PILOT-SCALE EVALUATION OF THE INHIBITION OF EXOTHERMIC RUNAWAY

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INTRODUCTION

Installations and operating procedures used for exothermic processes should be designed to minimise the possibility of a runaway reaction. This can be done, for example, by providing high integrity systems for controlling and monitoring the process and ensuring that the heat transfer characteristics of the heating and cooling system are sufficient to prevent temperature excursions which may lead to a runaway. In most cases it is not possible to completely eliminate the risk of a runaway reaction and the reactor will be provided with an emergency pressure relief system (ERS) in order to prevent catastrophic failure[1]. However, currently recommended ERS design methodology[2] has not been fully validated on industrial scale and problems arise in calculating the two phase flow capacity in the vent line and in predicting level swell and the flow regime in the reactor. High viscosity systems that may be found in the polymer industry can also present particular difficulties[3]. Additionally, even if the ERS successfully protects the reactor, there may be a significant release of toxic or flammable material to the atmosphere. For these and other reasons, mitigation techniques such as reaction inhibition are being considered as an alternative or in addition to the ERS.

Only limited guidance is currently available on the design of a reaction inhibition system (RIS)[4]. Companies use small-scale experimental data and theoretical considerations to design an RIS which is installed without the opportunity to test reliability against a full-scale runaway reaction. In the present study, RIS design methodology was evaluated using a facility specially designed for investigating runaway reactions on a scale which is reasonably representative of industrial installations. 340 litre pilot-scale trials were supported by 1 litre laboratory-scale runaway reaction experiments and adiabatic calorimetry.

The main difficulties in the design of an inhibition system arise in applying scale-up criteria to predict the rate of dispersion of inhibitor in the full size reactor using small-scale experimental data. The feasibility of using computational fluid dynamics to predict the effect of scale on the degree of mixing was investigated as part of this project and the results are reported separately[5]. This paper examines the simplified methods for selecting the conditions for reaction inhibition and back-up methods such pressure relief.

Laboratory-scale experimental data are used to illustrate scale-up procedures and predictions are compared with the pilot-scale runaway reaction experiments.

The polymerisation of styrene, initiated by 1%w/w benzoyl peroxide, was chosen for this investigation. The reaction can be inhibited by the addition of tertiary butyl catechol. This system has been studied extensively with detailed investigation of the reaction kinetics and the chemical mechanisms of polymerisation and inhibition[6]. Strictly speaking, the action of tertiary butyl catechol on the free radical polymerisation is a retardation effect. In the present investigation, the validity of general design principles and simplified interpretation of calorimetric data is examined without reference to the detailed chemistry. Temperature and pressure records from the laboratory and pilot scale experiments are used to establish the conditions under which the inhibition system may fail to stop the runaway.

ADIABATIC CALORIMETRY

A Phi-Tec calorimeter[7] was used to determine temperature and pressure variations as the polymerisation proceeds under adiabatic conditions. The instrument was charged with styrene and initiator and operated in heat-wait-search mode until exothermic polymerisation was detected at 77°C. Adiabatic conditions were then maintained and the temperature and pressure were recorded as polymerisation proceeded until a final temperature of 260°C was reached. The logarithm of the rate of temperature rise is plotted against reciprocal temperature in Figure 1. Under adiabatic conditions, the rate of heat production is approximately proportional to the rate of temperature rise. Figure 1 indicates complex

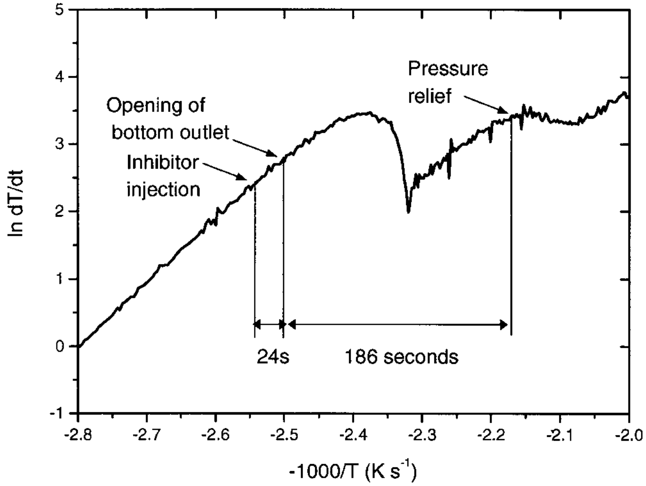

Figure 1. Relationship between self-heat rate, temperature and time intervals between inhibition and back-up measures, derived from adiabatic calorimetric data

variations in the rate of heat production with three separate local maxima in the rate of temperature rise. The relationship between the rates of heat production and the mechanism and kinetics of each stage of the polymerisation has been examined elsewhere[6]. The objective of the adiabatic calorimetry reported here was to establish whether a simplified interpretation of the adiabatic data could be used in the design of the inhibition system and to select conditions for laboratory and pilot-scale runaway reaction experiments.

THERMO-KINETIC EVALUATION

Figure 1 shows an approximately linear relationship between the logarithm of the self-heat rate and reciprocal temperature during the first phase of polymerisation. This suggests that the temperature dependence of the overall rate constant for the early part of the polymerisation follows the Arrhenius equation. Further analysis of the data in Figure 1 indicates a first order relationship between the rate of heat production and the degree of polymerisation in this first phase. The following expression for rate of heat production was found to give reasonably good fit to adiabatic data for the initial stages of the polymerisation.

$$\frac{dT}{dt} = A^{(-E_a/RT)} \cdot (1 - X) \tag{1}$$

Where T is the absolute temperature, t is the time, A is the pre-exponential Arrhenius factor, E_a is the activation energy, R is the universal gas constant and X is conversion.

The course of the polymerisation in a laboratory or pilot-scale reactor is determined by the rate of heat production and by the heat transfer characteristics of the process vessel. In the present investigation, the temperature of the heat transfer fluid at the inlet to the jacketed reactors was held constant during both the laboratory and pilot-scale experiments. Under these conditions, the rate of heat transfer from the reactor contents to the jacket is given by:

$$mC_p\frac{dT}{dt} = US \cdot (T - T_j) \tag{2}$$

where m is the mass of reactor contents, C_p is the heat capacity, U is the overall heat transfer coefficient, S is the heat transfer surface area and T_j is temperature of the reactor jacket.

