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NOVEL PROCESS APPLICATIONS USING PHI-TEC II ADIABATIC CALORIMETER

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Abstract

This paper presents several applications of the PHI-TEC II that are not commonly associated with adiabatic calorimeters but which have proved to be extremely valuable. These include simulation of a deep oil well for enhanced oil recovery, isothermal calorimetry of a semibatch reaction, catalyst research using flow through reactors (both plug flow and CSTR) with controlled feeds of high pressure liquid and gas.

Keywords: adiabatic calorimeter, calorimetry, exothermic, hazards, phi-factor, reaction, runaway, vents

Introduction

Conventional adiabatic calorimeters [1, 2] are used first and foremost to evaluate the temperature at which a liquid (or powder) begins to react at a 'significant' rate and they then follow, adiabatically, the subsequent rise in pressure and temperature. The 'onset' of reaction is indicated by a rate of temperature rise in the sample of around 0.02°C min^{-1} (or higher) and if this occurs at a temperature T_o, the heat release Q(J) may be calculated from:

$$Q = \overline{C_p}(T_f - T_o)\,\Phi$$

where T_f the final (maximum) temperature (K), $\overline{C_p}$ mean specific heat of the reacting sample (J g^{-1} K^{-1}) and Φ phi-factor

$$\Phi = 1 + \frac{(m\overline{C_p})_c}{(m\overline{C_p})_s}$$

where m is the mass, C_p the specific heat (subscript c is for sample container, s is for sample).

The adiabatic test data generated from a test (Fig. 1 for example) can also be used to evaluate the global kinetics for the reaction [1] .

Adiabatic conditions are ensured by holding the sample and its enclosure at the same temperature (Fig. 2); as the sample self-heats due to energy release the instrument control system ensures that the surroundings follow it precisely. The spherical

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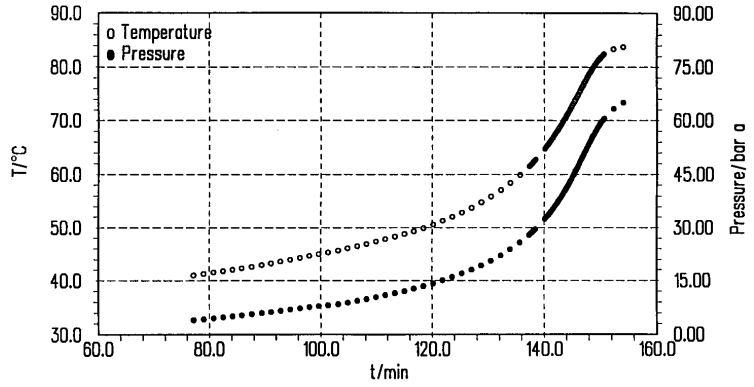

Fig. 1 Typical data from an adiabatic calorimeter

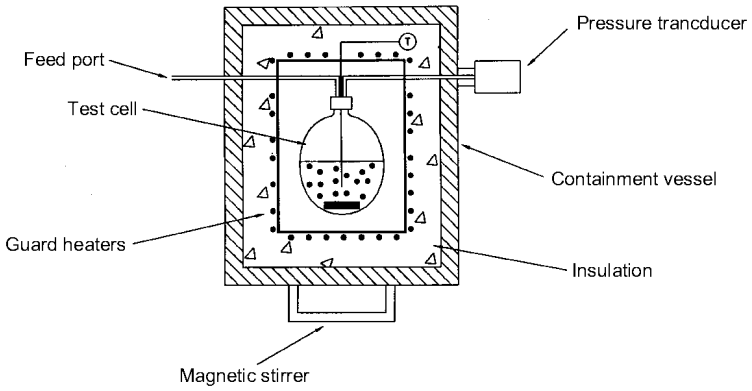

Fig. 2 Basic features of adiabatic calorimeter

test cell volume is normally around 10 ml and is designed to take fairly substantial pressures that may be generated during an exotherm. The phi-factor for conventional calorimeters of this type is around 2.0.

Important industrial applications of adiabatic calorimeters require that the phi-factor (also called thermal inertia) be close to 1.0 so that the data reflects more closely the characteristics of industrial systems (such as storage tanks and chemical reactors) and thereby allow reliable predictions of potential thermal runaways. This is done by inclusion of pressure compensation on top of the adiabatic conditions, see Fig. 3. The sample cell (~110 ml in volume) of very light weight construction is surrounded by three electrical heaters (which are controlled to give adiabatic conditions) and the entire assembly sits within a pressure vessel. As the sample pressure rises, nitrogen is added so as to maintain a relatively small differential across the walls of the cell. In this way a low mass test cell can be used but maximum pressures of 150 bar or more can be accommodated. Typically, Φ-factors of around 1.05 to 1.1 are achieved.

