Calorimetry & Hazard Assessment

Safe Scale-up Tools

H·E·L

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Product Selection Guide

For over 20 years HEL Group has been producing process safety and hazard assessment tools, offering now four main devices to assist in the evaluation of thermal hazards.

These complementary devices are all used in well equipped laboratories of large corporations, using a common software platform to produce similar data files, making it simple for users to move between the different systems.
Here is a quick selection guide:

APPLICATION	SOLUTION	
Chemical Stability Screening I Thermal stability of chemicals I Safe process/handling temperature I Potential temperature/pressure rise following exotherm	**TS^{u} (Thermal Screening Unit)** Uses only ~ 0.5 to 5g of sample, giving unambiguous data regarding hazards – including pressure.	TS^{u} replaces DSC as a screening device: **provides pressure data which is critical for safety assessment** and uses larger more reliable sample sizes.
Process Control & Scale-up Data I Cooling duty on scale-up I Time to complete reaction I Influence of feed rates I Total energy release (hence potential temperature increase) I Reaction Kinetics	**SIMULAR Reaction Calorimeter** A stirred and controlled reactor (typically 1 litre volume) that measures the RATE of heat release as the reaction is performed under controlled conditions of temperature, pressures, dosing etc.	SIMULAR is **the easiest system on the market to use**, allowing both safety experts and process development chemists to use it quickly and effectively. Calorimetry data displayed in realtime without any user input.
Precise Stability & Reaction Runaway Data I Same data as in TS^{u} but more precise I Plant-scale data following reaction runaway I Design relief vents	**Phi-TEC Adiabatic Calorimeters** For simulating reaction behaviour under plant condition and providing data to mitigate problem.	Phi-TEC I is the **classic 'ARC' – type calorimeter** used industry-wide for over 35 years. Phi-TEC II is a **unique low thermal inertia (or phi-factor)** device that directly allows vent sizing and all plant-scale incidents to be studied.

Common Software Platform

All devices use the same winISO software platform – intuitive, visual and with many unique features, such as:

I Real time graphical, tabular and mimic display of data
I Real time editing of experiments
I Alarms and shutdowns based on measured variables
I Data files can be imported directly into standard software packages

TS^u Simple, Rapid and Reliable Hazard Assessment

The Thermal Screening Unit (TS^u) has been developed for the first step in reaction hazards assessment, offering a more comprehensive solution than traditional screening by DSC/DTA.
For effective reaction hazards screening, two critical pieces of data need to be determined:

- the 'onset' temperature for the reaction
- the pressure generated by the runaway

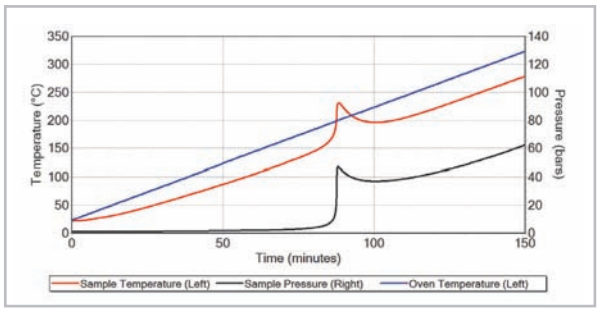
The TS^u offers you the simplicity of operation associated with DSC and DTA, whilst providing pressure data. In addition, by utilising sample cells from 1 to 8ml, representative samples and reaction mixtures can be tested.

