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Calibration of a discontinuous reaction calorimeter by a set of specific transient experiments

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Abstract

Batch heat flow calorimeters are frequently used to estimate thermal effects associated with chemical reactions. Batch chemical processes are also industrially relevant. In this paper, it is shown that classical energy balances obtained for a jacketted batch reactor (respectively the bulk phase, the walls and the jacket content) can be simplified to describe specific transient experiments. Each of these experiments allows the estimation of only one thermal parameter of the model, i.e. the heat transfer coefficients from both sides of the reactor inner wall, h_j and h_r, and the heat loss coefficient to the environment, K_L. The method used to estimate these coefficients is based on a classical least-squares minimization technique between the expected response of the models and the experimental one. This set of specific transient experiments constitutes the proposed calibration method which is applied to a calorimeter which was built in our laboratory. Statistical properties are given for each of the measured heat exchange coefficients.

INTRODUCTION

Discontinuous reaction calorimeters are often used for the measurement of kinetic and thermodynamic constants of chemical reactions. The main advantage of such devices is that they are very similar to industrial equipment [1]. Thus, other phenomena such as heat transfer capacities can be studied and correlated with stirring, and the results extended to production reactors.

Discontinuous reactors are also used for fine chemical production: in this case, we face specific control problems due to the non-linearities and the non-stationary nature of these processes. Furthermore, on-line estimation of some non-measured state variables is often necessary [2-4].

Generally, thermal effects in these reactors are subject to considerable attention because the bulk phase temperature is the main controllable state

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variable of the system. An accurate model for heat transfer in such systems thus needs to be devised, firstly to ensure good estimates of fundamental parameters and secondly to maintain the process under safely controlled evolution.

The main parameters for such models will refer to the thermophysical properties of the walls, the heat exchange coefficients between walls and fluids, and the heat loss coefficient with the environment.

In this paper, we propose a calibration procedure to estimate heat losses and heat exchange coefficients for a jacketted batch reactor based on specific transient experiments. This procedure has been described in part elsewhere [5,6]; it is here completed and applied to the calibration of a calorimeter which was built in our laboratory.

CALORIMETER DESCRIPTION

In their review [1], Karlsen and Villadsen give a classification for the different existing isothermal reaction calorimeters. According to this classification, our reactor belongs to type 2.3: its volume is 2×10^{-3} m^3 (less than 2.5×10^{-3} m^3), the sensitivity to q_r is about 0.5 W, and the temperature T_r is controlled by the jacket temperature T_{jo}. Figure 1 shows the system we built for calorimetric measurements. The reactor is insulated in a Dewar vessel. A jacket is formed between the inner wall of the Dewar and the reaction container. This inner container can be either in glass with a conventional 5 mm thick wall, or in stainless steel with a 1 mm thick wall; the characteristics are given in Table 1. Other materials could be used according to choice. The equipment was devised to allow complete change of the inner reactor wall. The refrigerating or heating fluid, which flows through the jacket, is regulated by the valve V_1. This fluid can also be changed from silicone oil to a water–ethylene glycol mixture. A Rushton type agitator is preferably used in our equipment. The jacket temperature is regulated by means of two heat exchangers and two valves, V_2, mounted in a split arrangement. The exchangers were built as two assemblies of coaxial tubing, allowing global heat exchange coefficients up to 1800 W m^{-2}°C^{-1} for hot and cold water. The flows, circulating in counter-currents, equal 2.8×10^{-4} m^3 s^{-1}. The exchanger characteristics are found in Table 2. The hot exchanger incorporates a primary regulated fluid loop, at temperature T_{bo}. Three electrical resistances each of 1000 W are mounted in the loop. All state and output variables listed in the following paragraphs are measured, and the data are transmitted to a microcomputer equipped with real time devices.

The computer is used to control q_j and T_{bo} using a discrete pole placement method [7]. The temperature T_r is controlled by the split range valves using a continuous pole placement method.

