

# LABORATORY SCALE INVESTIGATION OF RUNAWAY REACTION VENTING ©

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A simple esterification reaction was used to investigate runaway reaction venting phenomena in a laboratory scale reactor. The reactivity of the mixture was varied by adding small quantities of sulphuric acid as a catalyst, and the influence of initial temperature, relief set pressure and vent line diameter on the performance of the pressure relief system was explored. The experimental results are related to calorimetric data and the influence of reaction kinetics on the temperature and pressure records is discussed. Evidence for non-equilibrium conditions in the reactor is presented.

**Key Words:** venting; runaway; two-phase flow; calorimetry; reaction kinetics; pressure relief.

## Introduction

Chemical systems where there is a potential hazard due to runaway exothermic reaction are classified as tempered or non-tempered depending upon the vapour pressure of the reagents and products. A tempered system has a relatively high vapour pressure such that the heat generated by exothermic reaction can be removed as the latent heat of vaporisation required to generate the vapour which passes through the emergency pressure relief system (ERS). If the relief system has been designed correctly, the temperature remains approximately constant and only small overpressures are generated after the operation of the relief device. Low vapour pressure systems, or systems with permanent gasses as reaction products, exhibit little tempering. The ERS for a "gassy" system must be designed to cope with the very rapid rates of heat and gas generation encountered as the temperature rises to a maximum. Fortunately, many processes involve organic chemicals with relatively high vapour pressures such that a runaway reaction can be tempered by the operation of the ERS. Laboratory scale studies of these so called "vapour pressure" systems are reported in this paper.

ERS design for chemical reactors has been the subject of many recent experimental and theoretical investigations<sup>1</sup>. Several calculation methods have been developed for determining the vent line diameter and relief set pressure<sup>1,2</sup>. Earlier methods assumed vapour alone passed down the relief line but more recent treatments adopt the more realistic assumption of a two phase discharge which places more stringent requirements on the ERS<sup>3,4</sup>. Complex fluid mechanics are associated with the relief process and models have been developed to describe the main two phase flow regimes namely bubbly, churn turbulent and slug flow<sup>2</sup>.

The influence of chemical kinetics on reaction venting has received less attention. The rate of heat generation is dependent on temperature and chemical composition. Some of the calculation methods assume that these complex dependencies can be represented by the rate of temperature rise at the relief set pressure. More sophisticated methods include an apparent activation energy

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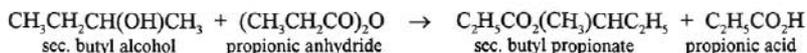
to represent the temperature dependence of the rate of heat generation but fail to take account of the effect of concentration changes. Reactant consumption will normally mitigate the increased rate of heat generation caused by the increase in temperature. This effect becomes important towards the end of the reaction and depends upon the reaction order. Complex reaction mechanisms or autocatalysis can result in an increase in rate at relatively low conversion. Concentration dependencies can therefore place reduced or increased demand on the ERS, depending on the reaction mechanism.

Experimental data are presented in this paper which demonstrate how isothermal chemical kinetics can influence the venting process. Some of the limitations of small scale experiments in reaction venting studies are identified. The experiments provide a qualitative understanding of venting phenomena and can be used to specify larger scale experiments which are more representative of industrial practice.

Process Hazards Section of HSE's Explosion and Flame Laboratory is currently undertaking a programme of research to assess the reliability of current methods for designing emergency pressure relief systems for chemical reactors. The programme will include pilot scale experiments on runaway reaction venting. The laboratory scale results reported here provide a basis for designing the pilot scale experiments.

### Reaction System

The esterification reaction between butanol (sec. butyl alcohol) and propionic anhydride was chosen as an example of a vapour pressure system.



