

A COMPARISON OF DSC AND RADEX FOR THE INVESTIGATION OF SAFETY PARAMETERS FOR INHOMOGENEOUS SYSTEMS

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INTRODUCTION

Reliable data on the decomposition of inhomogeneous reaction masses can be difficult to obtain.

Sampling can be a particular problem when carrying out small scale work and can lead to a wide variation in results, such variation could have potentially hazardous implications for process operations.

This paper highlights some of the advantages and disadvantages that can occur when using Differential Scanning Calorimetry and provides a comparison with an alternative experimental method using a RADEX.

DIFFERENTIAL SCANNING CALORIMETRY

When carrying out investigations into the process safety of a given chemical route one of the more commonly used techniques is that of Differential Scanning Calorimetry (DSC). The use of DSC as a screening tool for potentially hazardous materials is widely reported in the literature (D Dale, 2002), (Barton, 1997), (Baline, 1999).

DSC is a useful method for detecting potentially hazardous reactions and in estimating the temperatures at which these reactions will become apparent.

The technique has significant advantages in that it utilises a small sample size (a few mg) and can therefore be carried out at an early stage of the development cycle when material availability can be a problem. The test typically takes only a couple of hours to run and it provides very useful information on both the thermal stability and decomposition potential of a material.

For homogeneous samples good reproducibility between experiments can be obtained provided that care is exercised in sample preparation. The ASTM method (ASTM Standard test method E537-02) indicates that in an inter laboratory round robin test series the standard deviation for reproducibility with respect to onset temperature was 10 K and for reaction enthalpy 4.7%. The ASTM method does however include a number of caveats:

- 1) 'it is imperative that the qualitative results obtained from DSC be viewed only as an indication of the thermal stability of a chemical',
- 2) Onset temperature is affected by heating rate and only results obtained at the same heating rate should be compared.

Notwithstanding these comments, in the hands of a properly trained operator, DSC is an extremely powerful tool.

There are however a number of disadvantages with the technique which limit its use under certain circumstances.

Firstly it is not possible to obtain data on pressure generation. As the decomposition of materials is often accompanied by gas evolution (which manifests itself as a pressure rise in a sealed system) this is important information necessary for safe plant design.

Secondly, the generation of vapour pressure in sealed crucibles can lead to overpressurisation and rupture. This limits the effective temperature range over which the technique can be used.

Thirdly, although good reproducibility is relatively easy when pure liquids or solids are being tested inhomogeneous systems are difficult to examine. There are a number of ways that this problem can be overcome such as

- 1) repeated sampling in order to obtain a 'mean' result – as the sample size is of the order of a few mg it can be difficult to obtain a representative sample. A large number of tests could be carried out but there may not be a high degree of confidence in the results. This poses a dilemma, do we take the answer that gives us the least problems or do we assume the worst and over-design a solution. Neither option is satisfactory.
- 2) Separate the test substance into its component parts then test each material individually. An approximation of the overall heat output could then be made by proportion. This is unlikely to be successful as it would not show the effect of interactions.
- 3) Take a sufficiently large sample of material such that it can be broken down into separate phases (eg. solid and liquid). Take a representative sample of each phase then reconstitute the reaction mass in the DSC crucible. This could be the most sensible way of proceeding however experience has shown that the results obtained are not what is expected – sometimes the heat output differs significantly from predicted values. Although our experience has not shown any obvious trend sometimes we appear to over estimate other times it is an underestimate, it is thought that the lack of mixing has an effect on the heat transfer within the cell leading to unexpected results.

From the above we have concluded that none of the obvious 'solutions' actually provide us with data that enables us to have sufficient confidence in all cases to base safety upon the DSC results.

Clearly a system is needed that provides data on pressure and heat evolution at the same time as using a larger sample size which will overcome some of the problems associated with sampling of inhomogeneous materials. A number of such systems are available

within our Company but for the purposes of this paper we examine a comparison between results obtained from DSC with those obtained from RADEX.

RADEX (Schweizer Maschinenmarkt 1990), (Neunfeld 1993) (Figure 1).

This equipment was originally developed by SANDOZ in the 1970's and has subsequently been commercialised by SYSTAG.

The RADEX is a versatile tool and can be operated in a number of modes such as dynamic, isoperibolic and adiabatic. For the purpose of this paper we are concentrating upon its use as a dynamic screening tool, which provides data on thermal as well as pressure generating events.

