A STRATEGY FOR THERMAL HAZARDS ASSESSMENT IN BATCH CHEMICAL MANUFACTURING

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A strategy has been developed for the assessment of both thermal decomposition hazards and thermal runaway potential in intended exothermic reactions. The strategy is based on the application of simple, cost-effective experimental techniques. The results from these techniques have been compared with those from commercially available instruments, and indicate a similar level of sensitivity. Results are presented for representative experimental systems, which demonstrate the application of the developed test methods as part of an overall thermal hazards assessment.

Keywords: Strategy, Thermal decompositions, Runaway potential, Test methods.

INTRODUCTION

In 1984, Barton and Nolan (1) presented a paper on case histories of runaway incidents and proposed a plan for future research. This included the critical appraisal of existing equipment for thermal hazard assessment, the development of simple, cost-effective techniques for evaluating exothermic reaction hazards and the development of a logical testing strategy employing the developed and/ or existing test methods. Such a strategy was also required to take account of the effects of scale on experimental results and the possible effects of materials contamination.

Thermal decompositions of unstable chemical components occur in physical processing operations, such as drying and distillation, and as a consequence of the thermal runaway of desired exothermic reactions. Thermal runaway of reaction mixtures is attributable to heat release exceeding the available cooling capacity during a planned reaction stage.

Several manufacturing companies have devised their own testing strategies. These employ a variety of commercially available equipment and "in-house" test methods. Commercially available equipment includes the Accelerating Rate Calorimeter (for decomposition hazards assessment) and the Mettler Heat Flow Calorimeter (for heat evolution in reaction mixtures). The "in-house" techniques include those developed by the Association of the British Pharmaceutical Industry (2, 3) and Imperial Chemical Industries (4, 5). The sensitivity of any method for detecting exothermic reaction hazards depends on a number of factors, notably the size and physical properties of the experimental sample.

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For thermal decomposition hazards, experimental methods are required to identify the "initial" exotherm temperature (under specified conditions), the projected induction time for catastrophic decomposition in the bulk material, magnitude of energy release and characteristic heat generation and kinetic data. As most plant failures are ultimately due to uncontrolled vessel pressurisation, it is also desirable to specify the magnitude of associated gas generation.

For runaway reaction hazards, it is necessary to quantify the rate and magnitude of reaction heat release, and the consequent adiabatic temperature increase in the event of cooling and/or agitator failure. This requires the direct experimental measurement of the reactants' heat capacity, which is used in conjunction with heat release data.

Any strategy for exothermic reaction hazards assessment must indicate the appropriate application of specific test procedures, combined with confidence limits on the interpretation of results, based on operating experience and precedents set by past incidents.

A number of commercial instruments are available for quantifying specific aspects of exothermic reaction hazards. In practice, a manufacturer will require a combination of data to provide an overall assessment. The individual instruments tend to be expensive, and this has led to the development of the variety of purpose built "in-house" methods.

EXPERIMENTAL METHODS

Thermal Decomposition Hazards

In the study of thermal decompositions, both micro-thermal and gramme-scale (macro-thermal) methods have been evaluated. The commercial instruments employed were the Accelerating Rate Calorimeter, (ARC) (6), Sikarex (7), Sedex (8) and also a micro-thermal Differential Scanning Calorimeter. Two experimental methods have been developed at South Bank Polytechnic (9).

The first method, the Insulated Exotherm Test, allows early detection of initial exothermicity, calculation of pseudo-kinetic parameters, and estimation of scale effects on the initial temperature for self-sustaining reaction. The second method, the Decomposition Pressure Test, allows measurement of gas generation and pressurisation characteristics in the late stages of thermal decomposition.

    (i)   Insulated Exotherm Test

The equipment is shown in Figure 1. It is essentially a gramme-scale Differential Thermal Analysis technique. The sample and an inert reference are held in identical containers and heated at a constant rate within an internally lagged Dewar vessel. Sample temperature, and differential temperature between the sample and reference, are recorded as functions of time using a micro-computer. Self-heating of the sample relative to the inert reference can be determined under conditions of extremely low heat loss.

    (ii)   Decomposition Pressure Test

The equipment is shown in Figure 2. The sample is held in a glass-liner within a stainless steel pressure vessel. The vessel is provided with a bursting disc rated at 67 bar (1000 psig) and a bleed

valve for venting of decomposition products. The pressure vessel is mounted inside a temperature programmed oven, in such a way as to permit pressure relief to an external fume cupboard. A remote pressure transducer is linked to the vessel by a steel capillary. The oven is heated at a fixed rate over the experimental temperature range, and the sample temperature and vessel internal pressure are recorded as functions of time on a chart trace.

Runaway Reaction Hazards

Fewer commercial instruments are available for studying reaction mixtures; one such instrument is the Mettler RC 1 reaction calorimeter. A further experimental method has been developed in this study (10):

Power Compensated Dewar Calorimeter

The equipment is shown in Figure 3. It comprises a wide necked one litre Dewar vessel supported in a thermostatic bath and provided with internal cooling, turbine agitator, electrical heating and temperature sensors, which pass through a flanged glass top. Environmental heat losses from the vessel are minimised by insulation of the top, and by the surrounding medium being maintained at the initial reaction temperature. Residual heat losses are compensated by provision of a constant electrical power input (i.e. an auxilliary heater) to the vessel. Calibration heating allows direct experimental measurement of reactants' heat capacity. The elimination of extraneous heat losses allows reactions to be studied under effectively adiabatic conditions.