FEATURES

- Alternative to DSC/DTA as a primary thermal hazard screening method
- Wide temperature range
- Wide pressure range
- Simultaneous pressure and temperature data
- High pressure mid-test injections possible
- Rapid sample turn around
- Representative sample size
- Low running costs

KEY DATA PRODUCED

- 'Onset' temperature of exotherm
- Rate of temperature rise
- Rate of pressure rise
- Maximum temperature and pressure
- Indication of non-condensable gas generation
- Indication of energy released



Thermal stability tests using 2g of sample, gives clear pressure and temperature data, requiring virtually no user experience for result interpretation

OPERATING MODES

The standard procedure involves heating of the sample at a user defined rate (typically between 0.5 and 10°C/minute) whilst both the temperature and pressure are recorded. Deviation from linearity (e.g. a sharp rise) indicates the 'onset' of an exotherm. The subsequent rise shows the severity of the hazard directly, without the need for any calculation. Additional operating modes include isothermal, dual scan and soak-and-scan.

OPERATING RANGE

Temperature from ambient to 400°C, resolution of 0.01°C. Pressure transducers are available in several ranges, typically up to 200 bar.

TEST CELLS

Spherical test cells of approximately 8ml in stainless steel, hastelloy, and other alloys are available as well as in glass. The large volume allows for truly representative samples, and the study of liquids, solids and reaction mixtures.

TS^u Applications

Thermal screening of a series of nitrocellulose dyes
A series of nitrocellulose dyes (0.5g) were heated from ambient temperature to 280°C at a rate of 2°C/min to assess their thermal stability. The results obtained from a series of such tests are shown in the table. From these results the violet pigment can be identified as having the lowest thermal stability with an onset temperature (as determined from a dT/dt against temperature graph) of 127.4°C.

Pigment	Onset Temp (°C)	T Max(°C)	dT/dt Max (°C/Min)	dP/dt Max (Bar/min)
Violet	127.4	338.8	318.4	497
Yellow	139.5	302.5	269.5	550
Red	149.3	392.8	422.8	630

SIMULAR for Safe Process Scale-up without time consuming calibrations or off-line calculations

For safe and efficient scale-up, it is essential that your tools simulate your plant as closely as possible. In addition it is important that as much information and insight about the process be obtained.

FEATURES

- Ideal for both calorimetry experts and development chemists alike
- Gives real-time heat release data – automatically
- Requires no time-consuming calibrations
- Operation requires no prior knowledge of calorimetry theory
- Customised to your requirements

KEY DATA PRODUCED

- Reaction entalphy (△Hr)
- Heat accumulation
- Heat release rate (Q)
- Heat transfer rate (UA)
- Batch cycle times
- Scale-up data

CALORIMETRIC METHODS

Power Compensation and Heat Flow are provided as standard, selectable by the user for each experiment. In both cases, on-line calculations are performed without user input being necessary.

Reflux Calorimetry is also available as an option for reactions at boiling conditions.

REACTORS

The standard reactor is a 1 litre atmospheric pressure system. Optional volumes range from 0.2 to 20 litres in glass, stainless steel or resistant alloy, with pressure ratings of up to 200 bar.

OPERATING RANGE

Pressure - HEL offer a range of options for the study of reactions under pressure including 6 and 12 bar glass and 60 bar stainless steel reactors. There are other alloys and specialist material options. We even produce systems that operate over 200 bar reactor pressure.

Temperature - by using commercially available heater/chiller systems, we can offer you the temperature range you need, between -80 and over +350°C, with precision of better than +/-0.1°C. These systems also offer a small foot print and emergency cooling is available when required.

FEEDS

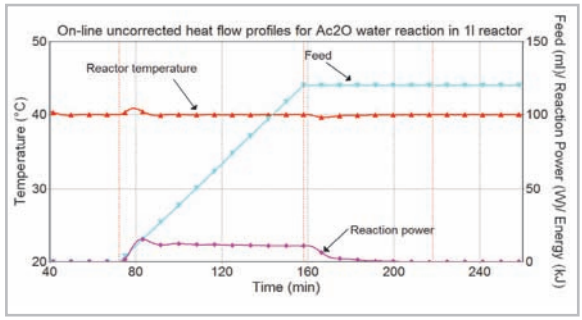
Reagent feeds - gas, liquid and solid feeds are all available using a variety of application-dependent techniques. Standard liquid feeds are pump and balance combinations, but options include syringe pumps for low flow rate feeds and pressurised vessels for faster rates and/or highly volatile reagents. Gas feeds can be controlled via constant reactor pressure, bottle/balance combinations or even mass flow control. Finally, automated solids addition is also made possible using a screw feed system developed exclusively by HEL.

