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Chilworth Technology Ltd
Beta House
Chilworth Science Park
Southampton SO16 7NS UK
Tel: +44 (0)23 8076 0722
Fax: +44 (0)23 8076 7866
Web: www.chilworth.co.uk
Email: info@chilworth.co.uk

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CONTENTS

DEVELOPMENTS OF THE ACCELERATING RATE CALORIMETER: INCLUDING LOW ϕ CAPABILITY AND VENT SIMULATION TESTING	I-1
<i>Stelios Mores, Martyn Ottaway</i>	
ADVANCES IN ADIABATIC DEWAR CALORIMETRY	I-6
<i>Stephen M. Rowe and Keith V. Middle</i>	
INCOMPATIBILITIES ON THERMAL RUNAWAY HAZARDS OF CUMENE HYDROPEROXIDE (CHP).....	I-16
<i>Chi-Min Shu, Yih-Wen Wang, Yih-Shing Duh, Chen-Shan Kao</i>	
FLAMMABILITY OF HFC/HCFC –AIR MIXTURES AT ELEVATED PRESSURES.	I-30
<i>Ya.A. Lissotchkin, V.I. Poznyak;</i>	
EXPLOSION-PROOF METHOD OF STORAGE OF LIQUID TETRAFLUOROETHYLENE	I-39
<i>Ya. A. Lissotchkin, S. I. Ozol, V. I. Poznyak</i>	

ADVANCES IN ADIABATIC DEWAR CALORIMETRY

Dr Stephen M. Rowe and Mr Keith V. Middle

Address for correspondence: Chilworth Technology Ltd, Beta House, Chilworth Research Centre, Southampton, Hampshire, England, SO16 7NS.

SUMMARY

The use of adiabatic calorimetry for the quantification of exothermic runaway reactions has considerably increased over the last 30 years or so. To a great extent this has been driven by the provision of emergency relief system design calculation methods which require adiabatic data input. Adiabatic Dewar calorimetry has existed for many years as an acceptable technique for such studies. This paper discusses the advances in adiabatic Dewar calorimetry with reference to specific recent developments and case studies (including polymerisation processes, a Grignard reaction, reaction inhibition studies and a chlorination process) which illustrate the versatility of the commercially available ADC II equipment.

Keywords:

Adiabatic, calorimetry, Dewar, exothermic, runaway, Grignard, polymerisation, chlorination, inhibition, ADC II.

INTRODUCTION

There are essentially three laboratory scale methods which can be employed to study reactions under low heat loss, low phi factor conditions. These are:

- I. heat flow calorimeters operated in “adiabatic” mode
- II. pressure compensation adiabatic calorimetry
- III. adiabatic calorimetry using pressure resistant reactors

As with any laboratory instrument, there are advantages and disadvantages associated with each type of system. The use of heat flow calorimeters (such as the Mettler Toledo RC1e) in adiabatic mode is uncommon due to the hazard involved in the conduct of such tests and, in the event of large adiabatic temperature rise reactions, the uncertainties in the changing heat transfer coefficient which is crucial in ensuring fully adiabatic conditions. In pressure compensation adiabatic calorimetry, low thermal inertia cells are employed (to minimise the phi factor) whilst their structural weakness is compensated by pressurising the outside of the vessel to match the internal pressure. The VSP II, APTAC and Phi Tec II are examples of this type of calorimeter. Each of these calorimeter systems has a reactor vessel of approx. 100 - 140 cm³ internal volume.

Adiabatic calorimetry using pressure resistant reactors encompasses techniques such as adiabatic pressure Dewar calorimetry and the accelerating rate calorimeter (ARCTM). The ARC, with its very high pressure capability, is ideal for the examination of single components (or homogeneous mixtures) but is significantly disadvantaged in its applicability by the relatively high thermal inertia of the test cell (the best attainable phi factor is ca. 1.5 but, more typically, values of 2 – 5 are exhibited).

The pressure compensation calorimeters have a much reduced thermal inertia (typical phi values of between 1.05 and 1.15 are obtained). This obviously represents a much closer correlation with the phi factor of large scale processing vessels. However, there are some disadvantages with such calorimeters. For example, the use of the equipment for the study of semi-batch processes and agitation of viscous systems with the standard magnetic agitator systems can be problematic. In addition, the adiabaticity of the equipment at high temperatures and pressures is compromised by high heat exchange with the pressure compensation gas.

Adiabatic calorimetry using Dewar vessels has long been established as a technique for the quantification of exothermic reactions under low heat loss, low thermal inertia conditions [1, 2]. Much of this work focused on the use of glass Dewar vessels. However, these systems have a severely limited pressure range. Subsequent developments were made with respect to the use of metal Dewar vessels.

The ADC II (adiabatic Dewar calorimeter) system is the first commercially available Dewar calorimeter system which offers high pressure capability in combination with a low heat loss, low thermal inertia environment. The scale of the apparatus (1.1 litre) makes it widely applicable for the study of exothermic runaway reactions under a variety of test conditions. Mechanical agitation is provided as standard with a number of different agitator designs available to simulate large scale manufacturing conditions.

This paper provides a summary of the specification and applications of the ADC II along with some more detailed discussion of recent developments.

