APPENDIX A

PHI TEC ADIABATIC CALORIMETRY DATA
PHI TEC ADIABATIC CALORIMETER

The PhiTec II is a low thermal mass adiabatic 100 ml calorimeter that can be used to study the potential hazard of reaction systems by operating with no nominal heat transfer to the surroundings. There is a built in pressure compensation feedback device to maintain the integrity of the calorimeter can. Temperature, pressures and time are logged throughout the test. Data can be analysed to obtain kinetic data. Adiabatic calorimeters are often used to determine the potential hazard of chemical reactions.

The calorimeter was charged with 60 g of styrene and 0.44 g of benzoyl peroxide initiator. The calorimeter was used in heat-wait-search mode which heats the can and contents in stages until an exothermic reaction is detected. This occurred for the criteria heat generation rate selected at 77°C. Thereafter the temperature and pressure generated are tracked by the instrument with zero nominal heat transfer to the surroundings.
Figure A1 Runaway Polymerisation of Styrene with Benzoyl Peroxide Initiator
(Phi Tec HWS test)

Figure A2 Activation energy & pre-exponential factor from Phi Tec PC46
APPENDIX B LABORATORY REACTOR STUDIES
INHIBITION OF STYRENE POLYMERISATION

EXPERIMENTAL PROCEDURE

The aim of the experiments is to determine whether tert. butylcatechol can successfully inhibit the runaway polymerisation of styrene under various conditions. The effect of the degree of mixing on inhibitor effectiveness is also studied in brief. The inhibitor concentration is expressed as a molar percentage and the initiator concentration as a percentage of the total mass of reactant.

The required amount of tert. butylcatechol inhibitor is mixed with a small amount of styrene and drawn into the double-acting air cylinder. The reactor is isolated and benzoyl peroxide initiator loaded directly into the glass sight vessel. The remaining styrene is then loaded into the feed vessel and heated to the required initiation temperature. On reaching this temperature, styrene is passed into the glass sight vessel where it mixes with the initiator. When the initiator has dissolved in the styrene, both reactants flow into the reactor. The reactor jacket is maintained at a constant inlet temperature during the experiment. When the reactor set temperature is reached, the air cylinder operates automatically and inhibitor solution is passed into the reactor. A check valve prevents return flow from the reactor.

Experiments are performed either with an open, or an initially closed, system. In the latter case, the reactor vent valve is closed and switched to automatic control after charging of the reactor is complete. The pressure vent controller is set to open the reactor vent valve at the desired set pressure. Temperatures and pressures are recorded by both fast and slow data logging systems during the reaction. The reaction is also observed remotely and recorded by video system.

The conditions of the experiments and a summary of the main results are given in Table B1. Graphs showing transducer reading versus time histories for key transducers in the reactor are given for each experiment as Figures B1 to B16.
<table>
<thead>
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<th>Experiment number</th>
<th>Lb26</th>
<th>Lb27</th>
<th>Lb28</th>
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<th>Lb31</th>
<th>Lb32</th>
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<td>Time to inhibitor solution Injection (s)</td>
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**Experiment 26**

Critical variables

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<td>Relief valve set pressure:</td>
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**Figure B1** Overall reactor temperature records

**Figure B2** Temperature and pressure profiles in the reactor during inhibition
### Experiment 27

#### Critical variables

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**Figure B3** Overall reactor temperature records

**Figure B4** Temperature and pressure profiles in the reactor during inhibition
## Experiment 28

### Critical variables

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**Figure B5** Overall reactor temperature records

**Figure B6** Temperature and pressure profiles in the reactor during inhibition
## Experiment 29

### Critical variables

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Figure B7  Overall reactor temperature records

Figure B8  Temperature and pressure profiles in the reactor during inhibition
## Experiment 30

**Critical variables**

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**Figure B9** Overall reactor temperature records

**Figure B10** Temperature and pressure profiles in the reactor during inhibition
# Experiment 31

**Critical variables**

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Figure B11 Overall reactor temperature records

Figure B12 Temperature and pressure profiles in the reactor during inhibition
### Experiment 32

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Figure B13 Overall reactor and catch tank temperature records

Figure B14 Temperature and pressure profiles in the reactor during inhibition
# Experiment 33

## Critical variables

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Figure B15 Overall reactor and catch tank temperature records

Figure B16 Temperature and pressure profiles in the reactor during inhibition
APPENDIX C PILOT REACTOR STUDIES
INHIBITION OF STYRENE POLYMERISATION

EXPERIMENTAL PROCEDURE

The benzoyl peroxide initiator was pre-weighed in the laboratory, then loaded into the glass feed column. The pre-prepared inhibitor solution was then charged to the injector vessel from a drum installed on a weigh scale. The injector vessel was then pressurised to 15 barg with nitrogen. The appropriate quantities of styrene were charged to the reactor and feed vessel 1 respectively. When the required initial temperature was reached in both the feed and reactor vessels, styrene was passed from feed vessel 1 into the feed column allowing the benzoyl peroxide initiator to be flushed through into the reactor. The reactor was then sealed. Heat transfer fluid was passed through the jacket at a constant flow rate and the temperature and pressure in the reactor were monitored during the course of the runaway reaction. Video recording was used to observe the various reactants passing into the reactor. In experiments 1 and 2, agitation continued throughout the tests. For the final experiment 3, agitation of the reactor contents was stopped automatically when a pre-selected temperature was reached. This allowed settling of the reactor contents. In all experiments, the valve between the injector vessel and the reactor was automatically opened on reaching a second pre-selected temperature, allowing injection of the inhibitor solution. The reactor temperature and pressure were continually monitored to ensure that inhibition of the reaction had been successful and that runaway polymerisation did not resume. Reactor contents were then allowed to cool while maintaining a constant jacket temperature. At the end of each experiment, the contents of the reactor were transferred to a storage vessel and weighed.

Test conditions were chosen which provided respectable self-heating rates at the start of runaway, while still allowing time for the successful inhibition of the reaction.