EXPERIMENTAL STUDIES

In the course of the research programme, a total of four materials have been evaluated for thermal decomposition hazards. This has allowed:

    (i)   a comparative study of the sensitivity of test methods (11),

    (ii)   the calculation of pseudo-kinetic parameters describing the decompositions (10),

    (iii)   the calculation of heat release and induction time data (10),

    (iv)   the prediction of scale effects on recorded initial exotherm temperature,

    (v)   the calculation of pressurisation characteristics (9).

For the assessment of exothermic runaway potential, two liquid-phase reactions were investigated following calibration of the power compensated Dewar calorimeter (PCDC) by measuring heats of dilution for sulphuric acid. Calibration measurements indicated an accuracy of ± 5% compared with published thermochemical data for this system. Experimental studies have demonstrated:

    (i)   the accurate calculation of heats of reaction,

    (ii)   the measurement of specific rate of heat release,

    (iii)   the measurement of reactants' heat capacity.

Other data which may be obtained include kinetic parameters describing homo-

geneous liquid-phase reactions (10).

Two illustrative examples of the experimental studies are provided:

    (i)   the thermal decomposition of Tertiary-Butyl Peroxybenzoate

$$C_6H_5-COO \cdot C(CH_3)_3$$
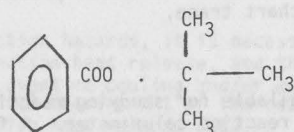
This is a liquid organic peroxide, which is used as a free radical initiator in polymerisation reactions. It is recognised as being thermally unstable; the manufacturers quote a Self-Accelerating Decomposition Temperature of 313 K (60°C), determined from a Heat Accumulation Storage Test (12).

    (ii)   the mono-nitration of toluene using mixed nitric/sulphuric acids

$$C_6H_5CH_3 + HNO_3 \xrightarrow[\substack{318 \text{ K} \\ (45°C)}]{H_2SO_4} C_6H_5CH_3NO_2 + H_2O$$
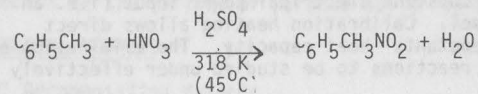
This is a two-phase aromatic nitration and is recognised as a hazardous unit process (13).

EXPERIMENTAL RESULTS

(i)   Thermal Decomposition Hazards

Preliminary results are presented to allow comparison of initial exotherm temperatures recorded, using commercially available instruments and the developed Insulated Exotherm Test (IET). These are shown in Table 1.

It can be seen that good agreement is obtained for recorded initial temperatures using commercial macro-thermal methods and the developed IET. The Sikarex instrument used had an extremely slow fixed scanning rate of 0.125°C min^{-1}, and the somewhat lower recorded initial temperature of 345 K (72°C) is possibly attributable to the autocatalytic decomposition characteristics of the test material. Microthermal DSC generally provides a less sensitive indication of initial temperature; however, this is greatly improved by reducing the scan rate from 10°C min^{-1} to 1°C min^{-1}.

Table 2 shows the comparison of "adiabatic" temperature increases determined using IET, ARC and SIKAREX (adiabatic) experiments, with associated heats of decomposition. The "adiabatic" temperature rise is taken as the product of the recorded experimental temperature increase ΔT_E, and the system thermal inertia, ϕ:

$$\Delta T_A = \phi \Delta T_E$$

The reaction energy is calculated as the product of the "adiabatic" temperature increase thus calculated, and the sample specific heat capacity:

$$\Delta H = C_p \Delta T_A$$

Comparative values for reaction energies measured using microthermal DSC with sealed high pressure pans is also given.

Table 1: Comparison of recorded initial exotherm temperatures for tertiary-butyl peroxybenzoate using different test methods

Test Method	Experimental Parameters	Sample Mass	Initial Exotherm Detected K (°C)	Apparatus/Comments
DSC	10°C min^{-1}	3.42 mg	395 (122)	Perkin-Elmer DSC 2 Sealed Stainless Steel pan (25 bar max.)
DSC	1°C min^{-1}	6.48 mg	366 (93)	Perkin-Elmer DSC 4 Sealed Stainless Steel pan
ARC	Start:50°C Heat Step: 10°C Wait:15 min Phi:2.39	3.57 g	354.8 (81.8)	CSI - ARC "Light" hastelloy bomb
Sedex	0.5°C min^{-1} "scanning" experiment	5.8 g	357 (84)	Systag TSC 510/511 open tube
Sikarex	0.125°C min^{-1} "scanning" experiment	5.0 g	345 (72)	Systag Sikarex 3 open tube
IET	0.5°C min^{-1}	3.0 g	353 (80)	

Manufacturer's data (12)
SADT temperature   : 333 K (60°C)
Emergency temperature : 328 K (55°C)

Table 2: Adiabatic temperature rise/heat of reaction data for tertiary-butyl peroxybenzoate using different test methods

Test Method (adiabatic)	Sample Mass	System Thermal Inertia	Recorded Temperature Increase ΔT_E °C	Corrected "Adiabatic" Increase ΔT_A °C	Indicated Heat of Reaction J g^{-1}
ARC	3.57 g	2.39	170	394.4	721.8
SIKAREX (adiabatic)	6.9 g	3.52	106	373.1	682.8
DSC (1°C min^{-1})	6.48mg	-	-	-	144.1
IET	3.0 g	3.75	119	446.3	816.6

With the exception of the DSC value, which is obtained from the integrated

differential power record, the heat of reaction has been calculated on the basis of a sample heat capacity of 1.83 J g^{-1}, which is a weighted average value for the decomposing material (14).