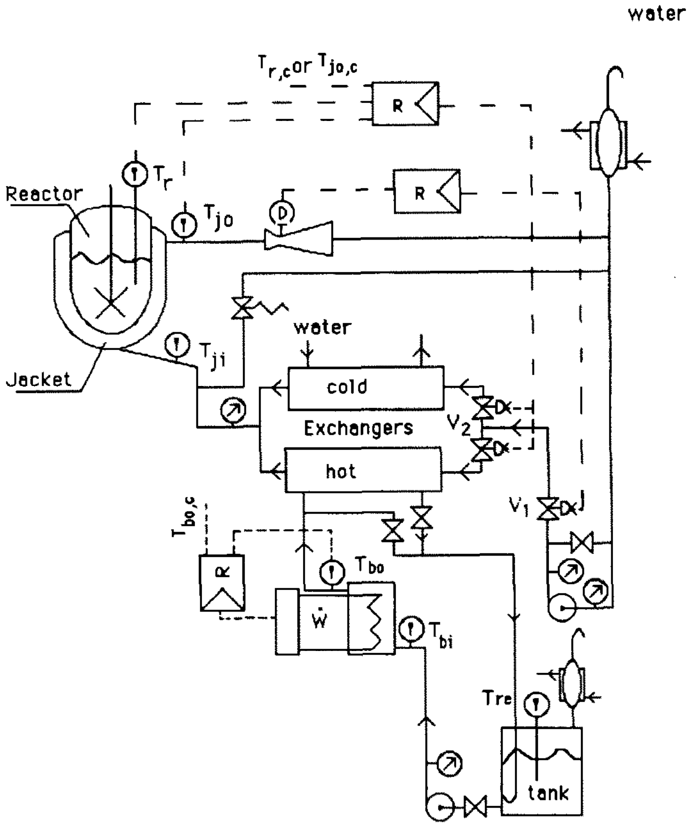

Fig. 1. Calorimeter scheme.

TABLE 1

Characteristics of reactor walls

Glass wall	$L = 5 \times 10^{-3}$ m	$\alpha_w = 6.332 \times 10^{-7}$ m^2 s^{-1}	$\tau_w = L^2/\alpha_w = 39.5$ s
Stainless steel	$L = 1 \times 10^{-3}$ m	$\alpha_w = 3.84 \times 10^{-6}$ m^{2}s^{-1}	$\tau_w = L^2/\alpha_w = 0.26$ s

TABLE 2

Heat exchanger characteristics

Inox tubing, thermally isolated from ambient air
Diameters of coaxial tubes, 0.103 m, 0.1143 m and 0.123 m
Length of tubing, 1 m
Volume of cooling compartment, 0.7×10^{-3} m^3
Volume of heating compartment, 0.7×10^{-3} m^3
Global heat exchange coefficient, 1800 W m^{-2} K^{-1}
Countercurrent fluids: water 40–70 °C, circulating flow 1 m^3 h^{-1}

THERMAL MODELLING OF THE REACTOR

This model is based on heat balances related to four subsystems: two systems for the fluids (the bulk phase in the reactor and the jacket contents) and two systems for the solids (inner and outer walls of the jacket).

Fluid subsystems

Bulk phase and jacket contents are assumed to be perfectly mixed. This assumption is very commonly adopted for the bulk phase model, although some authors have pointed out the influence of other flow patterns on the model [8].

The bulk phase heat balance related to the fluid mass M and an equivalent heat capacity Γ for inserts is then

$$(MC_p + \Gamma)\frac{\mathrm{d}T_r}{\mathrm{d}t} = \Phi_r + \Phi_f + \Phi_L \tag{1}$$

where Φ_r, Φ_f and Φ_L are respectively are respectively the heat production of the chemical reactions, the flux to the internal wall, and the heat losses toward the surroundings, the last being simply expressed by the Newton expression

$$\Phi_L = K_L(T_e - T_r) \tag{2}$$

Two flow patterns are generally deduced for the jacket contents from the mean residence time [9]: the perfectly mixed tank and the plug flow. In our case, the mean residence time equals 2 s, which is a very low value in comparison with the other time constants of our reactor. The flow pattern choice is thus relatively unimportant and we choose the perfectly mixed tank for the sake of convenience. Furthermore, we never observe any time delay effects. The heat balance is then

$$M_j C_{pj}\frac{\mathrm{d}T_{jo}}{\mathrm{d}t} = \Phi_1 + \Phi_2 + q_j C_{pj}(T_{ji} - T_{jo}) \tag{3}$$

where Φ_1 and Φ_2 are the heat fluxes exchanged with the inner and outer walls (see Fig. 2).

