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The role of calorimetry in chemical plant safety: a chlorination reaction[1]

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Abstract

The use of isoperibolic (near-isothermal) and adiabatic reaction calorimetry is discussed with particular reference to a chlorination reaction. The reaction, involving the semi-batch addition of a liquid substrate to a chlorine-saturated solution of dichloromethane containing a catalytic quantity of pyridine, was simulated under isoperibolic conditions (to assess the heat of reaction and extent of reagent accumulation at the proposed reaction temperature and with the maximum possible feed rate of substrate). This was followed by further adiabatic simulation of the reaction to assess the emergency relief size required to account for the worst case scenario (maximum substrate flow without vessel cooling). An assessment of the envelope of safe working conditions was then defined to allow continued safe manufacture.

Keywords: Adiabatic; Calorimetry; Chlorination; Safety

Nomenclature

U	overall heat transfer coefficient/W m^{-2} K^{-1}
A	active heat transfer area/m^2
ΔH_r	heat of reaction under process conditions/kJ mol^{-1}
n	quantity of reactant/mol
m	mass/g
C_p	specific heat capacity/J g^{-1} K^{-1}
ΔT_{ad}	adiabatic temperature rise/K

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T	temperature/°C
p	pressure/bar
t	time/min

1. Introduction

Isothermal (or isoperibolic) and adiabatic reaction calorimeters are key tools in the assessment of hazards posed by exothermic chemical reactions. The strategy generally employed when assessing such risks is;

i. A small scale assessment of thermal stability for reaction components, intermediates and products, and desk-based estimation of heats of reaction (from computational methods such as CHETAH [1] or simple bond energy calculations). When materials of unknown stability are present, small scale laboratory tests such as DSC/DTA [2] or Carius Tube [3] may be used to provide preliminary indications of thermal instability.
ii. A characterisation of the reaction under near-isothermal conditions to define the heat exchange requirements for the process and to define minimum temperatures and maximum feed rates outside which reagent accumulation may occur. Examples of commercially available isothermal calorimeters include Mettlers' RC1 [4], and Hazard Evaluation Laboratories' Simular [5].
iii. An adiabatic assessment of the reaction under low phi and low heat loss contitions which mimic the thermal characteristics of large scale plant. This stage of reaction assessment is normally undertaken to quantify the outcome of deviations from the normal operating procedure to enable the specification of safety measures. Techniques available commercially include the Adiabatic Pressure Dewar Calorimeter [6], Accelerating Rate Calorimeter [7], Pressure Compensated Adiabatic Calorimeters, (eg. the Vent Sizing Package [8] and Phi-Tec II [9]) and the Reactive Systems Screening Tool [10].

This strategy has been applied to a chlorination process currently operated on the manufacturing scale.

2. Process and plant details

The process involves the temperature-controlled pumped addition of a liquid substrate to a chlorine-saturated solution of dichloromethane containing catalytic quantities of pyridine. This is conducted in a 7.6 m^3 glass-lined reactor, having a design pressure of 6.9 barg and an emergency relief vent, fitted with a 0.2 m (8″) diameter, 2 barg, bursting disc. The substrate flowrate is controlled such that the total duration of the feed is 3–4 h. There is no facility for heating the reactor. The reactor is cooled by circulating chilled methanol through the jacket and the chlorine solution is pre-chilled to − 20°C before commencement of the addition. The heat of reaction associated with the initial high substrate feed rate results in the temperature rising to the control range of − 14°C to − 12°C, where feedrate control operates. The plant is DCS-controlled and a software interlock is provided to isolate the substrate feed in the event of temperature excursions above − 12°C. No high integrity trip systems (see EEMUA[11] recommendations) are fitted. The final product (substrate dichloride) is immediately reacted downstream and is not isolated or separated from the dichloromethane solution.

3. Process hazard assessment

A safety review of the process was conducted by the operating company. It was identified that conceivable process deviations included:

i. Addition of the substrate at the maximum pumping rate (the maximum possible flowrate would allow the feed to enter the vessel in 10 min).
ii. Failure of the DCS temperature control/interlock system allowing feed to continue above the high temperature set point.
iii. Loss of efficient cooling on the reactor jacket.

An examination of the plant instrumentation indicated a possible single failure which could account for all these maloperations. This involved failure of the reactor temperature probe. If the signal from this probe were to fail undetected at a constant low value, then the pump would continue at maximum rate, the cooling system would back off and the high temperature interlock would not be activated. This situation was deemed the most likely although other common process deviations were considered, i.e. mischarging materials, maintenance related problems, etc. It was decided to investigate the adequacy of the existing emergency relief system to cope with this failure scenario following recent extensive research to provide reliable techniques for vent sizing for two-phase venting systems, i.e. those that vent liquid and gas as a homogeneous mixture.