CONTROLS & SENSORS

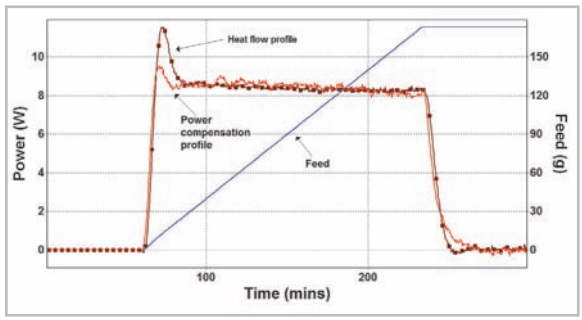
Software and electronics allow a variety of inputs to be logged and if necessary, used for feedback control. These include pH, turbidity, conductivity, FTIR, particle size, etc.

SAMPLING

HEL have developed tools for automatic sampling and dilution during chemical reactions. A portable sampler, software driven, is available as an option.



On-line (real-time) heat output data for semi-batch reaction

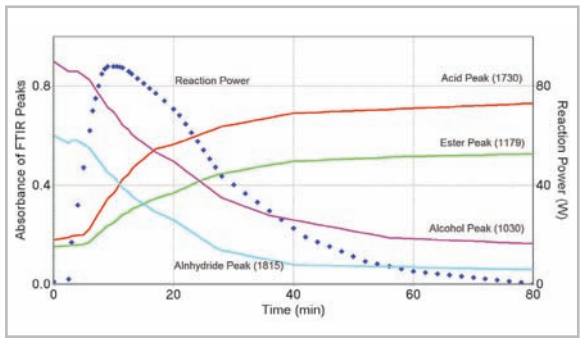


Comparison of heat-flow and power compensation profiles for water/acetic anhydride reaction

SIMULAR Applications

Process Optimisation
Yield, batch time
Optimisation of chemical reactions, to maximise yield, minimise side product formation etc., sometimes need complex combinations of measurements and control. SIMULAR is uniquely flexible in being able to take inputs from a range of sensors – FTIR, turbidity, particle sizing devices – and then using the data to gain a better understanding of the process.

Process Safety
Reagent accumulation
Most reactions are now run in a semi-batch manner: one or more reagents are held back and then dosed at a controlled rate. If the reaction rate is slow at the selected operating temperature, the dosed component can accumulate in the reactor – the amount of accumulation being a function of the feed rate.



Combined heat release and spectroscopy data from Simular with PAT capability

Scale-up Data
Heat transfer, cooling duty
Chemical engineering information necessary for the scale-up of reactions is readily obtained from the SIMULAR. This includes the cooling duty (Q) for either jacketed reactors or reflux condensers and heat transfer rate (UA). For multi-phase reactions where mixing is crucial, aspects of agitation can also be studied.

Heat Release (enthalpy)
Potential temperature rise
Total energy released by reaction can be used to calculate the potential temperature rise in the event of this energy release under adiabatic conditions. This can be used to assess the risk of explosion.

Reaction Kinetics
Dose or kinetic controlled reaction
Heat release rate data can directly provide kinetic information, allowing, for example, ready assessment whether the process is controlled by the rate of reagent addition or if kinetics are the limiting factor.

Specify SIMULAR around your chemistry

Phi-TEC I Classic Adiabatic Reaction Calorimeter

The Phi-TEC I is a computer-controlled adiabatic calorimeter that can be used to determine the heat evolved and pressure developed during an uncontrolled exothermic runaway reaction. It is the modern alternative to the classic 'ARC' developed by Dow Chemicals.