The thermochemical heat of reaction based on analysis of decomposition products is 1380 ± 150 J g^{-1} (14). This suggests that the DSC heat of reaction is closer to the true value; the substantially lower reaction energies indicated using macrothermal methods are attributable to the eventual expulsion of the hot decomposition products from the sample containment, which was observed with all of the latter methods for this material. This demonstrates the limitation of "adiabatic" temperature increase as a measure of reaction energy in violent decomposition reactions, when sample containment is not maintained due to highly energetic reaction.

Kinetic parameters describing the decomposition can be obtained by applying an "initial rate" (pseudo-zero order) model to the IET self-heat rate versus temperature data, in the early stages of reaction (fractional conversion < 0.05). Assuming adiabatic operation:

$$\rho C_p \left(\frac{dT}{dt}\right)_A = A \ \exp\left(\frac{-E}{RT}\right) \Delta H$$

$$S_T = \left(\frac{dT}{dt}\right)_E \cdot \Phi = \left(\frac{A\Delta H}{C_p}\right) \exp\cdot\left(\frac{-E}{RT}\right)$$

$$\ln \ S_T = \ln \left(\frac{A\Delta H}{\rho C_p}\right) - \frac{E}{R}\left(\frac{1}{T}\right)$$

The results of such a correlation are shown in Table 3 and Figure 4. The activation energy for the decomposition is 150 kJ mol^{-1}, determined directly from the gradient of the kinetic plot. The Arrhenius frequency factor, A may be isolated, if desired, provided reactant density, heat capacity and heat of reaction are known.

The induction time, τ is determined by numerical integration of the experimental self heat rate data:

$$\tau = \int_{T_o}^{T_f} \frac{dT}{S_T} \simeq \sum_{T = T_o}^{T = T_f} \frac{\delta T}{S_T}$$

This is then correlated with reciprocal absolute temperature, in accordance with Frank-Kamenetskii's approximate analytical solution (15):

$$\tau = \frac{C_p \rho}{A\Delta H} \cdot \frac{RT_o^2}{E} \cdot \exp\left(\frac{E}{RT_o}\right)$$

The latter expression may also be evaluated, using the previously determined kinetic data, for comparative purposes. The results are shown in Table 4 and Figure 5.

Table 3: Temperature/Rate data from thermal decomposition of t-butyl peroxybenzoate using Insulated Exotherm Test

Initial exotherm temp: 80°C   Sample size: 3.0 g
Temp at 5% conversion: 105°C   Thermal Inertia: 3.75
Sample heat capacity: 1.83 J g^{-1} C^{-1}
(Self heat rates evaluated at mid increment)

Run Time (min)	Sample Temp (°C)	Differential Temp (°C)	Self Heat Rate (°C/min)
130.30	80.64	-0.58	0.04
132.82	81.71	-0.56	0.05
135.58	82.80	-0.54	0.04
138.10	83.82	-0.49	0.06
140.74	84.87	-0.45	0.05
143.26	85.90	-0.41	0.08
145.90	86.96	-0.37	0.06
148.54	88.03	-0.31	0.08
151.17	89.07	-0.25	0.09
153.93	90.12	-0.19	0.10
156.57	91.19	-0.11	0.10
159.20	92.24	-0.04	0.11
161.84	93.35	0.05	0.15
164.59	94.41	0.17	0.13
167.12	95.46	0.27	0.21
169.64	96.49	0.41	0.24
172.16	97.55	0.60	0.25
174.57	98.58	0.76	0.31
176.87	99.61	0.97	0.38
179.16	100.68	1.23	0.44
181.34	101.75	1.50	0.55
183.52	102.86	1.88	0.72
185.47	103.94	2.31	1.00
187.08	105.01	2.82	1.40

Least Squares fit for zero order model:

$$\text{Ln } S_T = \text{Ln }\frac{d(\Delta T)}{dt} = 43.46 - \frac{18058.16}{T}$$

Activation energy = 150.14 kJ mol^{-1}

Modified pre-exponential factor = 7.45 x 10^{18}

Heat generation factor AΔH = 1.42 x 10^{25} W m^{-3}

Table 4: Numerical integration of experimental rate data for
adiabatic induction time

