Calorimetric Screening of Exothermic Reactions and Materials

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Abstract: Examples are given of how the Rapid Screening Device (RSD) can give vital information to allow safe processing, safe storage and safe transportation of hazardous and potentially exothermic materials. The RSD is a new technique of relatively low cost but rapidly and safety will give quality temperature and pressure data on any exothermic (and endothermic) reaction – up to 6 samples may be tested simultaneously. The RSD is an ideal first instrument for a company investing in chemical safety measurement. It is easy to use and the data produced is simple to understand. Applications (as given) range from low energy to high energy reactions; eg chemicals, monomers, reactive mixtures, propellants or explosives.

Key words: safety; calorimeter; exothermic reactions; thermal hazard; screening

1 Introduction

Knowledge of potential exothermic reactions is vital for safe processing, safe storage and safe transportation of chemicals and systems. A reliable safety calorimeter will provide much of the data that is needed to allow safe operation of any Chemical Processing facility.

However, many types of safety calorimeters have been devised. The world benchmark safety calorimeter is the Accelerating Rate Calorimeter (ARC™*). The true ARC™ is manufactured uniquely by Thermal Hazard Technology. This sophisticated system allows full time-temperature-pressure data under highly adiabatic conditions. An ARC™ test simulates any potential runaway reaction safely in the laboratory. The ARC™ has been commercially available for 25 years and is in use around the world (with instruments in use in China). It is used by most of the major Chemical and Pharmaceutical Companies as well as those making potentially hazardous materials.

Acquiring the ARC™, however, is a major investment and small or medium size chemical companies often do not have the resources or experienced personnel to purchase such an instrument and to make the best use from it. There has been extensive literature articles on the ARC™.

Smaller companies and those starting to develop safety testing techniques are often better suited to a smaller, simpler, lower cost instrument – an instrument that will produce quality data but more rapidly and with ease of use and data analysis. Until now, many such tests have been carried out with home-built apparatus or technologies (eg DSC) that are not purpose-designed for safety work.

To complement the Thermal Hazard Technology's ARC™, the Rapid Screening Device, RSD™ has been made commercially available. This is a screening and isothermal calorimeter designed to study exothermic materials. It has been designed to overcome limitations of other 'entry-level' techniques, for example "heat loss". The RSD can screen multiple samples simultaneously and a test may be set up to screen sample(s) ie to carry out a rapid test; or to operate more slowly to get good quality data on any exothermic reactions.

The requirement of a low cost, entry-level calorimeter is one that can be

Flexible and versatile in use
Quantify any exothermic reactions with quality reliable data

*ARC™ is a trademark of Thermal Hazard Technology in Europe

Yield reliable onset of reaction temperature and information on pressure generated
Be safe to use
Be rapid in use
Easy to use GUI software for control and data analysis
Low running and maintenance costs

These criteria have been met for the first time in the RSD™.

2 Experimental

The RSD incorporates patented novel and unique features. The calorimeter chamber is heated by a recirculating air bath. The chamber is of size that up to 6 samples can be accommodated. Sample holders may be "ARC-bombs", sealed tubes, glass vials or of any home-designed style. The samples are sealed with a head part through which goes the measuring thermocouple. There is a pressure tube that goes to individual low-cost pressure transducers and a burst disc can be incorporated to prevent the sample holder rupturing.

For safety, in addition to the burst disc, there is a double safety door interlock and proximity switch. The software activates fail-safe quench cooling. The calorimeter is rugged and of stainless steel construction. In operation all necessary components are within the hot zone (to give optimal data) and the calorimeter itself is within its sealed metal enclosure, for safety. During the test, there is continued extraction to negate any possibility of toxic or noxious fumes.

The system can ramp heat at up to 10°C/min for rapid screening tests or can be used at a slower rate (eg 0.5°C/min) or isothermally to obtain potentially better data. Though up to 6 samples can be used simultaneously, aften one 'sample' is a reference (empty container, solvent, or other inert material). Working this way, it is simple to enhance quality and presentation of data by plotting Temperature and Pressure Differences (sample minus reference).