EQUIPMENT SPECIFICATION AND FEATURES

The system comprises of essentially four components:

1. Dewar vessel and fittings
2. adiabatic enclosure
3. safety enclosure
4. data acquisition and control system.

A schematic of the equipment is provided in Figure 1. Each of the components of the system are described in more detail below. The standard system functions within an operating range of temperatures and pressures up to 350°C and 30 barg.

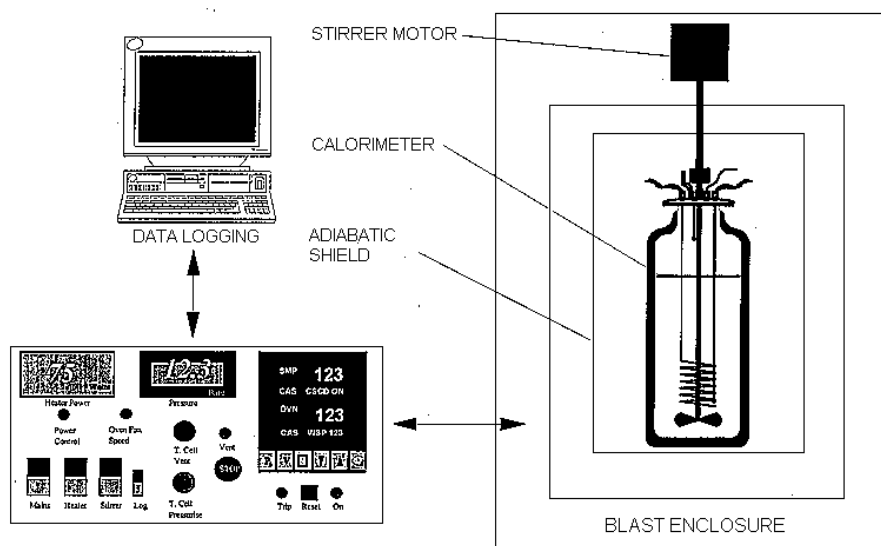


Fig.1 Schematic of the Adiabatic Pressure Dewar Calorimeter (ADC II)

DEWAR VESSELS AND ASSOCIATED FITTINGS

The standard vessels are 1.1 dm³ 304 L stainless steel Dewar vessels equipped with a stainless steel flange closure allowing a 45 mm diameter vessel access. The upper flange can be ported with up to 7 separate probes, sensors or addition lines. The upper flange is considerably reduced in size from previous designs. The vessels are found to withstand above 50 bar at ambient temperature although deformation generally occurs above 30 bar at elevated temperatures (above 200°C). The standard configuration has the following fittings:

1. Self-sealing stirrer gland with agitator (typically a pitched blade impeller is used for relatively mobile systems). The speed of the agitator system is externally variable whilst both speed and torque data are collected throughout experiments.
2. Temperature probes. Type-K stainless steel thermocouples are employed for temperature determination. Usually only one liquid phase probe is employed although duplicate liquid probes or vapour phase probes can be located as required for a specific purpose.
3. Pressure sensor. A 0 – 100 bar transducer and monitor are employed. The transducer is located just outside of the adiabatic enclosure via an oil-filled hydraulic linkage.
4. Relief devices. Dual relief devices are employed. The primary relief is provided by a 3/8" pneumatically activated plug valve (which is triggered to activate either manually or via the

computer control system). Back-up relief is provided via a bursting disc system (the standard disc is rated at 40 bar @ 200°C).

5. Calibration heater. A specially designed calibration heater can be used for a variety of purposes. The heated end of the heater is fully immersed when the calorimeter contains 350 cm³ or more of test fluid. This heater can then be employed for:
 - I. performing heat capacity determinations
 - II. heating a sample to a set temperature
 - III. heating a sample to simulate the heat input from vessel fire engulfment

The heater power is infinitely variable between 0 and 600 W.

6. Semi-batch feed. High pressure pumps can be connected to the equipment to simulate semi-batch process operations.

Other fittings that can be utilised include dip-pipe lines for subsurface additions (for example, for the study of hydrogenation or liquid / gas reactions). For the standard configuration, the thermal inertia of the vessel is found to be ca. 200 J.K⁻¹. This yields phi factors in the range 1.06 to 1.14 for typical initial fill levels of 700 g.

ADIABATIC ENCLOSURE AND CONTROL SYSTEM

The Dewar vessel itself minimises atmospheric heat losses to a great extent. In order to minimise heat losses further, the whole Dewar vessel assembly is located within a large volume, fan assisted oven. The oven is equipped with a 6 kW heating element which is capable of tracking exothermic rates of temperature rise of 60 K.min⁻¹. Above such values, the vessel is found to operate to a high degree of adiabaticity since thermal equilibration throughout the vessel is not attained. The oven is maintained under adiabatic conditions by provision of a PID temperature control unit. At rates of rise up to 30 K.min⁻¹, this control unit maintains the oven temperature to within ± 0.5 K. The high temperature and pressure stability of the equipment is highlighted in Section 4.1.