Adiabatic Temperature °C	Self Heat Rate °C min⁻¹	Induction Time from 80°C (min)	Reciprocal Absolute Temperature (1000/K)	Time to Explosion (min)
80.00	-	(0)	2.83	(239.20)
82.28	0.04	48.21	2.81	190.99
84.32	0.05	88.85	2.80	150.35
86.40	0.07	120.88	2.78	118.32
88.55	0.07	152.43	2.77	86.77
90.66	0.10	174.44	2.75	64.76
92.76	0.11	193.70	2.73	45.50
94.92	0.14	208.87	2.72	30.33
97.01	0.23	218.13	2.70	21.07
99.10	0.28	225.63	2.69	13.57
101.22	0.41	230.85	2.67	8.35
103.42	0.63	234.33	2.66	4.87
105.55	1.19	236.13	2.64	3.07
107.82	2.25	237.14	2.63	2.06
110.24	4.16	237.12	2.61	1.48
112.63	6.75	238.07	2.59	1.13
115.66	10.09	238.37	2.57	0.83
118.33	14.41	238.55	2.56	0.65
121.52	21.96	238.70	2.53	0.50
127.41	37.53	238.85	2.50	0.35
225.52	281.24	239.20	2.01	(0)

The scale-up correlation for experimentally determined initial temperatures is
based on an iterative calculation using extrapolated sample temperatures and
associated critical masses (16). This approach has been modified to
accommodate the apparent activation energy for the decomposition (determined
experimentally), which itself determines the attenuation of the decomposition
rate constant with decreasing temperature:

$$\frac{k_o}{k_i} = \frac{A \exp (-E/RT_o)}{A \exp (-E/RT_i)} = \exp \left[E \left(\frac{T_o - T_i}{RT_o T_i} \right) \right]$$

where k_o, k_i are the rate constants at T_o, T_i respectively ($T_i < T_o$). Results
are shown in Table 5 for an iterative computer calculation based on the above
treatment.

Table 5: Scale-up correlation for initial decomposition temperature

Critical Temperature (°C)	Mass kg
80	0.003
75	0.021
70	0.152
65	1.142
60	8.877
55	70.854

Typical decomposition pressures using the developed decomposition pressure test
are given in Table 6. The gas generation is calculated by assuming ideality of
evolved gas and applying Avogadro's hypothesis, i.e.

$$dn = \frac{dPV}{RT} \text{ at constant } T \text{ and } V$$

$$N_s = \frac{n_g}{n_s} = \frac{dn \, W_s}{m_s}$$

V = internal volume of vessel = $65 \times 10^{-6} \text{ m}^3$.

The number of moles of gas generated, n_g at maximum pressure was calculated as
0.025 mol while n_g at the residual pressure was 0.011 mol. The molar quantity
of sample was 0.0103 mol. The specific quantity of gas evolved during
decomposition were 2.43 mol mol⁻¹ and 1.07 mol mol⁻¹ at maximum and residual
pressure, respectively. The maximum specific volume of gas produced during
decomposition was calculated as 0.427 l g⁻¹ at 416 K and the residual specific
volume of gas was 0.180 l g⁻¹ at 398 K. The higher value is nearer that
predicted from analysis data on decomposition products. However, it is
possible that many of the ostensibly volatile decomposition products,
particularly the heavier aromatics, are recondensed after decomposition at
elevated pressures. It should be noted that the violent pressurisation
characteristics exhibited by this test material indicate that it would not be
practicable to design an effective relief and containment system for bulk
handling, and stringent storage conditions are stipulated.

Table 6: Decomposition pressure test data for tertiary-butyl
peroxybenzoate

Condition	Temperature K (°C)	Pressure (psig)
Prior to final decomposition	398 (125)	3
Maximum transient values	416 (143)	195
Residual values	398 (125)	84

(ii)   Exothermic Reaction Hazards

The mono-nitration of toluene using mixed acids was carried out in an
adiabatic Dewar, the Mettler RC 1 reaction calorimeter and the PCDC.

The results for heat of reaction recorded using the three instruments, together
with a theoretical value based on thermochemical considerations are given in
Table 7.

Table 7: Heats of reaction for toluene mono-nitration

Apparatus	Indicated Heat of Reaction kJ mol⁻¹	Potential Adiabatic Temperature Increase K mol⁻¹ accumulated feed acid *
PCDC +	-138.04	168
Adiabatic Dewar +	-140.41	171.2
Mettler RC 1	-148.03	172.4

* based on first decimolar addition.

+ based on initial reactants heat capacity indicated by PCDC.

The theoretical heat of reaction is -144.8 kJ mol^{-1}.

In the PCDC experiments, the heat of reaction is calculated as the product of the experimentally determined reaction temperature increase and the measured system heat capacity:

$$\Delta H = \Delta T_E \, (mC_p)_{ST}$$

The system heat capacity is determined before and after each addition stage, by means of a switchable fixed electrical heat input (ΔE) and recording of the reactor temperature response:

$$(mC_p)_{ST} = \frac{\Delta E}{\Delta T}$$

The reactants heat capacity is isolated by correction for the equipment heat capacity, which is itself determined by calibration using a liquid of known specific heat capacity (water).

The potential adiabatic temperature increase is obtained by dividing the experimentally determined heat of reaction by the calculated reactants' heat capacity:

$$\Delta T_A = \frac{\Delta H}{(mC_p)_R} \quad K \, mol^{-1} \text{ of unreacted material}$$

This is an important factor in the evaluation of the hazard presented by reactant accumulation; it ΔT_A is sufficient to heat the reactor contents to the boiling point or self heat temperature (bulk initial temperature) of one or more reaction components, a potentially hazardous operating condition exists in the event of cooling or agitator failure.