4. Experimental details

Following this review of the safety measures already installed on the plant (via a formal Hazop study conducted by the company operating the process), laboratory experimentation was recommended to assess:

i. The heat of reaction (under near isothermal conditions) when the process was conducted at −20°C with addition of substrate (not pre-chilled) over a period of 10 min. An isoperibolic reaction calorimeter was used for this purpose. Using this technique, the extent of any reagent accumulation considering the minimum addition period and minimum reaction temperature could be fully quantified.
ii. The consequences of continued addition of substrate at maximum flow rate in an unchilled vessel (considered following the hazard review and isothermal reaction calorimetry to be the worst conceivable scenario).

The results of the tests were used to assess the adequacy of the existing relief system using the methods proposed by the Design Institute for Emergency Relief Systems

(DIERS) for two-phase flow. It should be noted that initial screening tests are usually undertaken to identify areas of thermal instability. However, in the current assessment, the raw materials are known (from a review of the relevant literature) to be thermally stable up to high temperatures (> 200°C). However, the thermal stability of the reaction product was unknown.

4.1 Isothermal calorimetry

A low-cost reaction calorimeter has been developed by Starkie [12] based on isoperibolic (constant cooling load) rather than isothermal (constant temperature) conditions. A schematic of the equipment is provided in Fig. 1. In order to prevent the need for accurate determination of the heat transfer properties of the vessel, i.e. U (the overall heat transfer coefficient) and A (the total heat transfer area), electrical calibrations are undertaken before and after the reaction. The integrated area under the temperature curve for the reaction is then related to that under the calibration curves to provide a value of the heat of reaction. Additionally, the tail-off period, after addition has ceased, can be used to assess the extent of reagent accumulation under the reaction conditions of temperature, feed rate and components present.

For the chlorination reaction, the starting materials (dichloromethane and pyridine) were charged to the jacketed vessel and chilled to −20°C. The solution was saturated with chlorine and the reaction conducted with a constant feed rate of substrate over 10 min. Electrical calibrations were conducted before and after the reaction to account for changes in the heat capacity, viscosity and heat transfer properties of the system. Fig. 2 illustrates the temperature profile for the test. The electrical energy applied to the

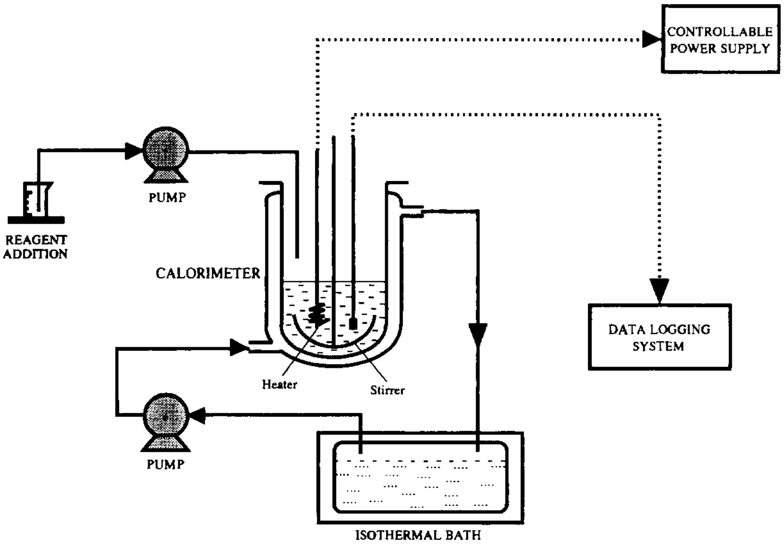

Fig. 1. Schematic of isoperibolic heat flow calorimeter.