Although the overall principle of the technique is similar to DSC with the RADEX calculating the heat output based upon the temperature difference between the sample and oven temperatures taking into account the effect of the cell (i.e. heat capacity, fill level, mass of cell etc), no reference cell is used.

The geometry of the crucible and the sample size (typically 1 to 3 g) means that sampling of inhomogeneous reaction masses can be carried out relatively easily, although once sampled it is not possible to provide further agitation.

Cells are available in steel, steel with a glass liner or simply glass. When the steel or glass lined cells are used then pressure measurements can also be obtained up to 200 bara (2900 psia) alternatively the cell can be connected to a gas flow meter and rates of gas evolution against time and or temperature can be measured.

Experience has shown that using a heating rate of 0.75 K/min is comparable to a DSC scanning rate of 4–5 K/min over the range 50–400°C.

The manufacturers claim a sensitivity of ca 1 W/kg, however we have found that a value of 5 W/kg is a better value to use. For comparison DSC is typically around 10 W/kg.

In the hands of an experienced operator a test (including calibrations and cooling down) would take around 24 hours.

EXAMPLE PROCESS

A synthesis route to an intermediate is being developed which involves a two phase (aqueous/organic) reaction carried out at 0–5°C. The reaction mass consists of 25% organic and 75% aqueous.

RESULTS

RADEX

(Two runs carried out to generate data for each sample – see appendix)

DISCUSSION

The results obtained from both DSC (Figures 2 to 8) and RADEX (Figures 9 to 12) cover a wide range of values we will now consider each situation in order to assess the validity.

Table 1. Summary of DSC results (see appendix)

Sample	Initial exotherm onset	Exotherm Peak	Heat output	ΔT_{ad} Assuming $C_p = 2 \text{ J/K/g}$
DSC 1	82°C	117°C	431 J/g	215 K
DSC 2	167°C	210°C	812 J/g	>400 K
DSC 3	–	–	–	
DSC 4	78°C	119°C	339 J/g	170 K
DSC 4_1	83°C	119°C	251 J/g	126 K
DSC 5	83°C	122°C	375 J/g	188 K
DSC 6	86°C	116°C	784 J/g	392 K

DSC 1 represents the sampling of the normal reaction mass by a highly trained technician, as such this should be representative.

DSC 2 represents the organic (product) layer after phase separation.

DSC 3 represents the aqueous phase from the reaction and shows no evidence of any appreciable thermal effects.

DSC 4 represents a sample made up from the individual phase as close to the proportions used in the reaction i.e., 25% organic and 75% aqueous as possible, in actual fact the ratios were 31% organic to 69% aqueous.

DSC 4_1 also represents a sample made up from the individual phase as close to the proportions used in the reaction, however the actual ratio used was 22.4% organic to 77.6% aqueous.

DSC 5 is an unrepresentative sample which is 50:50 organic:aqueous.

DSC 6 represents a mixture made up of ca 75% organic and 25% aqueous, i.e., the exact opposite of the normal batch.

If we assume that we have taken a ‘representative’ sample of our reaction mass correctly then we should take DSC 1 as the correct result. We would therefore conclude that although exothermic activity could be apparent close to the reaction temperature for a controlled reaction we should be able to operate safely. The results from RADEX 1 suggest

Table 2. Summary of RADEX results

Sample	Initial exotherm onset	Exotherm Peak	Heat output	ΔT_{ad} Assuming $C_p = 2 \text{ J/K/g}$	Comments
RADEX 1	99°C	137°C	354 J/g	177 K	Gas evolution from ca 97°C
RADEX 2	113°C	154°C	1358 J/g	>670 K	Gas evolution from ca 120°C

RADEX 1 represents the normal reaction mass.

RADEX 2 represents the organic (product) layer after phase separation.

