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Thermochimica Acta 310 (1998) 43–46

thermochimica acta

High-sensitive heat-flow calorimetry[1]

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Received 5 May 1997; received in revised form 27 June 1997; accepted 30 June 1997

Abstract

Heat production rates of chemical reactions or of biological cultures are a valuable signal, able to provide crucial information about the system under investigation. Commercially available bench-scale calorimeters reach a sensitivity of ≈100 mW/l. This sensitivity is usually sufficient for investigations in the field of reaction engineering or for safety studies. For the investigation of processes that exhibit only small exothermic or endothermic effects on the observation of the growth of biological material, the sensitivity of the calorimeter needs to be improved. This paper describes the modifications undertaken to reach a sensitivity of a few milliwatts per liter with an RC1 from Mettler–Toledo. © 1998 Elsevier Science B.V.

Keywords: Biological heat production; Fermentation; Heat-flow calorimeter; High-sensitive calorimetry; Reaction calorimeter

1. Introduction

Commercially available bench-scale heat-flow calorimeters reach a sensitivity of ≈100 mW/l, a value sufficient for investigation of normal chemical reactions. For investigations of reactions with small enthalpy changes, or for monitoring the growth of biological material, a higher sensitivity is required. There are several possible routes that lead to an improved sensitivity of the heat-flow measurements. One route is to employ a microcalorimeter [1]. Microcalorimeters are readily available, and they easily reach a sensitivity of a few milliwatts per liter. However, due to the small reaction volume, this type of instrument is not well suited for performing complex reactions in the instrument, or for placing sensors into the reaction mass. In the case of biological fermentation, where the pH, the aeration, and the substrate concentration need to be monitored and controlled in situ, such an instrument cannot be readily used. A second route is to equip a standard fermentation reactor with the controls and measurements needed for a calorimeter. This approach is chosen by the authors of Refs. [2,3]. These instruments reach a sensitivity of 20 to 50 mW/l with a working volume of ≈2 l. These instruments allow to perform a fermentation within the calorimeter, but are quite complex and difficult to operate. A third route to an increased sensitivity, employed in this work, is to

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[1]Presented at the Twelfth Ulm-Freiberg Conference, Freiberg, Germany, 19–21 March 1997

PII S0040-6031(97)00383-3

improve the sensitivity of a conventional bench-scale reaction calorimeter. The measures required to reach a sensitivity of ≈5 mW/l with a modified RC1 from Mettler–Toledo are described in this paper.

2. Principle of measurement and limitation of the sensitivity

A heat-flow calorimeter determines the reaction heat by making a heat balance over the reactor wall of a jacketed reactor. In the shell or jacket of the reactor, a powerful thermostat maintains a uniform temperature, which can be easily adjusted in order to control the temperature of the reactor contents. Eq. (1) shows the most important terms of this heat balance:

$$q_r + q_f + q_{accu} + q_{loss} = 0 \quad (1)$$

where q_f denotes the heat flow through the reactor wall, q_r the heat flow due to the reaction, q_{accu} the heat flow accumulated in the reaction mass and q_{loss} the heat flow to the environment. In order to compute the term of interest, q_r, all the other terms of Eq. (1) must be known. The heat flow through the reactor wall, q_f, is computed according to:

$$q_f = UA(T_r - T_j) \quad (2)$$

where U denotes the heat transfer coefficient, A the transfer area, T_r the temperature of the reaction mass and T_j the jacket temperature. q_{accu} can be computed according to:

$$q_{accu} = mc_p dT_r/dt \quad (3)$$

where m denotes the reaction mass, c_p the specific heat of the reaction mass, and dT_r/dt the derivative of the reaction temperature over time.

For a high-sensitive instrument, the different terms of Eq. (1) must also be measured with high sensitivity. From Eq. (2) it follows that an accurate measurement of the temperature difference is required for an accurate determination of the heat flow q_f. The option of reducing UA, in order to avoid the necessity of an accurate temperature difference measurement, is not attractive, since the UA value determines how much heat the calorimeter can exchange and how fast the reactor contents can be heated or cooled. In the presented results, a standard glass reactor with good heat transfer is employed.