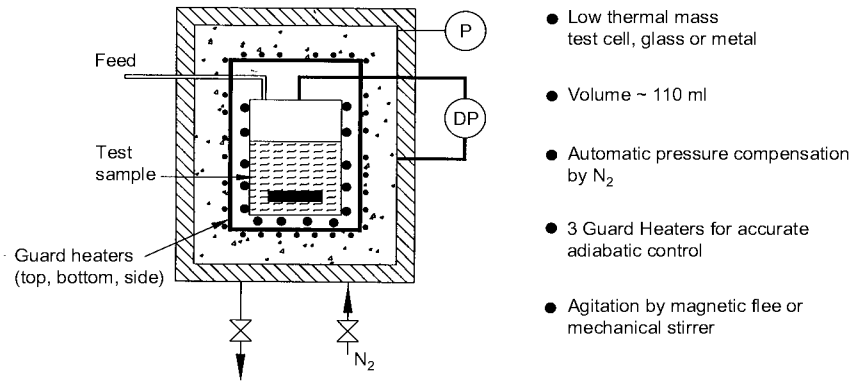

Fig. 3 Low PHI-factor adiabatic calorimeter (PHI-TEC II)

The larger (and low Φ-factor) test cell design permits a wide range of industrial 'accidents' involving exothermic reactions to be readily simulated. The experimental data can be used directly for design of safely features such as relief vents to protect industrial equipment [3].

Some specific aspects of PHI-TEC II

The PHI-TEC II adiabatic calorimetry is commonly used in the manner described above, as a tool for thermal analysis of chemicals and investigation of runaway reactions. A number of commercial units have also been equipped with other quite unusual features and this is made possible by the fact that the PHI-TEC II is a sub-set of a much more comprehensive system that has features such as:

- Isothermal operation of normally jacketed chemical reactors, where temperature is controlled by heat removal by a circulating oil.
- Power compensation and heat flow calorimetry, in support of a reaction calorimeter, as a special case of an isothermal reactor [4].
- Controlled dosing of liquid, gas or solid.
- Simultaneous control of other process variables (pressure, pH, etc.)

From the very broad list of features available, a specific instrument (such as PHI-TEC) is defined by the appropriate combination of three aspects:

- Mechanical

This determines the specific sensors, sizes of vessels, pressure rating, etc.

- Electronics interface

This is the facility that amplifies sensor outputs, provides the electrical power for valves, heaters etc. and is the link between the mechanical items and the software. The electronics rack is populated with the correct combination of 'cards' for a specific function.

- PC/software

The software is 'told' what signals are coming through which ports and what outputs are required for control. A very wide range of experimental routines are available from which those appropriate to a particular 'instrument' are selected. Thus, for the PHI-TEC for example, the 'heat-wait-search' routine is selected [1] as this is used to look for exotherms, but which is not relevant for normal chemical reactor control.

Thus the PHI-TEC II is just one special case of instruments that can be put together by an appropriate combination of features.

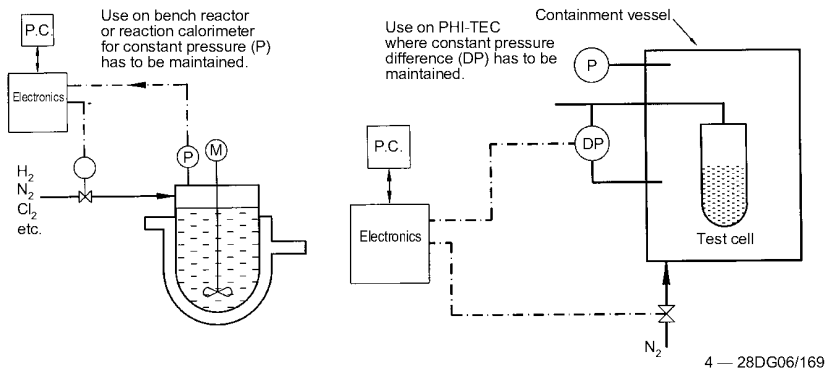

Fig. 4 Pressure control comparison in PHI-TEC II compared with stirred reactor

As an example, consider the control of pressure in a conventional chemical reactor and in the PHI-TEC (where pressure compensation is needed). As shown in Fig. 4, the same control logic (and indeed mechanical and electronic components) can be used for these two very different applications.

This design approach has the advantage that the PHI-TEC II can be easily expanded to include features that are not normally associated with adiabatic devices but which can be extremely useful; several examples will now be discussed.