Table 8 shows the variation in reactants' heat capacity over the course of a molar addition of feed acid.

Table 8: Variations in reactants' heat capacity during a molar addition of feed acid (based on the specific mixture considered of toluene and residual acid)

Additional Quantity mol HNO$_3$	Indicated System Heat Capacity J K^{-1}	Indicated Reactants Heat Capacity J K^{-1}
0.1	1210	820
0.2	1230	840
0.3	1270	880
0.4	1190	800
0.5	1340	950
0.6	1400	1010
0.7	1460	1070
0.8	1540	1150
0.9	1510	1120
1.0	1440	1050

Equipment heat capacity = 390 J K^{-1}

Total reactants' volume = 0.5 ℓ

The reaction heat release rate is shown in Table 9. This is determined using the relationship

$$q_R = (mC_p)_{ST} \left(\frac{dT_R}{dt} \right) \quad watt$$

The specific rate of heat release, q_S may then be determined using the relationship:

$$q_S = \frac{q_R}{V} \quad watts \, litre^{-1}$$

The mono-nitration of toluene is predominantly mass transfer controlled. However, the specific chemical rate of a kinetic controlled reaction may be also determined directly from heat generation data:

$$(-r) = \frac{q_S}{\Delta H} \quad mol \, s^{-1} \, l^{-1}$$

where ΔH is the reaction enthalpy in J mol^{-1}.

Table 9: Attenuated heat release calculation program

Initial reaction temp: 45°C   Feed Temp: 20°C   Addition mass (g): 21
Attenuation factor: 0.82   Mean CP value for feed (J/gC): 1.8
Total (system) heat capacity (kJ/C): 1.21

Run Time (min)	Bath Temp (^{o}C)	Reactor Temp (^{o}C)	Heat Rate (C/min)	Attenuated Power Output (Watts)	dH Increment (Joules)	Attenuated Heat Release (kJ)
1.20	44.80	44.50	0.00	0.00	0.00	0.00
2.10	44.77	44.74	0.26	4.33	233.98	0.23
2.60	44.83	45.20	0.93	15.34	460.16	0.69
3.00	44.81	45.72	1.29	21.39	513.42	1.21
3.40	44.83	46.29	1.43	23.64	567.25	1.77
3.80	44.82	46.95	1.65	27.33	655.93	2.43
4.20	44.85	47.65	1.76	29.03	696.65	3.13
4.60	44.79	48.37	1.78	29.49	707.80	3.84
5.00	44.86	49.11	1.86	30.74	737.64	4.57
5.40	44.81	49.84	1.81	29.94	718.68	5.29
5.80	44.81	50.54	1.76	29.06	697.48	5.99
6.20	44.86	51.23	1.73	28.61	686.61	6.68
6.60	44.88	51.86	1.57	25.92	622.19	7.30
7.00	44.87	52.44	1.46	24.16	579.80	7.88
7.40	44.84	53.08	1.60	26.48	635.57	8.51
7.80	44.83	53.56	1.19	19.66	471.87	8.99
8.30	44.86	54.08	1.04	17.12	513.70	9.50
8.70	44.85	54.51	1.08	17.92	430.04	9.93
9.30	44.83	55.11	1.00	16.54	595.41	10.52
9.90	44.82	55.65	0.90	14.86	534.90	11.06
10.50	44.87	56.16	0.86	14.18	510.63	11.57
11.10	44.86	56.62	0.76	12.57	452.63	12.02

11.70	44.76	57.06	0.73	12.02	432.55	12.45
12.40	44.89	57.55	0.70	11.63	488.32	12.94
13.10	44.88	58.01	0.67	11.03	463.22	13.41
13.90	44.84	58.12	0.13	2.10	100.96	13.51

Total (observed) heat release = 13.51 kJ
Cold feed correction = + 0.95 kJ
Corrected heat release = 14.45 kJ
Reaction enthalpy at 45.00°C = -14.45 kJ (exothermic)

THE STRATEGY

The purpose of a strategy is to

(i)   effectively identify materials and unit processes which are
        potentially hazardous,

(ii)   quantify the hazards which arise from these with a minimum of
        testing.

It is important that the results of experimental test methods can be interpreted with confidence. This may require the application of scale-up criteria and operational safety margins to the experimental data.

Figure 6 depicts an assessment strategy for thermal decomposition hazards. This provides a logical approach covering theoretical (thermochemical) evaluation, preliminary safety screening to identify possible detonating/deflagrating materials, preliminary exotherm screening and gas generation measurements, secondary (sensitive) exotherm screening (e.g. IET) and application of scale-up procedures to define safe operational temperatures. Safety margins have been specified based on operational experience with selected materials (10, 11). Safety margins can also be checked on subsequent testing.

Figure 7 shows the assessment strategy for chemical reaction hazards. The sequential approach includes thermochemical evaluation, reaction calorimetry, scale-up criteria and, if necessary, stability testing of potentially unstable reaction components in accordance with Figure 6.

As a final precautionary measure heat accumulation storage of individual components or reactants at the proposed safe processing temperature should be implemented using Dewar-based holding tests.

