TEMPERATURE OSCILLATING MINI-CALORIMETER

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Abstract

A small scale (100 mL) calorimeter is developed. It includes a glass vessel submerged in a thermostatic bath, a compensation electrical heater, and a control system. The typical operation mode consists on introducing the solvents and part of the reactants into the vessel, to stabilise a temperature of the bath (T_j) some degrees below the desired process temperature (T_p) and to adjust the reaction mass temperature (T_r) to T_p using the electrical heater. An oscillating set point is established for T_r, which produces an oscillating response of the applied compensation power ($\dot{Q}_C$). Finally, the rest of reactants are dosed to the vessel. A small deviation of T_r and T_p is observed. Even though it can be avoided improving the tuning of the controller, it can be useful for enhancing the calculation of the heat capacity of the reaction mixture (C_P).

The signals of T_r, $\dot{Q}_C$ and T_j are processed on-line using the FFT (Fast Fourier Transform) method as the mathematical tool used to analyse the data obtained, producing accurate values of the heat evolved ($\dot{Q}_C$) by the process, the heat transfer coefficient (UA), and the heat capacity of the reaction mixture (C_P).

Keywords: Fourier analysis, power compensation, reaction calorimetry, temperature oscillation

Introduction

The objective of this work is to develop the Temperature Oscillating Calorimetry (TOC) technique in a small volume (100 mL) reactor. This method is applied on a power compensation calorimeter, in which the temperature of the reaction mass is kept at a constant set-point value, by means of an electrical heater and a PI controller. The aim of this calorimetric technique is to obtain on-line the parameters involved in the heat balance of the reaction mass during a chemical reaction.

Theory

The principle of the temperature oscillation was first introduced in reaction calorimetry at the Technische Universität Berlin [1]. It has been widely applied in differential scanning calorimetry [2–5] and it has become one of the most innovative methods in thermal analysis nowadays [6–8]. It consists on the application of an oscillation of

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known parameters (frequency, amplitude) on the set-point of a power compensation calorimeter. This will produce an oscillation on the compensation power, and eventually another oscillation of the reaction mass temperature. Further mathematical treatment of both signals will provide a way to calculate continuously the values of UA and mc_p during the reaction [9].

In a typical power compensation calorimeter, considering without significance the contributions of dosing, agitation, reflux and losses on the system, the heat balance equation can be written as described in Eq. (1). If an oscillation is placed on the set-point, then the elements $\dot{Q}_C$ and T_r will become oscillating terms.

$$\dot{Q}_r + \dot{Q}_c = mc_p \dot{T}_r + UA(T_r - T_j) \tag{1}$$

Given that Eq. (2) is the general expression for an oscillating signal, and considering only the influence of oscillating terms on the heat balance, the previous equation can be written as in Eq. (3). Manipulation of this equation will yield Eqs (4), (5). The values of amplitude and phase for each signal during the course of the chemical reaction can be obtained applying the Fourier transform technique on each measured signal.

$$X = A_x e^{i(\omega t + \varphi_X)} \tag{2}$$

$$A_Q e^{i(\omega t + \varphi_Q)} = mc_p A_T \omega e^{i(\omega t + \varphi_T + \pi/2)} + UA A_T e^{i(\omega t + \varphi_T)} \tag{3}$$

$$UA = \frac{A_Q}{A_T} \cos(\varphi_Q - \varphi_T) \tag{4}$$

$$mc_p = \frac{A_Q}{\omega A_T} \sin(\varphi_Q - \varphi_T) \tag{5}$$

Experimental

In the first place, a theoretical simulation of calorimetry experiments is performed. A program has been developed in Simulink® environment to test the parameters that may have influence in power compensation and temperature oscillating calorimetry. The inputs for this program are the set point of the reaction temperature, the surroundings temperature, and the parameters of the forced oscillation (if working with TOC), as well as the evolution during the reaction of the values of U, A, V, ρ, c_p, the reaction time, the kinetic and the heat of the reaction. This program is useful to determine the possible values of maximum compensation power, or the optimum difference of temperature between reactor and surroundings.

The set-up of the designed calorimeter is described in Fig. 1. The reactor is a 100 mL flask with three openings, submerged in a thermostatic water bath. One temperature sensor (Pt-100) is placed in the reactor and two more in the bath, and the three of them are connected to electronic amplifiers. The voltages of the circuit for the reactor thermometer and one of the bath sensors are introduced into a differential amplifier, this way the value of ΔT can be determined in one single measurement.
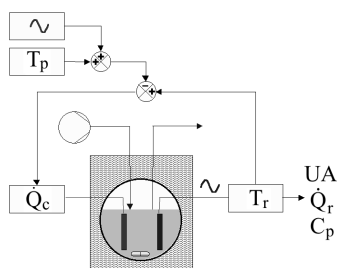
Fig. 1 Experimental set-up scheme

The temperatures measured are introduced in the control program (through FieldPoint® modules by National Instruments®). This program is a LabVIEW® application which determines the value of the compensation power required to keep the reaction temperature at the desired set-point, through a PI controller. The program also permits the user to determine the values of the different parameters needed to perform experiments of both power compensation or temperature oscillating calorimetry, as well as to observe the evolution of temperature and power signals.

