

WITH THERMAL SCREENING EXPERIMENTS MAKE SURE TO FOCUS ON THE REAL PROBLEM: THE ROLE OF THE TS^U

Simon Waldram, HEL, Barnet, UK

www.helrroup.co.uk

SUMMARY

The limitations of DSC as a tool for thermal screening are discussed and the Thermal Screening Unit (TS^U) is described. Ramped temperature experimental data for families of experiments on di tertiary butyl peroxide in toluene and azobis cyano valeric acid in dimethyl formamide are presented and used to illustrate the absolute necessity of recording pressure as well as temperature during any thermal screening tests.

Keywords: thermal screening, ramped temperature, exotherms, pressure generation, TS^U, runaway reactions

1. INTRODUCTION AND OVERVIEW

Thermal screening may be required for single pure components, for reaction mixtures, for crude reaction products or for samples of uncertain composition such as distillation residues or sludges from the bottom of vessels. The sample must be large enough to generate results that are representative and the experimental technique must be such as to give results that will reproduce what may happen in large scale equipment. By definition a screening test may have to be used to assess many samples, so it must be relatively cheap and quick to perform. Also, it must always be remembered that reactions can take place in many locations other than reactors, so the contents of storage tanks, evaporators and distillation columns will need to be assessed as well as reactor samples.

It is important to think with clarity about thermal screening and to identify the real hazard: it seldom is, per se, a high temperature but is almost always the high pressure that can be associated with that temperature. It is pressure that will cause relief valves to lift, bursting disks to rupture, equipment to fail and “missiles” to be hurled through the air. This leads to the potential loss of containment that results in environmental damage, toxic risk and fires and explosions. Well known examples include the relief valve lifting on the methyl isocyanate storage tank at Bhopal, (reference 1), the reactors that failed under pressure at Ringaskiddy (reference 2) or Huddersfield (reference 3) and the bursting disk that ruptured at the chemical facility at Meda, near Seveso (reference 4). This latter incident, of course, helped shape the EC Seveso Directive and associated national legislation such as the “Control of Major Accident Hazards Regulations 1999” in the UK.

Set against this background it is quite extraordinary to continue to hear of individuals and companies who advocate using Differential Thermal Calorimetry (DSC) for thermal screening. Not only does DSC fail to measure the primary hazard of interest (i.e. the

pressure), but as long as 15 years ago experienced practitioners demonstrated the difficulties (some would say impossibility) of applying the “onset” temperatures determined by DSC to the large scale and the folly of imposing arbitrary safety margins, for instance applying the “100 degree rule”.

DSC tests will not reveal the hazards of slow gassing associated with weak exotherms, the generation of non-condensable gases during an exotherm nor the dangers of weak endothermic decompositions that generate gas.

2. THE THERMAL SCREENING UNIT (TS^U)

The Thermal Screening Unit (TS^U) was designed to address some of the the particular problems outlined in section 1: it is illustrated in figure 1. The sample size is up to ~ 8 ml and pressure in the test cell headspace is measured as well as the sample temperature. The equipment can be operated isothermally or in ramped temperature mode and with a variety of test cell types: combinations of isothermal holds and temperature ramps can be combined into a single test. Details of the equipment and the ways in which the experimental data can be processed to reveal “onset” temperatures and thermokinetic parameters have been described previously, see reference 6.

The word “onset” is widely used but can be very misleading. The “onset” temperature is not a fundamental property of the sample but rather a reflection of the sensitivity of the instrument being used to search for thermal activity. Highly sensitive instruments will detect lower “onsets”, less sensitive ones higher “onsets.”

Figure 1: the TS^U equipment when both closed (left) and open (right)

3. EXPERIMENTAL RESULTS

Results from a typical ramped temperature experiment are shown in figure 2. These same data are re-presented in figure 3 but in the form of first and second derivatives of the sample temperature plotted as a function of temperature. The “onset” temperature that we report is defined by the point at which the second derivative of sample temperature starts to rise, see figure 3.