RADEX[®]

The safety calorimeter with test variations for thermal chemical testing

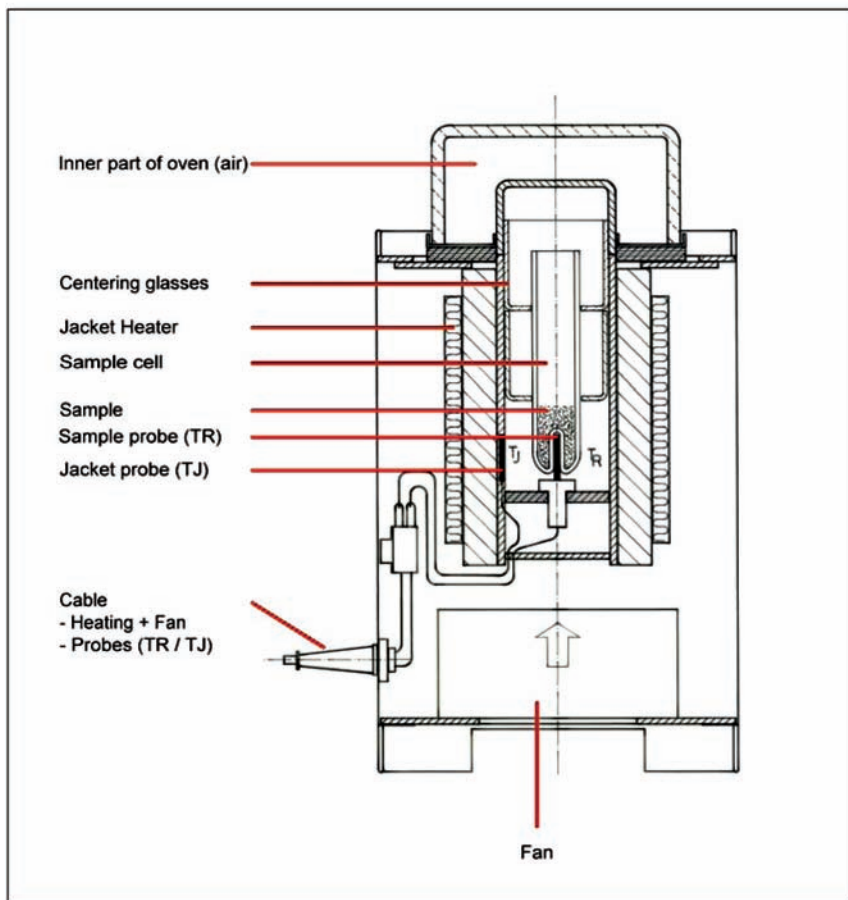


Figure 1

DSC 1 Normal Reaction Mass

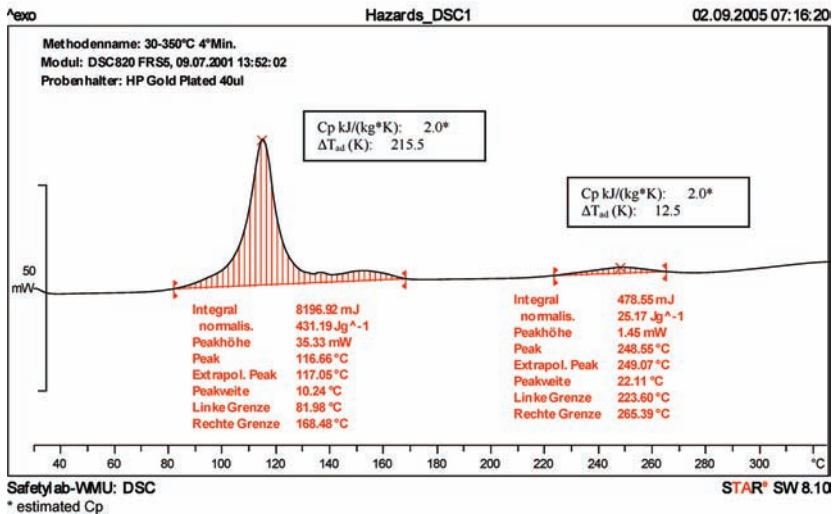


Figure 2

DSC 2 Organic phase

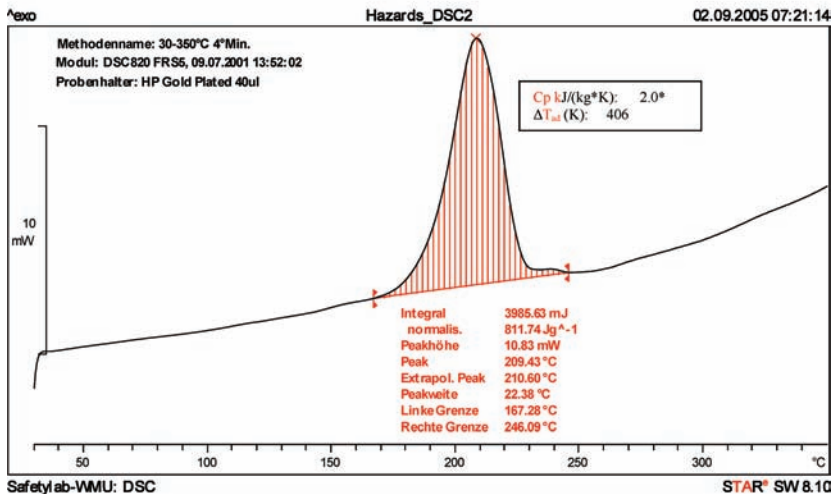


Figure 3

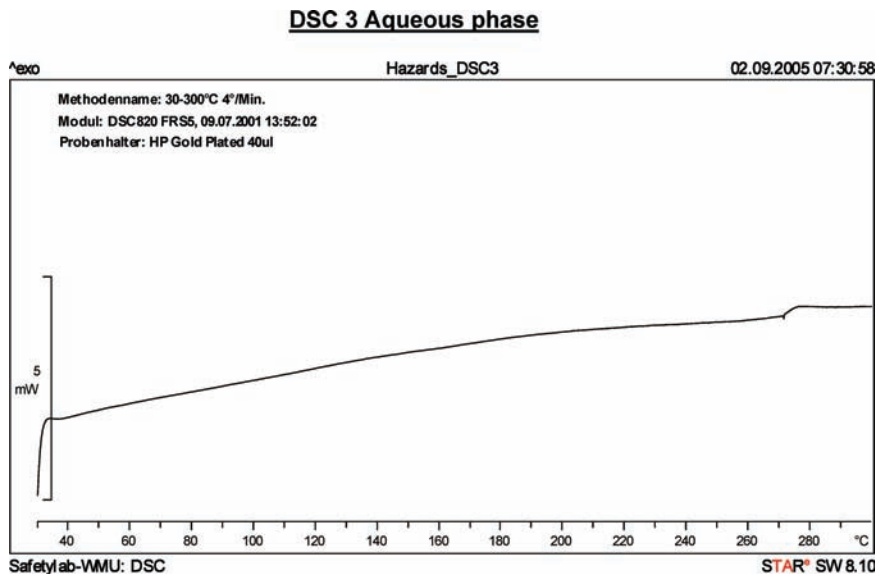


Figure 4

that the material is marginally more stable than the DSC indicates, notwithstanding this we would still be able to conclude that although there is the potential for a large temperature rise and the possibility of gas evolution from around 97°C we could still operate the process in a controlled manner.

If we were to assess the safety of the process based upon the stability of the separate phases then the following logic can be used,

We know from DSC 3 that the aqueous phase does not show any signs of exothermic activity therefore we could conclude that DSC 2 must represent the total heat output from decomposition of the system. By proportion (25% organic:75% aqueous) we should be able to compare this to the heat output in DSC 1 as follows

Heat output from DSC 2 = 812 J/g, heat output from DSC 3 = 0 J/g therefore expected heat output from reaction mass would be

$$(0.25 \times 812 + 0.75 \times 0) \text{ J/g} = 203 \text{ J/g}$$

i.e., heat output from the reaction mass should be ca 203 J/g, which would be sufficient to give us an adiabatic temperature rise of ca 100 K, this is only ca 50% of the value measured in DSC 1.