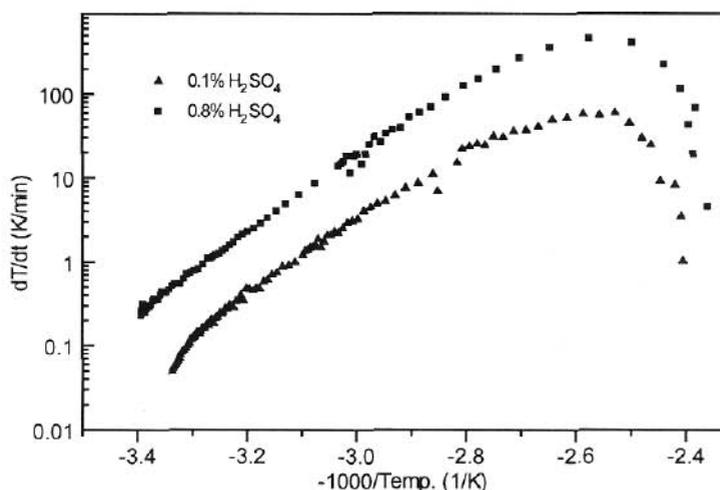
This reaction is moderately exothermic and leads to substantial vapour pressures when reaction is initiated at temperatures between room temperature and the boiling point of the reagents. The rate of reaction can be increased by the addition of small quantities of sulphuric acid as a catalyst. A range of rates of pressure rise can be obtained by varying the initial temperature or the sulphuric acid concentration without affecting the heat of reaction. Results are reported here for equimolar mixtures of anhydride and alcohol containing 0.1 and 0.8% sulphuric acid (expressed as a percentage of the weight of butanol). Equimolar mixtures would be expected to react to completion, compared with a 1:2 anhydride:alcohol molar ratio which would produce an equilibrium mixture.

### Adiabatic Calorimetry

#### *Experimental procedure*

The rate of reaction under adiabatic conditions was measured using the PHI-TEC calorimeter<sup>5</sup>. This instrument is similar to the Accelerating Rate Calorimeter<sup>6</sup> and the Vent Sizing Package<sup>3</sup>. The sample is held in a stainless steel container provided with a magnetic stirrer and with thin walls in order that the experimental results are not strongly influenced by the heat capacity of the container. Adiabatic conditions are maintained by using electrical heaters to match the temperature of the surroundings to that of the sample. A separate heater is

used to raise the temperature of the sample to the selected initial temperature and then adiabatic conditions are maintained as the temperature and pressure increase due to exothermic reaction of the sample. The sample container and electrical heaters are housed within a pressure vessel, and rupture of the thin walled sample container is prevented by automatically applying nitrogen pressure to the outside of the container to compensate for the internal pressure generated due to exothermic reaction. Reagents were added with the sample container positioned inside the calorimeter. The total sample mass was approximately 60g.



**Figure 1** PHI-TEC plots of the rates of self heating for the esterification reaction catalysed by 0.1% and 0.8% sulphuric acid.

#### Calorimetric results

Figure 1 shows plots of  $\log(\text{self-heat rate})$  against reciprocal temperature obtained using the PHI-TEC calorimeter for reaction mixtures containing 0.1 and 0.8%  $\text{H}_2\text{SO}_4$ . The effect of  $\text{H}_2\text{SO}_4$  concentration on the reaction rate is evident from the higher rates of self heating observed for the mixture containing 0.8%  $\text{H}_2\text{SO}_4$ . The catalyst concentration also affects the form of the isothermal dependence of rate on concentration such that higher sulphuric acid concentrations lead to a pronounced autocatalytic effect which can be seen from the results of reaction calorimetry reported elsewhere<sup>7</sup>. Isothermal reaction calorimetry on the uncatalysed composition showed a maximum rate of heat generation at the start of reaction, but in the presence of 0.8%  $\text{H}_2\text{SO}_4$ , the maximum occurred at approximately half conversion. Autocatalysis is not evident from the PHI-TEC data presented here because, under adiabatic conditions, particularly at low conversion, changes in self-heat rate are dominated by the exponential temperature dependence of the rate of reaction. Figure 1 indicates that catalyst concentration has no significant influence on the adiabatic temperature rise which is consistent with the expectation that addition of catalyst does not affect the heat of reaction.