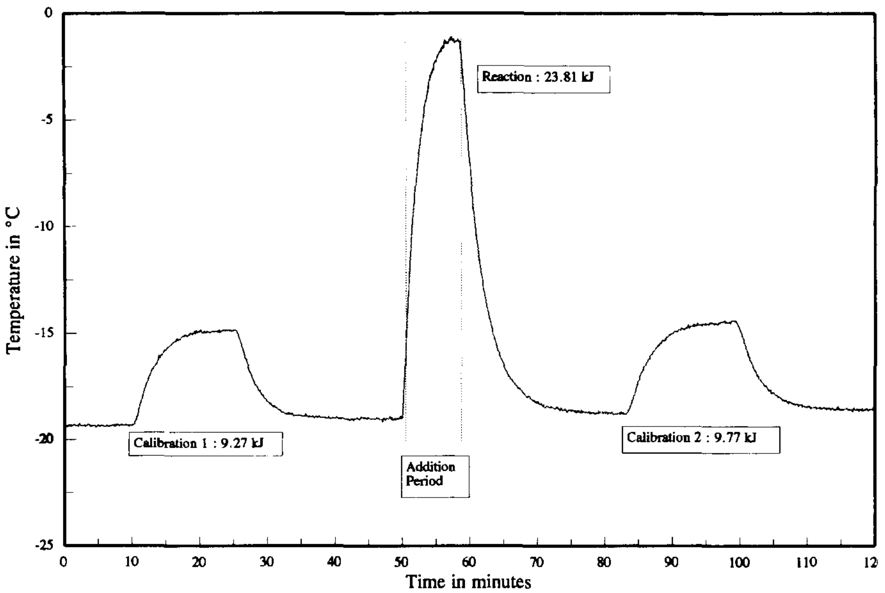

Fig. 2. Chlorination reaction; isoperibolic heat flow calorimeter experiment.

system before and after the reaction (in terms of the corresponding area under the temperture/time curve for each of these calibrations) can be directly related to the area under the curve for the reaction. It was determined that the heat of reaction for the process was -181 kJ mol^{-1} of substrate, and that negligible reagent accumulation occurs when the process is conducted under these conditions (this is a qualitative assessment of reagent accumulation only). The error associated with the determination was observed to be ± 8 kJ mol^{-1}.

At this stage of the process assessment, it is possible to estimate the adiabatic temperature rise, i.e. the temperature rise that would occur as a result of the reaction exotherm in a zero heat loss system, for the process using the following equation

$$\Delta H_r n = mC_p \Delta T_{ad}$$

Assuming the reaction mass has the heat capacity of pure dichloromethane, it is estimated that the adiabatic temperature rise would be 82°C. This would provide a peak temperature (from -20°C) of 62°C which is well in excess of the atmospheric boiling point (approx. 40°C), thus presenting a risk of overpressurisation.

It is therefore possible to state that at -20°C (the lowest conceivable process temperature) and with a feed duration of 10 min (the minimum possible on the plant scale), no accumulation of unreacted substrate occurs. It is also possible to calculate the heat output rate for a given feed rate to enable specification of heat transfer demands for the normal process. In the extreme, it is also possible to calculate vent sizes by generating temperature versus time data from the isoperibolic data, pressure versus temperature data from literature data on dichloromethane, and knowledge of the minimum plant addition period.

This approach to the specification of safety systems from isothermal (or near-isothermal) data involves the very significant assumptions that the reaction mechanism and heat of reaction do not change at elevated temperature, and that the final product (in solution) is thermally stable at the peak temperature attained during an uncontrolled reaction. In order to assess the applicability of these assumptions, it is necessary to simulate the process deviation under plant scale heat loss conditions. This can be achieved by using an adiabatic pressure Dewar calorimeter (or other adiabatic technique).

4.2 Adiabatic calorimetry

From the initial hazards assessment and the results of the isothermal test, it is conceivable that the uncontrolled addition of substrate could be achieved from −12°C (the highest allowable feed initiation temperature) without cooling being present. The simulation of the chlorination reaction was undertaken in an adiabatic pressure Dewar calorimeter. This apparatus consists of a stainless steel Dewar vessel (volume approx. 1.1 dm^3) which is situated in an adiabatic enclosure. The combination of the low heat loss Dewar vessel and adiabatic surroundings produce a system with heat loss characteristics similar to those of extremely large process vessels (up to approx. 25 m^3). The Dewar vessel is fitted with a mechanical agitator, temperature probes, heating coils, pressure measurement facilities and a dual vent system to prevent overpressurisation of the reactor (the vessel typically withstands pressures in excess of 30 bar). A schematic of the equipment is provided in Fig. 3.