The flow rate of water to the reactor jacket was maintained at 20kg min\(^{-1}\) for each experiment. The conditions of the experiments and a summary of the main results are given in Table 5.2 of the main report. Graphs showing transducer reading versus time histories for key transducers in the reactor are given for each experiment as Figures C1 to C12.
## Experiment 1

### Critical variables

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**Figure C1** Overall reactor temperature records

**Figure C2** Reactor liquid temperature and viscosity profiles
Figure C3  Temperature and pressure profiles in the reactor during inhibition

Figure C4  Reactor temperatures and inhibitor injection vessel pressure profile
## Experiment 2

### Critical variables

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Figure C5 Overall reactor temperature records

Figure C6 Reactor liquid temperature and viscosity profiles
**Figure C7** Temperature and pressure profiles in the reactor during inhibition

**Figure C8** Reactor temperatures and inhibitor injection vessel pressure profile
**Experiment 3**

Critical variables

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<td>Agitation stopped @</td>
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Figure C9  Overall reactor temperature records

Figure C10  Reactor liquid temperature and viscosity profiles
Figure C11  Temperature and pressure profiles in the reactor during inhibition

Figure C12  Reactor temperatures and inhibitor injection vessel pressure profile
Figure D1: Comparison Between the Simulation and Experiment Results (Pitched Blade Turbine, 100 rpm and Base Injection)
Figure D2: Comparison of the Tracer Disposition from Two Different Injection Positions
Figure D3: Effect of the Injection Duration on Mixing Time (Pitched Blade Turbine, 100 rpm)
Figure D4: Tracer Injection by Different Delay Times after Impeller Stops (Rushton, 100 rpm Before Impeller Failure)
The mixing behaviour at the same (V/Q) for different stirrer speed (pitched blade turbine)

Figure D5: The Tracer Spreading Views at Various Fraction and Multiple of (V/Qp) for Different Impeller Speeds (Pitched Blade Turbine)
Figure D6: Comparison Between the Tracer Spread in Agitated and Non-Agitated Cases at the Same Injection Pressure (Rushton, Top Injection, 100 rpm)
Figure D7: The Tracer Spread During Injection at Various Pressures (No Agitation, Top Injection)
Reaction Inhibition in the
Control of Exothermic Runaway

Ref : JC 0400065

VISCOSITY ANNEX :

Development and Testing of an In-situ Viscosity
Measuring System for the Adiabatic Dewar Calorimeter

Prepared by:

S.M. Rowe BSc, PhD, CChem and K.V. Middle BSc, CEng
Chilworth Technology Ltd
# TABLE OF CONTENTS

V1. INTRODUCTION ...........................................................................................................1

V1.1 IN-SITU VISCOSITY MEASUREMENT EXPERIMENTS ............................................2

V2. DEVELOPMENT OF AN IN-SITU VISCOMETER ......................................................3

V2.1 SUPPLIER RESEARCH – SOFRASER FRANCE ......................................................5

V2.2 VISCOMETER SYSTEM DESIGN ...........................................................................7

V2.3 COMMISSIONING THE SYSTEM ...........................................................................8

V3. PERFORMANCE TESTING OF THE IN-SITU VISCOMETER ...................................13

V3.1 CALIBRATION TEST RESULTS .............................................................................13

V3.1.1 Viscometer Calibration .....................................................................................13

V3.1.2 Modified Dewar Heat Capacity .......................................................................13

V3.2 EXPERIMENTAL TESTING ON THE POLYMERISATION OF STYRENE .............14

V3.2.1 Standard Styrene Runaway Reaction ..............................................................14

V3.2.2 5% Polystyrene Runaway Reaction .................................................................14

V3.2.3 10% Polystyrene Runaway Reaction ...............................................................15

V3.2.4 20% Polystyrene Runaway Reaction ...............................................................15

V3.2.5 Inhibitor Injection at 130°C (10% Polystyrene) .............................................16

V3.2.6 Inhibitor Injection at 150°C (10% Polystyrene) .............................................16

V3.2.7 Slow Inhibitor Injection at 150°C (10% Polystyrene) ......................................17

V3.2.8 Inhibitor Injection at 150°C (10% Polystyrene) without Agitation ...................18

V3.3 DISCUSSION OF TEST RESULTS .........................................................................27

V3.3.1 Uninhibited Polystyrene / Styrene Runaway Reaction Data ............................27

V3.3.2 Inhibited Polystyrene / Styrene Runaway Reaction Data ..............................30

V3.3.3 Effect of Varying Injection Conditions ...........................................................31

V4. CONCLUSIONS .........................................................................................................33
V1. INTRODUCTION

The prediction of the performance of large scale injection systems based on small scale adiabatic calorimetry studies requires accurate knowledge of a wide variety of chemical and physical characteristics of the system under investigation. The conclusions from the initial phase of the Reaction Inhibition (RI) project suggest that the more critical (and less easily defined) of these parameters are:

- the effect of jet mixing (which predominates in small scale studies but will have lesser, but potentially significant, impact under large scale mixing conditions), and
- the accurate definition of the viscosity of the reacting system throughout the course of the injection and subsequent intermixing process.

At the present time, there are no known (commercially available) techniques for the co-incident measurement of viscosity under adiabatic (runaway reaction) conditions. Viscosity can be approximated through a variety of techniques including:

- Monitoring of relative torque changes in agitator systems
- Sampling of the calorimeter contents throughout a reaction and subsequent use of conventional viscometer systems
- Conducting blowdown trials from a pressurised calorimeter to measure the flow of fluids through calibrated pipework (only able to measure a single condition)
- Extrapolation from physical properties data (if the components of the reaction system including intermediates and products are well defined and if suitable viscosity data exists).

However, all of these options are associated with appreciable uncertainty and can rarely be accurately applied.

For the specification of a large scale reaction inhibition system, modelling of the injection and subsequent intermixing processes requires precise knowledge of the viscosity of reaction system. There are a range of conditions for which the RI system would have to function effectively (e.g., the presence or absence of mechanical agitation, the presence or absence of jet mixing effects, injection at various stages through the runaway reaction, etc). To confirm the adequacy of RI for all of these conditions, accurate viscosity data is vital. The requirement for this data is particularly pertinent in the study of reactions that exhibit significant viscosity changes. Polymerisation reactions present a real challenge in this respect and are also one of the major intended chemical processes to which RI may be applied.

An extension to the original RI project was made possible by the sponsorship of ISPESL (the Italian Safety Authority). The aims of the project extension were to:

- Research, develop, design and implement a method of viscosity measurement under the demanding conditions of a runaway reaction
- Integrate the viscosity measuring system into the existing adiabatic Dewar calorimeter system (with minimal impact on the functioning of the calorimeter)
- Demonstrate the viscosity measuring system on the vehicle reaction previously studied for the RI project and examine the impact (on small-scale studies) of the viscosity of the reaction mass at the point of inhibitor injection.

The adiabatic Dewar calorimeter system can be considered to be a perfectly mixed environment for the study of inhibitor injection. In the context of the current project extension, this is advantageous (in that the effects due to injection and mixing can be considered to be fully dissociated). However, for large scale systems, the mixing conditions will be far from perfect and the effect of viscosity on the inhibitor delivery rate (and subsequent mixing time) will be highly significant.
V1.1 IN-SITU VISCOSITY MEASUREMENT EXPERIMENTS

Following successful implementation of a viscosity measuring system, a series of experimental trials have been performed to evaluate the performance of the viscometer and to examine the effect of viscosity on the mixing and distribution of inhibitor. Specifically, the following trials have been performed:

Styrene polymerisation reaction initiated at 70°C and catalysed with 0.5 % w/w benzoyl peroxide. This test was conducted to evaluate the performance of the modified Dewar calorimeter system compared with the standard unit.