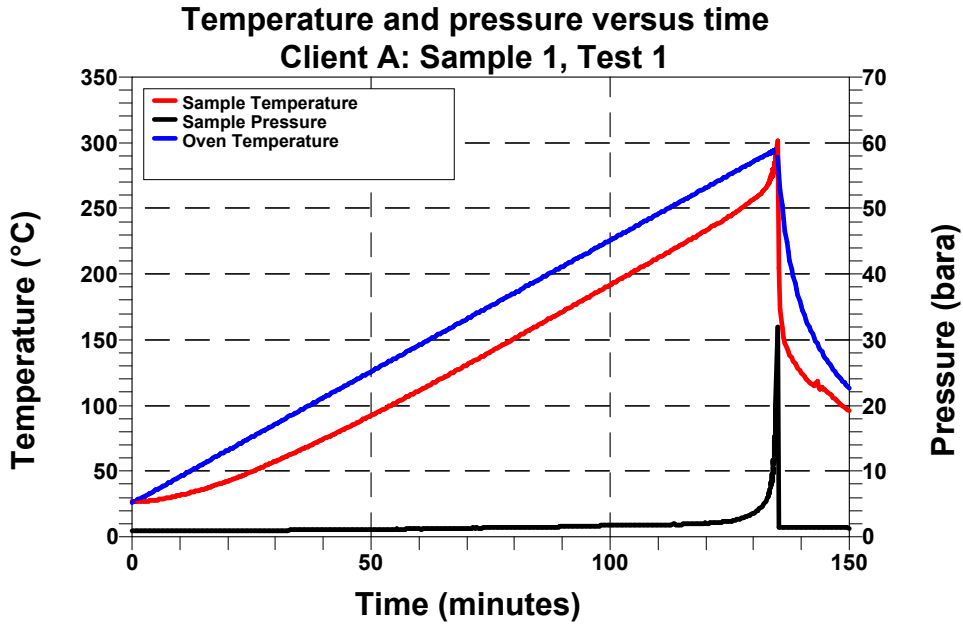


Figure 2: typical ramped temperature data

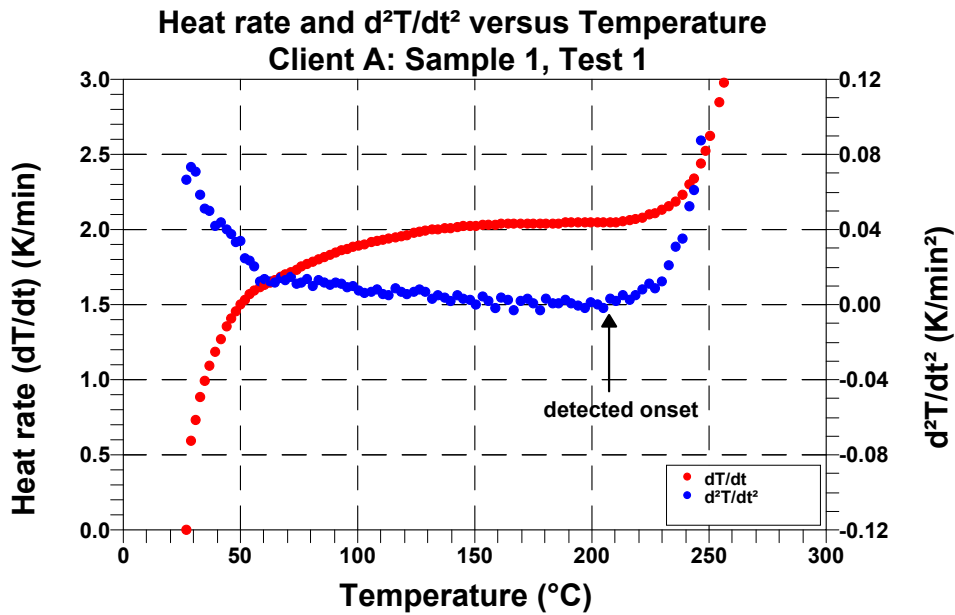


Figure 3: definition of the “onset” for thermal activity

From figure 3 the “onset” is seen to be $\sim 210^{\circ}\text{C}$, considerably lower than would be estimated by eye from figure 2 alone. Onset temperatures determined in this manner show good agreement with those evaluated from heat-wait-search experiments in adiabatic calorimeters: examples are provided in reference 6.