DSC 4 Mixture of 31% organic/69% aqueous layer

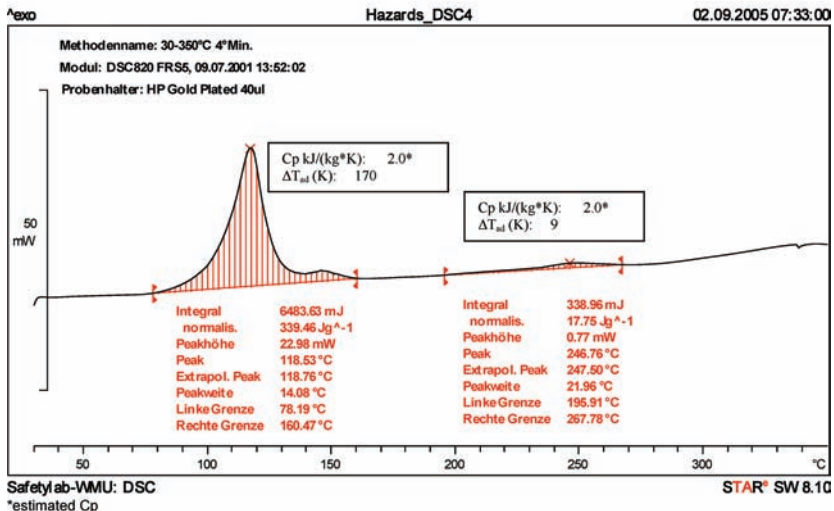


Figure 5

DSC 4 1 Mixture of 22.4% organic / 77.6% aqueous phase

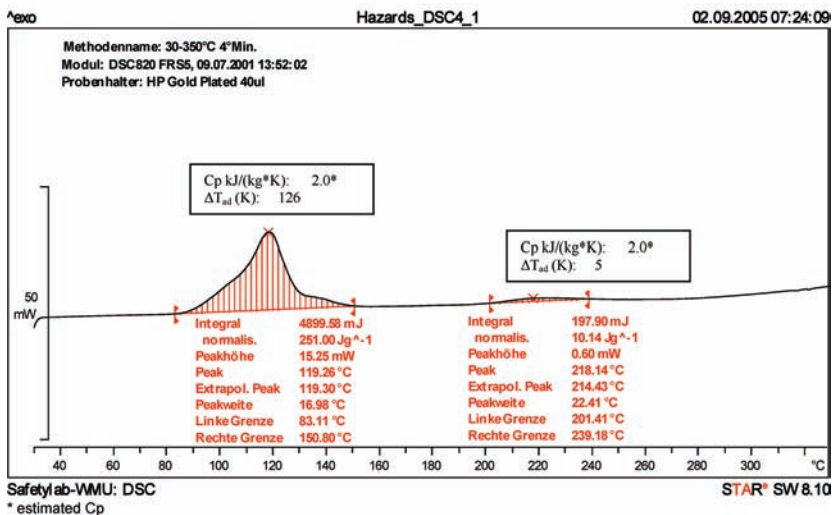


Figure 6

DSC 5 Mixture of 50% organic/50% aqueous layer

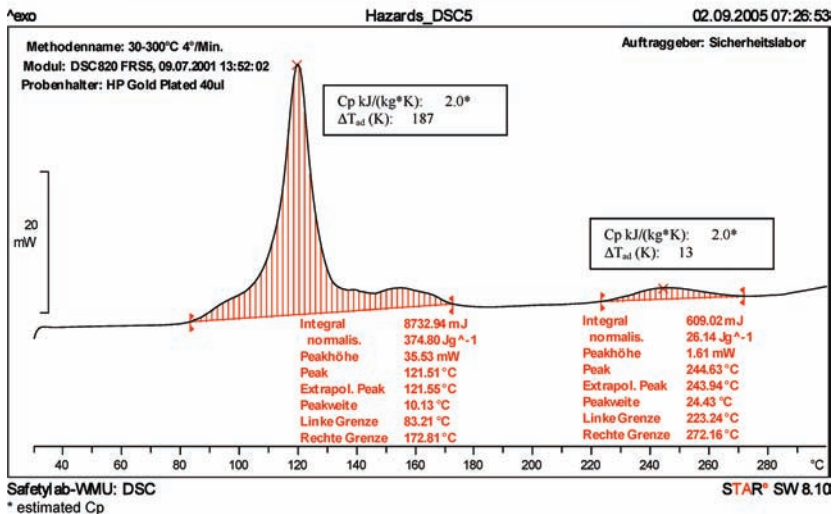


Figure 7

DSC 6 Mixture of 74.7% organic/25.3% aqueous phase

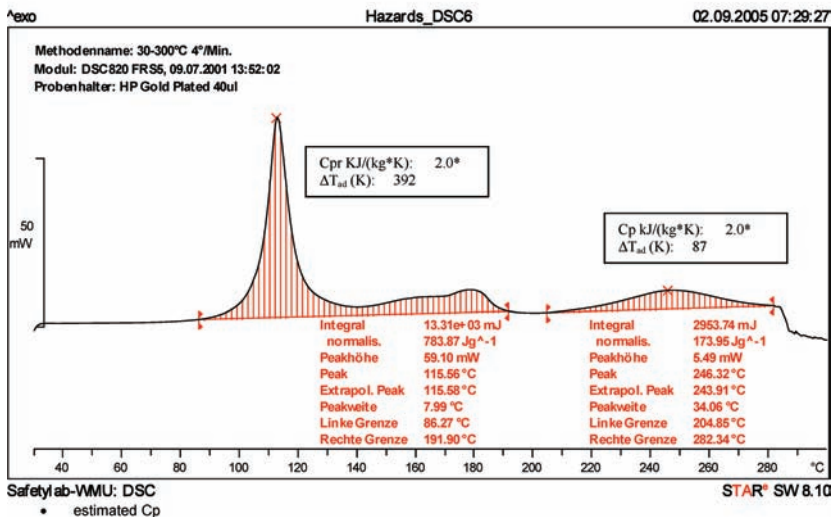


Figure 8

RADEX 1 Normal reaction mass- Pressure effects

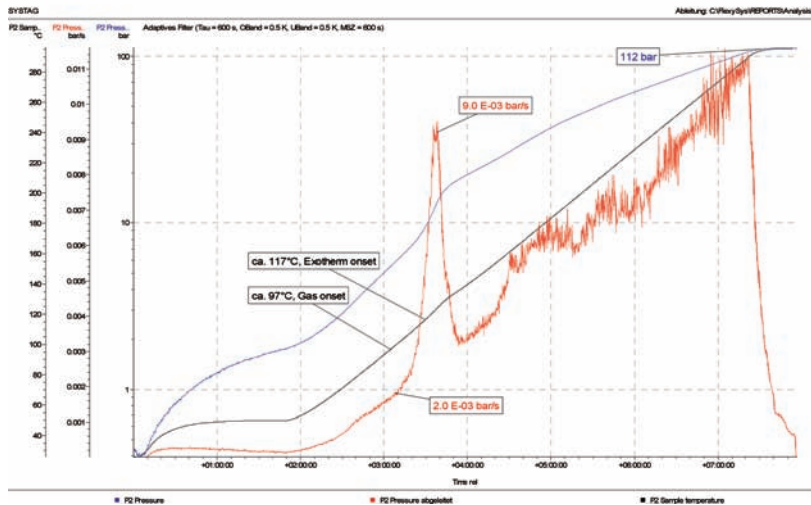


Figure 9

RADEX 1 Normal reaction mass- Thermal effects

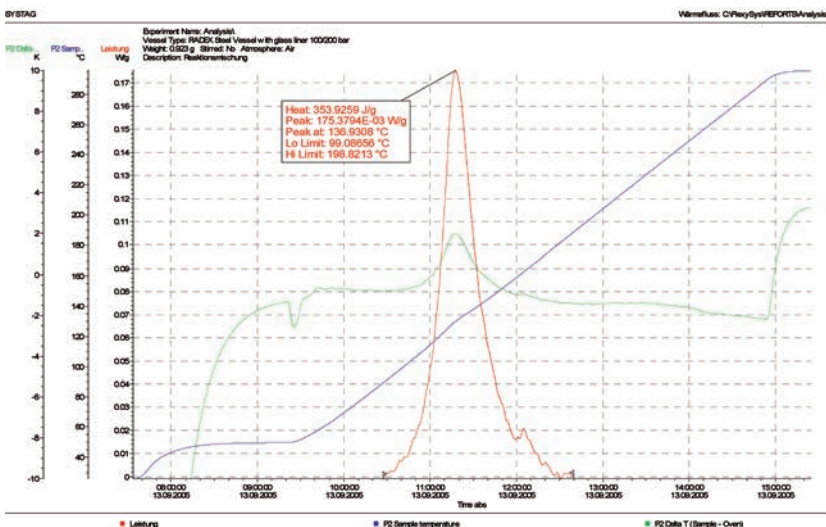


Figure 10

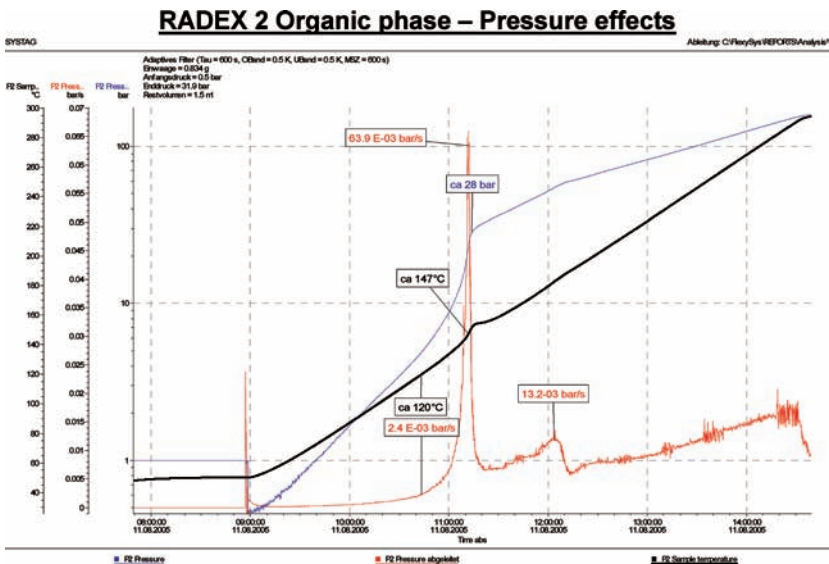


Figure 11

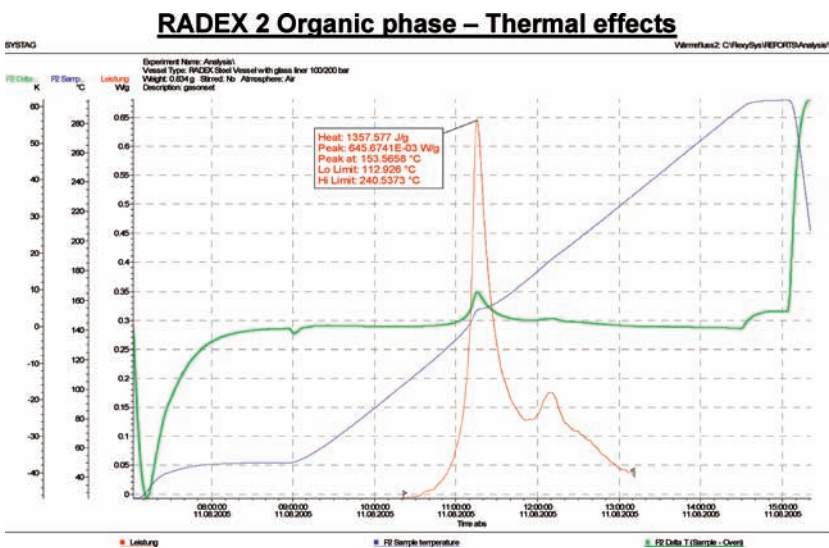


Figure 12

The data from the RADEX is much closer to the expected value as the 'mixture' has a heat of decomposition of around 354 J/g and the calculated value (making the same assumptions as above) based upon the organic phase alone would be 340 J/g.