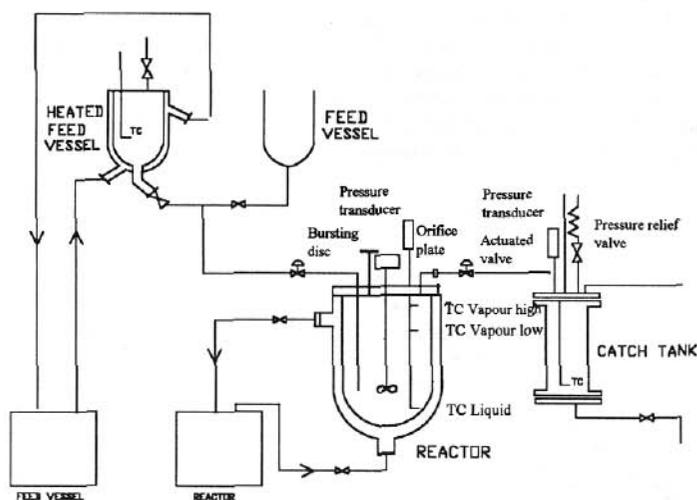


Figure 2 Schematic diagram of laboratory scale reactor system.

## Laboratory scale experiments

### Experimental procedure

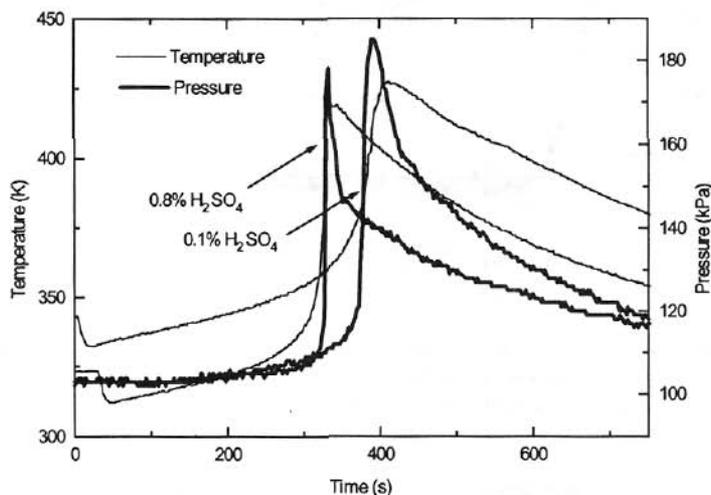
Laboratory scale venting experiments were performed using 1.6 dm<sup>3</sup> jacketed glass reactor with a maximum working pressure of 1200 kPa. The reactor system is shown schematically in Figure 2. The reactor is equipped with two feed vessel one of which is jacketed so that reagents can be preheated. Two independent thermostatic baths are used to circulate hot water through the jackets on the reactor and the heated feed vessel. The reactor is connected via a 10 mm diameter vent line to an 7 dm<sup>3</sup> capacity PTFE-lined catch tank. Remotely actuated valves have been installed in the pipework connecting the various vessels. Orifice plates of varying diameter can be installed in the reactor vent line to constrict the flow to the catch tank.

The reactor system is fully instrumented with temperature and pressure transducers connected to a computer data acquisition system with a sampling interval of 1 s. Some of the transducers are also connected to a high speed data logger with a sampling interval of 0.1 s so that rapid changes in temperature and pressure during exothermic runaway and venting can be accurately monitored.

Two fine thermocouples (0.5 mm diameter) are installed in the vapour space of the reactor at points 20 mm and 60 mm below the lid. Sharp temperature changes are recorded by these thermocouples when bubbles form in the reacting liquid causing the level to rise and fill the vapour space.

