A millifluidic calorimeter without contact for reaction enthalpy and kinetics measurements

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Kinetics and thermodynamics characterisation of chemical reactions is required for chemical process development and safety. We know that both phenomena, heat transfer and chemical kinetics, are present in chemical reactions. One way to control and measure those phenomena is calorimetry. The characterisation of exothermic chemical reaction is well developed and different kinds of calorimeter already exist [1]. Nevertheless, they are not simultaneously adapted to the use of microvolumes, high thermal sensitivity, good control of the reagent mixing and quasi isothermal conditions.

To this end, the recent development of MEMS (Micro-Electro-Mechanical Systems) allows the investigation of new approaches to measure the enthalpy of chemical reactions. The main advantage is the small size of the microchannels which permits the mixing control of the reactants with very low Reynolds number laminar flows.

The measurement of temperature at a small scale represents the main difficulty. However the temperature information in such devices is among the most important parameters. Today, only a few studies deal with this. One method consists in developing localised temperature microsensors [2]. Another one consists in measuring the infrared emission field of a surface without contact and leads to a qualitative analysis [3].

This work is devoted to the development of a new flow calorimeter without contact using an infrared camera. The main idea is to implement a millifluidic chip with integrated flow channels (diameter = from 250 μm to 1.6 mm) taken as a millireactor and an Infrared (IR) camera is used to measure the heat flux produced by the chemical reaction (figure 1). The advantages of this device are the followings: the use of small reagent volumes, the thermal properties of the millifluidic chip which offers specific thermal conditions and the non intrusive method. This 2D transient problem can be described as equations (1).
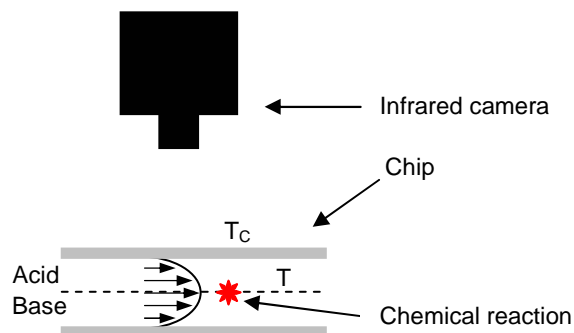
$$\rho.c_p.v.\frac{\pi.d^2}{4}\frac{dT}{dx} = \phi_{ch} - h.\pi.d.L.(T - Tc)$$

$$\phi_{ch} = \dot{m}.\Delta H.\frac{d\alpha}{dx}$$

$$T = T_{ch} + T_0$$

(1)

Fig. 1. *Experimental device*

Firstly, this device is calibrated. The calibration is composed of two steps, the calibration of the camera and the calibration of the chip.

The camera is calibrated when using a heat source produced by Joule effect. For that purpose, a tin wire is introduced inside the chip channel. Various electrical powers are applied to the tin wire and the temperature variation between the channel (T) and its surrounding (Tc) is measured thanks to the IR camera. Then, the relation between injected power and the temperature variation can be determined according to the following equation (2), the results are shown in figure 1.
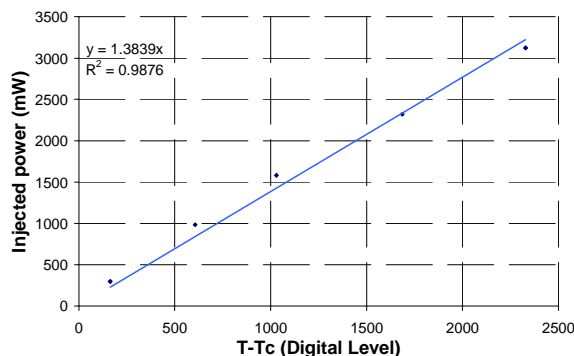
$$\phi = h.\pi.d.L.(T - Tc)$$ (2)

Fig. 1: *temperature variation versus injected power*

Then, the chip calibration is realised by maintaining the chip at a constant temperature (Tc=10°C) tha nks to a regulation system. The fluid is injected at different flow rates (figure 2). In order to determine the thermal transfer coefficient between the fluid and the millifluidic chip according to the equation (3) where To is the fluid temperature without chemical reaction.