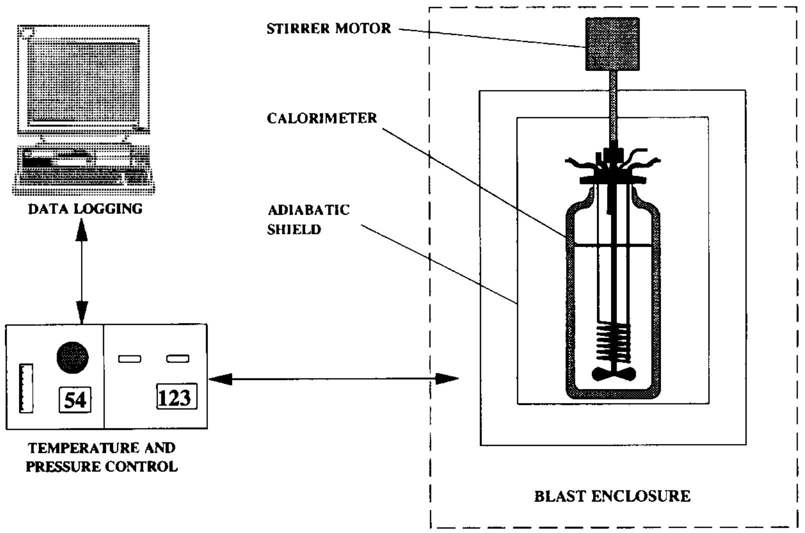

Fig. 3. Schematic of the adiabatic pressure Dewar calorimeter.

The chlorination reaction was undertaken using a Halar- (polyfluorinated hydrocarbon) lined vessel to prevent possible catalysis of the reaction (and corrosion of the vessel) by the interaction of chlorine with stainless steel. The reaction mixture (dichloromethane, pyridine and chlorine) was prepared in laboratory glassware at −20°C and charged to the pre-chilled Dewar vessel. The head of the vessel was assembled, the instrument placed within the adiabatic enclosure and then connected to all relevant logging and control systems. After a short baseline had been obtained (11 min), the substrate (at 20°C) was pumped into the vessel (using a high pressure dosing pump) over a period of 10 min. The resulting exothermic reaction is illustrated in Fig. 4.

The temperature increased linearly (at first) in a manner which could be predicted from the isoperibolic work. However, on reaching approx. 45°C, a secondary exothermic decomposition event was observed that increased the reaction mass temperature and pressure to 118°C and 14.5 bara. These conditions are markedly above those which could be predicted by the isoperibolic work (60°C (for a phi factor of 1.14) and 3.4 bar). Fig. 4 also illustrates the theoretical temperature and pressure profile which are derived from the isothermal study.

5. Determining the basis of safety for the plant

For any chemical reactor, a documented basis of safety should be available. This should contain a comprehensive review of hazards posed by the reaction in conjunction

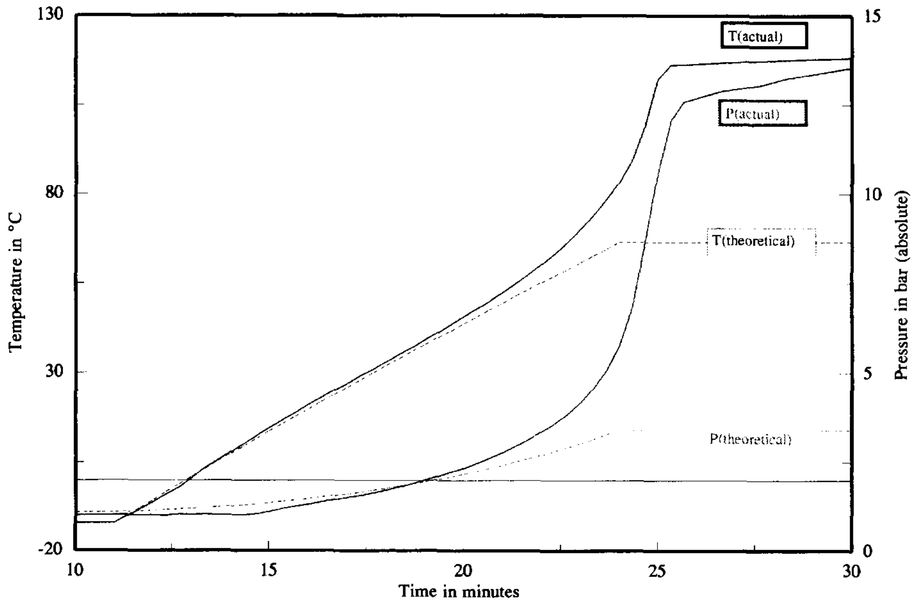

Fig. 4. Chlorination reaction; adiabatic Dewar calorimeter experiment.

with a thorough consideration of the engineering of the plant. The basis of safety should include the safety specific plant measures required to ensure safe manufacture by either;

(i) The incorporation of measures to prevent a runaway reaction occurring, or, more usually;
(ii) The incorporation of measures which minimise the risk of a runaway reaction occurring, coupled with systems that will protect the reactor in the event of a runaway reaction.