3.1. Data for Di-Tertiary Butyl Peroxide (DTBP) in toluene.

The first family of data presented are for Di Tertiary Butyl Peroxide (DTBP) at mass concentrations of 10, 15, 20 and 25% in toluene. Time is shifted for each test so that the oven temperature falls on a unique locus thus allowing the thermal data to be compared directly. Regions of no thermal activity are present at the start and end of the test whilst in the centre the exotherms of varying strength are seen. At mass concentrations of 20 and 25% these are sufficiently energetic to raise the sample temperature well above that of the surrounding oven. Figure 4 shows the thermal data for the 4 experiments whilst figure 5 shows the pressure data. In this latter figure the trend of the pressure data for 15% by wt of DTBP in toluene does not fit perfectly with the other data and indicates a possible small leak from the test cell. This may happen because the Swagelok fittings have been insufficiently tightened: for this reason a pressure test prior to the experiment is recommended. Small pressure leaks during any type of thermal screening can lead to evaporative cooling (tempering) and may mask an exotherm. It is always good practice to weigh the sample and cell both before and after the experiment to check for sample loss.

Note that if non-condensable gas generation is associated with the thermal activity then it is not unusual to be able to detect the onset of gassing in the pressure trace before the exotherm becomes detectable. This is simply because pressure transducers are very sensitive: as a result, gassing into a small, sealed test cell headspace is a very sensitive experimental method for detecting the onset of this type of decomposition.

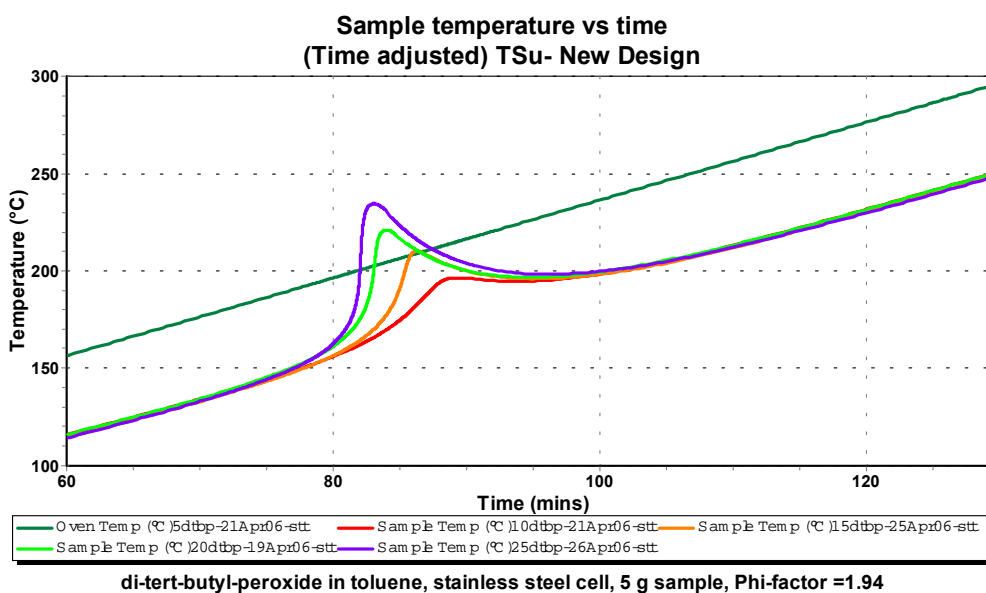


Figure 4: family of exotherms for DTBP in toluene at mass concentrations of 10, 15, 20 and 25%