- Styrene / polystyrene (95% / 5% w/w) reaction initiated at 70°C and catalysed with 0.475 % w/w benzoyl peroxide
- Styrene / polystyrene (90% / 10% w/w) reaction initiated at 70°C and catalysed with 0.45 % w/w benzoyl peroxide
- Styrene / polystyrene (80% / 20% w/w) reaction initiated at 70°C and catalysed with 0.35 % w/w benzoyl peroxide
- Styrene / polystyrene (90% / 10% w/w) reaction initiated at 70°C and catalysed with 0.45 % w/w benzoyl peroxide, with p-tert-butyl catechol (ptbc) inhibitor (0.01 mol\textsubscript{ptbc}.mol\textsubscript{styrene}^{-1}) injected at 130°C
- Styrene / polystyrene (90% / 10% w/w) reaction initiated at 70°C and catalysed with 0.45 % w/w benzoyl peroxide, with p-tert-butyl catechol (ptbc) inhibitor (0.01 mol\textsubscript{ptbc}.mol\textsubscript{styrene}^{-1}) injected at 150°C
- Styrene / polystyrene (90% / 10% w/w) reaction initiated at 70°C and catalysed with 0.45 % w/w benzoyl peroxide, with p-tert-butyl catechol (ptbc) inhibitor (0.01 mol\textsubscript{ptbc}.mol\textsubscript{styrene}^{-1}) injected at 150°C without agitation
- Styrene / polystyrene (90% / 10% w/w) reaction initiated at 70°C and catalysed with 0.45 % w/w benzoyl peroxide, with p-tert-butyl catechol (ptbc) inhibitor (0.01 mol\textsubscript{ptbc}.mol\textsubscript{styrene}^{-1}) injected at 150°C with a prolonged injection period.
V2. DEVELOPMENT OF AN IN-SITU VISCOMETER

Extensive research was conducted to source a viscometer sensor that:

- was small enough to fit inside a 1 litre adiabatic Dewar vessel
- has minimal impact on the thermal inertia of the adiabatic calorimeter (to retain phi factor (thermal inertia) values consistent with the nature of the calorimeter)
- was sufficiently resilient to resist pressures of up to 30 barg and temperatures of up to 350°C whilst retaining accuracy.

A thorough World Wide Web search was carried out for possible manufacturers of viscometers that would meet the projects requirements. Drawings of the adiabatic Dewar installation were submitted to various selected companies so that the problems associated with temperature, pressure and size limitations could all be addressed directly with the relevant manufacturers.

Figure V2.1 shows the standard adiabatic Dewar calorimeter (ADCII) assembly and physical size of the adiabatic shield internally. Figure V2.2 shows the plan view of the ADCII ported head. It can be seen that sourcing a small enough viscometer for top entry into the standard vessel would be challenging. It was therefore considered important, in the first instance, to investigate the availability of the smallest viscometer possible and then address the temperature and pressure criteria issues afterwards.

Overall, Chilworth Technology located at least 18 different viscometer manufacturers before selecting the one described within this report. Many of their products were found unsuitable for the project due to either the principle of operation (e.g. rotational viscometers), physical size, temperature rating, pressure rating, viscosity range and other influencing factors relating to the intended test reactions. Practicalities of cleaning the sensor between tests also played a major part in the assessment of possible viscometers.
Figure V2.1 Chilworth Technology standard Adiabatic Dewar Calorimeter installation.

Figure V2.2 Chilworth Technology standard ADC II head (shows amount of space available for a top entry viscometer).
V2.1 SUPPLIER RESEARCH – SOFRASER FRANCE

Supplier research highlighted that Sofraser in France manufacture perhaps the smallest viscometer transducer in the world of its type (the smallest that could be found in the extensive search of manufacturers conducted by Chilworth). The Sofraser MIVI sensor is shown in Figure V2.3.

The MIVI sensor was capable of withstanding 300°C and 60 barg and therefore the sensor electronics could potentially be installed within an oven.

The viscosity overall range of the sensor is dependent on the rod length and of the internal tuning capacitor and the overall properties of each sensor; this sensor worked on the vibration principle. The higher the damping of the vibration (and hence frequency), the higher the fluid viscosity. An important aspect of the sensor design was that normal Dewar system agitation should not affect the measured viscosity. This potential problem does not exist with the Sofraser MIVI sensor which has an imposed shear rate of 1000 – 2000 s⁻¹ compared with the agitator speed of up to 300 rpm.

It was decided that this viscometer had the most desirable overall capability although a modified Dewar vessel would be necessary to house the sensor (due to the fact that the sensor length is 80 mm and all of the sensor has to be immersed in the sample). Methods of installing this viscometer into a Dewar system were investigated, with Figure V2.4 and Figure V2.5 showing some of the work performed.
Figure V2.3 Sofraser MIVI sensor

Figure V2.4 Side entry of MIVI sensor to allow maximum probe coverage
Figure V2.5 MIVI sensor – bottom entry to allow maximum probe coverage and with adequate stirring action surrounding the probe.

Figure V2.4 illustrates the difficulty of side entry owing to the fact that the lower portion of the sensor would be located in a poorly agitated zone.

V2.2 VISCOMETER SYSTEM DESIGN

Based on the detailed investigation of potential sensors, it was concluded that the Sofraser MIVI sensor provided the best overall capability. It was, however, necessary to fabricate a custom manufactured stainless steel Dewar vessel of wider neck diameter design. Figure V2.5 was the chosen design (which also shows the gate stirrer design). Because the neck of the vessel would have to be wider, to allow for gate stirrer removal between tests, a custom manufactured head and head clamp were required. Figure V2.6 shows the custom design of the vessel.
Figure V2.6 Custom manufactured vessel design with special gate stirrer. Connection at bottom for accepting entry of viscometer sensor.

It was also noted that the new custom manufactured vessel and viscometer sensor would not fit directly within the Chilworth standard adiabatic shield (oven) due to the internal chamber height restriction. Therefore, it was decided that in order to align the vessel head automatic vent valve with the existing pneumatic piston it would be required that a large hole be drilled in the bottom of the oven, the vessel/viscometer lowered into the hole, the vent valve attached to the pneumatic arm and the hole insulated to minimise heat losses around the viscometer to outside the oven. This was therefore carried out and all the above parts ordered, including the viscometer sensor and processor electronics control unit.

V2.3 COMMISSIONING THE SYSTEM

All system components were received satisfactorily together with the MIVI sensor. The sensor had been pre-calibrated to standard Newtonian fluids in the range 0 - 4000 cP (although the sensor was capable of measuring viscosities up to 10,000 cP). The calibration of the unit was bench checked prior to installing into the custom manufactured vessel and proved to be very accurate. However, when the viscometer was installed on to the new vessel and inserted within the oven it was noted that the zero reading was unstable. Detailed investigation of the lack of stability indicated that the problem was
related to the critical mass of the vessel. Previous industrial systems in which the MIVI sensor had been installed had a minimum mass of 7 kg. This was vastly greater than the mass of the new vessel in the current design.