The power determined by the controller is supplied to the system as an intensity generated by a FieldPoint® module. This intensity goes through a power amplifier circuit, and is transmitted to the reaction media through an electrical resistance.

The system can be used to simulate the heat generated by a reaction, without needing to use chemical reagents. The control program allows the user to chose the generation of different heat curve types, which are transmitted to the reactor through a second set of power amplifier and electrical resistance. When performing experiments with real chemicals, the place of this second resistance is taken by a dosing device.

Results

Once the calorimeter has been set-up, the first experiences are performed in power compensation mode, with a simulation power resistance placed in 100 mL of water (Fig. 2). As described previously, the user can determine the heat profile generated by this resistance, simulating thus the heat generated during a chemical reaction. The heat balance
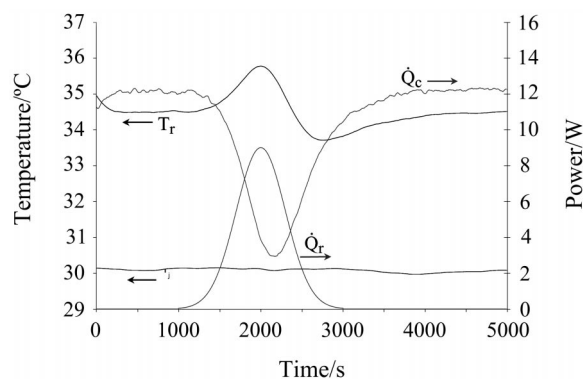

Fig. 2 Simulation of a batch reaction with Gauss type kinetics

performed with the terms of compensation power and reaction temperature, compared with the integral of the simulated power ($\dot{Q}_r$ line) yields a deviation of less than 5%. Figure 3 shows the same experiment, applying the TOC technique, and Fig. 4 shows the result of a semi-batch reaction, simulated at a higher oscillation frequency.
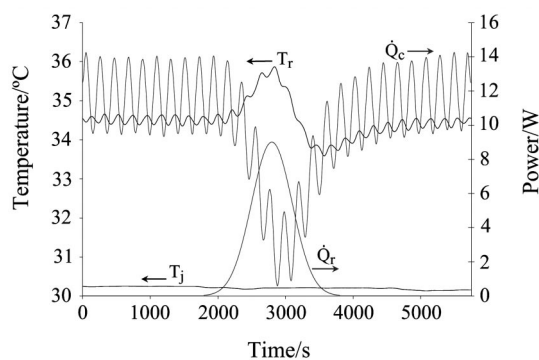

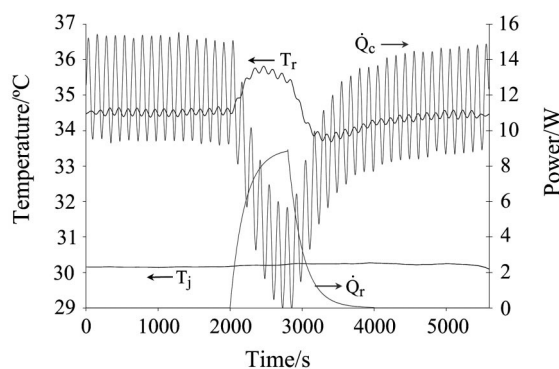**Fig. 3** Simulation of a batch reaction with Gauss type kinetics using TOC method (ω=0.03 rad s^{-1})

Fig. 4 Simulation of a semi-batch reaction with accumulation using TOC method (ω=0.05 rad s^{-1})

In the last step of a TOC experiment, the results obtained must be analysed in order to obtain the values for the UA and mc_p coefficients. A program has been developed in Matlab® environment to perform the Fourier analysis of the temperature and compensation power signals. This tool has been tested with the results obtained with the computer simulation of the calorimeter.