Acidified butanol was first charged to the reactor and an equimolar quantity of propionic anhydride was placed in the heated feed vessel. The temperatures of the reactor and feed vessel jackets were adjusted to give the desired initial conditions and time was allowed for the vessel

contents to reach thermal equilibrium. The propionic anhydride was then charged to the reactor and the valves in the feed line and vent line were closed. The valve in the vent line was set to open at a predetermined pressure by using the data acquisition system to trigger a relay. Initially, closed system tests were performed where a high relief set pressure was chosen so that the reaction could proceed to completion without venting. These initial experiments were followed by a series of tests over a range of initial temperatures, catalyst concentrations, relief set pressures and orifice diameters. Video tape recordings were made of each experiment.

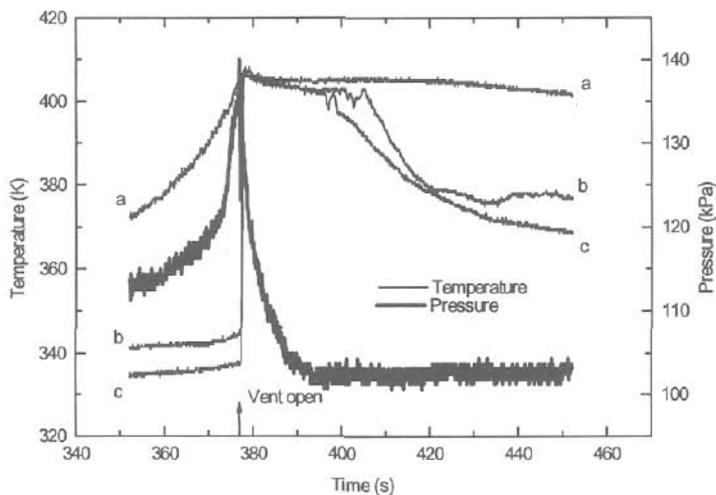


**Figure 3** Temperature and pressure records during the runaway esterification reaction in an unvented reactor.

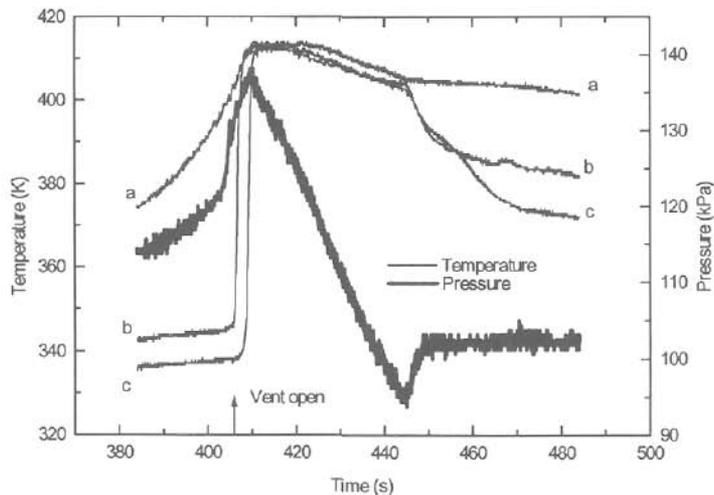
#### Laboratory Reactor Results

*Closed system tests.* Figure 3 shows the temperature and pressure records for reaction mixtures containing .1% and 0.8 %  $\text{H}_2\text{SO}_4$  with initial temperatures of 323 K and 343 K respectively. In both cases, the rate of heat generation exceeds the rate at which heat can be lost to the reactor jacket (and the cooler surfaces at the top of the reactor) and a runaway exothermic reaction occurs reaching a maximum temperature approximately 5 minutes after mixing. The initial drop in temperature is due to endothermic mixing of reagents. Induction times and maximum temperatures and pressures are similar for both compositions because a lower initial temperature was selected for the more reactive mixture (0.8%  $\text{H}_2\text{SO}_4$ ). It is clear from the PHI-TEC data that at the temperature maxima shown in Figure 3 reaction rates are very high for both compositions such that complete conversion and maximum temperature are virtually simultaneous. The pressure maxima occur before the temperature maxima due to the relatively high vapour pressure of the butanol which is rapidly consumed as the maximum temperature is approached.