Since computation of numerical derivatives from measured values is a notoriously difficult and noise-amplifying operation, one can try to minimise the accumulation by controlling the temperature of the reactor contents in a fast and accurate way, a strategy followed in this work. The term q_{loss} cannot be computed, and constructive measures must be taken to minimise it.

3. Measures

In order to improve the sensitivity of the commercial calorimeter three major measures were necessary. The most important measure was to improve the resolution of the jacket temperature measurement from 8 to 0.2 mK. Since the commercial calorimeter already had a resolution of 0.2 mK, for the measurement of the temperature of the reaction mass, the difference between T_r and T_j can now be measured with a resolution of 0.2 mK. The second measure was to improve the control of the jacket temperature to fully exploit the increased resolution. This improvement involved the use of a model-based predictive controller for a more precise and still highly dynamic control. In order to reduce the influence of the discretisation of heating, the maximal heating power of the jacket thermostat was reduced from 2000 to 500 W. For the temperature range of biological fermentations, these 500 W are absolutely sufficient. The third measure was to use a proportional-integral controller instead of a pure proportional controller for the control of the reactor temperature. This well-tuned controller minimises the accumulation to a degree that makes a computation of the accumulated heat obsolete.

4. Results

The achieved sensitivity of the instrument after the modifications described in Section 3 is shown in Fig. 1 and 2. Both figures show the measured heat flow for an experiment in which the electrical reference heater was switched on for 1 h. The reactor was filled with 1.6 l of water and stirred. A temperature setpoint of 28°C was used. No other operations, such as gassing or dosing were performed. Fig. 1 shows the signal as it is computed once every other second,

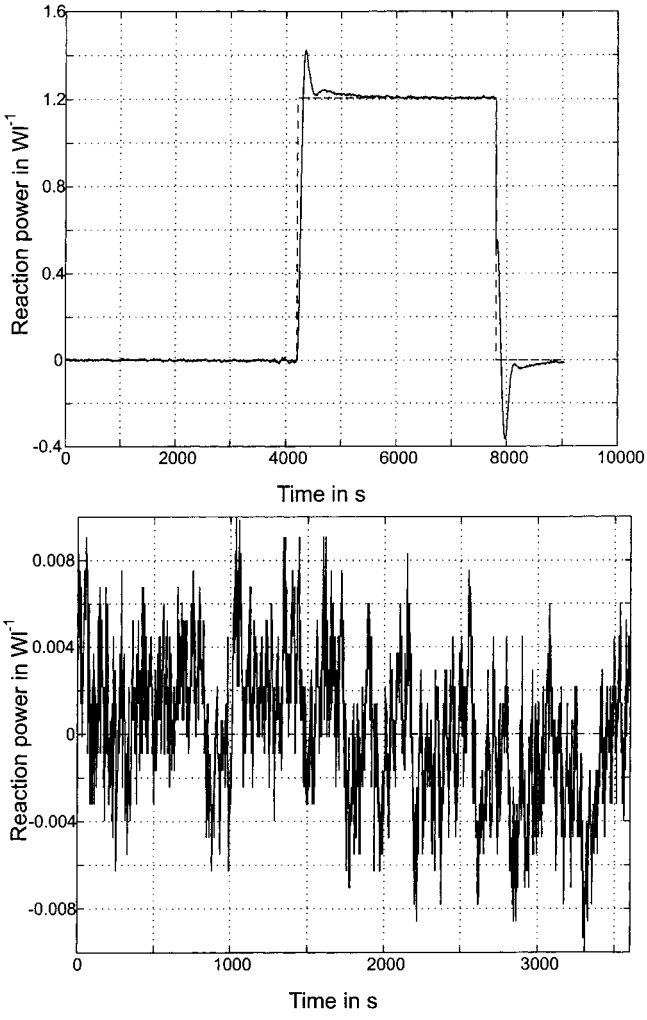

Fig. 1. Measured heat flow (———) and heat input from the reference heater (- - -), calculated every other second. The top graph shows the entire experiment, the bottom graph shows the first hour of the experiment.