Liquid C_p determination

Consider a liquid heated in a PHI-TEC test cell (adiabatically) by the addition of $\dot{Q}$(W) of electrical power. The following relationship can be used to determine the liquid specific heat:

$$C_p = \frac{\dot{Q}}{m_s(dT/dt)\Phi} \text{ J/gK} = \frac{1}{m_s}\left[\frac{\dot{Q}_c}{dT/dt} - (mC_p)_c\right]$$

where m_s is the liquid mass (g), (dT/dt) the rate of temperature rise (K s^{-1}) due to the input of $\dot{Q}$ and $(mC_p)_c$ the thermal mass (in J K^{-1}) of the container.

In order to do this test a specially modified test cell (Fig. 5), incorporating an internal heater is needed in addition to a known (and controlled) source of electrical heat ($\dot{Q}$). An experiment simply requires the application of heat and then a measurement of the resulting rate of temperature rise, (dT/dt) to directly give the liquid C_p.

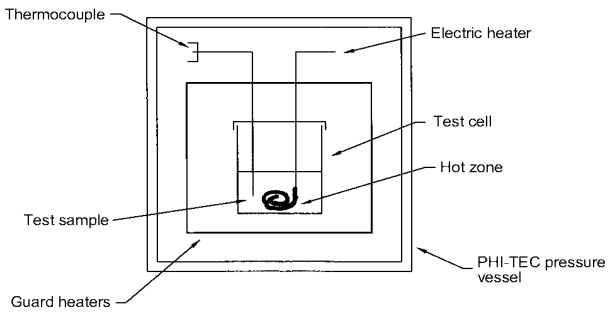

Fig. 5 Test cell for C_p determination and isothermal operation

Isothermal operation (with calorimetry)

There are at least two important situations where isothermal operation in the PHI-TEC II can be useful:

- To replicate in-situ, the precise conditions prior to an (adiabatic) runaway reaction.
- To obtain isothermal data, at relatively extreme conditions (high temperature and/or pressure), where a conventional bench-scale reaction calorimetry may not be available or would be too expensive.

The PHI-TEC is not equipped with any cooling capability and therefore the guard heaters around the test cell (which normally 'track' the sample temperature) are deliberately held at a lower temperature in order to induce cooling by heat loss. At temperatures close to ambient, this arrangement may need to be supplemented by the circulation of cold air (or N_2) through the vessel.

Thus, if a reaction is to be carried out isothermally at T_r, the guard heaters might be held at T_g, some 20 to 50°C lower; provided this difference in temperature is held constant, the cooling rate will also be constant. The test cell to be used is again fitted with an internal electrical heater which is now used to hold the temperature at T_r by compensating for the heat loss from the test cell to the surroundings. As changes occur in the test cell, due to addition of chemicals and/or exothermic effects, the power to the electrical heater will be adjusted in order to maintain T_r. The dosing facilities necessary for semi-batch operation can also be automated (see discussion of flow through systems).

Measurement of thermal changes during the isothermal period can be made using the power compensation technique. This simply involves comparing the heat applied (by the internal heater) during the chemical reaction with the baseline power in the absence of reaction (e.g. at the start of the experiment).

If the isothermal step is the first part of a hazard assessment, it is possible at any time to switch to adiabatic conditions. This will require switching the electrical power to zero and changing the control on the guard heaters so that they will 'track'

the sample temperature adiabatically. Recent examples of isothermal process investigation include hydrogenations, involving units designed to operate at 325 bar.

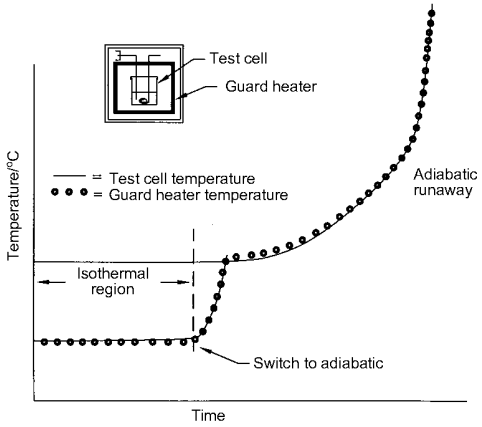

Fig. 6 Schematic representation of isothermal operation followed by adiabatic runaway

This would be rather like starting a reaction normally and then simulating loss of cooling part of the way into the reaction (Fig. 6).

Flow through system

Another interesting application of the PHI-TEC is for continuous flow (rather than closed) systems. These units typically consist of (Fig. 7):

- controlled dosing (gas and/or liquid)
- pre-heter
- reactor

The reactor could be a stirred tank (giving a CSTR) or a pipe (i.e. a plug flow reactor). The pre-heater can be controlled to ensure the feed is at a user defined temperature or alternately it can be set to follow the reactor temperature. The guard heaters will track the sample temperature (hence operating adiabatically) or can hold the sample at a user-defined value.