SAFETY ENCLOSURE

The large sample size employed with the ADC II system (and the lack of provision for cooling) infers a high degree of risk in the event of vessel rupture. Our internal procedures dictate that each material tested within the adiabatic calorimeter must be screened first to identify potentially explosive or extreme high rate decomposers. Such materials are excluded from study in the ADC II. However, in certain circumstances, the relief devices on the calorimeter are inadequate to prevent overpressurisation and rupture. Within our laboratories, we have two blast-proof chambers in which the ADC II system is housed. These chambers incorporate a 1 m² explosion relief panel to prevent internal overpressurisation. The commercial unit is supplied with an optional explosion resistant spherical chamber capable of withstanding 10 bar internal pressure and preventing shrapnel projectile escape.

DATA ACQUISITION AND CONTROL SYSTEM

A PC based data acquisition package is utilised for data collection and experiment control. Two sampling rates are employed. The first (slow log) rate can be set at any time interval (typically we employ 30 s intervals) whilst a rapid log system triggers at high rates of temperature or pressure rise to collect data at 10 Hz. The main ADC II control unit houses all of the displays, activation switches and control functions. The computer display provides real-time data on all process variables and signals via graphical and meter displays.

STANDARD OPTIONS AND RECENT DEVELOPMENTS

With the standard configuration, the following options are available:

1. Tempering cell system (for assessing whether venting at a set pressure will relieve sufficient vapour to temper a runaway reaction). In addition, this vessel can be used as a collection vessel for blowdown experiments.
2. Pressure pump systems (for accurate semi-batch dosing even at elevated pressures)

3. Gas evolution measurement system (for determination of gas generation rate and quantity for untempered reaction systems)
4. Bomb injection system (for pressurised header tank injections)
5. Dip-pipe addition system (for subsurface gas or liquid addition).
6. Corrosion resistant components. In order to extend the range of application of the system to corrosive chemical systems, a range of Hastelloy Dewar components and coated vessels are available. Perfluoroalkoxy (PFA) polymer lined Dewar vessels (or even gold lined Dewar vessels and fittings) can be supplied.

The system is highly versatile and easily manipulated for a specific application. The ease of access to the vessel head and relatively large scale of the calorimeter present many options not easily applied to other (smaller scale) pressure compensation calorimeter systems. In order to expand the applications of the system further, a number of developments are currently being investigated. These developments are nearing completion and should, in the near future, allow us to offer the enhanced ADC III system. Existing users will be offered the developments as system upgrades. There are several areas where the system is being enhanced:

1. Pressure Capability : Bespoke calorimeter vessels have been designed and constructed with increased structural integrity. The intended range of pressures which can be studied with the new vessels is 0 – 100 bar. This overcomes one of the most significant disadvantages of adiabatic Dewar calorimeter systems over their pressure compensated rivals. The vessels are constructed via electron beam welding under high vacuum.
2. Corrosion Resistance : As well as increasing the structural integrity of the vessels, the bespoke design allows the use of more corrosion resistant alloys such as Hastelloy. The supply and use of vessels and fittings manufactured entirely from Hastelloy is hence possible.
3. Data Acquisition System : The data acquisition and control system of our laboratory units have been upgraded from DOS-based systems to Windows™-based systems. This system has enhanced facilities over the previous DOS-based version and allows data display in colour with on-line historical trend analysis options. Additionally, the upgraded software allows enhanced automation for procedures such as dosing and heat-wait-search operation.
4. Agitator Designs : The single impeller agitator system provided adequate mixing for homogeneous, low viscosity reaction systems. For heterogeneous systems and high viscosity reaction systems, this design can prove inadequate. For this reason, specially designed agitator systems have been developed (including an anchor agitator system).

MODES OF OPERATION AND APPLICATIONS

The equipment can be operated in a variety of modes for a variety of applications. The equipment can be utilised for the following typical applications. Some actual case studies are provided for illustration purposes.

As well as the specific (closed cell) applications detailed below, vent sizing tests (tempering tests and blowdown trials) can easily be conducted in the ADC II. For these tests, a specially designed containment pressure vessel is connected to the Dewar system. The system pressure can then be controlled at a set level (tempering test) or discharged via the large bore connection line into the containment vessel (blowdown test).

THERMAL STABILITY AT ELEVATED TEMPERATURE AND PRESSURE

Maintaining truly adiabatic conditions at elevated temperatures and pressures is an important characteristic of any adiabatic calorimeter. In the case of certain pressure compensation calorimeters, thermal characteristics at elevated conditions deteriorate due to increased heat exchange through the compensation gas and dense vessel headspace. The ADC II maintains excellent adiabaticity up to 30 barg, 300°C.

This feature is demonstrated by a heat-wait-search test conducted on a 700 g sample of ethyl benzene with a reaction product. Figure 2 illustrates the result of the test.

The detection limit for exothermic activity is typically 0.015 K.min⁻¹. In the case of the ethyl benzene

test, temperature drift of less than 0.1 K over 4 hours is observed at 300°C (22 barg). The importance of adiabatic performance at elevated conditions becomes particularly important when assessing the thermal stability of materials at elevated temperatures. Any deterioration in adiabatic performance can considerably decrease the quality of the test result and give rise to false conclusions.