It is necessary to assess chemical batch reactions for both types of hazard; purely physical processes, such as batch drying operations, generally need only be assessed for thermal decomposition hazards.

CONCLUSIONS

(i)   Thermal Decomposition Hazards

The experimentally determined "initial" temperature of a thermal decomposition depends on a number of factors, independent of the chemical properties of the test material. It is possible to construct relatively simple tests to evaluate the primary decomposition hazards of heat and gas generation. The developed Insulated Exotherm Test and Decomposition Pressure Test allow quantification of these factors.

Comparative studies of thermal decomposition reactions indicate that the

Insulated Exotherm Test compares favourably, in terms of detection sensitivity, to the more expensive commercial instruments investigated.

(ii)   Exothermic Reaction Hazards

A Power Compensated Dewar Calorimeter has been constructed, with which it is possible to measure the rate and magnitude of heat generation in controlled, exothermic liquid-phase reactions. The advantages achieved over simple Dewar calorimeters include elimination of residual heat losses, direct measurement of specific rate of reaction heat generation, and determination of reactants' heat capacity. These data can be applied by direct scaling to the industrial process. The results for the calibration system indicate that the developed method is suitable for heat release measurement in liquid systems; those for the hazardous unit process compare favourably with results obtained from Heat Flow and Adiabatic Dewar Calorimeters.

(iii)   Assessment Strategy

A strategy has been developed for the analysis of thermal hazards in batch chemical processing. This separately identifies the hazards from unintended thermal decompositions and intended exothermic reactions, and demonstrates the inter-relation of these in a potential thermal runaway reaction. The effects of scale have been considered as part of the experimental programme. The implication of these, together with the possible effects of contaminants and appropriate operational safety margins, are considered as part of the overall strategy.

REFERENCES

1. P. F. Nolan and J. A. Barton; "Runaway reactions in batch reactors", IChemE Symposium Series No. 85, 1984, p 13.

2. Association of the British Pharmaceutical Industry; "Guidance notes on chemical reactions hazards analysis", London, 1981.

3. C. F. Coates and W. Riddell; "Assessment of thermal hazards in batch processing", Chemistry and Industry, February 1981, p 84.

4. N. Gibson, D. J. Harper, R. L. Rogers; "Evaluation of the fire and explosion risk in drying powders", Plant Operations/Progress, Vol. 4, No.3 July 1985, p 181.

5. T. K. Wright and R. L. Rogers; "Adiabatic dewar calorimeter", IChemE Symposium Series No. 97, 1986, p 121.

6. D. I. Townsend; "Accelerating rate calorimetry", IChemE Symposium Series No. 68, 1981, paper 3/Q:1.

7. L. Hub; "Adiabatic calorimetry and sikarex technique", ibid, paper 13/K:1.

8. J. Hakl; "SEDEX - sensitive detector of exothermic processes", ibid, paper 13/L:1.

9. J. L. Cronin and P. F. Nolan; "Laboratory techniques for the quantitative study of thermal decompositions", AIChE Annual Meeting, Miami Beach, November 1986, Session No. 115, 'Advances in Calorimetry with Applications in Engineering'.

10. J. L. Cronin; "A strategy for thermal hazard analysis in batch chemical manufacture", PhD thesis, CNAA (South Bank), January 1987.

11. J. L. Cronin and P. F. Nolan; "Comparative sensitivity of test methods for determining initial temperatures in thermal decompositions", J. Hazardous Materials, Accepted for publication, 1987.

12. Trigonox C. Technical Data Sheet, Akzo Chemicals UK.

13. F. P. Lees; "Loss prevention in the process industries", Vol. 1, Butterworths, 1979.

14. J. Verhoeff; "Experimental study of the thermal explosion of liquids", Prins Maurits Laboratium, TNO Rijswijk, Netherlands, 1978.

15. D. A. Frank-Kamenetskii; "Diffusion and heat transfer in chemical kinetics" Plenum Press, NY, 1969.

16. G. F. P. Harris, N. Harrison, P. C. MacDermot; "Hazards of the distillation of mononitrotoluenes", IChemE Symposium Series No. 68, 1981, paper 4/W:1.

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NOMENCLATURE

Symbol	Quantity	Units
A	Arrhenius zero order frequency factor	$mol\ s^{-1}\ m^{-3}$
C_p	Specific heat capacity	$J\ kg^{-1}\ K^{-1}$
E	Arrhenius activation energy	$J\ mol^{-1}$
ΔH	Reaction enthalpy	$J\ mol^{-1}$
k	Zero order rate constant	$mol\ s^{-1}\ m^{-3}$
m	Mass	kg
n	Molar quantity	mol
N_s	Specific gas generation	mol/mol
q_r	Reaction heat generation	W
q_s	Volumetric heat generation	$W\ dm^{-3}$
R	Universal gas constant = 8.314	$J\ mol\ K^{-1}$

-r	Kinetic rate	$mol\ s^{-1}\ dm^{-3}$
S_T	Adiabatic self-heating rate	$K\ s^{-1}$
t	Time	s
T	Absolute temperature	K
T_o	Initial temperature	K
ΔT_A	Adiabatic temperature increase	K
ΔT_E	Experimental temperature increase	K
V_s	Specific volume of gas	$dm^3\ g^{-1}$
W_s	Sample molecular weight	$g\ mol^{-1}$
ϕ	System thermal inertia $= 1\ +\ \dfrac{M_c\ C_{pc}}{M_s\ C_{ps}}$	
ρ	Reactant density	$kg\ m^{-3}$
τ	Adiabatic induction time	s