*Venting tests.* Figures 4 and 5 show the temperature and pressure records when reactions catalysed by 0.1%  $\text{H}_2\text{SO}_4$  were initiated at 343 K with a relief set pressure of 130 kPa with restricting orifices in the vent line of 5.5 and 1 mm respectively. Figure 4 shows that the larger



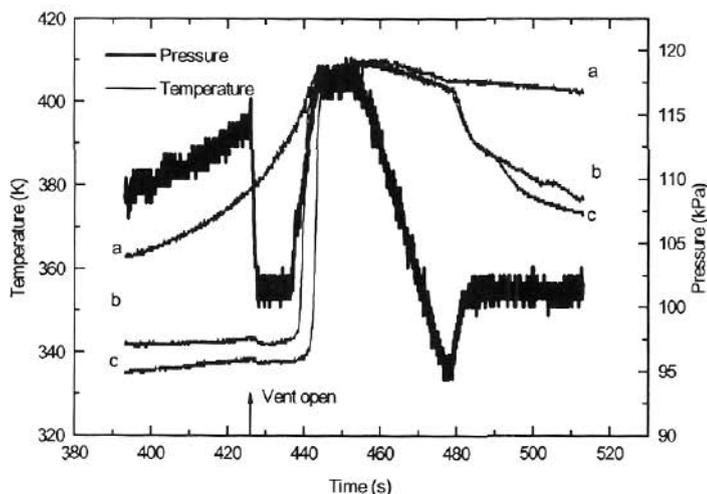
**Figure 4** Temperature and pressure records during runaway esterification reaction catalysed by 0.1% H<sub>2</sub>SO<sub>4</sub> with a relief set pressure of 130 kPa and a vent line diameter of 5.5mm. a: liquid temperature b: vapour temperature (low) c: vapour temperature (high)



**Figure 5** Temperature and pressure records during runaway esterification reaction catalysed by 0.1% H<sub>2</sub>SO<sub>4</sub> with a relief set pressure of 130 kPa and a vent line diameter of 1 mm. a: liquid temperature b: vapour temperature (low) c: vapour temperature (high)

orifice leads to a rapid decline in pressure when the vent line is opened. The reaction is effectively tempered, with the liquid temperature remaining approximately constant during venting. It was clear from the video record that there was a two-phase discharge from the reactor. This is confirmed by the vapour space temperature records which show sharp discontinuities as the liquid level in the reactor rises due to bubble formation. These discontinuities are virtually simultaneous indicating a very rapid rate of level swell.

The 1 mm restricting orifice leads to a more gradual decline in pressure when the vent line is opened at the relief set pressure (Figure 5). Pressures in excess of the relief set pressure are recorded. A two phase discharge occurs but the time difference between the discontinuities in the two vapour space temperature records indicates that the rate of level swell was less rapid with the smaller orifice diameter.



**Figure 6** Temperature and pressure records during runaway esterification reaction catalysed by 0.1% H<sub>2</sub>SO<sub>4</sub> with a relief set pressure of 115 kPa and a vent line diameter of 1 mm. a: liquid temperature b: vapour temperature (low) c: vapour temperature (high)

Figure 6 shows the results for the 1 mm restricting orifice where the reaction is vented early in the course of the runaway, at a relief set pressure of 115 kPa. Initially a vapour only discharge occurs which has little influence on the rate of temperature rise in the liquid. This is followed by a two-phase discharge which tempers the reaction. This tempering is partly associated with increased heat losses as the swelling liquid comes into thermal contact with the cooler surfaces at the top of the reactor.