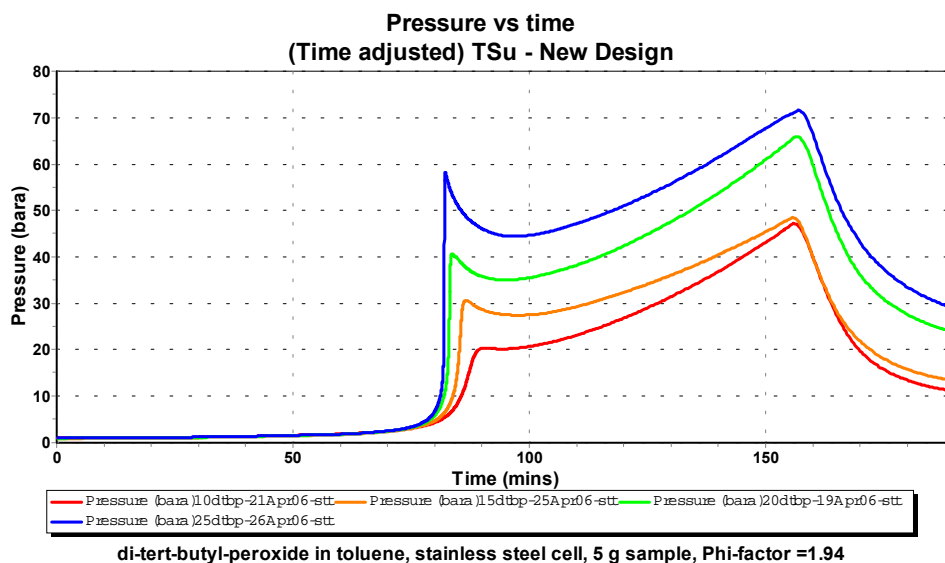


Figure 5: family of pressure traces for DTBP in toluene at mass concentrations of 10, 15, 20 and 25%

It is often very useful to take the data presented in figures 4 and 5 and to present it in the form of a pressure vs temperature plot as illustrated in figure 6.