Subscripts

A	Adiabatic
c	Container
E	Experimental
g	Gas
s	Sample
R	Reactants
ST	System total

OUTPUT
TO
PRESSURE
TRANSDUCER

FLEXIBLE STEEL
TUBE

SAFETY
HEAD

BURSTING
DISC

RELIEF
VALVE

GLASS
LINER

PRESSURE
VESSEL

SAMPLE
MATERIAL

THERMOCOUPLE

OUTPUT TO
AMPLIFIER

FIGURE 2
DECOMPOSITION
PRESSURE TEST

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DIFFERENTIAL
TEMPERATURE

TUBE
CLOSURE

SAMPLE
TEMPERATURE

REFERENCE
TUBE

BOILING
TUBE

GLASS
SHEATH

SAMPLE
TUBE

REFERENCE
MATERIAL

DEWAR

HEATING
TAPE

INSULATION

FIGURE 1   INSULATED EXOTHERM
TEST

DEWAR

BATH
COOLER

CALIBRATION &
AUXILLIARY HEATER
POCKET

AGITATOR

T, ΔT THERMOCOUPLE
OUTPUTS

CONTROLLED ADDITION

THERMOSTATIC
BATH HEATER

COOLING
COIL

CONSTANT
TEMPERATURE BATH

FIGURE 3   POWER COMPENSATED
DEWAR CALORIMETER

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$$E_a = 150 \cdot 14 \text{ kj mol}^{-1}$$

$$1000 \, \text{Ln} \, S_2 / S_1$$

$$\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

FIGURE 4 ARRHENIUS PLOT
T - BUTYL PEROXYBENZOATE

ANALYTICAL
SOLUTION

NUMERICAL
INTEGRATION

FIGURE 5 INDUCTION TIME PLOT
T BUTYL PEROXYBENZOATE

* Data Required
** Process Variables

Thermal Decomposition Hazards

Thermochemical Evaluation

* Reactive Groupings
* Oxygen Balance
* Heat of Formation
* Heat of Combustion
* Heat of Possible Decomposition
* Potential Toxicity of Decomposition Products

* Auto Ignition Temperature
* Melting and Boiling Point Data
* Vapour Pressure/Temperature Data
* Flash Point

Detonation Potential? — Yes / No

Preliminary Safety Screening

Specialist Testing Required ← Yes — Explosive or Deflagration Potential? — No → Thermal Stability Testing - - - (** Effects of contaminants, proposed operating conditions.)

Preliminary Exotherm Screening   Enclosed Heating Test: Gas Generation Potential   Bulk Drying Stability

* Initial Temperature

* Initial Temperature
* Magnitude & Associated Temperature of Gas Generation

* Initial Temperature
* Induction Time

Exotherm or Pressurisation @ Top + 100 K? — No

Yes

Sensitive Exotherm Screening

* Initial Temperature
* Induction Time
* Apparent Activation Energy
* Magnitude of Heat Release

Exotherm @ Top + 50 K? — No

Yes

Redefine Operating Conditions

Apply Scale-up Criteria

Exotherm @ Top + 25 K

Yes

Exotherm Detected? — No

Heat Accumulation Storage @ Top + 25 K

* Long Term Stability
* Inductive Self-Heating Potential

Proceed to Pilot Plant

FIGURE 6: ASSESSMENT STRATEGY, THERMAL DECOMPOSITION HAZARDS

* Data Required
** Process Variables

```
Chemical
Reaction
Hazards
```

Thermochemical Evaluation

* General Process Hazards
* Heat of Desired Reaction
* Total Reactants Heat Capacity
* Adiabatic Temperature Increase
* Thermal Stability of Reaction Components
* Potential Toxicity of Reaction Components

Thermally Stable? — No → * Thermal Decomposition Potential of Reaction Mixture and Components

Yes

(** Effects of agitation, ---- Reaction Calorimetry
cooling, contaminants,
mischarging)

* Heat Release Rate
* Specific Cooling Requirements
* Indicated Reaction Enthalpy
* Indicated Reactants Heat Capacity
* Indicated Adiabatic Temperature Rise
* Accumulation Potential
* Kinetic Data
* Gas Generation Potential

(** Scale up criteria) ----------

(** Plant cooling capacity
and proposed operating
conditions. Effect of ---- Potential Runaway? — Yes → * Thermal Decomposition Potential of Reaction Mixture and Components
cooling or agitator
failure.)