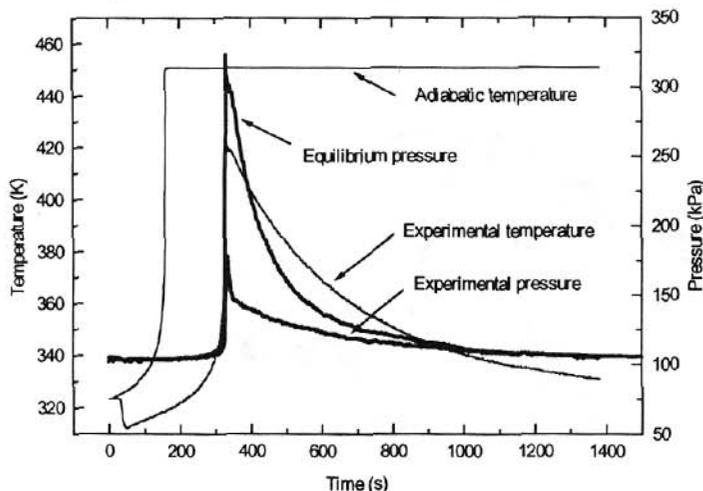
## Discussion

Direct comparison of the PHI-TEC data with the closed system reactor experiments is not possible because of the differences in the conditions of heat transfer and the temperature at which the reaction is initiated. The influence of the initial temperature on the PHI-TEC data can

be quantified by first assuming particular forms for the dependence of reaction rate on temperature and concentration. The following rate equation was used to predict the variation of rate of conversion with temperature and concentration.

$$\frac{dx}{dt} = (1-x)^2 \left( \frac{x}{B-\sqrt{x}} + C \right) A \exp\left(\frac{-E}{RT}\right) \quad (1)$$

Isothermal and adiabatic calorimetric data which form the basis of Equation (1), and the procedure for determining A, B, C and E, are reported elsewhere<sup>8</sup>.

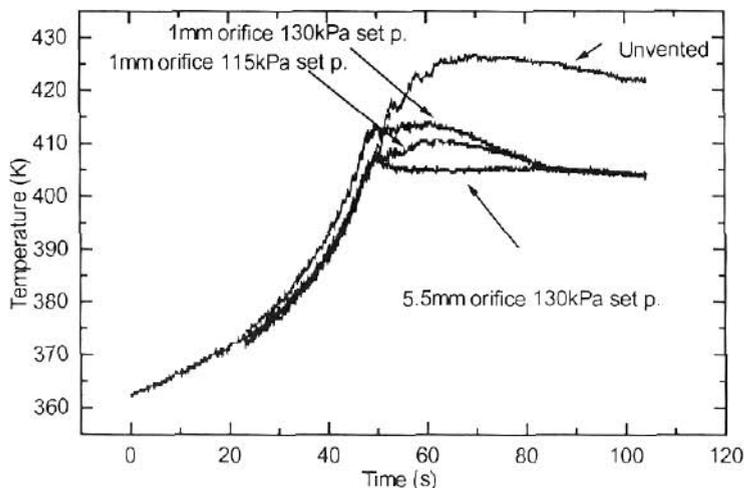


**Figure 7** Comparison of experimental temperature and pressure records for closed system runaway esterification reaction of the mixture containing 0.8%  $\text{H}_2\text{SO}_4$  with theoretical predictions.

The temperature-time profile for the esterification reaction proceeding under adiabatic conditions from a particular starting temperature can be predicted by numerical integration of Equation (1). Such a prediction is shown in *Figure 7* for the reaction mixture containing 0.8%  $\text{H}_2\text{SO}_4$  with an initial temperature of 323 K. The experimental temperature time history in the 1.6 dm<sup>3</sup> reactor is shown for comparison. Conditions in a jacketed reactor are clearly not adiabatic but, as the reaction accelerates during runaway, rates of heat loss are low compared to the rate of heat generation. *Figure 7* indicates that approximately 20% of the total heat of reaction is lost to the jacket during the period up to the maximum temperature. The induction time in the jacketed reactor is significantly longer than the adiabatic induction time because Equation (1) does not predict cooling due to endothermic mixing of reagents. Otherwise, the temperature time history is broadly consistent with Equation (1). A more detailed simulation of the temperature evolutions including the effect of endothermic mixing and a rigorous treatment of the heat transfer characteristics of the reactor produces good agreement with the experimental curves<sup>8</sup>. Failure to include the correct form of concentration dependence in the

rate equation leads to simulated temperature-time curves which are inconsistent with the experimental data <sup>8</sup>.

