Thermal Hazard Technology, 1 North House, Bond Avenue, Bletchley MK1 1SW, England.
Phone: +44 1908 646800 Fax: +44 1908 64520 Email: martyn.ottaway@science.org.uk W eb: www.thermahazardtechnology.com

Technical Information Sheet No 12

Low Phi Testing with the Accelerating Rate Calorimeter

The THT 60ml container has been designed for 'low phi' tests in a closed vessel state and also for stirring tests with the THT Sample Stirring Option. With a second tube, the containers can be used with the THT Vent Size Unit for tempering and hydrodynamic tests.

For normal low ϕ tests these containers can be used within either the THT or the CSI/ADL instrument. However prior to selling the containers THT insist on acquisition of the Burst Disc Assembly.

The containers can be used for solids or liquids. Prior investigation needs to be carried out before using the low ϕ containers such that experimental conditions are well defined and a safety cut-off temperature is defined (if necessary) – and cooling air is in use for rapid cooling.

The test used as standard with the normal bombs (20% DTBP in Toluene) may not be the best for these containers. Calculation would suggest fast heat rates and significant pressure rise (near to the limit of the burst disc). In addition the final temperature with the solvent (near 200°C) is maybe high compared to normal use.

However since data from DTBP is very well know, the choice may be to keep to this sample but with a somewhat lower peroxide concentration.

We have chosen 15%.

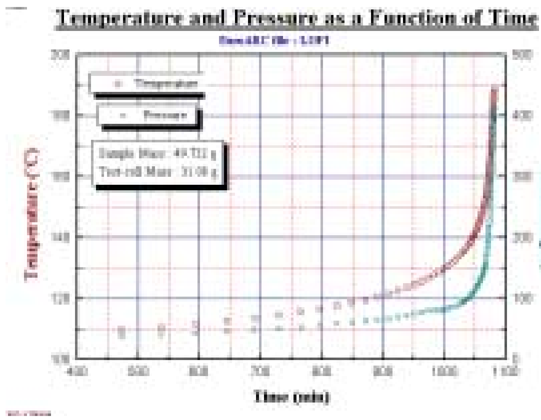
Data from a sample of 14.96% by weight DTBP (98% pure) with Toluene (Analytical Reagent Grade) was made. The low ϕ container was essentially filled. The sample mass was 49.732g and the Stainless Steel container mass 31.080g. The test was carried out under normal conditions. Start temperature 90°C, heat step 3°C, wait time 30 minutes, sensitivity 0.01°C/min.

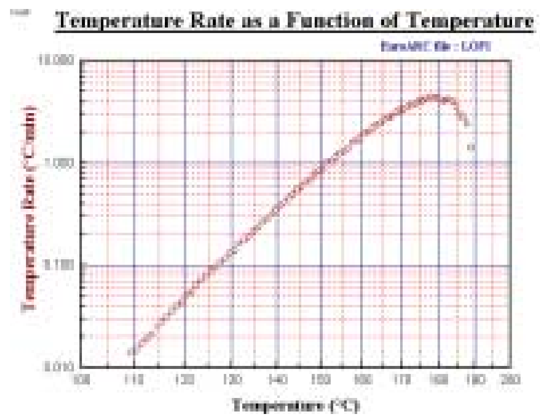
These results can be compared to earlier data from both 15% and 20% DTBP.

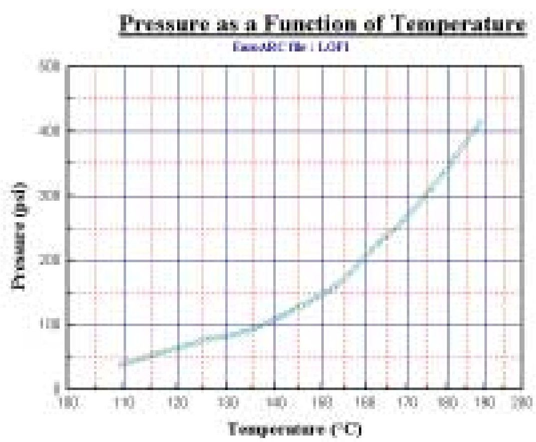
The value of ϕ is 1.125. However this is determined from specific heats of the container as 0.418J/g°C (0.1cal/g°C) and the sample (both components) 2.09J/g°C (0.5cal/g°C).