To overcome this problem a robust clamping system was required. A special band clamp (with eyelets) was manufactured. Eyelets were riveted in each corner of the oven interior base. A tubular stainless section was also fabricated. This was used to seat the vessel and the viscometer passed through the centre of this tube. Rigging screws were then used from each clamp eyelet to each oven corner eyelet and tightened. This had the effect of tightening down the new vessel against the large tubular mass at the oven base (centrally located) with the result of increasing the overall mass of the new vessel. The viscometer was again tested and the zero-in-air reading rechecked. The reading was found to be very stable and further testing to evaluate the performance of the system was conducted. Figure V2.7 shows the MIVI sensor prior to installation within the new project vessel.

Figure V2.7 MIVI sensor

Figure V2.8 and Figure V2.9 show photos of the newly designed and manufactured vessel head and stirrer assembly for the project.
Figure V2.8 New wider head, with head stirrer assembly, custom manufactured gate stirrer and heater.

Figure V2.9 New head design plan view
Figure V2.10 Viscometer system

Figure V2.11 Viscometer system (prior to solving critical mass issues)

Figure V2.11 shows the set-up within the adiabatic shield prior to establishing that there were critical mass issues associated with this set-up which would result in the “zero-in-air” instability initially experienced.
Figure V2.12 Viscometer system (shows solution to critical mass issues)

The MIVI sensor electronic processor (not shown) was located on a remote workbench and the viscosity measurements were re-transmitted via a 4 - 20 mA link to the existing laboratory Dewar acquisition software. The viscometer cables (not shown) are shrouded within a heat proof flexible conduit and passed through the base of the oven.
V3. PERFORMANCE TESTING OF THE IN-SITU VISCOMETER

Following the identification of an appropriate in-situ viscosity measuring system and the specification and construction of a fully modified Dewar vessel and assembly to incorporate the measuring device, a series of adiabatic Dewar tests have been undertaken to evaluate the performance of the modified calorimeter.

Prior to commencement of the styrene tests, a series of calibration trials were performed to evaluate the heat capacity of the modified Dewar system and calibrate the viscometer against a Newtonian calibration fluid. Additional tests were conducted to confirm that the Dewar agitator speed (or internal Dewar pressure) did not affect the measured viscosity.

V3.1 CALIBRATION TEST RESULTS

V3.1.1 Viscometer Calibration

The viscometer was calibrated using N1000 Viscosity Oil (for which a temperature / viscosity relationship was provided by the supplier). Trials performed at different agitator stirring rates (100 – 300 rpm) showed clearly that the agitator speed did not affect the measured viscosity. However, for the viscous oil tested, it was observed that appreciable heat input occurred at higher rates of stirring (ie. 0.17 K.min⁻¹ at 30°C for a stirrer speed of 300 rpm). This is not an unexpected finding for the high viscosity fluid used (2200 cP at 30°C) but does illustrate the potentially significant effect of stirrer heat input in the adiabatic study of high viscosity systems.

The reproducibility of the viscosity measurements (following disassembly / re-assembly of the Dewar system) was initially found to be very poor (completely different results were noted each time the equipment was re-assembled). As previously explained, this was attributable to the critical mass of the Dewar assembly. The system was modified to incorporate substantial bracing (a strong retaining clamp system (bolted to the oven floor) with a modified circular stand on which the system was supported). This modification provided a system which was reliable and reproducible between tests (without the need for re-linearisation of the viscometer prior to every test). Subsequent tests were performed on the modified system. The high shear rate of the viscometer (1000 – 2000 s⁻¹) was sufficiently in excess of the normal range of stirrer speeds (up to 300 rpm) that interference of the agitator with the measured viscosity was not observed when trials were performed at various stirrer speeds.

V3.1.2 Modified Dewar Heat Capacity

Step-wise heating experiments were performed using 800 g of water in the range 35 to 90°C (and with a heating rate of 80 W). The mean (static) heat capacity determined for the Dewar vessel was found to be 620 J.K⁻¹. This equates to a phi factor (for the styrene / polystyrene reaction system) of 1.379. The heat capacity determined is appreciably higher than that of the standard Dewar system (250 J.K⁻¹ which equates to a phi factor of 1.15).

The cause of this appreciable increase is believed to be two-fold. Firstly, the modified Dewar system is appreciably heavier than the standard system (predominantly due to the inclusion of the bulky viscometer). Secondly, and most significantly, the inclusion of the viscometer into the base of the Dewar system means that there is a large un-protected surface area on the base of the vessel through which heat can transfer from the inside to the outside of the vessel.

With the viscometer intimately attached to the base of the vessel (and protruding through the base of the oven) it is observed that the isothermal temperature stability of the Dewar system is poor in relation to the standard system. During the isothermal hold periods following heat capacity
calibrations, a downward drift in temperature of around 0.07 K.min$^{-1}$ (4.1 K.hr$^{-1}$) was observed at 90°C, despite the heat input of the agitator previously discussed. This value would be expected to increase at higher temperatures as the differential temperature between the sample and the outside of the oven increases. This significantly impacts on the adiabaticity of the system and requires appreciable attention as further work.

Despite the short-comings in the adiabaticity of the Dewar system, further trials to examine the efficacy of the system under runaway conditions were conducted. The reaction vehicle selected for study was the same system previously examined in the RI project (i.e. the peroxide catalysed polymerisation of styrene). In order to evaluate the efficiency of the in-situ viscosity system, the original styrene formulation was modified by the addition of polystyrene (an amorphous polymer with an average molecular mass of ca. 230,000 (average molecular number ca. 140,000); glass transition temperature of 94°C). An experimental programme of work was performed to evaluate the efficacy of the viscometer in the presence of different concentrations of polystyrene. In addition, trials were performed to evaluate the effect of inhibitor injection to the more viscous formulation.

### V3.2 EXPERIMENTAL TESTING ON THE POLYMERISATION OF STYRENE

#### V3.2.1 Standard Styrene Runaway Reaction

Date of Test : 10$^{th}$ September 2002  
Filename : D10402P/Q.ASC  
Operator : P.J. Carter

Data currently exists on the styrene (BPO catalysed) runaway reaction initiated from 70°C using the standard Dewar system. The first test in the modified system was performed to compare the data from the standard test with that from the modified test system (whilst also recording the viscosity of the system).

Styrene (696.5 g) and benzoyl peroxide (3.5 g (of dry material)) were charged to the modified Dewar system. The internal Dewar heater was employed to heat the reaction mass up to 70°C at which point the reaction was maintained under adiabatic conditions. Figure V3.1 illustrates the temperature / pressure / viscosity / time data obtained. After reaching 70°C, the reaction accelerated (slowly at first) reaching maximum conditions of 306.5°C and 7.0 barg at maximum rates of 53.5 K.min$^{-1}$ and 3.5 bar.min$^{-1}$. The time to maximum rate was noted to be 67.9 minutes.