Measures to protect against runaway reactions may include emergency relief venting, additional (back-up) cooling facilities, reaction inhibition or a total containment system, i.e. constructing the reactor or reactor housing to withstand the peak pressure from a runaway event. Choice of the appropriate measures will involve an assessment of the reliability of the protection system, the ease of engineering, cost implications, and ease and cost of maintenance.

For the chlorination reactor, process control (backed up with reactor venting) was the preferred basis of safety. Based on the isothermal test results, the calculated peak pressure from the reaction (3.4 bar) would not be sufficient to overpressurise the reactor (design pressure, 6.9 bar). It may therefore have been interpreted (incorrectly) that an emergency relief vent is not required for this runaway reaction and that containment can be defined as the basis of safety. From the adiabatic test result, a peak pressure of 14.5 bar would occur (hence presenting a risk of overpressurisation in a sealed or inadequately vented system).

A vent sizing analysis using DIERS [13] equations for a vapour pressure system was conducted based on the adiabatic test results. These calculations indicated that a minimum vent diameter of 6.2 inches (including a safety factor of 1.5 and allowance for the down-rating effect of the vent line) would be required to protect the reactor pressure from exceeding 6.9 bar.

The following measures are also recommended to minimise the risk of any additional runaway reaction scenarios arising.

(i) High reliability engineering and procedural measures to ensure that the maximum reactor temperature at the start of the addition is $-12°C$.
(ii) High reliability engineering and modification control measures to prevent substrate feed durations of less than 10 min.
(iii) High reliability engineering measures to ensure that the agitator is interlocked to the feed to prevent feed without agitation and consequent stratification. This scenario could potentially lead to an all-in batch process with uncontrollable rates of temperature rise.
(iv) High reliability engineering and procedural measures to ensure the use of correct reagent quantities added at the correct stage of the process. For example, the consequence of undercharging solvent (given that chlorine is in excess for the desired reaction) would be a reduced system heat capacity, and increased adiabatic temperature rise, and thus the installed vent system would be under-specified. In addition, not charging the catalyst at the correct stage of the process could lead to accumulation of unreacted substrate.

It was recommended that adequate two-phase, i.e. liquid and vapour, separation and containment facilities were designed to prevent exposure of plant and external personnel, and the environment, to the release that may occur during a venting incident.

6. Conclusions

This paper clearly illustrates (with reference to a specific example) the role of isoperibolic and adiabatic reaction calorimetry in the assessment of a chemical process with respect to its reaction hazards. The need for detailed assessment of plant conditions and investigation of all possible failure scenarios is also highlighted. The most important conclusion from the article is that isothermal (or near-isothermal) calorimetric data should be interpreted with consideration of the applicable ranges of the data only. The extrapolation of isoperibolic data to adiabatic conditions is a dangerous exercise in which secondary reactions which occur at elevated temperature can be overlooked. It is often these secondary reactions which give rise to the major process hazard since, as illustrated in this chlorination reaction, the semi-batch chlorination process (when conducted with inadequate cooling) leads to a rapid and violent batch decomposition process. The use of isoperibolic heat flow and adiabatic calorimetric techniques in deriving the necessary data are also highlighted.

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References

[1] C.A. Davies, et al., The ASTM Chemical Thermodynamics and Energy Release Evaluation Program, 2nd edn., ASTM, Philadephia, DS 51A, 1990.

[2] K. Dixon-Jackson, The use of advanced DSC techniques in the assessment of thermo-chemical hazards, 4th Int. Conf. on the Assessment and Control of Chemical Reaction Hazards, IBC Tech, Services (E7770), London, December 1993.

[3] J. Barton and R.L. Rogers, Chemical Reaction Hazards–A Guide, IChemE, Rugby, England, 1993, pp. 30–32.

[4] W. Regenass, Thermal and kinetic design data from a bench scale heat flow calorimeter, ACS Symposium Series No. 65, 1978, Houston, p 37.

[5] S.P. Waldram, Isothermal calorimetry: extracting kinetic information from heat flux measurements, Chemical Industry Digest, March (1993) 111–114.

[6] R.L. Rogers, The use of Dewar calorimetry in the assessment of chemical reaction hazards, IChemE Symp. Series No. 115, 1989, p. 97.

[7] C.F. Coates, The ARC in chemical hazard evaluation, Thermochim. Acta, 85 (1985) 369–372.

[8] Bench Scale ERS Sizing Tools: Equipment Details and Test Procedures, Design Institute for Emergency Relief Systems Report,. FI/84-4, AIChE, 1984.