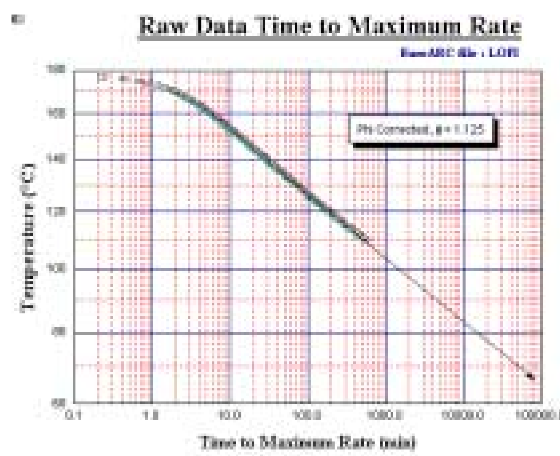
Other values might be used but these specific heat values are those historically used and those used for the earlier 15% and 20% DTBP samples.

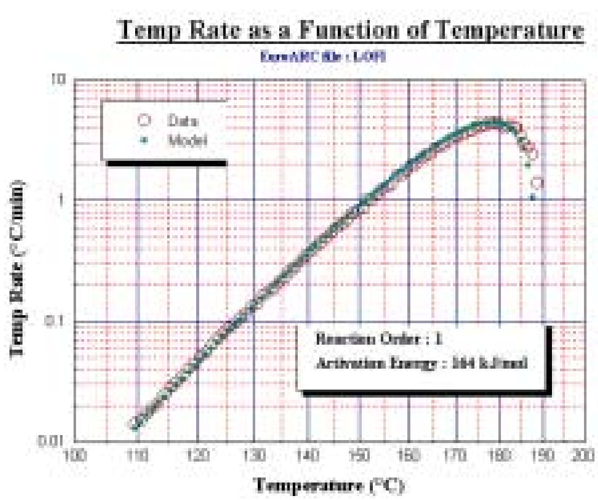
Data has been presented in graphical form using both the THT ARCCal software and CSI ARCWin software, these being the two packages mostly used. The figures below are self-explanatory.