Fig. 2 shows the signal after filtering with a moving average filter over 2 min.

The results show an impressive improvement of the sensitivity due to modifications. The signal settles within a few minutes to a stable value and reaches a sensitivity of ca. 5 mW/l.

5. Conclusion

The presented modifications allow to reach a sensitivity of ca. 5 mW/l with an RC1. The modified calorimeter still shows an excellent dynamic response with a short settling time. The powerful thermostat is able to reach the desired temperature quickly and to hold the temperature of the reaction mass accurately at the setpoint. The usability of the calorimeter is not hampered by the presented modification and the reactor can be sterilised in situ. The instrument shows, in addition to the excellent sensitivity a good baseline stability over the extended time required for fermentations.

Further work is needed to optimise the operations specific for fermentations, such as gassing, pH control and substrate feeding, in order to reduce the disturbances on the calorimetric signal. So far, a sensitivity

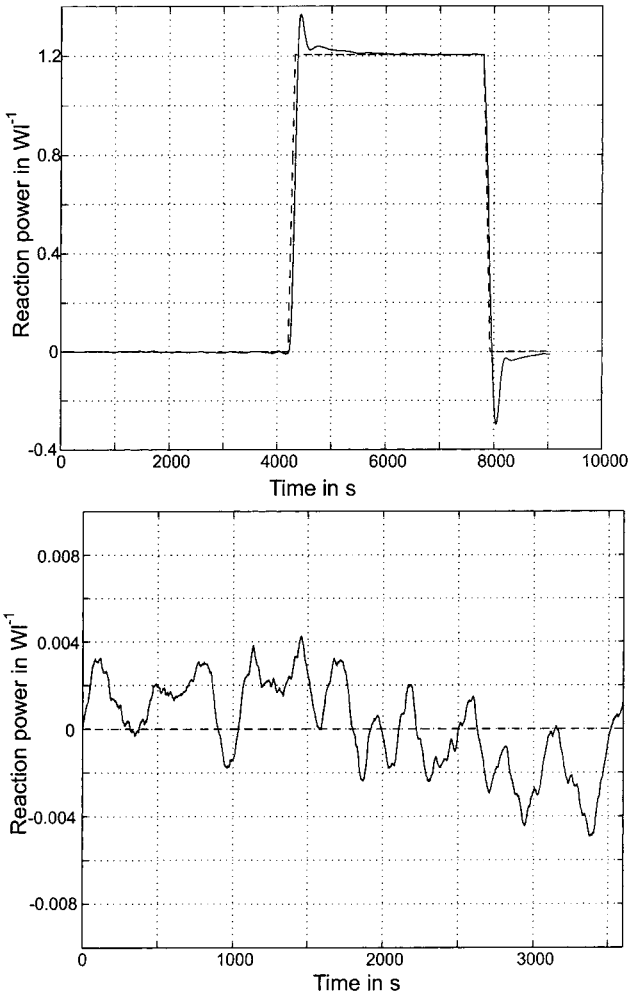

Fig. 2. The curves of Fig. 1 after filtering with a moving average filter over a time interval of 2 min.

of <20 mW/l is reached under typical fermentation conditions.

The high sensitive calorimetric signal is to be used to monitor and control on-line fermentations of different cultures. Preliminary results are very promising and indicate that the heat production rate of biological cultures provides an excellent additional signal that allows a deeper insight into the fermentation process and a more precise and highly efficient control of the growth of the cultures [4].

Acknowledgements

The authors would like to thank Dr. Jing Song Liu and Dr. Sylvia Ampuero for valuable discussions and various measurements, which helped to improve the calorimeter, and for performing the measurements presented in Section 4.

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