Combining Equations 1 and 2 gives the following relationship for the rate of temperature raise as a function of conversation.

$$\frac{dT}{dt} = A^{(-E_a/RT)} \cdot (1 - X) \cdot \frac{\Delta H}{C_p} - \left(\frac{US}{mC_p}\right) \cdot (T - T_j) \tag{3}$$

where ΔH is the heat of reaction.

The variation in reactor temperature during the early stages of the polymerisation can be predicted for the laboratory and pilot-scale reactor by numerical integration of

Equation 3 using the appropriate value for the heat transfer coefficient. Estimates of the heat transfer coefficients for the laboratory and pilot-scale vessels were determined by observing the rate of cooling when hot, chemically inert fluids, were charged to the reactors with the jacket temperatures held constant.

Before proceeding with the detailed design of the inhibition system for the pilot-scale facility, the validity of the thermo-kinetic interpretation was investigated using laboratory-scale experiments described in the following section.

LABORATORY-SCALE EXPERIMENTS

Laboratory-scale experiments were designed to achieve the following objectives.

1. Assessment of the validity of the interpretation of the adiabatic data and the simplified assumptions regarding heat transfer.
2. Investigation how the effect of the inhibitor might be influenced by the reactor temperature at which it is injected.
3. Qualitative assessment of the how the rate of agitation influences the efficiency of reaction inhibition.

Laboratory-scale experiments involve only small inventories and can be performed relatively easily. A wide range of conditions can be investigated safely, including experiments where the inhibition system may fail to stop the runaway. The experimental conditions were selected to investigate the influence of key parameters on the performance of the inhibition system. Some experiments were performed at elevated jacket temperatures and with little or no agitation so as to challenge progressively the efficacy of the inhibition system. However, the small-scale data alone cannot provide a direct indication of the reliability of reaction inhibition in industrial scale vessels. Scale-up procedures must be applied, with regard to both heat transfer and mass transfer, including agitation.

The laboratory-scale facility for studying runaway exothermic reactions is shown schematically in Figure 2. The reactor comprises a 1.5 litre jacketed glass vessel with maximum operating pressure and temperature of 12 bara and 200°C, respectively. The reactor is provided with a jacketed feed vessel and is connected via a 12 mm diameter vent line to a 10 litre catch tank. The reactor contents are heated by circulating silicone oil through the reactor jacket from a thermostatic bath, which is also used to preheat reagents in the feed vessel. The system is installed in a blast cell with remote operation so that energetic reactions can be studied safely. Addition of reagents, pressure relief and bottom discharge can be initiated using remotely operated actuated valves. Fine thermocouples are used to monitor the temperature at various levels in the reactor and at the inlet and outlet of the reactor jacket. Pressure transducers are fitted to the reactor and catch tank. The signals from the transducers are connected to a data acquisition system and to controllers which can initiate inhibitor injection and pressure relief at pre-selected temperatures and pressures, respectively. A more detailed description of the facility is available elsewhere[8].

The polymerisation reaction was performed on laboratory-scale by heating styrene in the feed vessel and charging the initiator to a small vessel installed in the feed line to the

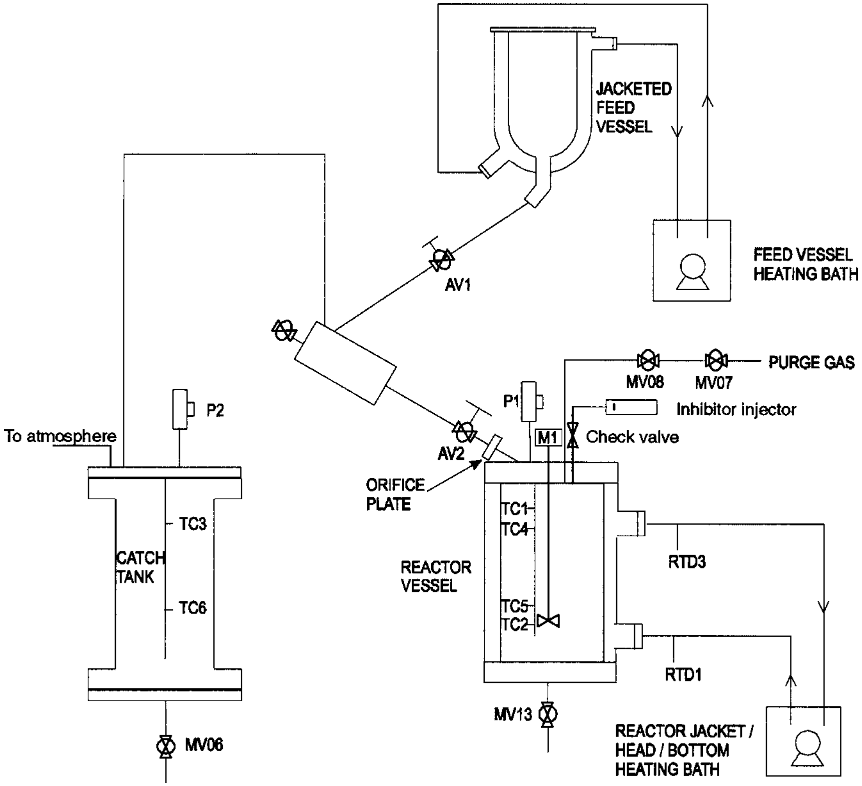

Figure 2. Laboratory-scale facility

reactor. When the styrene had reached the same temperature as the reactor jacket the feed valve was opened and the initiator dissolved in the styrene as it flowed into the reactor. The inhibitor (a solution of tertiary butyl catechol in styrene) was held in a cylinder with a piston, which was actuated automatically when a pre-set inhibition temperature was exceeded.