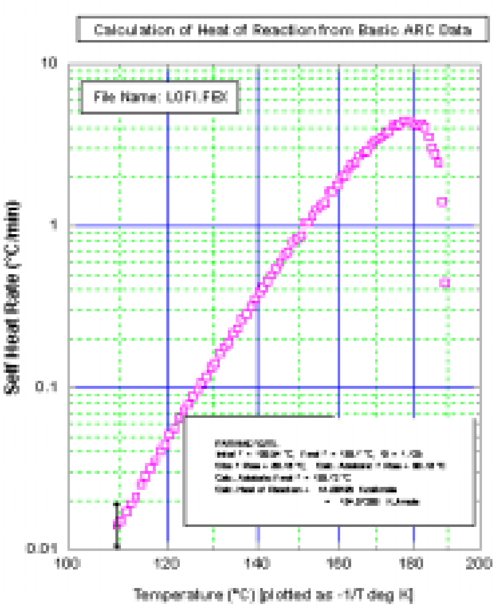


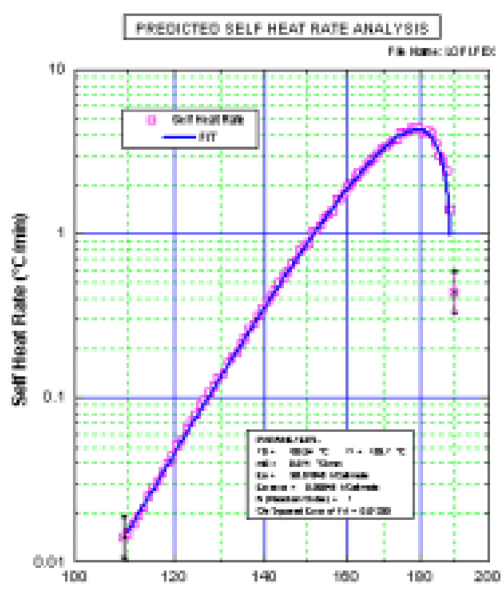


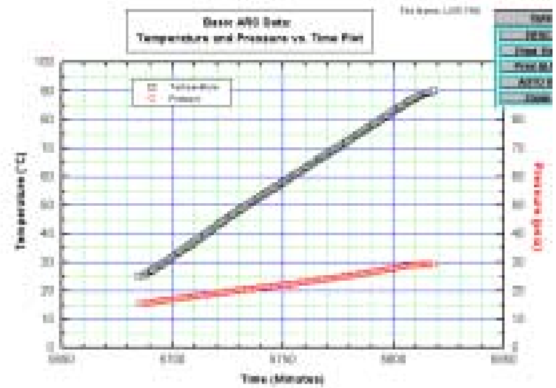




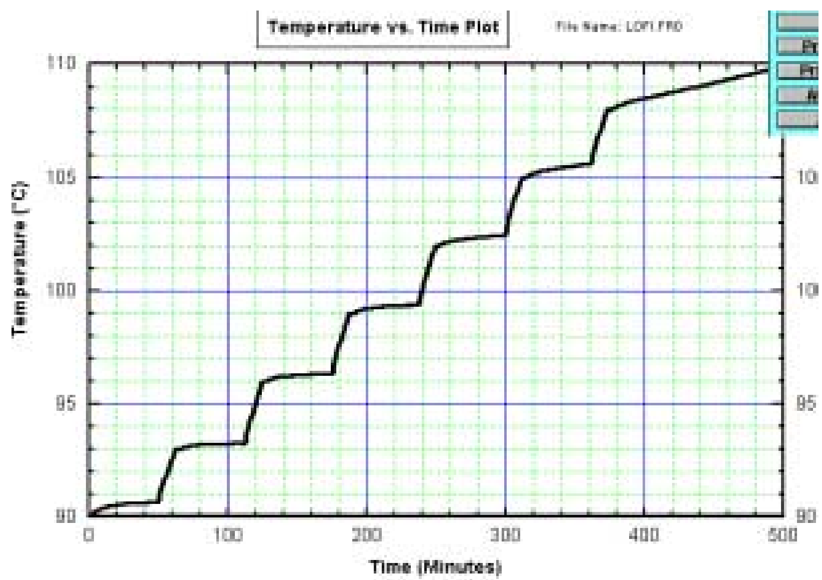
Sample Identity :	LOFI
Sample Mass (g) :	49.732
Sample Cp (J/gK) :	2.09
Sample Density (g/l) :	900
Sample RMM (g/mol) :	146
Test-cell type :	ss63
Test-cell Mass (g) :	31.08
Test-cell Cp (J/gK) :	0.42
Phi-factor :	1.12559
Onset Temp (° C) :	109.54
Onset T Rate (° C/min) :	0.014
Max Rate Temp (° C) :	177.65
Max T Rate (° C/min) :	4.4
Max P Rate (bar/min) :	36.08696
Final Temp (° C) :	188.68
Max Pres (bar) :	413.2
Adiab Temp Rise (° C) :	79.14
Total Enthalpy (J) :	9258.86401
Heat of Reaction (J/g) :	186.17518
Reaction Order :	1
Act. Energy (J/mol):	164307.06086
Frequency Factor (/s) :	4.4049E18
Kinetic Max Temp (° C) :	178.36394
K. Max T Rate (° C/min) :	4.45885
Heat of Reaction (J/mol)	181695.02861
Percent Purity (%) :	14.96