Solid subsystems

The models to take into account for the inner and outer walls are given by the classical linear heat conduction equation; considering the relatively small wall thickness (5 mm) in comparison with their curvature (the internal radius equals 0.1 m), they may be considered as plane walls, and a simple monodimensional model is sufficient [1] (Fig. 2):

$$\alpha_w \frac{\partial^2 T_{wk}}{\partial^2 x_k} = \frac{\partial T_{wk}}{\partial t} \tag{4}$$

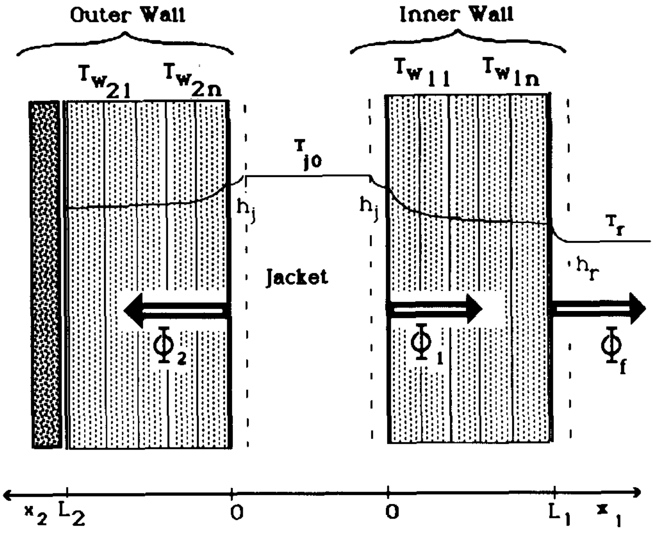

Fig. 2. Reactor wall modelling.

with $k = 1$ and $k = 2$ respectively for the inner and outer wall. This model is completed by the following limit conditions:

$$\Phi_f = h_r S_r \left[T_{w1}(L_1, t) - T_r(t)\right] = -\lambda_w S_r \frac{\partial T_{w1}}{\partial x_1}(L_1, t) \tag{5}$$

$$\Phi_1 = h_j S_j \left[T_{w1}(0, t) - T_{jo}(t)\right] = +\lambda_w S_j \frac{\partial T_{w1}}{\partial x_1}(0, t) \tag{6}$$

$$\Phi_2 = h_j S_j \left[T_{w2}(0, t) - T_{jo}(t)\right] = +\lambda_w S_j \frac{\partial T_{w2}}{\partial x_2}(0, t) \tag{7}$$

The outer wall being well insulated in a Dewar vessel, we assume that

$$\Phi_3 = -\lambda_w S_j \frac{\partial T_{w2}}{\partial x_2}(L_2, t) = 0 \tag{8}$$

THERMAL PARAMETER ESTIMATION

Principle

Parameters α_w, S_j and S_r are known, and h_j, h_r and K_L are unknown. To estimate separately these unknown parameters, we present here three specific transient experiments leading, after model simplications, to the successive estimation of only one parameter from each experiment. An estimation procedure is conducted using the Marquardt algorithm [10], which minimizes a quadratic criterion giving the distance between measured and simulated trajectories. These simulated trajectories are obtained by

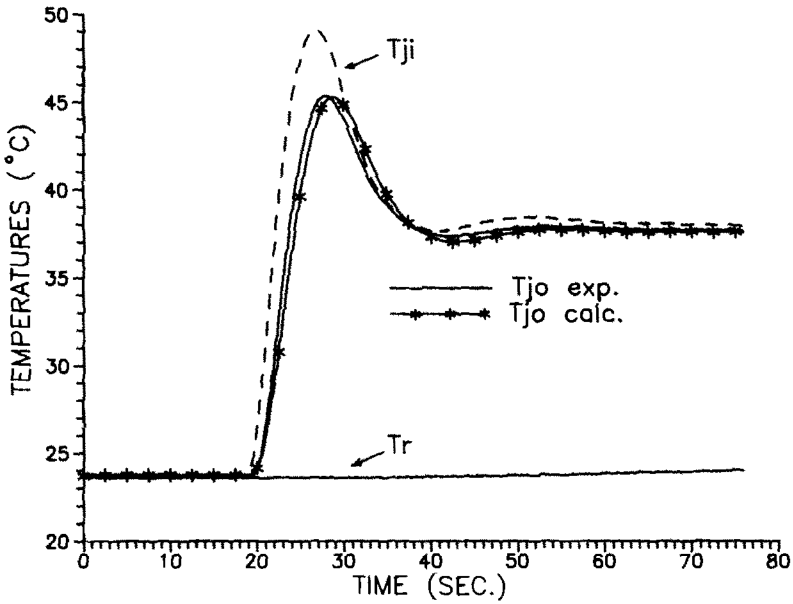

Fig. 3. Jacket response with the reactor empty.