The viscosity began to increase detectably from ca. 150°C with the most rapid rate of viscosity increase observed at around 260°C. The peak viscosity noted was 1908 cP at 302°C (this was observed 4 minutes after the main exothermic reaction was noted to be complete).

#### V3.2.2 5% Polystyrene Runaway Reaction

Date of Test : 12$^{th}$ September 2002  
Filename : D10402R/S.ASC  
Operator : P.J. Carter

The standard pure styrene formulation was modified to incorporate 5% polystyrene (with a corresponding reduction in the BPO concentration to retain the same ratio of styrene to BPO).

Styrene (665 g), polystyrene (35 g) and benzoyl peroxide (3.325 g (of dry material)) were charged to the modified Dewar system. The internal Dewar heater was employed to heat the reaction mass up to 70°C at which point the reaction was maintained under adiabatic conditions.
Figure V3.2 illustrates the temperature / pressure / viscosity / time data obtained. After reaching 70°C, the reaction accelerated (slowly at first) reaching maximum conditions of 297.8°C and 6.0 barg at maximum rates of 44.8 K.min\(^{-1}\) and 2.81 bar.min\(^{-1}\). The time to maximum rate was noted to be 72.8 minutes.

The viscosity began to increase detectably from ca. 150°C with the most rapid rate of viscosity increase observed at around 270°C. At the end of the exothermic heat release, the viscosity was 1661 cP although over the following 35 minutes, this increased appreciably to 3730 cP.

V3.2.3 10% Polystyrene Runaway Reaction

Date of Test : 16\(^{th}\) September 2002
Filename : D10402T/U.ASC
Operator : P.J. Carter

The standard pure styrene formulation was modified to incorporate 10% polystyrene (with a corresponding reduction in the BPO concentration to retain the same ratio of styrene to BPO).

Styrene (630 g), polystyrene (70 g) and benzoyl peroxide (3.15 g (of dry material)) were charged to the modified Dewar system. The internal Dewar heater was employed to heat the reaction mass up to 70°C at which point the reaction was maintained under adiabatic conditions.

Figure V3.3 illustrates the temperature / pressure / viscosity / time data obtained. After reaching 70°C, the reaction accelerated (slowly at first) reaching maximum conditions of 288.9°C and 5.0 barg at maximum rates of 40.8 K.min\(^{-1}\) and 2.28 bar.min\(^{-1}\). The time to maximum rate was noted to be 92.1 minutes.

The viscosity began to increase detectably from ca. 130°C with the most rapid rate of viscosity increase observed at around 270°C. At the end of the exothermic heat release, the viscosity was ca. 3000 cP although over the following 15 minutes, this increased appreciably to 5432 cP.

In a preliminary test on this formulation, a significant increase in viscosity was noted to occur from 210°C which reached 8500 cP within 1 minute. The viscosity remained constant through the subsequent exothermic reaction decreasing sharply on reaching the peak temperature. The remainder of the viscosity profile after this discontinuity was essentially the same as that noted for the repeat test. The cause of this discontinuity is discussed in more detail in the discussions section of this report (section V3.3). In summary, it is believed to have been caused by localised cooling of the reaction mixture in the base of the calorimeter (where the heat losses are highest) causing partial solidification of the mass around the viscometer.

V3.2.4 20% Polystyrene Runaway Reaction

Date of Test : 13\(^{th}\) June 2002
Filename : D10402K/L.ASC
Operator : H.E. Gair

The standard pure styrene formulation was modified to incorporate 20% polystyrene (with a corresponding reduction in the BPO concentration to retain the same ratio of styrene to BPO).

Styrene (560 g), polystyrene (140 g) and benzoyl peroxide (2.8 g (of dry material)) were charged to the modified Dewar system. The internal Dewar heater was employed to heat the reaction mass up to 70°C at which point the reaction was maintained under adiabatic conditions.
Figure V3.4 illustrates the temperature / pressure / viscosity / time data obtained. After reaching 70°C, the reaction accelerated (slowly at first) reaching maximum conditions of 268°C and 4.5 barg at maximum rates of 33.7 K.min⁻¹ and 1.78 bar.min⁻¹. The time to maximum rate was noted to be 77.1 minutes.

The viscosity began to increase detectably from ca. 150°C with the most rapid rate of viscosity increase observed at around 240°C. The viscometer reached its limiting value at 250°C (hence viscosity data above this point could not be determined).

This test was performed prior to the attachment of the enhanced securing devices (and re-calibration of the sensor from 0 to 8000 cP (rather than the initial setting of 0 to 4000 cP). These additions were noted to cause significant additional heat loss from the base of the calorimeter. The time to maximum rate in the current test is therefore less than that for the 10% polystyrene sample (test V3.2.3).

V3.2.5 Inhibitor Injection at 130°C (10% Polystyrene)

Date of Test : 18th September 2002
Filename : D10402V/W.ASC
Operator : P.J. Carter

The standard pure styrene formulation was modified to incorporate 10% polystyrene (with a corresponding reduction in the BPO concentration to retain the same ratio of styrene to BPO). In addition, the effect of a 1% mol/mol injection of p-tert-butyl catechol inhibitor was assessed.

Styrene (605 g), polystyrene (70 g) and benzoyl peroxide (2.8 g (of dry material)) were charged to the modified Dewar system. The internal Dewar heater was employed to heat the reaction mass up to 70°C at which point the reaction was maintained under adiabatic conditions. On reaching 130°C, ptbc (10.0 g) in styrene (25 g) was injected into the calorimeter from an air-pressurised bomb (to ensure rapid injection in < 1 s). The bomb volume of 75 cm³ and a 6 barg air pressure was used to force the injection.

Figure V3.5 illustrates the temperature / pressure / viscosity / time data obtained. After reaching 70°C, the reaction accelerated (slowly at first) reaching 130°C after 80 minutes. At this point, the inhibitor injection was performed causing a decrease in the sample temperature (owing to the addition of the cold inhibitor solution). From this point, the sample temperature continued to decrease (ultimately reaching 73°C some 17 hours after the injection).

It is believed that the extremely slow rate of residual heat release after inhibitor injection was of lesser magnitude than the heat loss from the system caused by the attachment of the viscometer. The viscosity of the system was 73 cP immediately after the injection increasing to 180 cP during the cooling period to 73°C. A further test was performed with an injection temperature of 150°C.