Figure 5 shows the result of the computer simulation of a semi-batch reaction. The values of the coefficients are calculated for each oscillation period. Figure 6 shows the heat capacity calculated for this reaction, compared to the simulated value, and Fig. 7 presents the reaction power determined in this case. It can be seen that the calculated value draws near to the simulated profile. However, a slight deviation is observed, especially in the base line of the power curve. This might be due to an incorrect selection of the intervals of temperature and power compensation to be analyzed at each set of data periods, which suggests that the coefficient determination
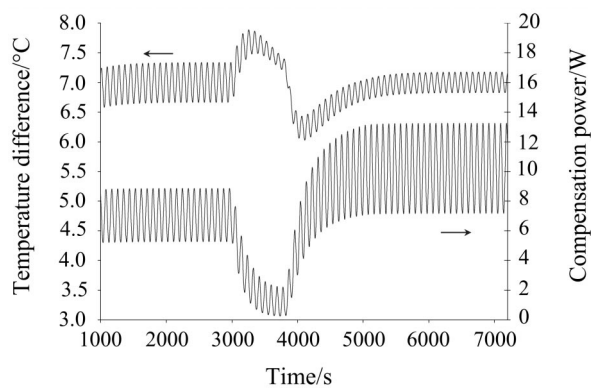
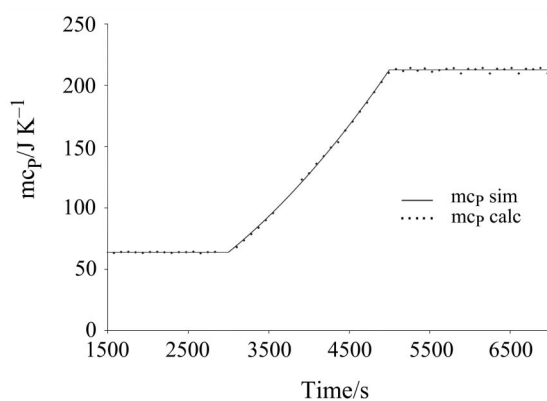**Fig. 5** Computer simulation of a semi-batch reaction

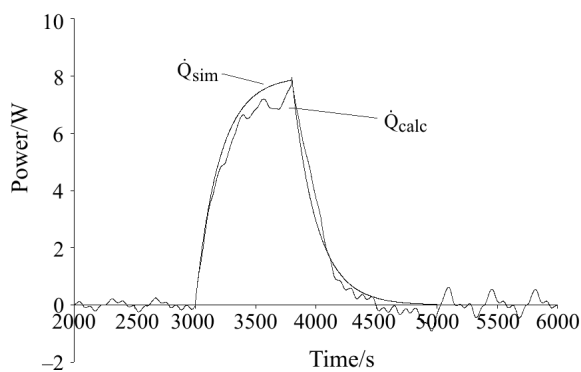**Fig. 6** mc_p coefficient calculated by Fourier transform

Fig. 7 Reproduction of reaction power in the simulation of a semi-batch reaction

can be improved. It must also be noticed that some points have been eliminated from results in Figs 6 and 7. Those points correspond to oscillation periods at the beginning and at the end of the simulated dosage, which generate discontinuities in the results.

For the calculation of the final result, linear interpolation has been used to complete the reaction power profile, which might generate the deviations in the results at the levels of maximum power generated seen in Fig. 7.

Conclusions

A prototype of reaction calorimeter has been built. After an initial theoretical simulation, the different elements of the calorimeter have been put together, with reliable results for data acquisition and control systems. The prototype has been used as a power compensation calorimeter with good results in the determination of the reaction power.

The Temperature Oscillation method has been applied on the calorimeter. The results show a good behaviour in the response of the system at different oscillation parameters. A mathematical tool has been developed for the continuous calculation of the parameters during the reaction, using the Fourier transform technique.

Some of the elements of the reaction calorimeter, such as agitation, control and data treatment systems can still be improved, in order to obtain more accurate results in the determination of the heat balance coefficients.

Nomenclature

A	Transfer area	m^2
A_Q	Amplitude of the oscillating power signal	K
A_T	Amplitude of the oscillating temperature signal	K
A_x	Amplitude of an oscillating signal X	K
C_P	Heat capacity of the reaction mixture	$J\,K^{-1}$
c_P	Specific heat of the reaction mixture	$J\,kg^{-1}\,K^{-1}$
m	Mass of the reaction mixture	kg
$\dot{Q}_C$	Compensation power	W
$\dot{Q}_r$	Power generated by the chemical reaction	W
t	Time	s
T_j	Temperature of the cooling fluid	K
T_p	Desired process temperature	K
T_r	Reaction mixture temperature	K
$\dot{T}_r$	Variation of the reaction temperature with time	K
U	Global heat transfer coefficient	$W\,m^{-2}\,K^{-1}$
V	Reactor volume	M^3
X	Variable signal	Adim
ΔT	Temperature difference between reactor and surroundings	K
ρ	Density of the reaction mixture	$kg\,m^{-3}$
φ_Q	Phase of the oscillating power signal	rad

φ_T	Phase of the oscillating temperature signal	rad
φ_x	Phase of an oscillating signal X	rad
ω	Oscillation frequency	rad s^{-1}

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