We could have a reasonably high degree of confidence in the result from the RADEX based upon this approach but would not place the same degree of confidence in the DSC results.

Also what do we consider to be the 'onset' temperature. As no thermal effect was observed in the aq phase the only 'onset' we have from DSC is the organic phase which shows a detected onset temperature of 167°C which is nearly 85 K higher than the value obtained from testing the reaction mass itself. From the RADEX we have similar (though not identical) values for the 'onset' temperature, so we would have a higher degree of confidence in the validity of this result.

Basing safety on the DSC data would lead us to believe that although we had a potential for a temperature rise of around 100 K under adiabatic conditions, the likelihood of experiencing this under normal operating conditions would be small. The RADEX results suggest a higher potential adiabatic rise and a less thermally stable system, this would be one which could be less safe to operate on a larger scale.

RECONSTITUTED PHASES

If we consider reconstituted phases then this can be split into two scenarios;

Scenario 1 where we have got close to the correct proportions in our tests and scenario 2 where we have significantly different proportions.

For scenario 1 DSC 4 was carried out with a small excess of the organic phase. The results indicated a slightly lower onset temperature (78°C) compared to DSC 1 this difference is not particularly significant. However the heat output is around 339 J/g compared to 431 J/g seen previously, i.e., even though the organic content (the supposedly unstable material) is higher the heat output is lower.