The system is versatile, allowing sample agitation, dosing and cryogenic options. The outer enclosure is fully self-contained, it houses the calorimeter and all electronic components. Serial and USB connections to any PC, for test set-up and control and data analysis. Fig. 1 and Fig. 2 show the overall unit.

Fig. 1

Fig. 2

Fig. 3 and Fig. 4 zoom in to the calorimeter sample chamber. Fig. 5 details the types of sample holder that may be used and also shows the connecting head. The latter illustrates the thermocouple entry and the burst disc, there is no pressure line connected.

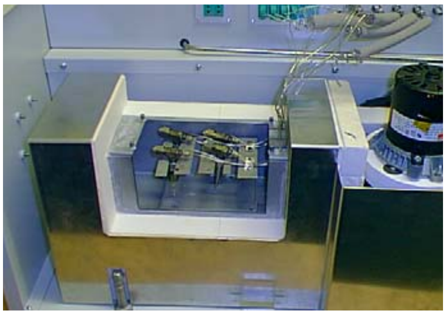


Fig. 3

Fig. 4

Fig. 5

In operation, the system may ramp (at the chosen rate) and then soak (isotherm). Fig. 6 and Fig. 7 show performance of the unit.

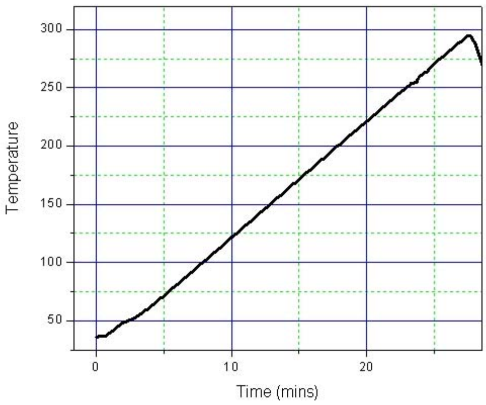


Fig. 6

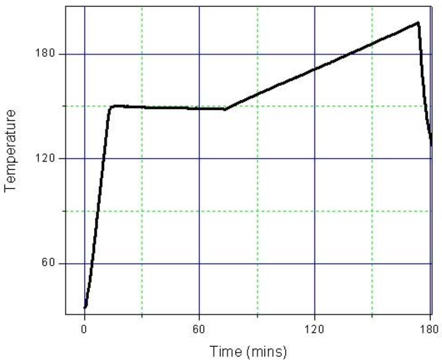


Fig. 7

3 Results

Di-tertiary Butyl Peroxide (DTBP) is a suitable ‘standard’ material to illustrate performance and indicate application possibilities of this (or any) safety calorimeter. DTBP decomposition (kinetics and thermodynamics) is well documented and over the years it has been used as a standard material for testing the ARC™ and other calorimeters. It is an energetic material and usually tested as a 20% solution in toluene.

3.1 20% DTBP-Toluene

Tests have been carried out with two identical samples and with a third ARC-bomb containing toluene as a reference. Sample data is shown here. The ramp is linear until the exotherm commences and with the increasing temperature ramp, the reaction proceeds and causes large temperature excursion within the sample. Fig.8 shows the thermal data to be expected from this standard sample. It is plotted alongside the pure toluene reference. 20% → 140°C. Fig. 9 shows the Temperature data from all four thermocouples. The ramp rate of the test is controlled by the control thermocouple, this is in the air of the chamber. The data also shows the thermocouple in the two 20% DTBP samples and the thermocouple in the pure toluene reference.