V3.2.6 Inhibitor Injection at 150°C (10% Polystyrene)

Date of Test : 20th September 2002
Filename : D10402X/Y.ASC
Operator : P.J. Carter

The standard pure styrene formulation was modified to incorporate 10% polystyrene (with a corresponding reduction in the BPO concentration to retain the same ratio of styrene to BPO). In addition, the effect of a 1% mol/mol injection of p-tert-butyl catechol inhibitor was assessed.
Styrene (605 g), polystyrene (70 g) and benzoyl peroxide (2.8 g (of dry material)) were charged to the modified Dewar system. The internal Dewar heater was employed to heat the reaction mass up to 70°C at which point the reaction was maintained under adiabatic conditions. On reaching 150°C, ptbc (10.0 g) in styrene (25 g) was injected into the calorimeter from an air-pressurised bomb (to ensure rapid injection in < 1 s). The bomb volume of 75 cm³ and a 6 barg air pressure was used to force the injection.

Figure V3.6 illustrates the temperature / pressure / viscosity / time data obtained. After reaching 70°C, the reaction accelerated (slowly at first) reaching 150°C after 86 minutes. At this point, the inhibitor injection was performed causing a decrease in the sample temperature (owing to the addition of the cold inhibitor solution). From this point, the sample temperature continued to decrease to 109°C over 20 hours before starting to increase once more. Over the following 75 hours, the temperature increased to 175°C. The test was terminated at this point as the viscosity had reached a high level (7400 cP) and the rate of temperature rise was very low.

It is believed that the extremely slow rate of residual heat release after inhibitor injection was of lesser magnitude than the heat loss from the system caused by the attachment of the viscometer. However, over the 20 hours taken to reach 109°C, the activity of the inhibitor had reduced to such an extent that the power output from thermal polymerisation was increasing significantly (this aspect is discussed in Section 4.2 of the main report). The rate of heat release at this point began to exceed the rate of heat loss from the calorimeter and slow self-heating occurred. The viscosity was successfully measured throughout the test.

V3.2.7 Slow Inhibitor Injection at 150°C (10% Polystyrene)

Date of Test : 6th November 2002
Filename : D10402cc.ASC
Operator : P.J. Carter

The standard pure styrene formulation was modified to incorporate 10% polystyrene (with a corresponding reduction in the BPO concentration to retain the same ratio of styrene to BPO). In addition, the effect of a 1% mol/mol injection of p-tert-butyl catechol (a known inhibitor) was assessed. As opposed to test 3.2.6, the inhibitor solution was pumped into the calorimeter over 2 minutes rather than being injected instantaneously using gas pressure.

Styrene (605 g), polystyrene (70 g) and benzoyl peroxide (2.8 g (of dry material)) were charged to the modified Dewar system. The internal Dewar heater was employed to heat the reaction mass up to 70°C at which point the reaction was maintained under adiabatic conditions. On reaching 150°C, ptbc (10.0 g) in styrene (25 g) was injected into the calorimeter via a high pressure pump over a total duration of 2 minutes.

Figure V3.7 illustrates the temperature / pressure / viscosity / time data obtained.

After reaching 70°C, the reaction accelerated (slowly at first) reaching 150°C after 100 minutes. At this point, the inhibitor injection was performed over a 2 minute duration. The sample temperature showed evidence of slowing at 168°C before finally stabilising at 180°C. The sample temperature continued to rise (albeit slowly) ultimately reaching a peak temperature of 203°C (3.7 barg) some 103 minutes after commencement of the addition. The sample temperature then essentially stabilised remaining between 194 and 214°C over the following 20 hours. The test was terminated at this point as the viscosity had reached a high level (7550 cP) and the rate of temperature rise was very low.

The viscosity had increased steadily following completion of the addition (at which point the measured viscosity was 418 cP). The slow addition clearly causes a delay in stabilising the increasing
temperature. Once stabilisation was achieved (at 180°C) the rate of continuing reaction was sufficiently high to overcome the modified calorimeter heat losses.

**V3.2.8 Inhibitor Injection at 150°C (10% Polystyrene) without Agitation**

Date of Test : 23rd October 2002  
Filename : D10402aa.ASC  
Operator : P.J. Carter

The standard pure styrene formulation was modified to incorporate 10% polystyrene (with a corresponding reduction in the BPO concentration to retain the same ratio of styrene to BPO). In addition, the effect of a 1% mol/mol injection of p-tert-butyl catechol (a known inhibitor) was assessed. As opposed to test V3.2.6, the inhibitor solution was added via an air-pressurised bomb but with the calorimeter agitator isolated at 130°C (such that nominally static conditions were present in the vessel at the point of injection).

Styrene (605 g), polystyrene (70 g) and benzoyl peroxide (2.8 g (of dry material)) were charged to the modified Dewar system. The internal Dewar heater was employed to heat the reaction mass up to 70°C at which point the reaction was maintained under adiabatic conditions. On reaching 130°C, the agitator was switched off and at 150°C, ptbc (10.0 g) in styrene (25 g) was injected into the calorimeter from an air-pressurised bomb (to ensure rapid injection in < 1 s). The bomb volume of 75 cm$^3$ and a 6 barg air pressure was used to force the injection. The inhibitor was injected into the headspace of the vessel (ie. not sub-surface).

Figure V3.8 illustrates the temperature / pressure / viscosity / time data obtained.

After reaching 70°C, the reaction accelerated (slowly at first) reaching 150°C after 86 minutes. The agitator was isolated at 130°C. At 150°C, the inhibitor injection was performed but, due to the absence of agitation, no appreciable decrease in the rate of reaction was observed until the temperature had reached 163°C. After a short settling period, the temperature began to increase once more reaching a peak of 249.3°C (2.8 barg) some 3.2 hours after the injection had been conducted. Having reached the peak value, the temperature began to subside (due to heat losses) with the test finally terminated 16 hours after completion of the injection. The viscosity had initially decreased for ca. 60 minutes after the injection (reaching a minimum value of 1381 cP) before increasing steadily throughout the duration of the test reaching the limit of the sensor (10000 cP) 7 hours after the injection.

The absence of agitation clearly has an adverse effect on the initial intermixing process. In this case, the temperature is seen to rise an additional 13 K above the injection point before the temperature increase is halted. This in turn leads to a more rapid recovery after injection. The magnitude of the effect of agitation is likely to be much more appreciable in larger scale vessels where the initial jet mixing effect of the injected stream will be less significant.
Figure V3.1 Experimental Data from Pure Styrene / BPO Runaway
Figure V3.2 Experimental Data from Styrene / Polystyrene (5%) / BPO Runaway
Figure V3.3 Experimental Data from Styrene / Polystyrene (10%) / BPO Runaway
Figure V3.4 Experimental Data from Styrene / Polystyrene (20%) / BPO Runaway
Figure V3.5 Experimental Data from Styrene / Polystyrene (10%) / BPO Runaway with Inhibitor Injection at 130°C
Figure V3.6 Experimental Data from Styrene / Polystyrene (10%) / BPO Runaway with Inhibitor Injection at 150°C
Figure V3.7 Experimental Data from Styrene / Polystyrene (10%) / BPO Runaway with Slow Inhibitor Injection (over 2 minutes) at 150°C
**Figure V3.8** Experimental Data from Styrene / Polystyrene (10%) / BPO Runaway with Inhibitor Injection at 150°C (Agitator Switched off at 100°C)
V3.3 DISCUSSION OF TEST RESULTS

V3.3.1 Uninhibited Polystyrene / Styrene Runaway Reaction Data

The in-situ viscometer system has proved highly effective in providing detailed viscosity analysis during the progression of a runaway reaction. Unfortunately, the integration of the viscometer into the Dewar calorimeter assembly substantially impacts on the thermal characteristics of the system. Data is compared in Table V3.1 and Figure V3.9 for the BPO catalysed polymerisation of styrene when conducted in the standard ADC II and the viscometer-modified calorimeter.