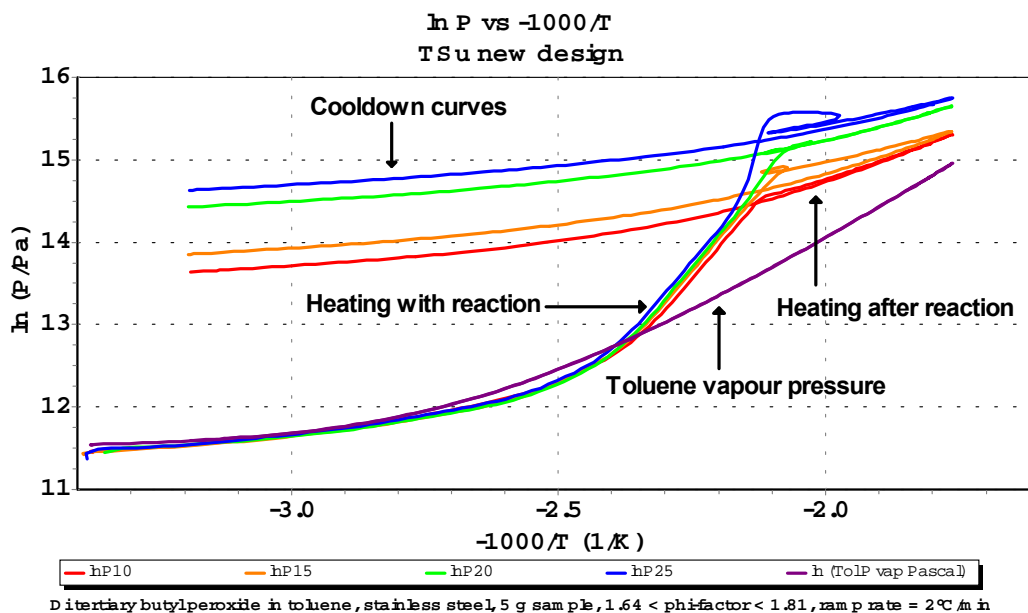


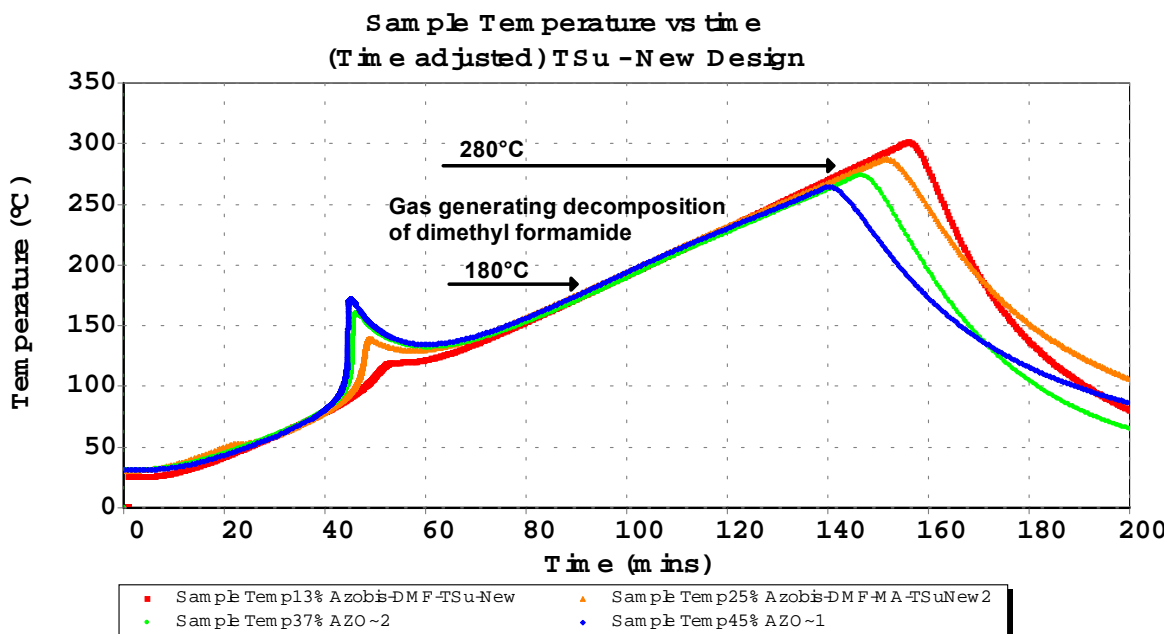
Figure 6: family of pressure vs temperature traces for DTBP in toluene at mass concentrations of 10, 15, 20 and 25%

This shows clearly the early phases of the experiments during which the test cell pressures agree well with the saturated vapour pressure for toluene. Then there are the periods of exothermic activity during which the temperature and pressure are increasing rapidly. In the case of the more concentrated tests the samples then cool and as this happens the pressure reduces: finally the reaction product mixtures are raised to the maximum temperature in the tests. It is important to note that during the final cool down the pressure vs temperature trajectories are such as to retrace the curves corresponding to the post-reaction heat up of the reaction products. This demonstrates conclusively that the reaction products produce no further non-condensable gas as they are heated: they also show no evidence of any subsequent exothermic or endothermic activity.

Note that the final cooldown curves are elevated with respect to their early heat-up counterparts. This is clear evidence of non-condensable gas generation associated with the exothermic activity. Note also that the trace for 15 wt % of DTBP in toluene confirms the likelihood of a small leak from the test cell in that the initial cool down curve from the highest temperature does not overlay that of the analogous heat-up curve.

3.1. Data for AzoBis (4-Cyano Valeric Acid) (ABCVA) in Dimethyl Formamide (DMF)

The second family of data are for ABCVA at concentrations of 13, 25, 37 and 45 % by weight in Dimethyl Formamide (DMF). The temperature traces are shown in figure 7. Phases of exothermic activity are clear but what is not revealed is that there is also non-condensable gas generation between temperatures of ~ 180°C and 280°C.



azobis (4-cyanovaleric acid) in dimethylformamide, hasteby cell, 5 g sample, 1.73 < phi-factor < 1.95, ramp rate = 2 °C/min

Figure 7: family of exotherms for ABCVA in DMF at mass concentrations of 13, 25, 37 and 45%

This is revealed most clearly in figure 8, the counterpart plot to figure 6. For this system non-condensable gas generation continues to take place even after the exotherm has expired. This in fact is due to the decomposition of the DMF and can be confirmed by independent TS^U or adiabatic (PHI TEC) tests on pure DMF. Because this decomposition is only very weakly exothermic it is not revealed in figure 7. However, in figure 8 it is clear that the heat-up and cooldown of the reaction products remaining in the test cells after exothermic activity has ceased do not over lie each other. More non-condensable gas is being generated: this part of the hazard associated with the samples can never be revealed in a test that records temperature alone.