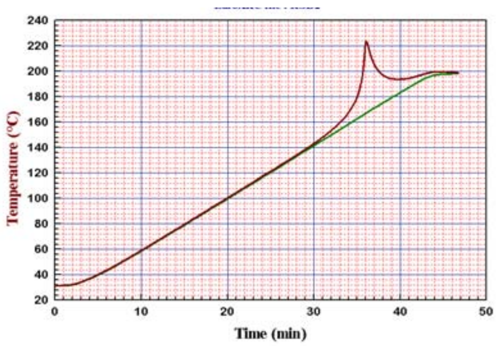


Fig. 8

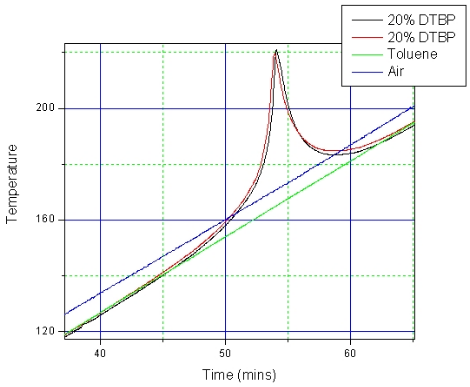


Fig. 9

A standard method of graphical presentation with the RSD is temperature difference or Delta T (sample temperature minus reference temperature). This of course is only possible when a reference sample has been run. Such a plot is shown in Fig. 10. From this plot the exotherm can most clearly be seen.

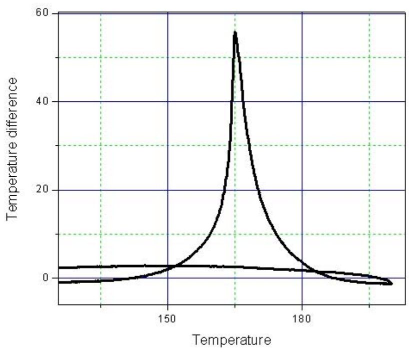


Fig. 10

3.2 5 – 20% DTBP

As the percentage of DTBP in toluene is decreased, the solution simulates a less energetic sample. The tests and data detailed here have been carried out in just one experiment. Four titanium ARC-bombs contained 6gms of 5%, 10%, 15% and 20% DTBP in toluene and a fifth similar sample container had 6gms of toluene. The samples were heated at 4°C/min. The Heat of Reaction of DTBP is approximately 175 kJ/mole or 1200J/g. Therefore 6gms of a 5%, 10%, 145% and 20% solution would decompose to give approximately 350 Joules, 700 Joules, 1050 Joules 1400 Joules respectively.

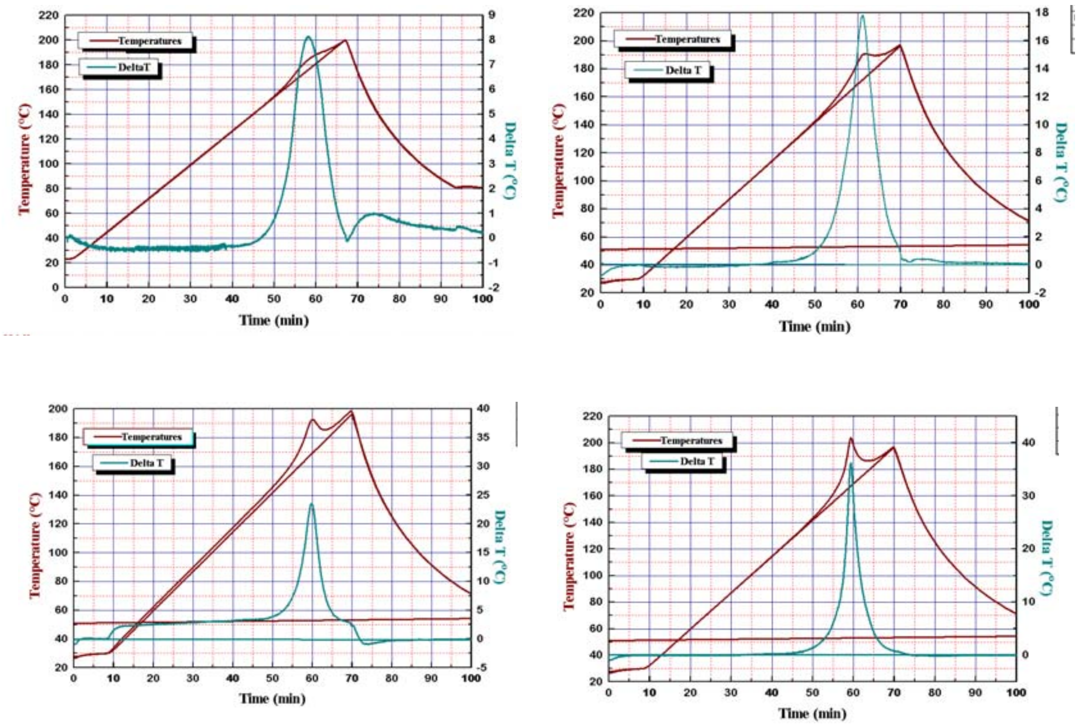
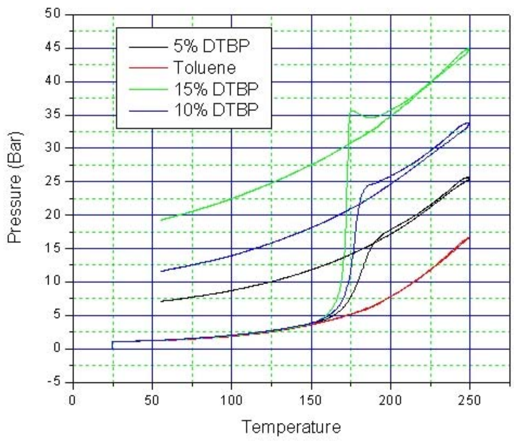