LABORATORY-SCALE RESULTS

Validity of thermo-kinetic model

The temperatures of the reactor jacket which would produce a runaway were selected by using Equation 3 to predict the temperature-time profiles for the polymerisation in the laboratory-scale reactor. The result of one of these simulations for a jacket temperature with a set point of 120°C and a batch volume of 1 litre is shown in Figure 3 along with

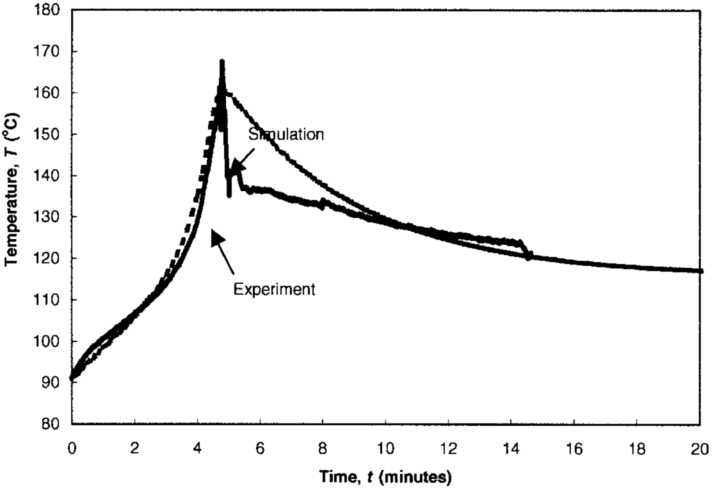

Figure 3. Comparison of simulation prediction with laboratory-scale result

the corresponding experimental data. The jacket temperature actually attained is a few degrees less than the set point due to heat losses in connecting heat transfer fluid piping. A reduction in temperature occurs as the styrene passes through the feed line and is mixed with the cold benzoyl peroxide. The initial temperature used in the simulation shown has been set to correspond to the initial temperature of the reactor contents observed experimentally. There is good agreement between the calculated and experimentally observed temperature profiles for the early stages of the runaway.

Effect of jacket temperature and injection temperature

Laboratory-scale experiments were performed over a range of reactor jacket temperatures (T_j) and inhibition temperatures (T_i). Results from some of these experiments are summarised in Table 1. In all these cases the inhibitor was injected when the temperature of the reactor contents exceeded the jacket temperature by 10°C. An increase in T_j and T_i increased the rate of temperature rise, measured just before the inhibitor was injected. These rates of temperature rise are listed in Table 1 along with the corresponding rates from the adiabatic (Phi-Tec) data at T_i. The rates in the laboratory-scale reactor are similar to those obtained from the adiabatic calorimeter, particularly at the higher values of T_j and T_i. This implies that the rate of heat production at T_i substantially exceeds rate of heat transfer to the jacket giving quasi-adiabatic conditions with the rates of heat production proportional to the rates of temperature rise.

Figures 4 and 5 show the temperature and pressure records from experiments with jacket temperatures of 110°C and 120°C, respectively and with relatively vigorous

Table 1. Laboratory-scale experimental results

Jacket temperature (°C)	Injection temperature (°C)	dT/dt Phi-Tec at T_i (°C min^{-1})	dT/dt pre-injection (°C min^{-1})	dT/dt post-injection (°C min^{-1})	Maximum temperature (°C)	Maximum pressure (bara)	Agitator speed (rpm)
100	110	6	4	decreasing	110.1	1.29	300
110	120	11	10	decreasing	121.2	1.35	300
120	130	20	22	decreasing	133.0	1.39	300
120	130	20	30	29	167.6	2.04 (vented)	300 (off at 126°C)

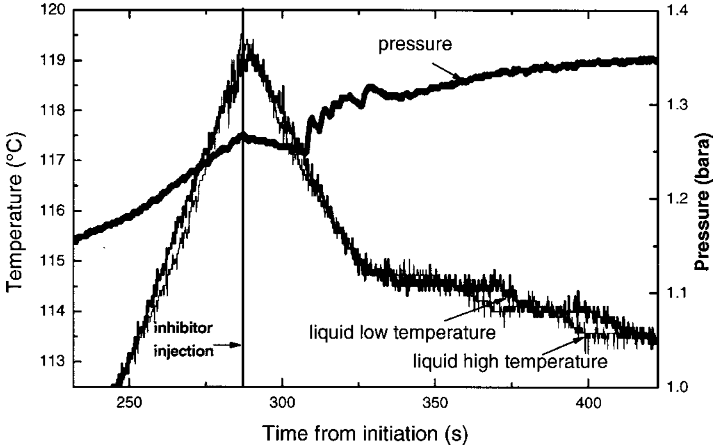

Figure 4. Laboratory-scale polymerisation with inhibition at 120°C: temperature and pressure changes at time of injection. (pressure relief 2 bara, agitator 300 rpm)

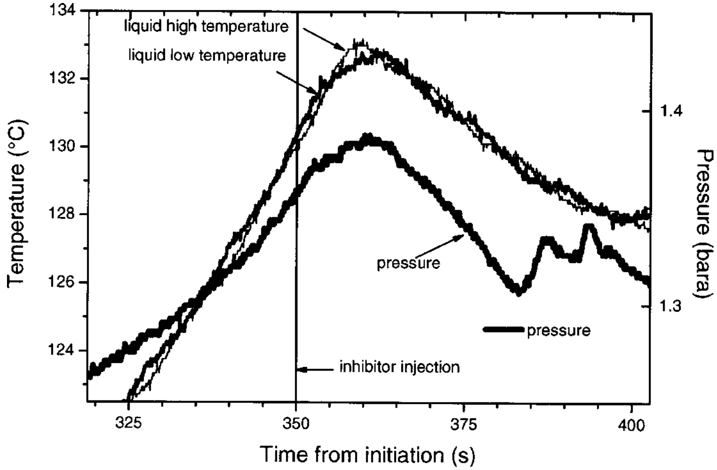

Figure 5. Laboratory-scale polymerisation with inhibition at 130°C: temperature and pressure changes at time of injection. (pressure relief 2 bara, agitator 300 rpm)

agitation at 300 rpm. Just before inhibition, rates of temperature rise are 10 and 22°C/min, respectively. With the lower values of T_j and T_i, Figure 4 shows that inhibitor injection produces an immediate and sustained decline in reactor temperature. With the higher values of T_j and T_i (Figure 5) the increased reaction rate presents a greater challenge to the inhibition system and injection at T_i produces a more gradual reduction in the rate of temperature rise.

Compared with industrial vessels, it is relatively easy to achieve good mixing in laboratory-scale equipment. The experiments shown in Figures 4 and 5 were performed at a high rate of agitation. There are no significant differences in the temperature records from thermocouples near the upper and lower surfaces of the liquid. This implies that, in these experiments, the rate of inhibition is limited not by the agitation rate but by the kinetics of chemical interaction between the inhibitor and the reaction mixture. This conclusion can inform the choice of conditions for reaction inhibition on industrial scale. The inhibition temperature should be less than the temperature at which reduced rates of inhibition are observed in the laboratory. On industrial scale the rate of inhibition may be further diminished due to less efficient mixing. Direct scale-up using dimensionless group to relate the laboratory and pilot-scale results was not feasible because of the lack of geometrical similarity between the two reactors.