Consider for example a liquid mixture at T_f(K) fed continuously at a rate $\dot{m}$(g s^{-1}) to a small stirred test cell containing a solid catalyst. If as a result of reaction the liquid leaves the test cell at T_r, achieved under adiabatic conditions, then the reaction heat is given by (assuming no phase change):

$$\dot{Q}_r = \dot{m}C_p(T_r - T_f)$$

where C_p is the mean specific heat of the liquid. With T_f fixed, T_r *effectively becomes an on-line monitor of reactivity or heat output. A typical temperature profile is shown in Fig. 8. If product samples are analysed (e.g. on-line gas chromatograph, GC), then the heat output can be correlated with conversion. Thus for a stirred reactor, thermal ad kinetic data can be easily at a wide range of pressures and temperatures.*

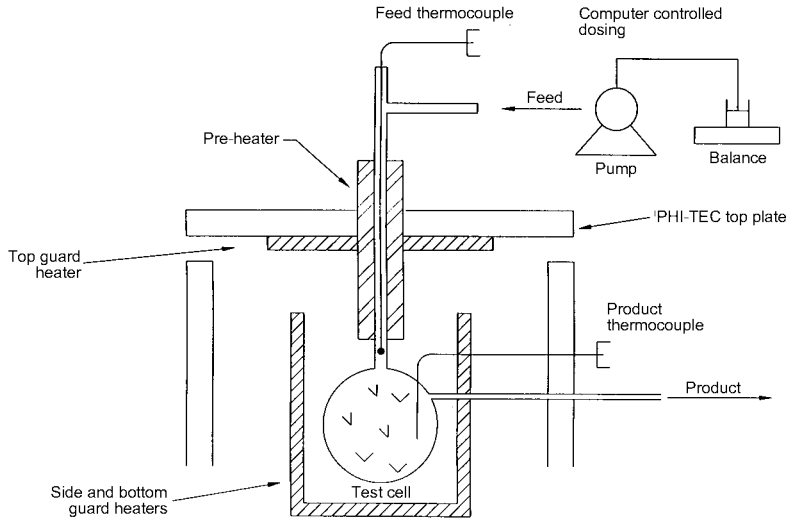

Fig. 7 Flow through (CSTR) testing in PHI-TEC II

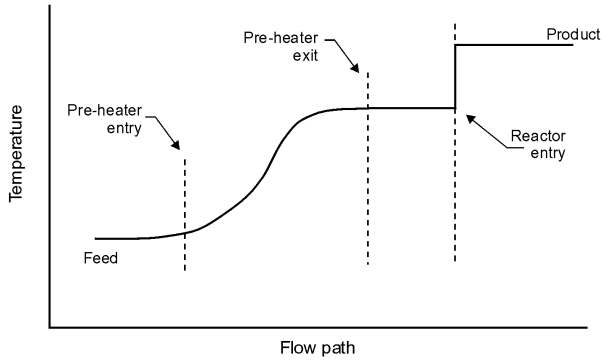

Fig. 8 Typical temperature profile through CSTR system

If the reactor is a plug flow type the temperature will increase gradually down the reactor. Thermal data is now more difficult to interpret because there is now no single temperature for the reactor and hence no easy way to ensure adiabatic conditions. This is the only difference between two modes of operation – changing from one to the other is very simple.

Deep sea oil recovery

Conventional oil drilling from deep sea beds typically results in 30 to 50% recovery of the oil, even after enhancement with pressurized liquids. The remaining 50 to 70% represents an enormous resource that is potentially wasted. One method of reducing this waste down to 30% or less (i. e. over 70% recovery) is by pumping com-

pressed air into the oil bed and forcing the oil out. When this is done, oxidation reactions can occur within the deep sea bed leading to the release of heat. It is anticipated that the ability to generate pressures in the region of 400 bar and temperatures in excess of 200°C will be necessary in order to investigate the reaction kinetics in the oil beds together with a wide range of operating modes (isothermal, adiabatic and flow through).

A specially designed PHI-TEC with an operating pressure limit of 400 bar and temperature of 500°C has recently been developed and is being used for enhanced oil recovery research [5].

Conclusions

The conventional use of adiabatic calorimeters can be substantially extend by the addition of additional peripheral devices such as pumps, heaters, flow controllers which are coupled to flexible control software.

The PHI-TEC II adiabatic calorimeter is proving valuable in catalyst research, high pressure/temperature oxidation and hydrogenation reactions and for isothermal experimentation.

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