solving the equations of the preceding linear model. The reactor walls are described by a distributed parameters model (eqns. (4)–(8)). This model is spatially discretized, and in conjunction with eqns. (1) and (3) a linear lumped parameters model is derived:

$$\dot{T} = \mathrm{A}T + \mathrm{B}u \tag{9}$$

The model input u depends on the jacket inlet temperature T_{ji}. According to our technique, the initial and the discretized models are simplified to represent each of the three transient experiments described in the following section.

Jacket size heat exchange coefficient h$_j$

The first experiment is conducted after having emptied the reactor (if possible under vacuum). The jacket outlet temperature T_{jo} is registrated as the system response to a variation in the inlet jacket temperature T_{ji}. The reactor being empty, Φ_{f} is negligible and the model is reduced to eqns. (3)–(8). Figure 3 shows the comparison between the experimental results and the model response. The model, being numerically solved, gives $h_j = 350 \pm 10$ W m^{-2} °C^{-1}, leading to a good fit between model and experiment.

Furthermore, it can be seen on that figure that the assumption $\Phi_{\mathrm{f}} = \Phi_3 = 0$ is a valid one, because at steady state $T_{\mathrm{ji}} = T_{\mathrm{jo}}$.

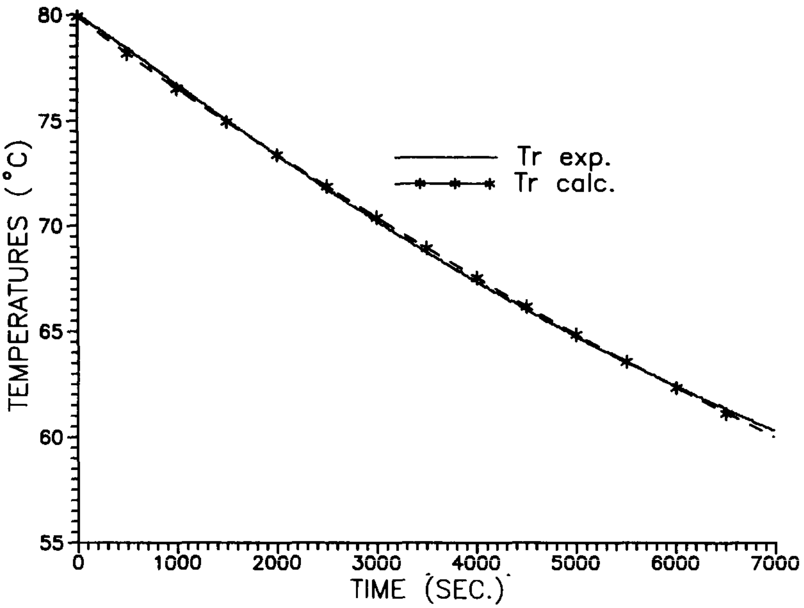

Fig. 4. Free evolution of T_r.

Reactor heat loss coefficient K_L

We have seen on Fig. 3 that the jacket heat losses may be neglected, so that the main heat losses are associated with the cover. To estimate K_L, it is then sufficient to empty the jacket and to measure the bulk phase temperature free evolution of an inert charge in the reactor. For a calorimeter equipped with an electric calibration heater this experiment can be conducted easily. In our case, we fill the reactor with a previously heated inert fluid; we can also heat the fluid through exchange with the jacket fluid. After that, we empty the jacket and measure the free evolution of T_r. The model is reduced to eqn. (1) with $\Phi_r = \Phi_l = 0$. Figure 4 shows a comparison between the model and the measurements for an initial temperature T_r of 80 °C. One can see a good fit of the model and measurements for the value $K_L = 0.470 \pm 4 \times 10^{-4}$ W $^\circ C^{-1}$. Considering the area involved in this exchange, approximately the area of the cover, the corresponding heat exchange coefficient equals 35.5 W m^{-2} $^\circ C^{-1}$, which corresponds to natural convection in ambient air.