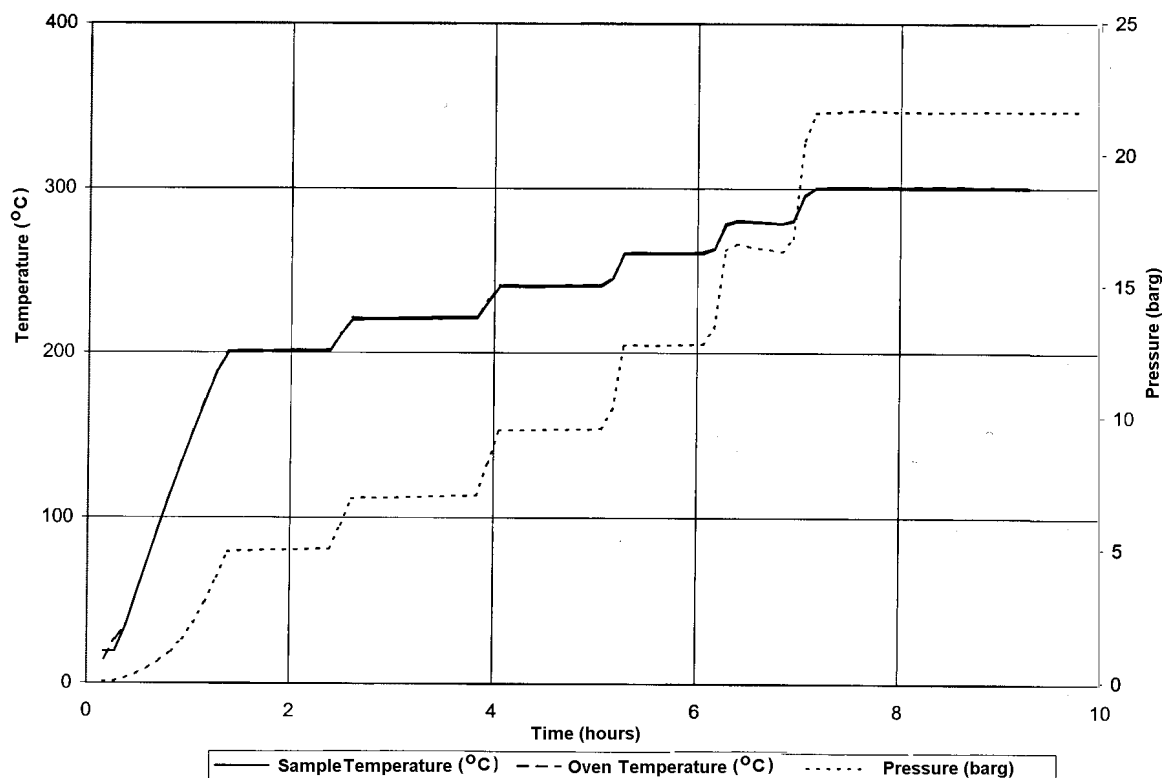


Fig. 2 Ethyl Benzene/Substrate. Adiabatic Heat-Wait-Search Analysis in ADC II

BATCH PROCESS INVESTIGATION: GRIGNARD REACTION STUDY

Exothermic batch processes, by their very nature, present a significant risk of runaway reaction if not adequately controlled. A simple and foreseeable process deviation (loss of cooling) will readily result in the potential for exothermic runaway. Grignard reactions are highly exothermic reactions (heat of reaction typically -200 to -250 $\text{kJ}\cdot\text{mol}^{-1}$) which are generally conducted in semi-batch mode. The processes are usually conducted by the controlled dosing of a halo-organic substrate to a slurry of magnesium (raspings) in solvent. It is common to employ a “initiator” which activates the magnesium and ensures rapid reaction initiation.

However, omission of the initiator, delayed addition of the initiator or stalling of the reaction (by some other means) can cause almost total substrate accumulation. The semi-batch process is then converted to a batch process which presents a considerable hazard. A study conducted in our laboratories indicates the potential hazard posed by delayed initiator addition. The large scale of the Dewar access was highly amenable to the charging of the magnesium raspings (typical particle diameter 2 – 5 mm). This operation may be considerably more difficult in smaller calorimeter systems with very limited cell access. In addition, the mechanical agitation characteristics of the ADC II ensured representative stirring of the vessel and suspension of the metal throughout the test.

The process involved a halo-aromatic substrate and was conducted in THF / toluene at 70°C. An ADC II test was conducted to simulate the process when the initiator was added after the substrate (i.e. reverse addition scenario). The substrate was added over 90 minutes with the initiator being added 30 minutes after completion of the substrate addition.

Figure 3 illustrates the test data. An adiabatic temperature rise of 154 K was noted with rapid peak rates of rise of temperature and pressure of 1.35 $\text{K}\cdot\text{s}^{-1}$ and 0.106 $\text{bar}\cdot\text{s}^{-1}$. Following analysis of the pressure characteristics of the reaction, the data was subsequently used for emergency relief system design assuming the two-phase relief of a vapour pressure controlled reaction.