Changes in composition are proportional to the change in temperature under adiabatic conditions (assuming that the heat capacity of the reacting mixture remains constant). If an exothermic reaction proceeds rapidly to runaway under conditions which are close to adiabatic, temperature changes are approximately proportional to changes in reactant conversion ( $x$ ). This means that the composition of the reacting mixture can be estimated from the change in temperature. The corresponding vapour pressure can be calculated using Raoult's law, and assuming that the vapour pressure of each component follows the Clapeyron equation. Values for the constants in the Clapeyron equation can be obtained from published data <sup>9</sup>. The pressure time dependence, predicted on the basis of the above assumptions, is shown in *Figure 7*, along with the experimental data. The experimental pressures are substantially less than the predicted pressures. This difference is partially attributable to non-adiabatic conditions due to the temperature difference between the reacting liquid and the jacket. However, the discrepancy is largely due to condensation on the cooler surfaces at the top of the reactor which prevents the equilibrium vapour pressures being achieved. Further evidence for non-equilibrium conditions can be seen from the experimentally recorded vapour temperatures which are substantially less than the corresponding liquid temperatures.



**Figure 8** Temperature variations during venting of runaway reaction of mixtures catalysed by 0.1% H<sub>2</sub>SO<sub>4</sub> with various set pressures and orifice diameters.

Some of the implications of non-equilibrium conditions with respect to interpretation of the laboratory scale experiments can be seen from the temperature records, shown in *Figure 8*, for a series experiments under identical conditions apart from the relief set pressure and orifice diameter. *Figure 8* shows that a 5.5 mm orifice diameter and a relief set pressure of 130 kPa leads to effective tempering of the reaction, as can be seen from the temperature and the

pressure records. The results for the experiments using a 1 mm diameter orifice plate all show a constant or reducing pressure after the onset of two-phase venting (as detected by the thermocouple at the high point in the vapour space) suggesting that the reaction has been tempered. The temperature records, however, show an increase after the onset of two phase flow indicating an untempered reaction. In a larger vessel where conditions are closer to adiabatic due to the reduction in surface to volume ratio, the temperature increases would lead to substantial overpressures. Significant scale effects can also be expected associated with the flow characteristics of the vent line, particularly when the limiting orifice diameter is smaller than the bubble diameter.

The temperature records for the experiments using a 1 mm diameter orifice plate (*Figures 5 and 6*) indicate that the increase in temperature which occurs after the onset of two phase venting is relatively small when the highest relief set pressure is selected (130 kPa). This is consistent with autocatalysis predicted by Equation (1). Autocatalysis implies that at relatively low conversion, and correspondingly low temperatures and pressures, increases in conversion and temperature both result in an increase in rate. At high conversion, the decline in autocatalysis causes the rate to subside more rapidly than would occur with normal reaction kinetics.

## Conclusion

The laboratory-scale experiments have provided a qualitative appreciation of many the important features of runaway reaction venting. Chemical kinetics have been shown to have an important influence on the temperature and pressure evolutions. Quantitative interpretation of the results and extrapolation to large vessel sizes is difficult because of non-equilibrium conditions in the reactor and the complex influence of small vent line diameters on the two phase flow regime. Pilot scale experiments which should allow more quantitative interpretation and extrapolation are planned for the future <sup>10</sup>.

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**Nomenclature**

A	Pre-exponential factor (1/s)
E	Activation energy (kJ/mol)
B,C	Constants in rate equation.
R	Universal gas constant (kJ/mol/K)
t	time (s)
x	Conversion (for equimolar mixtures $x = 1 - \text{molar concentration}/\text{initial concentration}$ )

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