$$\rho.c_p.v.\frac{\pi.d^2}{4}\frac{dT_0}{dx}=h.\pi.d.L.(T_0-Tc) \qquad (3)$$
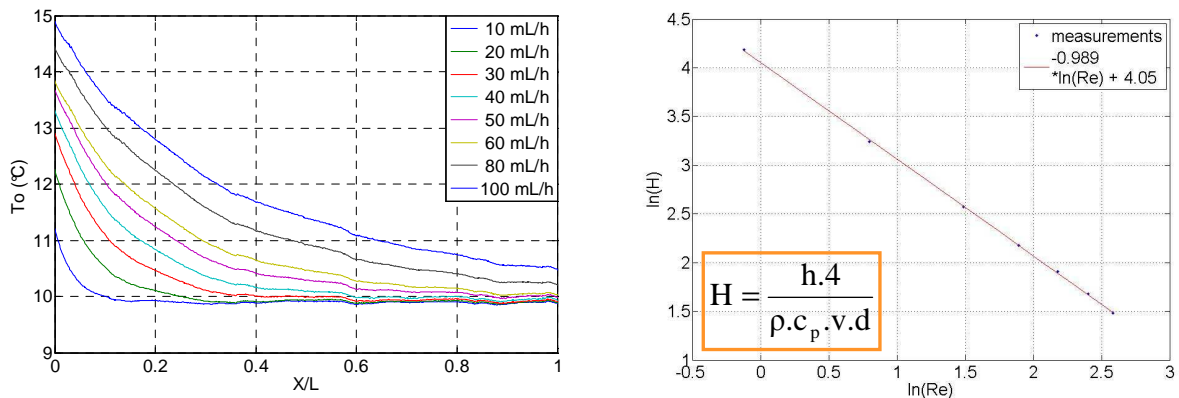

$$H=\frac{h.4}{\rho.c_p.v.d}$$

Fig. 2: left: water temperature variation versus chip length at different flow rates at 10 °C, right: and ch ip calibration, ln(H)=f(ln(Re))

Secondly, the enthalpy estimation of a well known reaction (strong acid-base) is performed in order to validate this device. The experiments are realized at different flow rates and the temperature is the same as in calibration. As the calibration coefficient (H.S) and the product $\rho.c_p$ are known, the integration of the emitted heat flux (corresponding to the reaction enthalpy) can be estimated thanks to the thermal model (1).
In order to obtain the temperature profiles from the reaction only, the superposition principle is used:

$$T_{ch}=T+T_0 \qquad (4)$$

Thanks to these temperature profiles, the analytic solution of equation (1) and the calibration the chemical heat flux variation can be estimated such as the chemical reaction conversion (figure 3). The reaction enthalpy can be determined: 55.7 kJ/mol. This result is closed to the literature data of 56 kJ/mol [4] and allows the validation of this flow calorimeter. The kinetics agrees the kinetics of acid-base reaction and all the curves are correctly overlapped in time.
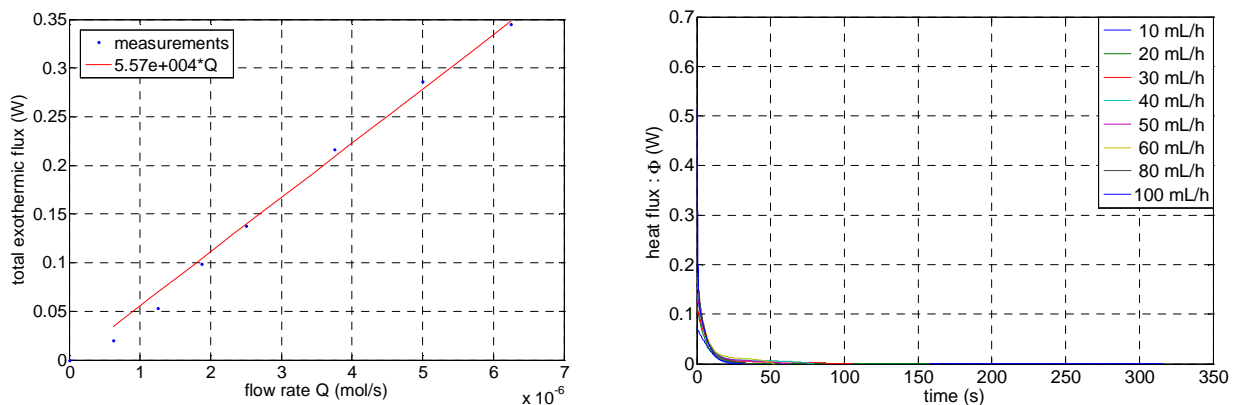

Fig. 3: left: Integrated heat flux versus molar flux, right: heat flux versus time

To conclude, it is relevant to note that the calorimeter we developed allows the determination of global information such as reaction enthalpy and the local temperature information of chemical reaction. The main advantage of this device is the use of an infrared camera which allows the measurement without contact between the reaction volume and the temperature sensor.

[1]   A. Zogg, F. Stoessel, U. Fischer, and K. Hungerbühler. Isothermal reaction calorimetry as a tool for kinetic analysis, *Thermochimica Acta,* 419 (2004) 1-17.
[2]   J.M. Köhler, and M. Zieren. Chip reactor for microfluid calorimetry, *Thermochimica Acta,* 310 (1998) 25-35.
[3]   K. P. Mollmann, N. Lutz, and M. Vollmer. Thermography of microsystems. *Inframation proceedings*, ITC 104A, 07-27, 2004.
[4]   Handbook of chemistry and physics, 85 th, 2004-2005.