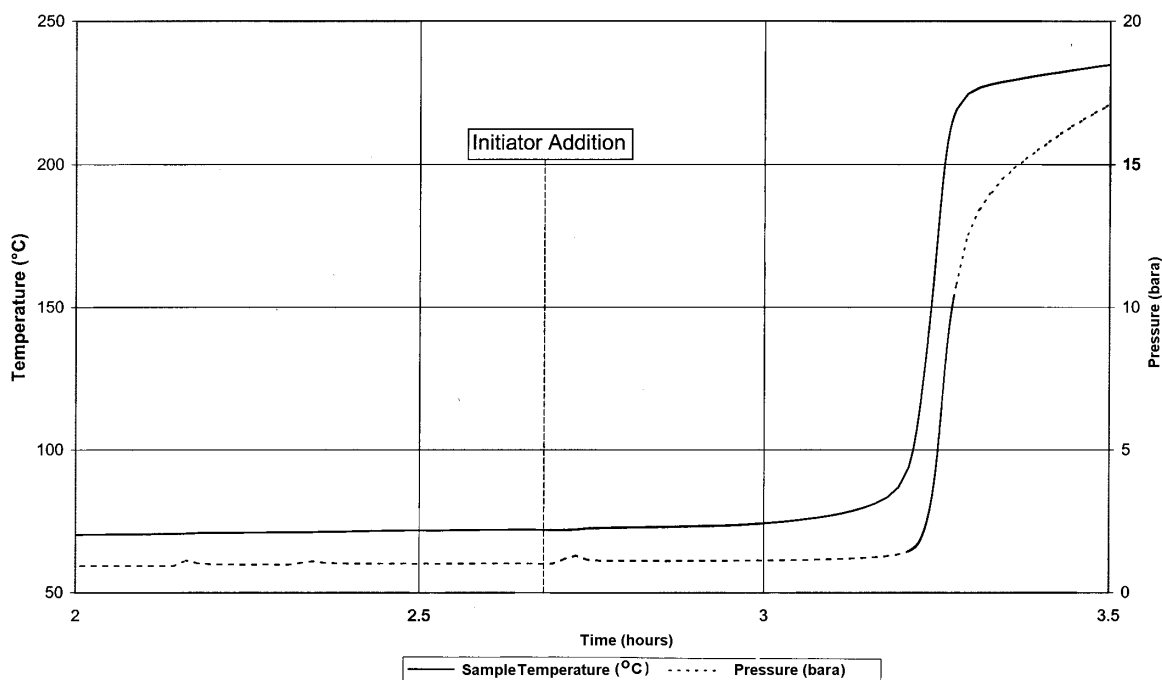


Fig. 3 Gringard Reaction Investigation. ADC II Test Data for Delayed Initiator Addition

SIMULATION OF FIRE ENGULFMENT OF REACTIVE CHEMICAL STORAGE FACILITIES

Emergency relief systems for liquid storage tanks are often designed based on single phase, vapour only relief resulting from external fire engulfment. Determination of heat input is easily achieved using an appropriate standard or recommended practice (API, NFPA, etc). This approach, whilst acceptable for non-reactive liquids, can give rise to dangerously undersized relief systems when exothermic reaction (eg. self-polymerisation) or decomposition commences below the relieving conditions.

In order to correctly evaluate the required relief size it is necessary, with reactive fluids, to simulate the heat input from a fire under adiabatic test conditions and then monitor the kinetic characteristics of the resulting runaway reaction. The data obtained can then be used directly in conjunction with hand calculation methods for emergency relief system sizing.

The ADC II is an ideal tool for such analysis since the heat input associated with fire engulfment can be continuously simulated by activation of the internal Dewar heater at the required power.

A typical test of this nature is described below. The impact of sizing technique (and experimental design) is highlighted in the example of an initiator solution storage vessel.

The vessel has a volume of 3.0 m^3 , is equipped with a bursting disc (set pressure of 1.0 barg) and has a maximum allowable working pressure of 1.1 barg. The initiator (benzoyl peroxide) was stored as a 10% w/w solution in ethyl benzene. If relief system design calculations are undertaken assuming single phase fire relief of a vapour pressure system, the required nozzle relief diameter is determined to be 6.7 cm.

However, it is known that the initiator solution will decompose exothermically. In order to accurately determine the required relief size for fire engulfment an ADC II test was conducted on the mixture by continual heating of the mixture at a heat input equivalent to the fire heat input (93 W for the 500 g sample tested). The test results are illustrated in Figure 4.