Table V3.1 Comparison of Data for Standard and Modified Dewar Systems

<table>
<thead>
<tr>
<th></th>
<th>Standard Dewar</th>
<th>Viscometer Dewar</th>
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<tbody>
<tr>
<td>Tmax (°C)</td>
<td>339.6</td>
<td>306.6</td>
</tr>
<tr>
<td>Pmax (barg)</td>
<td>12.6</td>
<td>7.0</td>
</tr>
<tr>
<td>dT/dtmax (K.s⁻¹)</td>
<td>1.16</td>
<td>1.09</td>
</tr>
<tr>
<td>dP/dtmax (bar.s⁻¹)</td>
<td>0.094</td>
<td>0.059</td>
</tr>
<tr>
<td>Time to peak temperature from 70°C (minutes)</td>
<td>49</td>
<td>69</td>
</tr>
<tr>
<td>Phi Factor (calculated)</td>
<td>1.15</td>
<td>1.379</td>
</tr>
</tbody>
</table>

Figure V3.9 Comparison between Modified and Standard Dewar Data for Styrene

It is clear that all measured thermal parameters are adversely affected by the integration of the viscometer. However, the magnitude of the effect is not sufficiently large to render the data meaningless. The theoretical phi factor (assuming a Dewar vessel heat capacity of 620 J.K⁻¹) for the
modified Dewar vessel is calculated to be 1.379 whereas the “apparent phi factor” is observed to be 1.31 (this is the ratio between the known adiabatic temperature rise for the reaction and the measured temperature rise for the modified Dewar). This anomaly is likely to be attributable to the variation in the vessel heat capacity at different self-heat rates.

For the purposes of providing thermal data for detailed safety system design, the standard Dewar configuration should be employed for the runaway characteristics. However, viscometry data obtained from the modified system at the emergency relief system design temperature is also considered valid for design purposes, since the viscosity data is likely to be marginally conservative owing to the higher phi factor – at a given temperature in a higher phi factor apparatus, a higher conversion would have occurred compared to the standard Dewar, leading to a higher, conservative, viscosity value.

The influence of initial polystyrene content on the viscosity of the reaction mass is clearly demonstrated by tests V3.2.1 to V3.2.4. Data relating % conversion, temperature and viscosity are provided in Table V3.2 and Figure V3.10 for these trials.

**Table V3.2 Viscosity of Reaction Mixture**

<table>
<thead>
<tr>
<th>Temperature</th>
<th>0% PS</th>
<th>5% PS</th>
<th>10% PS</th>
<th>20% PS</th>
</tr>
</thead>
<tbody>
<tr>
<td>%PS</td>
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<td>%PS</td>
</tr>
<tr>
<td>70°C</td>
<td>0</td>
<td>0</td>
<td>5</td>
<td>0</td>
</tr>
<tr>
<td>100°C</td>
<td>12.7</td>
<td>8</td>
<td>17.5</td>
<td>9</td>
</tr>
<tr>
<td>125°C</td>
<td>23.3</td>
<td>15</td>
<td>27.9</td>
<td>24</td>
</tr>
<tr>
<td>150°C</td>
<td>33.8</td>
<td>27</td>
<td>38.4</td>
<td>39</td>
</tr>
<tr>
<td>175°C</td>
<td>44.4</td>
<td>57</td>
<td>48.8</td>
<td>74</td>
</tr>
<tr>
<td>200°C</td>
<td>55.0</td>
<td>107</td>
<td>59.2</td>
<td>127</td>
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<tr>
<td>225°C</td>
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<td>176</td>
<td>69.6</td>
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<td>920</td>
<td>90.5</td>
<td>828</td>
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<tr>
<td>300°C</td>
<td>97.3</td>
<td>1263</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Notes:
- %PS is the percentage of polystyrene in the reaction mixture during the polymerisation process. This is calculated from the percentage of thermal conversion plus the initial polystyrene content.
- Viscosity units are cP

At initial polystyrene concentrations of 0 and 5% w/w, there is little discernible difference in the measured viscosities of the mixtures throughout the runaway. However, increasing concentrations to 10 and 20% w/w makes an appreciable difference to the measured values. At 20% w/w, it is seen that the initial mixture is fairly viscous. The viscosity of this solution decreases in the early stage of the runaway (indicating that the temperature effect dominates over the conversion effect).

The absolute viscosity values should be regarded as indicative although the calibration testing conducted on the sensor suggests a tolerance within 10%.
Analysis of the rate of temperature rise profiles for the various initial polystyrene concentrations examined reveals that the kinetic mechanism of the reaction remains unaltered by the presence of the initial polystyrene (Figure V3.11). Three rate peaks are observed in all tests corresponding with two stages of BPO initiation followed by pure thermal polymerisation. However, owing to the increased loading of polystyrene, the magnitude of each peak is seen to diminish; that is the kinetics are slowed due to concentration effects.

**Figure V3.10** Viscosity versus Temperature Profile

**Figure V3.11** Comparison of Rate of Temperature Rise for PS Formulations
V3.3.2 Inhibited Polystyrene / Styrene Runaway Reaction Data

Injection of inhibitor into the runaway reaction of 10% polystyrene / styrene mixture at 130 and 150°C provides effective inhibition of the runaway reaction. A comparison of temperature and viscosity data for the inhibited reactions is provided in Figure V3.12.

The initial stages of the data (i.e. prior to inhibitor injection) demonstrate the reproducibility of the thermal data from the modified Dewar system. Following execution of the (rapid) injection, immediate cessation of reaction is observed. The increased viscosity of the reaction mass at the point of injection (compared with the pure styrene runaway) does not adversely affect the subsequent inhibition of the reaction. However, since the small scale Dewar system can be considered to be near-perfectly mixed, this is not particularly surprising. The duration of intermixing at larger scales would be expected to increase considerably with increasing viscosity.