Fig. 11

Fig. 11 show both temperature and temperature difference for these four samples. The temperature rise in the sample is clearly seen in all four samples. However, plotting this temperature on the same graph as the reference sample shows the temperature excursion very clearly. From this it can be seen that the exotherm would be observed in this way for materials with even lower heat output.

But the plot showing temperature difference is more revealing. Clearly this plot shows the exotherm most distinctly – and is the best plot to display the onset of exothermic reaction. Looking just at the temperature plot may suggest an onset near 140^{o}C, but from the different plot, the onset is seen 15 – 20^{o}C lower, near 120^{o}C. The temperature rise of 8^{o}C, 18^{o}C, 23^{o}C, 36^{o}C approximately is in uniform variation with the percentage of DTBP and the heat output. This is not to suggest that there is quantative operation of the RSD with samples of this heat output – but as a 'rule of thumb' the relationship between temperature rise and heat output can be useful.



Pressure vs Temperature for Different Concentrations of DTBP

Fig. 12

Pressure data of 5 – 15% DTBP is shown in Fig. 12. The red curve is the data from the reference sample and it is clear that the pressure of all four tests deviate at a similar temperature with the pressure rise approximately linear with DTBP content. The cool-down pressure data differentiates condensible from non-condensible gases.

3.6 1 – 3% DTBP

With a very small amount of active material in the sample, a simulation of very low energetic samples is possible. With the ARC™ detection of reaction from below 3% DTBP is not possible (this is because the sample thermocouple is not within the sample and the temperature is not ramped). A 6gm sample of 1% solution would decompose to give approximately 72 Joules and this figure would be doubled for a 2% solution etc. The tests are shown in Fig. 13.