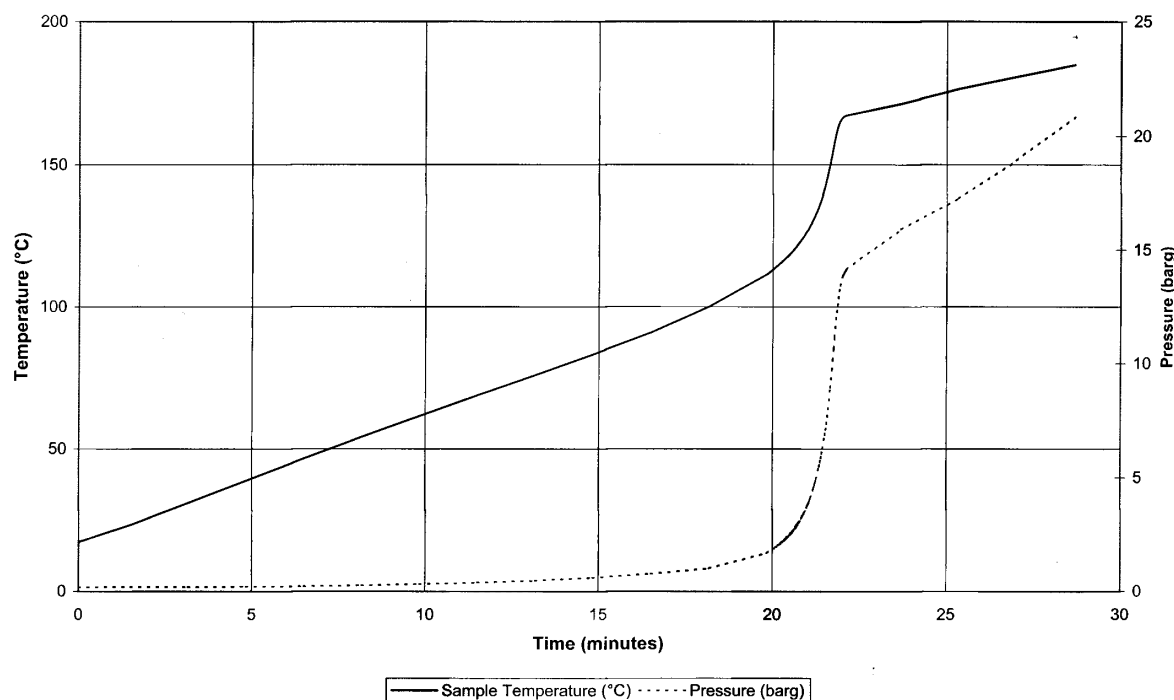


Fig. 4 benzoyl Peroxide (10% w/w) in Ethyl Benzene. Decomposition in ADC II (93 W Continual Heat Input to Simulate External fire Engulfment)

Peak conditions of 170°C, 14 barg were observed after the rapid runaway decomposition. More importantly, the rates of rise of temperature and pressure are considerably increased over those anticipated for fire heat input of a non-reactive system. Using the peak rate of pressure rise, it is calculated that the peak rate of gas generation is $0.55 \text{ m}^3 \cdot \text{s}^{-1}$ (at 1.1 barg, 160°C). Assuming two-phase discharge, the required nozzle relief diameter for a gassy system is calculated to be 24.8 cm.

This example illustrates the importance of experimental design and the versatility of the ADC II system as well as highlighting the consequences of selecting an inappropriate vent sizing methodology.

SEMI-BATCH PROCESS INVESTIGATION : CHLORINATION STUDY

The large scale of the Dewar technique makes it feasible to accurately simulate semi-batch operations as well as simple batch (or rapid addition) processes. A previously published case study relating to a chlorination reaction adequately illustrates an adiabatic, semi-batch process investigation which was undertaken to provide data for emergency relief system design [4].

The process involved the semi-batch addition of a liquid substrate to a chlorine saturated dichloromethane solution (containing catalyst). The normal process temperature was -20°C . After a hazard identification exercise, it was identified that the worst case scenario (for relief system design) was addition of the substrate at maximum pumping rate without activation of cooling. This scenario would result from a single failure of the temperature probe at a constant, low value. Within the process control DCS, this would initiate maximum feeding rate and cessation of cooling.

From isoperibolic reaction calorimetry (at -20°C), the heat of reaction for the process was determined to be $-181 \text{ kJ} \cdot \text{mol}^{-1}$ (of substrate). This equates to an adiabatic temperature rise of 82°C . For the process solvent (dichloromethane), this would result in a final temperature of 62°C and a theoretical vapour pressure of 3.4 barg. Since this was below the vessel design pressure (6.9 barg) it was possible to conclude that the worst case scenario was inherently safe. In order to confirm this, an ADC II test was conducted. The substrate was added over 10 minutes (simulating feeding at maximum rate) at an initial batch temperature of -14°C . A PFA lined Dewar vessel and fittings were employed (due to the presence of the highly corrosive chlorine solution). It should be noted that the short set-up time of the equipment allows for rapid transfer of the sub-ambient temperature starting mixture. Figure 5 illustrates the experimental data obtained (with the superimposed, theoretical data assuming a feed rate

controlled process).