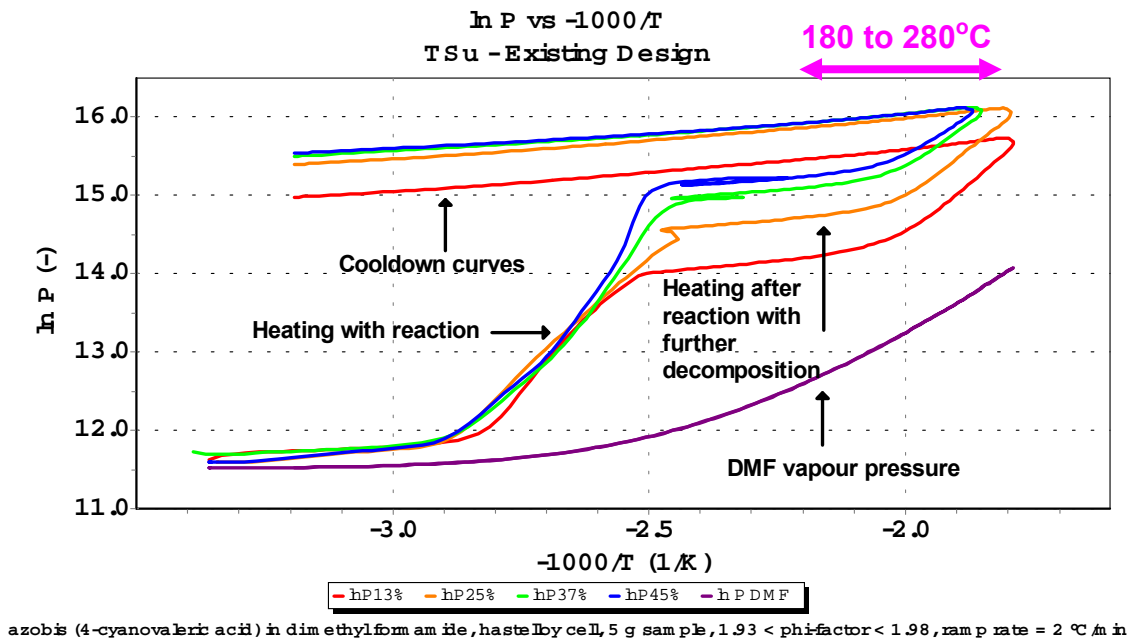


Figure 8: family of pressure vs temperature traces for ABCVA in DMF at mass concentrations of 13, 25, 37 and 45%

4. DISCUSSION AND CONCLUSIONS

The main hazard associated with exothermic activity is the pressure that may be generated. Thermal screening methods in which temperature alone is measured will never reveal the extent to which pressure may rise during the exotherm, nor whether this is attributable solely to the vapour pressure of the sample or whether non-condensable gas is being generated. To continue to advocate and use thermal screening methods that do not measure temperature is at best naïve and at worst foolhardy.

5. REFERENCES

1. Lees F P, Loss prevention in the process industries, Second Edition, Butterworth Heinemann, 1996, ISBN 0 7506 1547 8, Vol. 3, Case histories, Bhopal, A5/1 to A5/11
2. “Report of investigation into a major accident at Hickson PharmaChem Ltd., Loughbeg, Ringaskiddy, Co. Cork,” Health and Safety Authority (Ireland), October 1994, ISBN 0 7076 0448 6
3. Partington S, Waldram S P, “Runaway reaction during production of an azo dye intermediate”, Trans IChemE, Vol. 80, part B, Jan 2002, pages 33 – 39
4. Lees F P, Loss prevention in the process industries, Second Edition, Butterworth Heinemann, 1996, ISBN 0 7506 1547 8, Vol. 3, Case histories, Seveso, A3/1 to A3/14
5. Hofelich T C and Thomas R C, “The use/misuse of the 100 degree rule in the interpretation of thermal hazard tests”, International symposium on runaway reactions, Cambridge, Massachusetts, March 7 – 9 1989, AIChE, ISBN 0 8169 0460 X, pages 74 to 85
6. McIntosh R D, Waldram S P, “Obtaining more, and better, information from simple ramped temperature screening tests”, J of Thermal Analysis and Calorimetry, Vol. 73, 2003, pages 35 to 52.

SPW\My documents\TSU performance .doc