FEATURES

The entry-level Phi-TEC I uses high pressure cells, or bombs, of approx 7-11ml volume to determine the heat evolved and pressure developed during the reaction. Sample sizes from 0.5 to 5g are typical and give rise to a thermal inertia (or phi-factor) of around 1.5 or higher with organics.

I TEST CELLS
Uses common glass, stainless steel & hastelloy test cells, typically 7-11ml volume.
Custom test cell designs available.

I SAMPLE AGITATION
Magnetic stirring, controlled by the software, is a standard feature of Phi-TEC.
This is useful in many situations but absolutely essential when non-homogenous or immiscible samples are tested. To enable simple and inexpensive use of this feature, special non-standard test cells are supplied.

I DIRECT TEMPERATURE SENSING
Traditional designs of the 'ARC' system attach the thermocouple to a clip on the outside wall of the test cell. The Phi-TEC I design allows direct temperature sensing, giving a more representative measurement and greater sensitivity.

KEY DATA PRODUCED

Specifically, the following information can be obtained:

- Exotherm 'onset' temperature with sensitivity of 0.20°C/minute (or better)
- Heat release (or temperature rise)
- Pressure increase
- Global reaction kinetics
- Time to maximum rate (TMR)
- SADT (used in storage/transportation studies)

Phi-TEC I is also available as a BATTERY TESTING CALORIMETER (BTC)

AA Batteries after a test in a 'Standard' Phi-TEC BTC

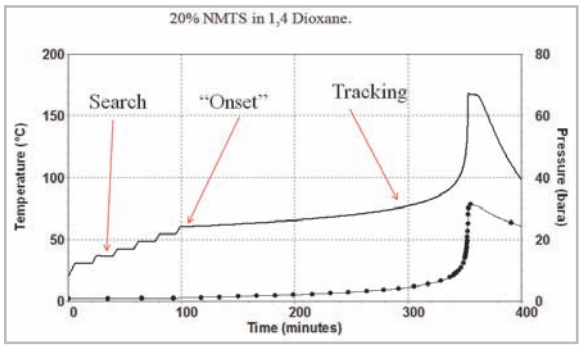
TWO STANDARD TESTS ARE NORMALLY PERFORMED:

Rapid Screening

For preliminary screening of chemicals it is possible to ramp the sample temperature until an exotherm is induced. This simulates a large scale DSC but with the added advantage of being able to measure the pressure and stir the sample.

Heat-Wait-Search

This is the classic test for detailed sample evaluation initially developed by Dow Chemicals for the original 'ARC'. The sample is heated in small steps and at the end of each, the software 'searches' for an exotherm within the sensitivity of the instrument. This is continued until a reaction is detected and adiabatic tracking of the sample then commences.



Phi-TEC II Industry Leader, Low Ø-Factor Calorimeter

Phi-TEC II is a computer controlled adiabatic calorimeter with the capability of simulating the behaviour of a large-scale chemical reactor under conditions virtually identical to a large scale plant using only 10-100ml of sample. This is due to the low phi-factor data obtained from the Phi-TEC II.

Phi-TEC I and TS^{U} type tests can also be performed on Phi-TEC II.

FEATURES

Sample cells
Test cells can be made of glass or a range of metals. For screening tests, metal or glass cells (~10ml) may be used, but for detailed studies of reactions, larger (100 to 120ml) cells are appropriate.

Sample agitation
Agitation of viscous liquids or multi-phase samples can be performed by use of mechanical agitation driven by a conventional electric motor. This design can be used on thin-walled test cells and is often essential if reliable design data is to be generated.