On the other hand DSC 4_1 which represents a sample with a slightly lower proportion of organic shows a similar onset temperature to DSC 1 but the heat output is only around 251 J/g.

This difference in heat output does not appear to be logical based simply upon the proportions of the reactive material present.

For scenario 2 we have simulated what could happen when a relatively inexperienced operator makes up the samples incorrectly.

The two examples here show a 50:50 mixture (DSC 5) and a 75:25 mixture (DSC 6). Although they exhibit similar onset temperatures the heat outputs (and hence potential adiabatic temperature rises) are significantly different at 375 J/g and 784 J/g respectively and do not correlate well with the value for 100% organic layer or for that matter with the value from the reaction mass (431 J/g).

The differences between these results indicate that if we sample our reaction mass incorrectly then there could be safety implications associated with this. Although the detected onset temperatures are similar 78–86°C the magnitude of the associated

exotherms (and indeed the profile) is somewhat different and could result in an adiabatic temperature rise of anywhere between 126 K and 392 K.

IMPLICATIONS

On its own each DSC test result appears to be valid. However, on cross checking there does not appear to be a very high degree of consistency between the results and it is difficult to conclude which is the correct or indeed the safe result to use. We could have a detected onset temperature anywhere between 78°C and 167°C and a potential temperature rise between 100 K and 392 K. This could have potentially serious consequences when the results are applied to a larger scale operation of the process. The RADEX results are much closer to each other, although by comparison with DSC they do not provide confirm the level of sensitivity claimed, nevertheless for the less experienced practitioner it would appear easier to obtain reproducible results.

We are unable to predict the thermal stability of the two phase mixture based upon either the single phase or by reconstituting the reaction masses with any degree of confidence. Inefficient sampling of the mass or the use of incorrect proportions could therefore markedly affect our result and hence our ability to ensure safety for a process.

From the chemistry involved we know that this material will produce gas when it decomposes yet from the DSC results we do not have any indication of the temperature from which this will be apparent nor the quantities that will be produced.

The DSC results do however provide a rapid indication of the thermal stability of a system and can be used to screen out potential problems.

By using a larger sample size errors introduced by sampling can be reduced as it is easier to obtain a representative sample. With a larger sample we will also be able to obtain data on the potential for gas/pressure evolution.

The residual pressure in the RADEX at the end of the test allows calculation of the quantity of gas produced per unit quantity of material. For the organic phase such a calculation suggests that decomposition is incomplete. Given the thermal events observed this seems unlikely, a more plausible explanation for a lower than expected value for the residual pressure is that the evolved gases are in solution. Supporting evidence for this theory was obtained when a sample of the organic phase was heated in a glass tube fitted via Swagelok connections to a pressure transducer. After cooling back to ambient, pressure was released from the tube and bubbles were observed in the reaction mass. Re-sealing the tube resulted in the pressure re-equilibrating. On the basis of this it can be concluded that the residual pressure value obtained provides an indication that gas evolution has occurred it is not however a quantitative measurement.

After carrying out DSC testing an additional method of experimental investigation such as the RADEX does provide a relatively easy way of obtaining more information on a process. However it may not provide the complete picture and other experimental investigations could be necessary to ensure a safe process, either by confirming the data obtained from screening tests or providing additional data.

OVERALL CONCLUSIONS

- 1) In the hands of an experienced technician it may be possible to obtain good data from DSC on which safety critical decisions regarding the thermal stability of a multiphase mixture can be based.
- 2) Due to the small sample size used in DSC accurate reconstitution of a reaction mass cannot be carried out with a high degree of confidence.
- 3) Basing the stability of a reaction mass on the stability of the individual components could lead to an unsafe situation.
- 4) An operator would have a higher degree of confidence in obtaining a representative sample for use in the RADEX as opposed to the DSC.
- 5) Analysis of the pressure data allows an indication of the likely temperature from which gas evolution will be observed.
- 6) Residual pressure measurements obtained in the RADEX provide a qualitative indication of the quantity of gas evolved.
- 7) The sensitivity of the RADEX may not be as good as is claimed and further work across a range of samples would be beneficial in investigating this.
- 8) Basing the safety of a process on results obtained from a single technique could lead to an unsafe situation.

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