Effect of reduced rates of agitation

The main problems in the design of an inhibition system for an industrial-scale vessel arise because of uncertainties in scale-up of mixing. Laboratory-scale experiments were performed to explore the effects of reduced agitation and to determine how inefficient mixing is evident from the temperature variations before and after inhibitor injection.

Figure 6 shows the results of a laboratory-scale experiment under conditions similar to those for the experiment shown in Figure 5 except that the agitator was switched off when the reactor contents had reached a temperature of 126°C. The loss of agitation produced no immediate changes in the rate of changes of temperature in the liquid but there was a decline in the rate of pressure rise. This reduction is attributable to reduction in rate of heat transfer to the vapour space and top flange of the vessel as reduced agitation caused a diminishing vortex in the liquid. The temperature of the vapour space was, generally, significantly below that of the liquid, indicating that vapour-liquid equilibrium had not been achieved, resulting in a reduction in the vapour pressure above the liquid.

The effect of inhibitor injection shown in Figure 6 differs significantly from the results of the two previous experiments, shown in Figures 4 and 5. After injection, there is no reduction in the rate of temperature rise and the temperatures within the liquid begin to diverge. This shows that, with the agitator off, the rate at which the inhibitor is mixed with the reactants is insufficient to stop the runaway. This is consistent with a video record of the experiment which showed the colour change associated with presence of inhibitor confined to the volume immediately around the end of the injection pipe. The continuing increases in temperature caused corresponding increases in pressure which triggered the pressure relief system at 2.0 bara. Pressure relief causes a two-phase discharge from the reactor during which the vapour and liquid temperatures become

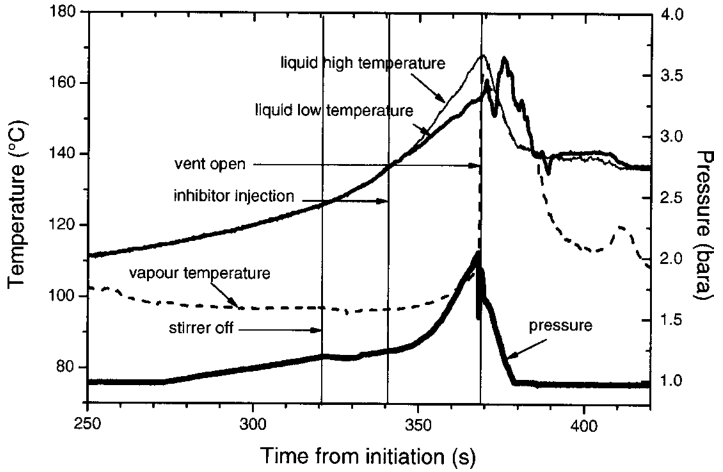

Figure 6. Laboratory-scale polymerisation with agitator off at 126°C and inhibition at 130°C: temperature and pressure changes in the reactor. (pressure relief 2 bara, agitator 300 rpm)

equal and the pressure and temperatures decline as the reactor contents cool due to the production of styrene vapour. The qualitative features of this experiment provide an indication of how reduced agitation or agitator failure can affect the performance of the inhibitor. Insufficient mixing is evident from increasing temperature variation within the liquid, particularly as any residual agitation subsides once the agitator has been switched off.

PILOT-SCALE EXPERIMENTS

The main aim of the pilot-scale investigation was to determine the reliability of the design and operation of a reaction inhibition system on a scale which is reasonably representative of industrial processes. Full-scale evaluation of inhibition systems under runaway conditions is precluded because of the associated hazards. The pilot-scale experiments were designed to evaluate criteria that can be used in the design of an industrial-scale reaction inhibition system.

PILOT-SCALE FACILITY

A schematic diagram for the pilot-scale facility is shown in Figure 7. The system comprises a 340 litre jacketed glass-lined reactor which is provided with glass feed vessels and is connected via a vent line to a 2500 litre catch tank. The vent line includes a relief valve which is opened automatically when the pressure in the reactor exceeds a pre-selected value. The reactor and catch tank have maximum operating pressure of

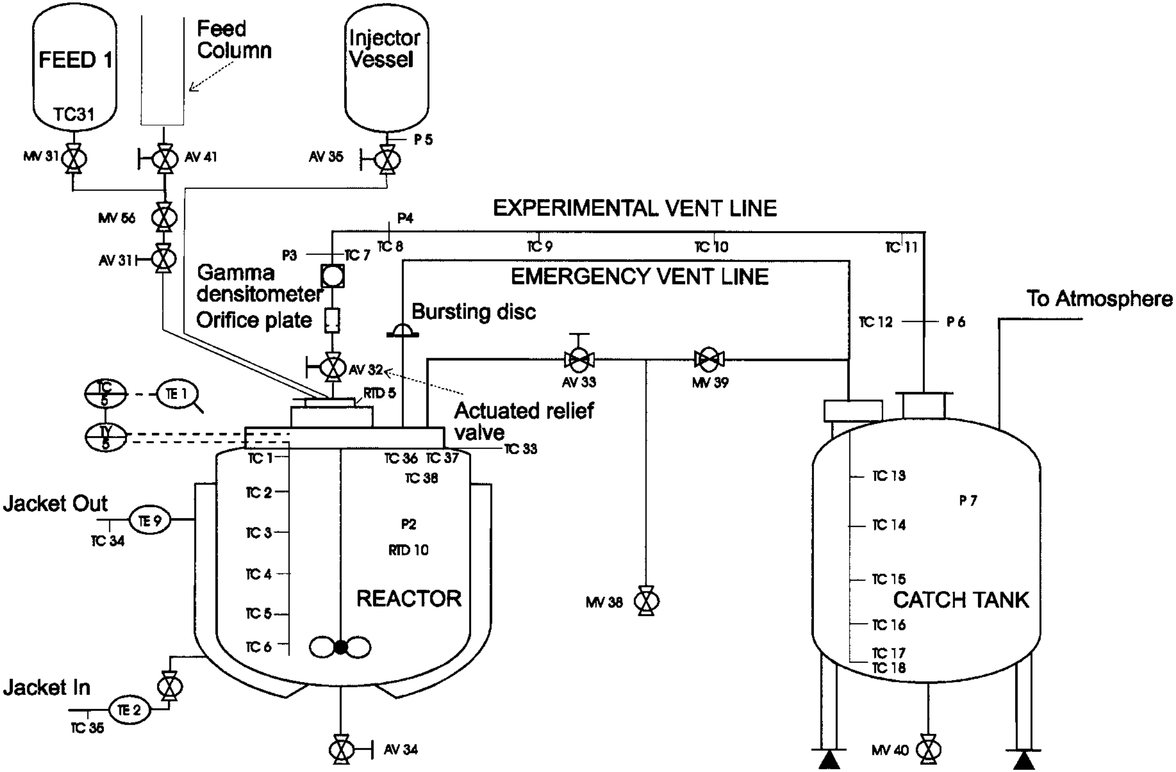

Figure 7. Pilot-scale facility

6 barg and maximum operating temperature of 250°C. The facility can be operated and monitored from a control room located 100 m from the main reactor building. Further detail on the design and construction of the facility is available elsewhere[9].