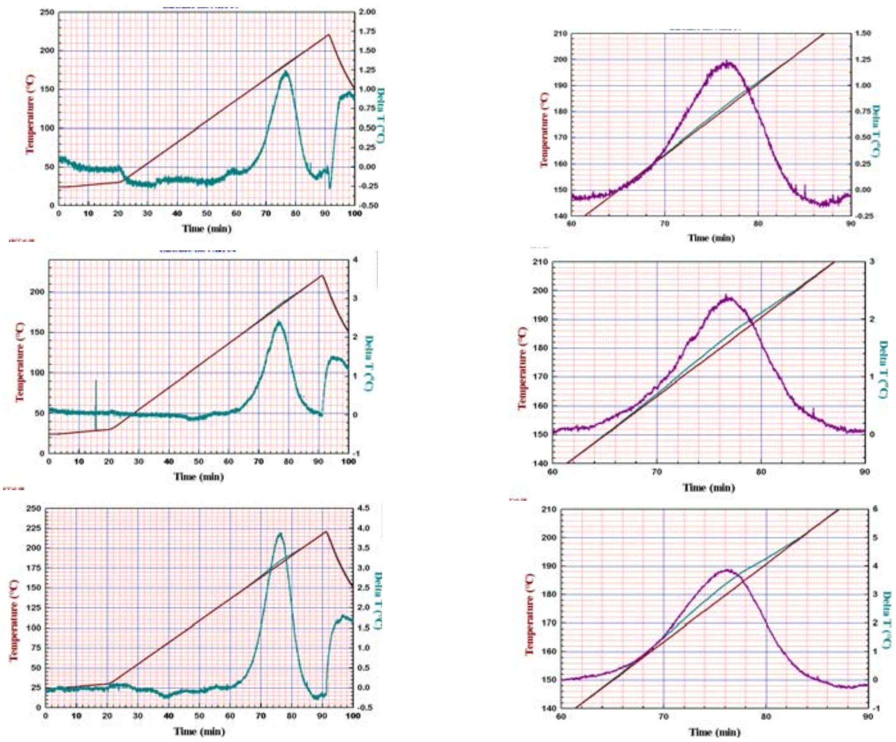


Fig. 13

The sample data is compared with the reference data and automatically subtracted to give differential temperature data. The results are shown graphically and clearly with all three samples the heat of decomposition is shown. Whilst this is not clear from the raw temperature data, the differential data makes the results very clear. Further tests have shown that DTBP solutions of 0.5% give measurable heat outputs. The results imply that under these experimental conditions – conditions that are perhaps 'standard for screening' the RSD will record heat outputs down to the 20 Joule level. It is also possible to see the decomposition by the pressure rise – though data is not presented here. Comparison of the graphs may be done as shown in Fig. 14.

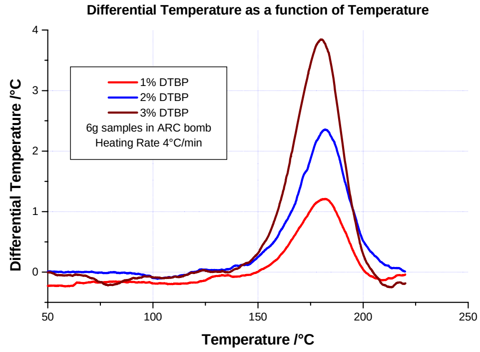


Fig. 14

The quantative nature of the RSD can be seen by this data. Quantative data analysis can be achieved if the area under the peaks is integrated and the data plotted (Fig. 13 and Table 1). Measuring the peak areas has shown a linear relationship between the recorded heat output and the sample DTBP content. As such, and probably over a DTBP range from below 0.5% to above 5%, the heat output peak could be used to measure the DTBP content. Alternatively, the peak size from similar systems could then be converted into heat output, ie Joules. An important application of this would be in the field of solvent recovery and distillation. Often solvents are used in industry and they are contaminated with a small percentage of reactive chemical. After recycling, they are returned and re-used. The RSD offers a simple and inexpensive way to determine the hazards from contaminated solvents. The RSD can determine the percentage of reactive chemical in the solvent before and after distillation – and can of course determine the hazard associated with the still bottom residue a product that would increase in volume and hazard with time!

% DTBP	Raw Integrated Area
1	204
2	416
3	620

Table 1

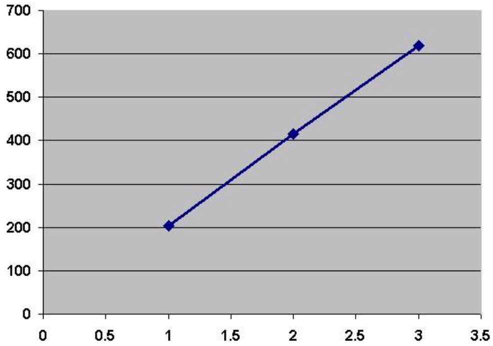


Fig. 15

4 Other Samples

RSD tests showing applications from a range of machine and hazardous chemicals will be added during presentation of this paper. The full text will be available on the THT website, they are not included here to prevent the paper being overlong.

5 Conclusions

The data highlighted illustrates the versatility and wide applicability of the RSD. It shows the importance of using a reliable screening calorimeter in any safety testing protocol. For safety testing a sample of significant size is needed and pressure data is essential. As chemical industries expand and develop in new geographical regions – as is now happening in China – the need for safety testing (as well established in the developed western countries) becomes vitally important. Though sophisticated, techniques are available, a rapid and easy to use safety calorimeter, like the RSD, is the instrument required to start a professional safety testing program.