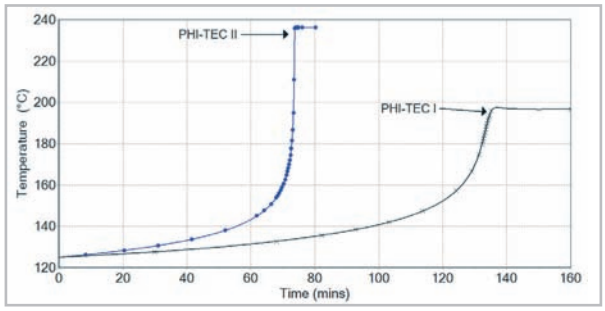
Sample addition
The sample can be loaded into the test cell at any stage: prior to placement in the containment vessel, whilst in situ, or during the experiment.

Temperature/pressure measurement
A fast-response, type k thermocouple is placed inside the test cell directly in contact with the sample, range 0 to 500°C. Maximum pressure is typically 138 bar (2000psi).

Exotherm detection-sensitivity
In general, exotherm detection down to 0.02°C/min or lower. Heaters can track rates of over 200°C/min.

KEY DATA PRODUCED

- Accurate 'onset' temperature of exotherm
- Runaway data suitable for DIERS RELIEF LINE SIZING
- Determination of venting behaviour (Gassy, tempered, hybrid)
- Determination of flow regime (two-phase or single phase)
- Kinetic data (e.g. for TMR or TNR calculations)



Effect of Ø-factor (thermal inertia) on runaway reaction

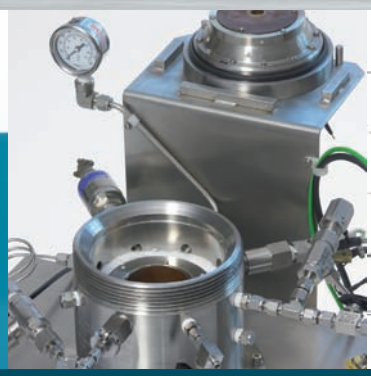
Phi-TEC Applications

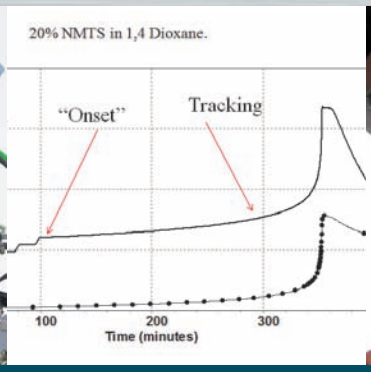
The consequence of a runaway in a large-scale reactor can be explored under a variety of situations. In this way hazards can be truly quantified without the need for reaction modelling, extrapolation or expensive pilot plant trials.

Relief sizing to prevent equipment damage following an unwanted reaction is another application of Phi-TEC II. The equipment allows investigation of gas generating reactions, vapour pressure dominated systems, checking for two-phase flow and design of external dump tanks.

25% DTBP Decomposition

This graph shows why phi-factor data is so important. Small changes in phi-factor can lead to huge differences in reaction rate. Phi-TEC II emulates conditions essentially the same as in a large scale plant (i.e. a low phi-factor). The data is produced from tests with di-tertiary butyl peroxide in test cells which have a different mass and hence produce different phi-factors. Phi-TEC II can generate both types of data.





ABOUT HEL

HEL is an international company that specialises in research and pre-pilot scale chemical reactors and related data logging/automation tools for process R&D in the pharmaceutical, fine chemical and petrochemical industries. Established in 1987 and with clients worldwide our key strengths are:

Knowledgeable staff - highly qualified and experienced chemical engineers and chemists
Quality - underpinned by ISO9001 certification for over 16 years
Service - choice of service contracts backed by established culture of unmatched client support
Range of products - both off-the-shelf and custom designs, manual and fully automated controls, low and high pressure/temperature applications, single and parallel/multi-vessel products

CONSULTANCY & TESTING SERVICES

Over the past 20 years we have developed expertise and become industry experts in:

- Reaction hazards calorimetry, vent sizing
- Process development and optimisation
- Dust and powder flammability
- Other hazard consultancy services, including expert opinion, HAZOPS, DIERS, incident and accident investigation and professional training

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