Reactor side heat exchange coefficient

Using an inert fluid as bulk phase (in our case, a charge of water) leads the term Φ_r in eqn. (1) to equal zero. It is then possible, knowing h_j and K_L and using the same mathematical procedure as that described previously, to estimate h_r by measuring the bulk phase temperature T_r response to a T_{ji}

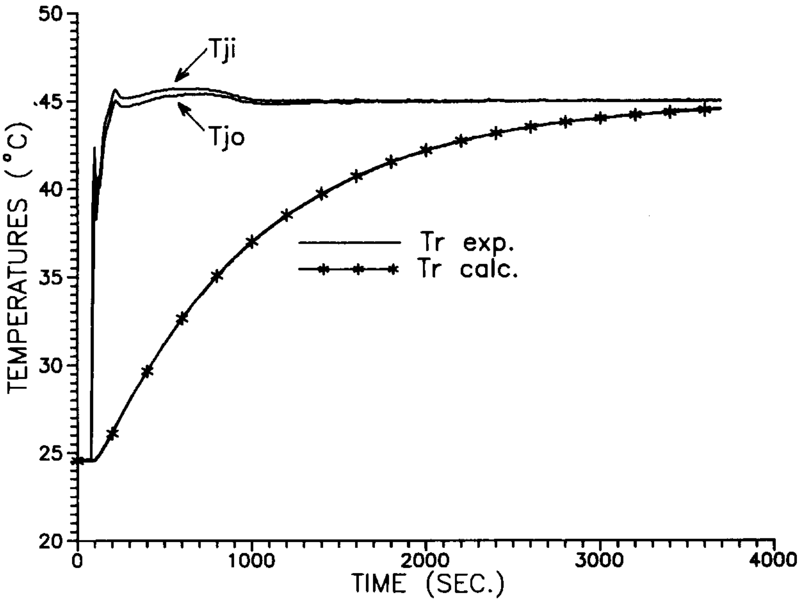

Fig. 5. Inert bulk phase temperature response.

input variation. Figure 5 shows an excellent fit of the model and the measured data for an estimated value $h_r = 1680 \pm 15$ W m^{-2} °C^{-1}.

CONCLUSION AND SIGNIFICANCE

The basic idea of this method is to minimize the number of parameters estimated simultaneously by choosing specific experiments which allow us to eliminate some of them in the model. We have used the transient approach, but this is not the only possibility that can be used to measure the unknown parameters. For example, the steady state results of the first experiment (empty reactor) would allow, if necessary, calculation of the jacket heat losses from the difference between T_{ji} and T_{jo}.

Concerning the determination of h_j and h_r, the main advantage of our approach is that these two parameters are measured independently by comparison with the Wilson method, which is generally used elsewhere [11,12]. Using this step-by-step method, dimensionless correlations for h_j and h_r can be determined by changing the fluids, the jacket flow-rate, and the agitator type and speed.

Furthermore, the basic idea of our method, that is, to empty such and such parts of the system, can be applied to other thermal equipment.

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APPENDIX: NOMENCLATURE

A, B	discretized model state and input matrices
C_p	specific heat capacity (J °C^{-1} kg^{-1})
h	heat exchange coefficient (W m^{-2} °C^{-1})
K	heat loss coefficient (W °C^{-1})
L	wall thickness (m)
M	bulk phase mass (kg)
q	mass flow-rate (kg s^{-1})
S	surface area (m^2)
T	temperature (°C)
u	model input

Greek letters

α	thermal diffusivity (m^2 s^{-1})
λ	thermal conductivity (W m^{-1} °C^{-1})
Γ	equivalent heat capacity of inserts (J °C^{-1})
Φ	heat flux (W)
τ	time constant (s)

Subscripts

1,2,3,4	walls or fluxes toward walls
e	environment
f	flux toward inner wall from the bulk phase
i	inlet
j	jacket
k	wall number
L	loss
o	outlet
r	reaction or bulk phase
w	walls