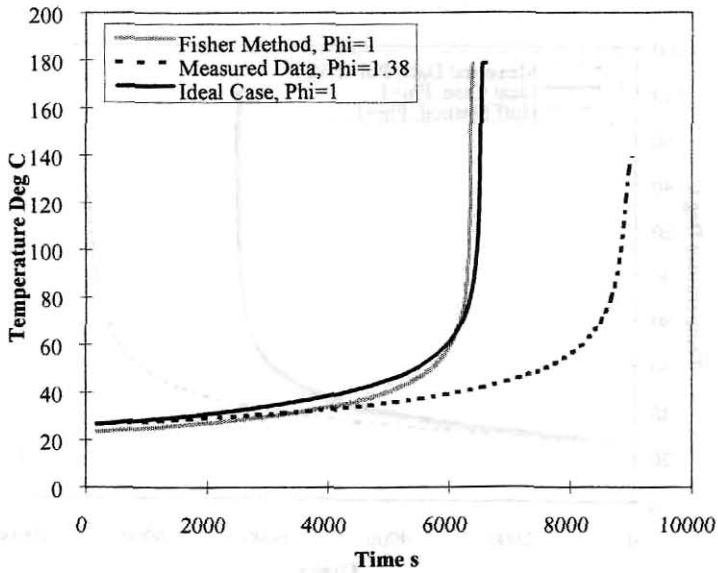


Figure 6 - Fisher Method

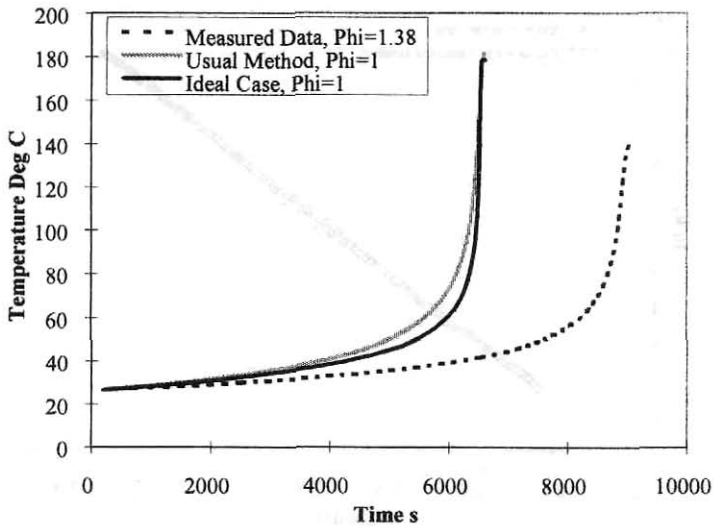


Figure 7 - Usual Method

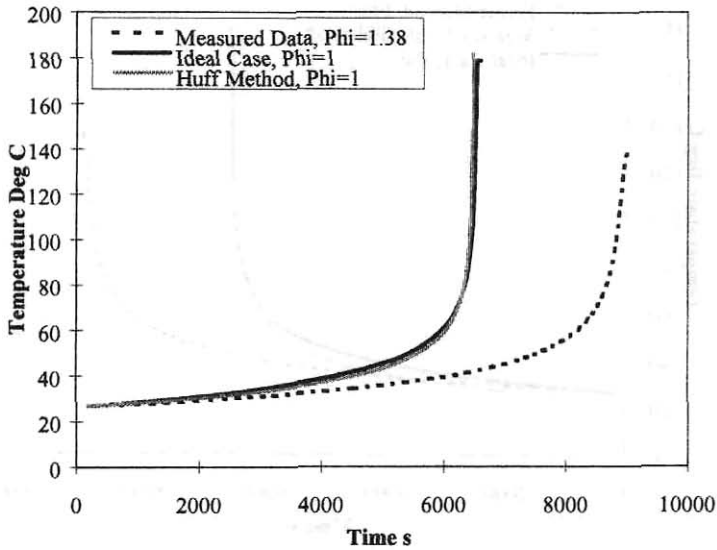


Figure 8 - Huff Method