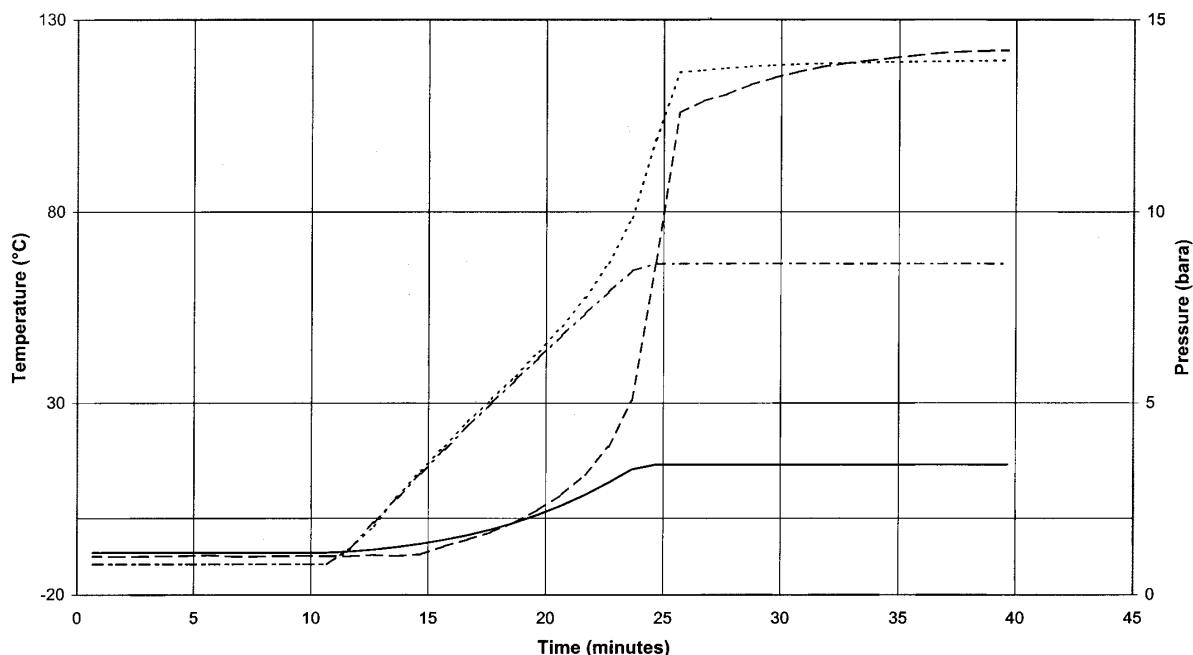


Fig. 5 A Semi-Batch Chlorination Reaction Investigation. ADC II Test Simulating Semi-Batch Substrate Addition at Maximum Rate

The initial stages of the test proceeded as anticipated, a linear rate of temperature rise was observed according to the theoretical. However, on reaching ca. 45°C, an upturn in the rate of rise was noted and a self-accelerating secondary reaction (possibly a decomposition) occurred. The peak conditions attained (118°C, 14.5 barg) were well in excess of those predicted from extrapolation of the (low temperature) isothermal heat of reaction data.

The application of the ADC II to semi-batch process characterisation (using highly corrosive process materials) is highlighted. The study also indicates the importance of confirming the thermal stability of process streams at elevated temperature. The extrapolation of isothermal calorimetry data to pseudo-adiabatic conditions should not be undertaken without detailed knowledge of potential secondary reactions. For the study in question, the potential hazard of the reaction was ascertained before large scale processing was initiated (through the conduct of a thorough process safety testing program and hazard identification study).

STUDY OF AGITATION FAILURE : AN EMULSION POLYMERISATION STUDY

One of the most potentially hazardous process deviations that can occur during batch or semi-batch processing is agitator failure. This is particularly true for heterogeneous reaction systems where the agitation not only provides heat transfer but also mass transfer. The potential hazard of such occurrences is highlighted in a study conducted for an emulsion polymerisation reaction.

As part of the reaction hazard assessment, the worst case reaction scenario (for relief system design) was identified as agitator failure and stratification of the (vinyl) monomer and aqueous phases during a batch emulsion polymerisation. From the monomer / aqueous feed present, the calculated peak conditions which would result from polymerisation of a well mixed system were 130°C and 3.4 barg.

The scenario of agitation failure was simulated in the ADC II. After heating the batch mixture up to the reaction temperature (65°C) with efficient agitation, the stirrer was halted and the batch maintained under adiabatic conditions. The resulting runaway reaction is depicted in Figure 6. For the purposes of this study, the ADC II was equipped with dual temperature sensors. These sensors were situated within the lower (aqueous) and upper (monomer) layers of the settled mixture.

The peak conditions attained within the reactor were 221°C and 21 barg. The peak rates of rise were noted to be 24 K.s⁻¹ (within the upper layer) and 6 bar.s⁻¹. Examination of the two temperature sensor readings indicates how the temperature of the aqueous phase is virtually unchanged during the rapid upper layer polymerisation. Thermal equilibration between the aqueous and organic phases is obtained

some 3 hours after completion of the exothermic reaction. A repeat experiment with inefficient agitation yielded similar results.