The polymerisation was performed by first charging styrene to the reactor and to one of the feed vessels. The styrene was heated by circulating hot water through the reactor jacket and through a heating coil in the feed vessel. The initiator (benzoyl peroxide) was held in a glass column and, when the styrene had reached the required initial temperature a valve was opened to allow styrene to flow from the feed vessel into the glass column. A short time was allowed for the initiator to dissolve in the styrene and then the connection to the reactor was opened to allow the initiator solution and the styrene from the feed vessel to flow into the reactor. This could be viewed remotely from the control room.

The inhibitor solution (tertiary butyl catechol in styrene) was held in an injection vessel that was pressurised with nitrogen. The injection vessel is connected to the reactor via a feed line with an actuated valve which was opened automatically when the reactor contents reach a pre-selected temperature. This caused the pressurised contents of the injection vessel to be transferred to the reactor.

During the polymerisation experiments, a connection was provided between the reactor and catch tank via the bottom outlet valves. The bottom outlet valve from the reactor was set to open automatically when the reactor contents reached a preset temperature, causing the contents of the reactor to be discharged to the catch tank, as an additional safety measure.

Only a limited number of pilot-scale tests could be performed and, it was important to select conditions where the possibility of forming solidified polystyrene in the reactor was eliminated. If the injection of inhibitor failed to stop the runaway, the bottom outlet valve would be opened automatically to discharge the contents of the reactor to a catch tank. If bottom discharge failed to stop the runaway and the temperature and pressure in the reactor continued to rise, pressure relief would be provided by the rupture of the bursting disc in the vent line to the reactor. The catch tank is permanently vented to atmosphere.

Three pilot-scale experiments were performed each with the same reactor jacket temperature. The jacket temperature and the conditions for initiating inhibitor injection, bottom discharge and pressure relief were selected by analysis of the adiabatic data and the laboratory-scale results and by the application of scale-up procedures. The criteria for the selecting the experimental conditions are described in the following section. Similar procedures would be required in the design of an inhibition system for a full-scale process.

Selection of conditions for pilot-scale experiments

The conditions which were selected for the three pilot-scale experiments are summarised in Table 2 and the selection criteria for key parameters are outlined in the following sections.

Table 2. Pilot-scale results

Experiment number	Exp't 1	Exp't 2	Exp't 3
Styrene mass before inhibitor solution injection (kg)	170	170	170
Reactor jacket temperature (°C)	90	90	90
Agitator speed (rpm)	103	51.5	103
Reactor temp when agitator stopped (°C)	N/A	N/A	119.5
Injection set temperature (°C)	120	120	120
Max temperature rate before injection (°C/min)	10.53	9.38	10.59
Temperature rate at injection (°C/min)	12.07	11.11	17.05
Maximum temperature rate after injection (°C/min)	14.4	18.29	17.62
Maximum temperature (°C)	121.75	122.25	122.00
Maximum pressure (bara)	2.62	2.45	2.60
Time to inhibitor solution injection (s)	895	962	912

Initial temperature

In order to select the jacket temperature for the pilot-scale experiments, Equation 3 was integrated numerically to produce predicted reactor temperature-time profiles for a range of jacket temperatures. These calculations were performed for a batch volume of 200 litres, selected in order that, with the agitator running, the wetted surface area corresponded to the jacketed area of the vessel. An appropriate overall heat transfer coefficient could then be estimated from previous experiments on other chemical systems but with some allowance for the influence of viscosity on the inside film heat transfer coefficient.

The surface to volume ratio for the pilot reactor is much less than that of the laboratory-scale vessel and therefore runaway polymerisation can be initiated at lower jacket temperature. This is evident from Figure 8 which shows temperature variations predicted for the early stages of the polymerisation with values of T_j ($= T_i$) from 80°C to 100°C. The calculations indicate that a pronounced runaway polymerisation would occur if T_j is greater than 90°C. This value was chosen for the pilot-scale experiments. On industrial scale, induction times leading to runaway would tend to be longer than those shown in Figure 8. The predictions indicate that at 90°C the induction time will be strongly influenced by the heat transfer characteristics of the pilot reactor and the experimental results can be expected to provide a reasonable test of scale-up criteria, particularly with respect to heat transfer.

Injection temperature

Laboratory-scale experiments showed that, when inhibitor was injected with the reactor contents at 120°C, there was an immediate turnaround in the rate of temperature rise. At 130°C (Figures 4 and 5), there was a delay of approximately 10 s before the reactor temperature began to decrease. On pilot-scale, the efficiency of mixing is more likely to affect the rate of inhibition. An injection temperature of 120°C was chosen in order that

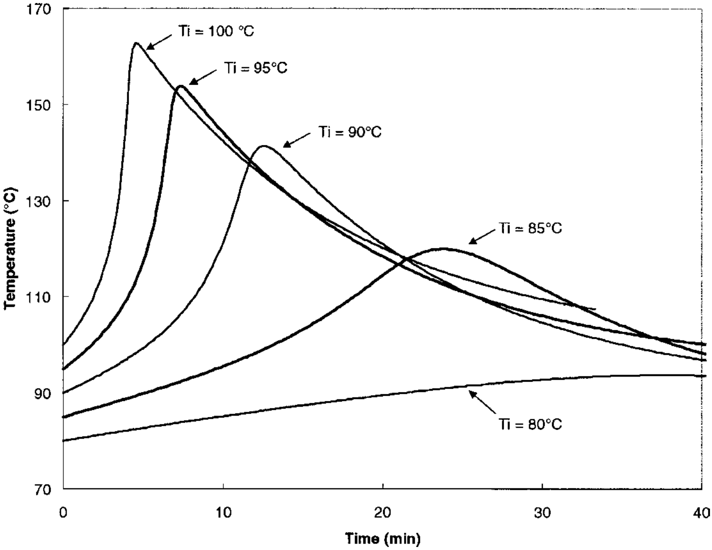

Figure 8. Simulation predictions for pilot scale tests (US/mC$_p$ = 0.00124)

inhibition would stop the runaway but under conditions where the effect of mixing would be evident from the temperature variations after injection. This criterion differs from recommended industrial practice where the injection temperature would be chosen to be as low as possible once the onset of runaway had been detected.