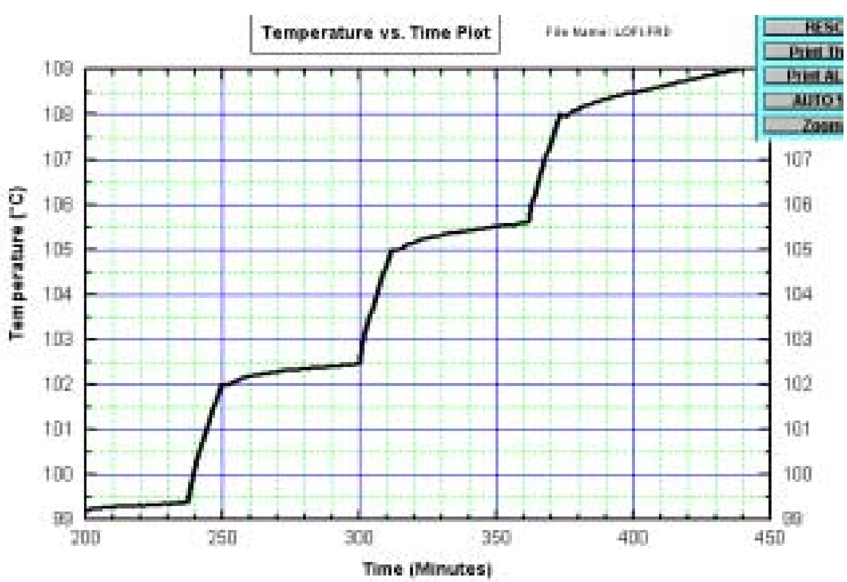


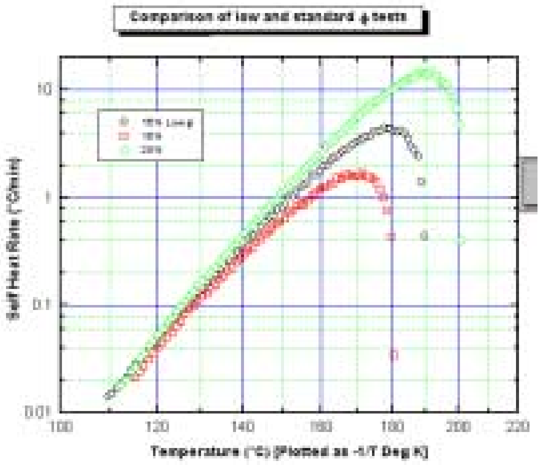


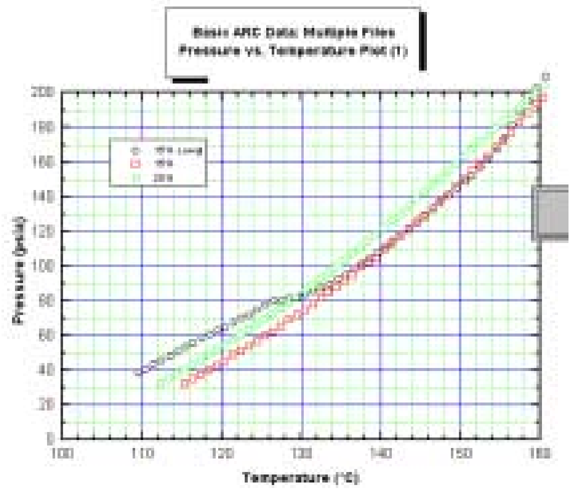

Basic ARC Data:
Temperature and Pressure vs. Time Plot
Time (Minutes)
Temperature (°C)
Pressure (psia)

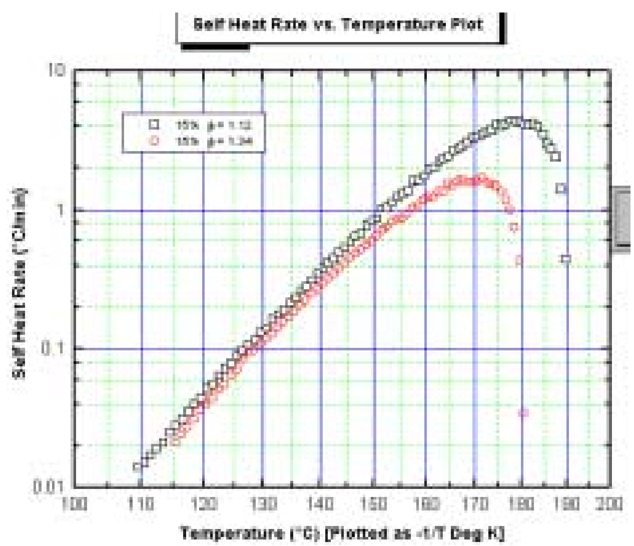

Pressure vs. Time Plot
Time (Minutes)
Pressure (psia)