The relatively poor thermal stability characteristics of the modified Dewar assembly are such that on completion of the injection, the low rate of continued propagation is appreciably less than the heat loss from the reactor. For example, with injection at 130°C, the rate of temperature rise associated with continued reaction has previously been observed to be 10.8 K.hr\(^{-1}\). In the case of the modified Dewar system, a temperature rise rate of – 49.5 K.hr\(^{-1}\) is observed, despite the heat input of the agitator into the advancing viscosity of the polystyrene. The viscosity in the reactor after settling, is observed to drift upwards very slowly whilst the reactor contents cools. Over the 17 hours post-injection, the temperature decreases from 130°C to 73°C whilst the viscosity increases from 74 cP to 180 cP.

![Figure V3.12 Comparison of Data for Inhibitor Injection Studies](image-url)
Under large scale heat loss conditions (i.e. near adiabatic), it would be anticipated that the temperature would remain essentially constant after injection whilst the viscosity would continue to rise slowly due to continuing (albeit slow) reaction.

For injection at 150°C, the initial rate of temperature rise associated with continued reaction has previously been observed to be 32.4 K.hr⁻¹. In the case of the modified Dewar system, a temperature rise rate of – 4.5 K.hr⁻¹ is observed, despite the agitation effect. The viscosity in the reactor after settling, is observed to drift upwards very slowly whilst the reactor contents initially cools (down to 109°C) and then increases. Over the 93 hours post-injection, the temperature reaches a peak of 175.4°C whilst the viscosity increases from 1700 cP to 7400 cP.

From initial inspection of the inhibitor injection studies, it is not possible to ascertain whether the viscosity after injection is increasing due to the temperature decreasing or to a combination of falling temperature and continuing conversion. Although there is an appreciable amount of data collected on the uninhibited polymerisation, it has not proven possible to identify whether the viscosity change is solely attributable to the temperature change due to the inherent variability in the data. Further studies would be required to enable this type of data analysis.

### V3.3.3 Effect of Varying Injection Conditions

The effect of varying injection conditions is seen to make an appreciable difference to the overall efficacy of the inhibition process (Figure V3.13). This is likely to be substantially affected by the increased viscosity of the batch at the moment of injection, which will significantly reduce the rate of inhibitor diffusion.

Injecting into the (headspace of the) Dewar vessel with the agitator inactive gives rise to an overshoot in the baselining temperature (i.e. the equilibrium temperature at which the reaction is brought under control). The reaction is seen to be inhibited but the baselining temperature is sufficiently high that the rate of continuing reaction is able to overcome the modified calorimeter heat loss (and hence self-heating continues).

Provision of a relatively long (2 minutes) inhibitor delivery duration by pumping through a narrow bore feed line into the headspace with continued agitation, similarly causes an overshoot in the baselining temperature (by a higher margin). In this trial, jet mixing effects are likely to be absent and hence the mechanical agitation is the sole means of inhibitor distribution. By contrast, with the pressurised injection system used for all other trials, a significant contribution to the overall mixing efficiency would be likely to result from the turbulence caused by the high rate injection below the liquid level and the subsequent jet of pressurising gas. It is likely that during plant scale injection studies, viscosity will have a pivotal role in the effectiveness of these jet mixing effects. At high viscosity, the level of turbulence invoked by the (sub-surface) jet of inhibitor and gas is likely to reduce considerably (hence diminishing the overall efficiency of the intermixing process).
Figure V3.13 Comparison of Varying Inhibitor Injection Conditions
V4. CONCLUSIONS

Integration of an in-situ viscometer into an adiabatic calorimeter unit has been successfully achieved and demonstrated. The adiabatic Dewar calorimeter system is likely to be one of the only commercially available adiabatic calorimeters in which such a system would be feasible, owing to the relatively large test cell volume. Although the smallest possible viscometer sensor was sought, the size of the smallest unit identified remained fairly substantial for laboratory use.

An appreciable number of technical obstacles were successfully overcome yielding a reliable and reproducible calorimeter system with in-situ viscosity capability. The stability of the Dewar assembly was found to be critical in overcoming problems associated with vessel vibration interfering with the oscillation of the viscometer sensor.

As would be anticipated, deterioration in performance of the calorimetric function of the system was noted due to the appreciable mass of the viscometer system. This performance deterioration was exacerbated by enhanced heat losses from the calorimeter (caused by heat transfer through the main body of the viscometer to the ambient temperature environment). The as-built modified Dewar suffers significantly from heat losses from the base of the calorimeter, through the viscometer. The magnitude and consequences of this effect were only identified once elevated temperature, low self-heat rate reactions were tracked (i.e. during the inhibitor injection trials). This precluded the possibility of re-design of the system during the study.

In order to enhance the performance of the system, future work will attempt to mount the entire viscometer assembly within the oven (this will require a larger (taller) oven than standard). It may also be necessary to modify the coupling of the viscometer to the Dewar vessel to reduce the rate of heat loss to the body of the viscometer. This may decrease the phi factor (i.e. improve the thermal response).

The viscometer unit works well and reliably. It is relatively easy to clean. The modifications to the Dewar ensure that all normal operations remain possible (e.g. pumped additions, pressurised injections, agitation options, etc). Further work should be undertaken to re-design the coupling system to focus on improving the thermal characteristics of the vessel. On completion of this modification, a further programme of experimental work should be performed to further evaluate the injection and intermixing process in viscous systems. The current work has considered only a limited range of injection conditions.

The use of the system in the styrene examples is clearly demonstrated. However, with the current system, the kinetics and thermodynamics have been compromised to an unacceptable extent.

The significance of adding on-line viscometry to the normal functions of an adiabatic calorimeter should not be underestimated. As well as providing crucial information of the design of a RI system, viscosity data is vital in the specification of other basis of reaction safety. For example, in emergency relief system design, standard vent sizing equations are only valid for vented fluids with a viscosity of below 100 cP. Alternative calculation techniques exist for sizing relief systems for fluids that exceed this viscosity. Clearly, the implications of transporting a viscous fluid through a relief vent system can be appreciable. There is presently no known practical technique for confirmation of (a reacting) relief stream viscosity under experimental conditions. The same critical requirement for viscosity data also exists for quenching and drown-out techniques (both of which require rapid and reliable intermixing of the relieved stream with the diluent).

For specification of large scale reaction inhibition systems, the viscosity of the fluid during runaway will be a significant parameter, particularly for polymerising systems. Using a technique such as Computational Fluid Dynamics (CFD), modelling of the inhibitor injection flow patterns and the intermixing processes is possible to confirm adequate delivery and mixing times within the constraints of the runaway reaction kinetics. CFD is required for its ability to model fluid dynamics, whereas the
Network-of-Zones simulation is only able to simulate the concentration and reaction profiles once the flow patterns are known. Therefore, for this application, on-line viscometry is crucially important in the design of successful inhibition systems.

From initial pilot scale trials it is observed that jet mixing of the inhibitor into the (mobile) reaction media provides rapid and effective intermixing and distribution of the inhibitor. With increasing viscosity at the point of injection, the effect of this jet mixing will diminish appreciably. The impact of this effect can only feasibly be considered through the conduct of CFD modelling of the large scale injection process.