Bottom discharge

The facility to open the bottom outlet valve from the reactor, at a pre-selected temperature (T_b), was provided as a back up measure if inhibition failed to stop the runaway. Transfer from the reactor to the catch tank is likely to reduce the rate of polymerisation via the following mechanisms:

1. The thermal mass of the catch tank would result in a reduction in the temperature of material transferred from the reactor.
2. Transfer from the reactor is also likely to result in additional mixing improve the dispersion of the inhibitor solution in the reaction mixture.
3. Transfer from the jacketed reactor to the stainless steel catch tank would increase the rate of heat transfer from the reaction mixture.

Ideally, injection of inhibitor in the reactor should be sufficient to stop the runaway polymerisation without recourse to other measures. The temperature for opening of the bottom outlet valve was selected so that transfer to the catch tank would take place only after sufficient time had been allowed for the inhibitor to stop the runaway in the

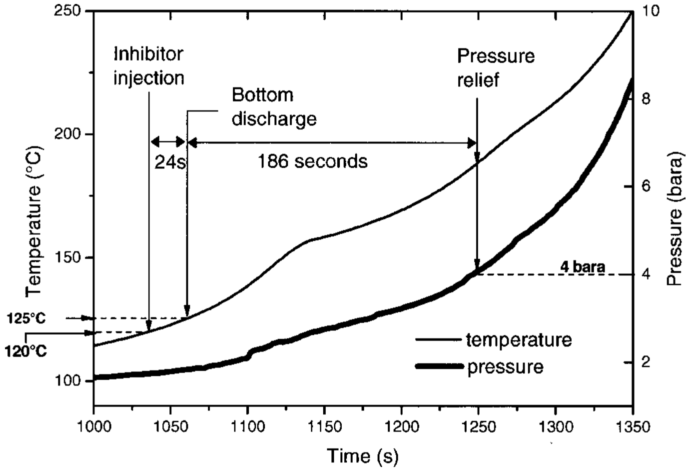

Figure 9. Temperature and pressure variations from adiabatic calorimetry, showing the relationship between trigger levels and time intervals associated with each mitigation technique

reactor. Pilot-scale tests were to be performed over a range of agitation speeds and there are considerable uncertainties in the scale-up procedures for estimating mixing time and the influence of reaction kinetics and micro-mixing on the rate of inhibition in the pilot-scale vessel. The laboratory-scale experiment with an injection temperature of 130°C (Figure 5) showed a delay of 10 s before the inhibitor became effective. On pilot-scale, even with a lower injection temperature, a longer period is required because of reduced mixing efficiency and the period required to complete the injection of the inhibitor solution (estimated at 5 s).

An indication of the minimum time available for inhibition to be effective can be obtained from the adiabatic temperature-time curve. Figure 9 shows that, under adiabatic conditions, the interval between T_i (120°C) and the temperature chosen to initiate bottom discharge ($T_b = 125°C$) would be 24 sec. Heat transfer to the jacket affects the time between T_i and T_b. The temperature-time curve obtained from Equation 3 predicted an interval of 40 sec between T_i and T_b. In practice, the time between T_i and T_b is much longer because, even if inhibitor injection fails to stop the runaway, there will be a significant reduction in the rate of temperature rise due to the chemical interaction with the inhibitor and due to cooling caused by injection of cold inhibitor solution.

Pressure relief

The following criteria were used to select the relief set pressure (T_s) and the vent diameter of the emergency pressure relief system (ERS) for the pilot-scale experiments:

1. The ERS should be designed in accordance with currently recommended methodology for vapour pressure systems.
2. The increase in reactor pressure caused by injection of inhibitor should not cause premature operation of the relief system.
3. The time between T_b and pressure relief should be sufficient to allow transfer to the catch tank via the bottom outlet valve.
4. Pressure relief should be initiated before the increase in the viscosity of the reaction mixture causes a significant reduction in the flow capacity of the vent line.

The adiabatic calorimetric data form the basis of the vent sizing calculations. The details of these calculations lie outside the scope of the present discussion of scale-up criteria but the methodology has been described elsewhere[2]. The calculated relief set pressure and temperature identified are shown on the adiabatic temperature and pressure curves in Figure 9. This shows an interval of 186 s between T_b and T_s, which is in excess of the estimated time for discharge via the bottom outlet valve. The relief set pressure of 4 bara is higher than that chosen for the laboratory-scale experiments but takes account of the increase in pressure which occurs when the inhibitor solution is injected.

Agitation speed

It is difficult to assess the effect of scale on the degree of mixing by agitation and the rate of inhibitor dispersion and reaction. The following factors were taken into account in order to select the rates of agitation for the pilot-scale experiment:

1. Because of uncertainties in the methods used to assess the affect of scale on the rate of mixing and inhibition, a high rate of agitation should be chosen for the first experiment. The effect of reduced rates of agitation can then be investigated in subsequent experiments.
2. The rate of agitation should not be so high as to produce a large vortex, gas entrainment or excessive bubbling in the reactor. This may reduce the rate of mixing, particularly if vortex formation causes the liquid surface to fall below the end of the injection pipe.
3. Methods used to scale-up the effect of mixing require geometric similarity between the laboratory and full-scale equipment. There are significant differences in the type of agitator, baffling and the aspect ratios for the laboratory and pilot-scale reactors available for the present investigation.

Water was used to establish that the maximum rate of agitation that could be used, without causing a large vortex in the reactor, was 103 rpm. This estimate included consideration of the influence of the differences in the physical properties of water and hot polymerising styrene. This rate of agitation was selected for the first pilot-scale test and proved to be satisfactory with styrene charged to the reactor at the start of the experiment.