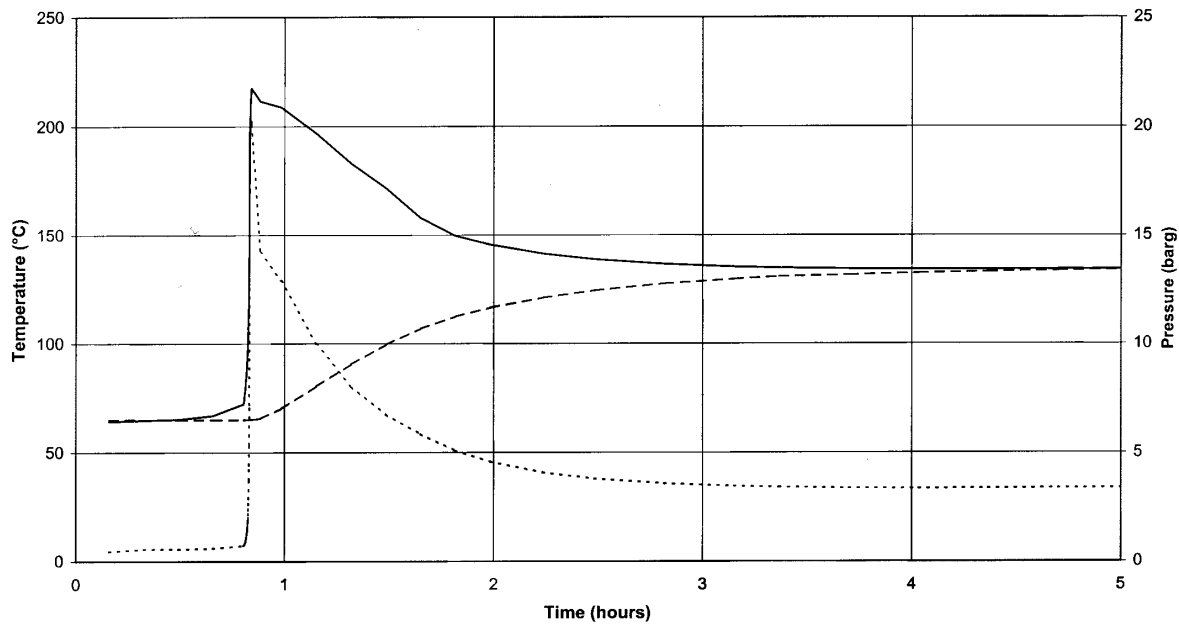


Fig. 6 Emulsion Polymerisation Reaction. ADC II Simulation of Agitation Failure after Heating to the Reaction temperature

Emergency relief sizing for systems such as this is highly complex. The study highlights the importance of agitation for heterogeneous reaction systems and indicates the severity of runaway reaction in a stratified mixture. The use of the ADC II in studying such systems (and monitoring multiple-point temperatures) is clearly illustrated.

INJECTION OF INHIBITORS : A BULK POLYMERISATION INHIBITION STUDY

For reasons of increasing environmental awareness (and associated legislation), the use of safety measures which prevent loss of containment are highly desirable. One such methodology which is rapidly developing is reaction inhibition (ie. the injection of small quantities of active materials which inhibit further reaction).

This technology most favourably lends itself to free radical polymerisation processes whereby the free radicals can be consumed by known inhibitors. A research programme conducted at Chilworth Technology highlights the use of the ADC II in examining potential reaction inhibitors and ideal inhibition conditions [3]. The peroxide catalysed bulk polymerisation of styrene has been assessed with rapid inhibitor (*tert*-butyl catechol) injection during the runaway reaction.

Figure 7 illustrates the ADC II data obtained with and without the injection of a solution of *tert*-butyl catechol. The inhibitor was injected from a pressurised cylinder which was triggered by the attainment of a set temperature (150°C). The rate of temperature rise at this point is relatively high (1 K.s⁻¹). Clearly, the 0.015 mol/mol (inhibitor/styrene) inhibitor does not stop the reaction, however, it significantly reduces the rate of reaction offering time (in this case up to 1 hour) for corrective measures.



Fig. 7 Peroxide Catalysed Polymerisation of Styrene. ADC II Data for p-tert-butyl Catechol Injection at 150°C

CONCLUSIONS

The ADC II adiabatic Dewar calorimeter provides a versatile and easy to use technique for the study of exothermic runaway reactions (under low heat loss, low phi factor and reliable agitation conditions). Recent developments have extended the range of pressure capability and corrosion resistance of the system. These enhancements, coupled with continued development of the control and automation systems, extend the range of application of the equipment to virtually any chemical reaction type. The case studies presented illustrate the variety of modes of operation of the equipment and the quality of the data produced from such studies.

- ADC II data can be used for a variety of purposes:
- evaluating thermal stability at elevated conditions
- determining power output from runaway reactions for cooling system design (including provision of time to maximum rate data)
- determining the consequences of process deviations
- providing kinetic data (and tempering and blowdown test data) for emergency relief system design or kinetic reaction modelling.
- simulating fire engulfment of reactive chemical storage facilities
- evaluating the efficacy of chemical reaction inhibitors

Of these applications, provision of data for emergency relief system design calculations is the most common. In many circumstances, the relatively large sample size makes the equipment more desirable than the smaller sample size of the pressure compensation calorimeter systems.

REFERENCES

1. Grever, Th., "Dewar Test Methods for Exothermic Reactions", Conference on Techniques for Assessment of Chemical Reaction Hazards, December 1990, Amsterdam.
2. Wright, T.K. and Rogers, R.L., "Adiabatic Dewar Calorimetry", presented at "Hazards from Pressure Symposium" at UMIST (England), IChemE Symp. Series 97 (Rugby, England), 1986, pp 121 – 132.
3. Rowe, S.M., "The Role of Calorimetry in Chemical Plant Safety: A Chlorination Reaction", *Thermochimica Acta*, **289**, 1996, pp 167-175.
4. Rowe, S.M., "The Use of Reaction Inhibition Techniques for Control of Runaway Polymerisation Reactions", PhD Thesis, South Bank University (University of London), 1996.