No

Heat Accumulation Storage

@ Top + 25 K

* Long Term Stability
* Inductive Self-Heating Potential

Exotherm Detected? — Yes → Define Maximum Safe Holding Time at Reaction Temperature

No

Proceed to Pilot Plant

OR

Specify Minimum Cooling Required After Completion of Reaction

OR

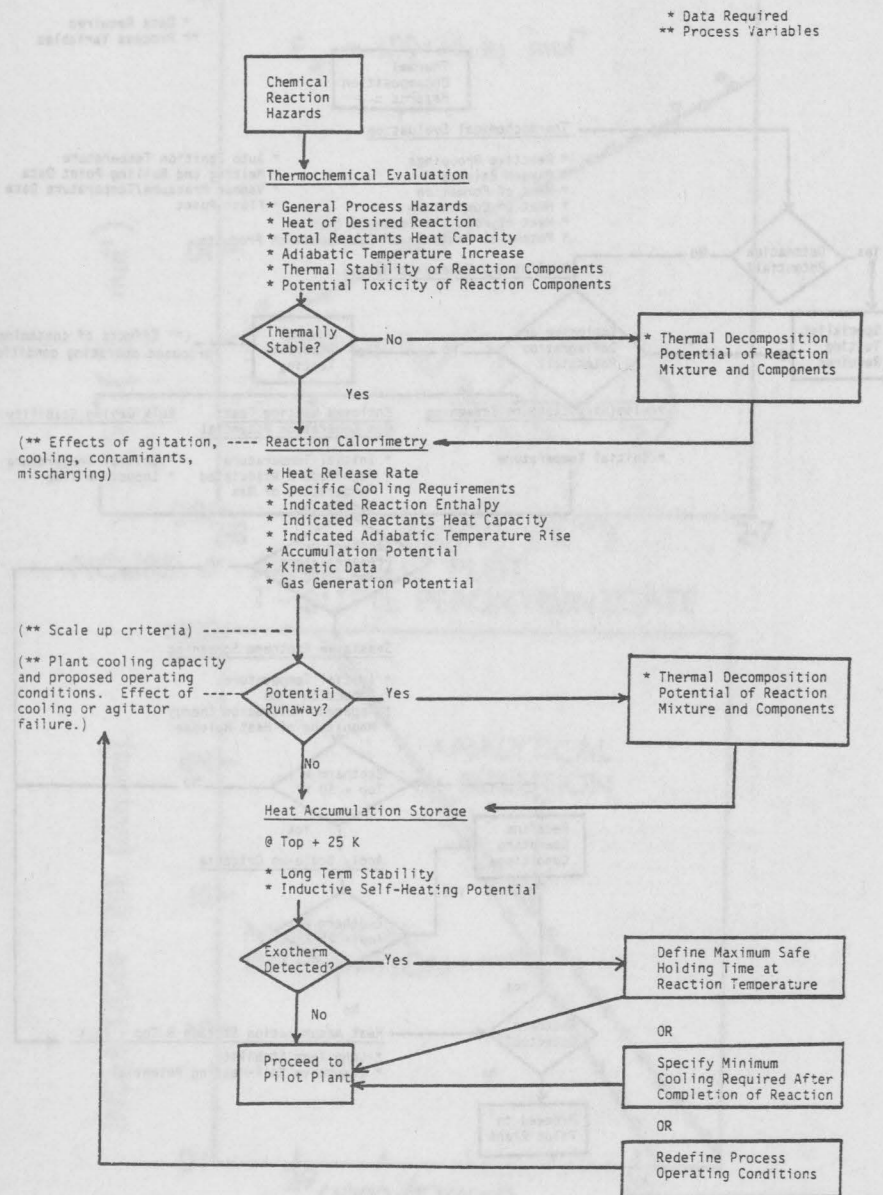Redefine Process Operating Conditions

FIGURE 7: ASSESSMENT STRATEGY, CHEMICAL REACTION HAZARDS

PRESSURE RELIEF AND VENTING: SOME PRACTICAL CONSIDERATIONS RELATED TO HAZARD CONTROL

Hans K. Fauske*

Newly developed practical methods for assessing pressure relief requirements for reactive and non-reactive systems are summarized. Considerations include runaway of liquid-phase exothermic reactions and fire exposure to liquid-filled storage vessels. Special emphasis is given to emergency releases involving two-phase flows.
Keywords: Relief, Venting, Reactors, Two-phase flow.

INTRODUCTION

Hazard control in connection with both reactive and non-reactive systems requires considerations of pressure relief. Inadequate relief may lead to severe explosions, extensive property loss, injury and environmental insult (1). In case of reactive systems several steps need to be taken in order to assure adequate relief. Hazard identification and system characterization are especially important steps. Wrong recipes, uncontrolled addition, catalyst mischarge, solvent mischarge, etc., can have a profound impact on the chemical energy release rate (see Figure 1). Such mistakes can alter the temperature rise rate (commonly known as the self-heat rate in runaway reactions) at relief conditions by up to several orders of magnitude (2). For non-reactive systems energy release characteristics in connection with fire exposure are of special interest (3).

Recognizing that the relief vent area is directly proportional to the self-heat rate, clearly establishes the overall importance of hazard identification and system characterization in the relief system design process. If these steps are done poorly, the level of hazard control achieved will be equally poor. An example is the case where the relief system design is based on fire exposure alone ignoring the potentially large additional contribution from chemical energy release if heating can lead to chemical reaction.

The actual design of the emergency relief system to mitigate or control the hazards involves two major aspects. These include establishing the vent size to relieve the pressure and disposal of the emergency release safely. In this paper methods for assessing vent sizing requirements for both reactive and non-reactive systems will be reviewed. Some special considerations involving disposal of two-phase (liquid-vapor) emergency releases are provided in (2).

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