The rate of agitation for the second experiment was chosen in order that the experimental results would show the effect of reduced rates of agitation but without reaching the point where the inhibitor may fail to stop the runaway. Classical mixing theory indicates that the rate of dispersion of the inhibitor would be approximately proportional to the agitation speed. Once the inhibitor has been dispersed, the kinetics of the inhibition process are likely to be affected by the degree of micro-mixing. The adiabatic calorimetry and laboratory-scale runaway reaction experiments were not designed to investigate the effect of micro-mixing. However, approximate calculations based on the power input per unit volume suggested that, on pilot-scale at an agitation speed of 50 rpm, the rate of micro mixing would be similar to that in the laboratory-scale equipment.

An overall assessment of how agitation might influence the rate of inhibition, suggested that reducing the rate of agitation by 50% would produce a significant effect which would be evident from the temperature records from the reactor before and after inhibitor injection. On this basis the rate of agitation for the second pilot-scale experiment was set at 51.5 rpm.

The final pilot-scale experiment was designed to investigate the effect of agitator failure on the performance of the inhibition system. The agitator was stopped automatically when the reactor temperature reached 119.5°C. The adiabatic data indicate that inhibitor injection would occur approximately 2 s later when the temperature reached 120°C. Preliminary experiments, using partially polymerised styrene from the second experiment, showed that liquid continued to circulate in the reactor for period of approximately 10 s after the agitator was switched off. This indicated that residual, diminishing agitation would continue for 8 s after inhibitor injection. No attempt was made to predict the efficiency of mixing under these complex conditions. Given that approximately 5 s is required for transfer of the inhibitor solution to the reactor, the rate of dispersion due to residual agitation is likely to be much less than the rate of mixing in the previous experiments.

Jet mixing

The rate of dispersion of the inhibitor is determined not only by the rate of agitation but also by entrainment of the reaction mixture in the inhibitor solution as it enters the reactor. The initial pressure of nitrogen in the inhibitor vessel was selected to achieve rapid transfer of the inhibitor solution to the reactor. This was necessary to ensure the safety of the first pilot-scale experiment. Subsequent experiments were performed using the same initial pressure of nitrogen in order that the effect of varying agitation speed in these experiments could be compared directly with the results of the first experiment.

PILOT-SCALE RESULTS

The initial conditions and results for each pilot-scale experiments are summarised in Table 2. In each case the injection of inhibitor at 120°C successfully stopped the runaway polymerisation, with the maximum temperatures in the reactor exceeding the inhibitor injection temperature by no more than 3°C. Table 2 shows that the initial conditions for each experiment were successfully reproduced and gave good agreement between induction times from initiation to inhibitor injection.

Figure 10 shows the temperature variations in the reactor and the pressures in the reactor and injection vessel for Experiment 3 at the point when the injection valve was

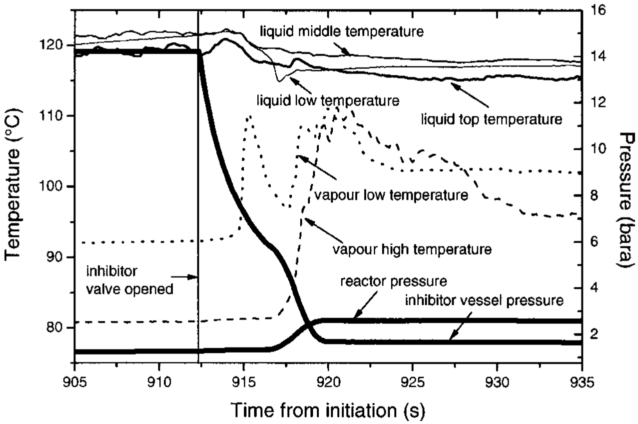

Figure 10. Temperature and pressure variations from pilot-scale Experiment 3. (agitator off at 119.5°C, inhibitor injection at 120°C)

opened. The pressure transducers in the reactor and inhibitor vessel respond in bar gauge and bar absolute respectively. The pressure in the inhibitor vessel falls over a period of about 5 s as the inhibitor solution is transferred to the reactor, causing a small increase in reactor pressure. At the end of liquid transfer, the pressure in the inhibitor vessel falls sharply and the reactor pressure increases as nitrogen flows from the inhibitor vessel until the pressures equalise.

The detailed variation in the temperature within the liquid in the reactor is considered later in this discussion. The temperature in of the vapour space initially was much less than that of the liquid. However, vapour-space thermocouples show sharp increases in temperature during the transfer from the inhibitor vessel (see Figure 10). The temperature increase recorded by the "vapour low" sensor occurs during transfer of liquid and may be due to level swell as nitrogen in the injected fluid comes out of solution as the pressure falls. Additionally, the chemical interaction between the between inhibitor and the initiator may result in gas production. At the end of liquid transfer, the "vapour high" and "vapour low" sensors show an increase in temperature which is attributable to level swell caused by bubbles forming in the liquid as nitrogen flows from the inhibitor vessel.

COMPARISON WITH PREDICTED TEMPERATURE-TIME PROFILES

Figure 11 shows the variation in the temperature of the reactor contents for each pilot-scale experiments. These data were obtained from the platinum resistance thermometer that was located in the liquid and connected to the controller used initiate reaction inhibition. The tests were performed under the same conditions, apart from the rate of agitation. The results have been plotted from the point when the temperature of the reactor contents

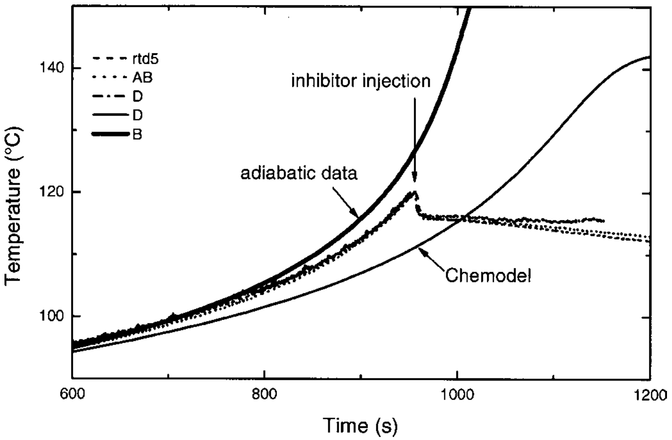

Figure 11. Comparison of adiabatic, simulation and pilot scale measurements

becomes equal to the jacket temperature, which was held constant at 90°C, and show good reproducibility up to the point of reaction inhibition at 120°C. This implies that, in the initial stage of the polymerisation, the rate of heat transfer to the reactor jacket was not strongly affected by the reduced rate of agitation used for Experiment 2. After inhibitor injection, the cooling curves for each experiment begin to diverge. This indicates that, with increased viscosity, reductions in the rate of agitation produce significant reductions in the inside film heat transfer coefficients. With the agitator switched off, Experiment 3 shows the largest divergence from the other cooling curves, as would be expected.