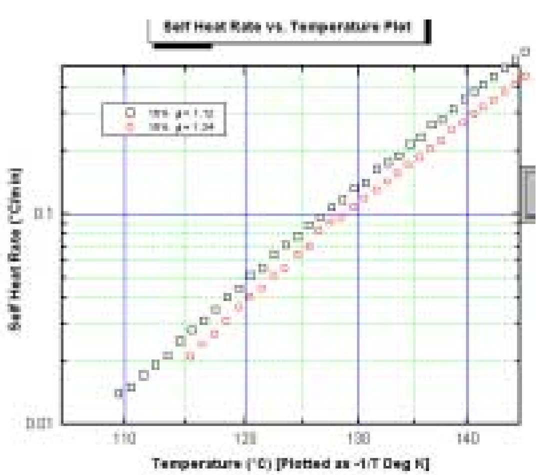

Temperature vs. Time Plot
File Name: LOF1.FRD
Temperature (°C)
Time (Minutes)


Temperature vs. Time Plot
File Name: LOF1.FRD
Temperature (°C)
Time (Minutes)


Comparison of low and standard φ tests
15% Low φ
15%
20%
Self Heat Rate (°C/min)
Temperature (°C) [Plotted as -1/T Deg K]


Basic ARC Data: Multiple Files
Pressure vs. Temperature Plot (1)
15% Low φ
15%
20%
Pressure (psia)
Temperature (°C)


Self Heat Rate vs. Temperature Plot
15% φ= 1.12
15% φ= 1.34
Self Heat Rate (°C/min)
Temperature (°C) [Plotted as -1/T Deg K]


Self Heat Rate vs. Temperature Plot
15% φ= 1.12
15% φ= 1.34
Self Heat Rate (°C/min)
Temperature (°C) [Plotted as -1/T Deg K]

The data from the Low ϕ test shows the expected self-heat rate curve. The First Order Activation Energy and Heat of Reaction for this data has been calculated using both the THT and CSI software. Modelling shows a very good fit – perhaps better than with the higher ϕ tests.

THT	ΔH	181.7kJ/mol	43.3kcal/mol	CSI	ΔH	181.8kJ/mol	43.4kcal/mol
	Ea	164.3kJ/mol	39.1kcal/mol		Ea	162.7kJ/mol	38.8kcal/mol

Prior to exothermicity being recorded there was self-heating observed below the sensitivity. At 90°C, 0.002°C/min; 93°C, 0.001°C/min, 96°C, 0.002°C/min and 99°C again 0.002°C/min. This indicated the 'baseline' and shows good stability of these low ϕ containers. But there is no indication by heat rise or indeed there was no indication by pressure rise of any reaction at this temperature. This is no doubt due to stabilizers in the DTBP. The stability of the system might be expected due to the thermal mass.

At 102°C the rate was 0.004°C/min and there was pressure rise of 0.01psi/min and at 105°C these rates were 0.008°C/min and 0.04psi/min.

This shows that the low ϕ containers can readily be used to detect at high sensitivity, probably as low as 0.003°C/min if required. (The system was calibrated prior to the test with the low ϕ container, but no special conditions were used).

The reaction below the onset is shown in the figure.

Previous work has been published with a range of DTBP concentrations at normal (though perhaps relatively low) ϕ. (See THT TI Sheet No 23). Figures also show comparison with the 15% and the 20% DTBP solutions given. In these tests a 6g solution was used in a bomb weighing just under 8g, $\phi = 1.34$.

Clearly the low ϕ result lies between these two results and direct comparison of the two 15% DTBP shows the effect of lowering the ϕ value.

It is suggested that these low ϕ containers can be used with both the THT and the CSI Accelerating Rate Calorimeters to give reliable results at ϕ values near 1.1. It can be noted that, in this low ϕ region, the ϕ value depends greatly upon the specific heat of the sample. With an aqueous sample, $\phi = 1.05$ may be obtained.

The low ϕ container might be considered for the following types of test:

High sensitivity tests for reliable 'onset' determination
Investigating impurity reactions (small reactions at low temperatures)
Low energy samples
Storage simulation tests, including SADT simulation
Reaction engineering tests
Closed vessel low ϕ tests for vent sizing requirements
Direct vessel simulation tests