Heat transfer to the reactor jacket is evident from the difference between the experimental results and the adiabatic temperature-time curve shown in Figure 11. The temperature variations predicted by numerical solution of Equation 3, also shown in Figure 11, lie below the experimental curves and indicate that the rate of heat transfer has been overestimated in the calculations. The calculations were based on single value for the overall heat transfer coefficient and the effect of increased viscosity was not included. It was also difficult to predict the temperature of the reactor contents after the styrene had been charged from the feed vessel and mixed with the initiator because of the cooling effects of the pipe work and the thermal mass of the initiator. A more rigorous model could have been developed but the simplified analysis was sufficient for the design of the pilot-scale experiments.

DETAILED TEMPERATURE VARIATIONS

The objective of the pilot-scale experiments was to evaluate the inhibition system and the criteria used for detecting the runaway, triggering inhibition and initiating back-up measures such as pressure relief and bottom discharge. In order to carry out this assessment, the pilot-scale data should provide evidence of the conditions under which inhibition system becomes less effective. This type of information can be used to optimise the design parameters and gives a better indication of the margin of safety provided by the inhibition system.

On laboratory-scale, temperature gradients within the liquid in the reactor were observed only in the experiments where the inhibition system had failed to stop the runaway. Figure 6 shows that, as the reaction rate accelerated with the stirrer off, the temperature near the surface increasingly exceeds the temperature lower in the liquid. In the laboratory tests the inhibitor was injected near the bottom of the vessel. The temperature gradients can be seen as evidence that the inhibition system has become less effective and may fail to stop the runaway.

On pilot-scale, significant temperature gradients are evident from the temperature records up to inhibitor injection and larger variations occurred after injection. Figure 12 shows the liquid temperature variations observed in Experiment 3 before and after inhibitor injection. The temperature variations between the top, middle and bottom thermocouples cover a range of approximately 1.8°C. After injection, the temperature spread was 4.1°C. Before injection the middle thermocouple records the highest temperature but after injection the highest temperature occurs at the bottom of the vessel. Earlier in the induction period, the bottom temperature record lies close to the top temperature but moves towards the middle temperature as the reaction accelerates up to the point of inhibitor injection. The temperature records for all three pilot-scale experiments at around the time of inhibitor injection have been examined and the results are summarised in Table 3.

The detailed temperature variations must be interpreted with care because of the limitations on the accuracy of the fine thermocouples installed in the reactor. The

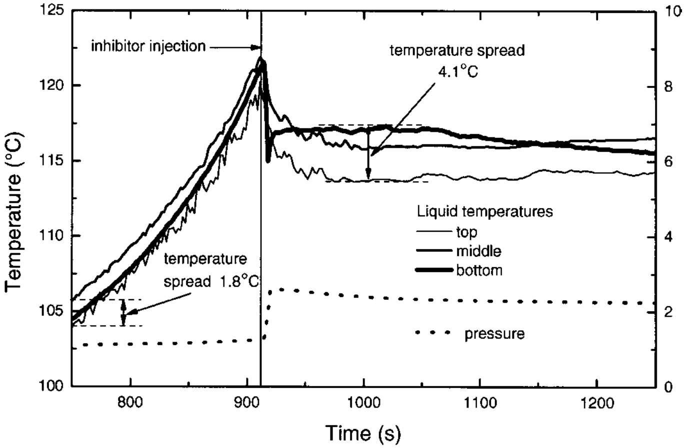

Figure 12. Temperature spread before and after inhibitor injection for pilot-scale Experiment 3

Table 3. Temperature distribution in the pilot-scale reactor before and after inhibitor injection

	Before injection		After injection	
Experiment No. (agitation)	Temperature spread (°C)	Highest temperature location	Temperature spread (°C)	Highest temperature location
Experiment 1 (103 rpm)	1.8	middle	1.5	middle
Experiment 2 (51.3 rpm)	2.4	middle	3.1	middle
Experiment 3 (103 rpm, off $T_r = 119.5$)	1.8	middle	4.1	bottom

changes in temperature distribution before and after injection are of more significance than the absolute value of the temperature spread. The following conclusions can be drawn from temperature records and the data summarised in Table 3.

1. The temperature spread before injection is related to the rate of agitation and increases with reducing agitator speed.
2. As the reaction accelerates up to the point of injection, the temperature at the bottom of the vessel increasingly exceeds the temperature at the top.
3. With the highest rate of agitation (Experiment 1), inhibitor injection results in a small reduction in the temperature spread whereas with slower agitation (Experiment 2), the temperature spread increases.
4. After inhibitor injection, with the agitator off (Experiment 3), there is large increase in the temperature spread and a change in temperature distribution.

These conclusions suggest that an increase in the temperature spread and changes in temperature distribution indicate reduced rates of inhibition. The changes are consistent with effects that would be expected from progressive reductions in the rate of agitation. The conclusions are broadly consistent with the interpretation of the laboratory-scale experiments. However, the effect of inhibitor injection on the temperature distributions was different from that observed on laboratory-scale, where low rates of inhibition produced higher temperatures at the top of the reactor. This difference is attributable to differences in the relative rates of heat transfer to top of each reactor. Furthermore, on pilot-scale the inhibitor was injected just below the liquid surface whereas, on laboratory-scale, the inhibitor was injected at the bottom of the vessel.

CONCLUSIONS

The pilot-scale experiments on the polymerisation of styrene have demonstrated that with a simplified kinetic model and analysis of heat and mass transfer it is possible to predict the conditions which will lead to runaway on large-scale. The adiabatic data have been used in the design of the reaction inhibition system and selection of the conditions for detecting the runaway and triggering inhibition and additional mitigation systems. Laboratory-scale results have been used to predict the effect of mixing on the performance of the inhibition system so that pilot-scale runaway reactions could be performed with reasonable confidence that inhibition would stop the runaway. Conditions were carefully chosen so that temperature variations in the reactor would provide evidence of reductions in the efficiency of the inhibition system. In an industrial installation, lower values of the inhibitor injection temperature could be chosen. This would make the inhibition system more effective and provide a greater margin of safety than that which applied to the pilot-scale tests. More sophisticated analysis of the mass transfer mechanisms may enable better scale-up predictions if validated. Further details and information on other work carried out as part of this project are available in the project report[5].

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