



# Quantitative kinetics and enthalpy measurements of biphasic underflow chemical reactions using infrared thermography



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## ABSTRACT

The aim of this paper is to present an experimental infrared thermography study of a well-known chemical reaction in a biphasic millifluidic droplet flow. Through a simple thermal evaluation, it is possible to characterize the kinetics and enthalpy of exothermic chemical reactions. The originality of this work lies in the combination of two versatile techniques and a thermal evaluation based on a homogenized thin body approximation to perform calorimetric estimations. This novel calorimeter requires thermal calibration to estimate the heat losses. A correlation method was therefore applied for the simultaneous estimation of the heat source ( $\phi$ ) and the characteristic coefficient due to convective heat transfer effects ( $H$ ). This methodology was applied to an acid-base chemical reaction performed at different flow rate ratios. The reaction enthalpy was estimated with an error smaller than 2% compared with the literature value. In addition, the procedure for the estimation of the mixing kinetics of the reaction is revealed by the time-integrated heat flux. Finally, a non-contact thermal calorimeter based on millifluidic and IR thermography was developed. The proposed methodology is demonstrated to be a convenient and powerful tool for the characterization of chemical reactions performed in a droplet flow.

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## 1. Introduction

Micro and millifluidic droplet-based systems are recognized as high-throughput screening platforms. In the chemistry field, reactive droplet flow platforms are currently being used as a tool for a wide range of tasks including analysis, process intensification, and data acquisition [1]. Thus, infrared thermography (IRT) is a versatile technology that can be applied across several domains and scales ranging from macroscopic applications to the characterization of miniaturized systems such as electronic devices or biological and chemical systems. Indeed, the principal motivation for the development of a non-intrusive tool for the online monitoring of small-scale chemical reactions is to benefit from the combination of flexible and original techniques. Specifically, quantitative IRT studies offer the possibility to measure important experimental parameters such as convective heat transfers [2] and temperature distributions. The latter may be one of the most important parameters in certain experimental studies, e.g., chemical reaction kinetics and thermodynamic characterizations. However, many

chemical or physical processes are associated with thermal phenomena commonly characterized using calorimetric methods, which are used to obtain thermodynamic and kinetic data by measuring the heat flux. In such cases, the evolution of the heat flux is reproducible and directly proportional to the reaction conversion rate. Among these methods, some in situ calorimetric applications have been developed for both miniaturized and flow-based systems. Despite their potential, most of these techniques are intrusive, difficult to adopt, and have been tested only on single-phase flows. Therefore, they are not suitable to be used as flexible online analysis tools. In light of these limitations, the aim of this work was to develop a simple thermal evaluation device designed for microfluidic droplet flows. Through successive steps, an estimation of the dissipated energy (enthalpy) of the chemical reaction (heat source) taking place inside the droplet was performed.

## 2. Experimental setup and materials

The millifluidic isoperibolic chip, schematized in Fig. 1, was fabricated using a bulk piece of brass for thermal control and small-sized commercial Teflon tubing and junctions (from Jasco) for the flow setup. The typical dimensions of the main tubing are 3.17 mm (OD) and 1.6 mm (ID), while the tubes used for supplying the reactants have outer and inner diameters of 500  $\mu\text{m}$  and

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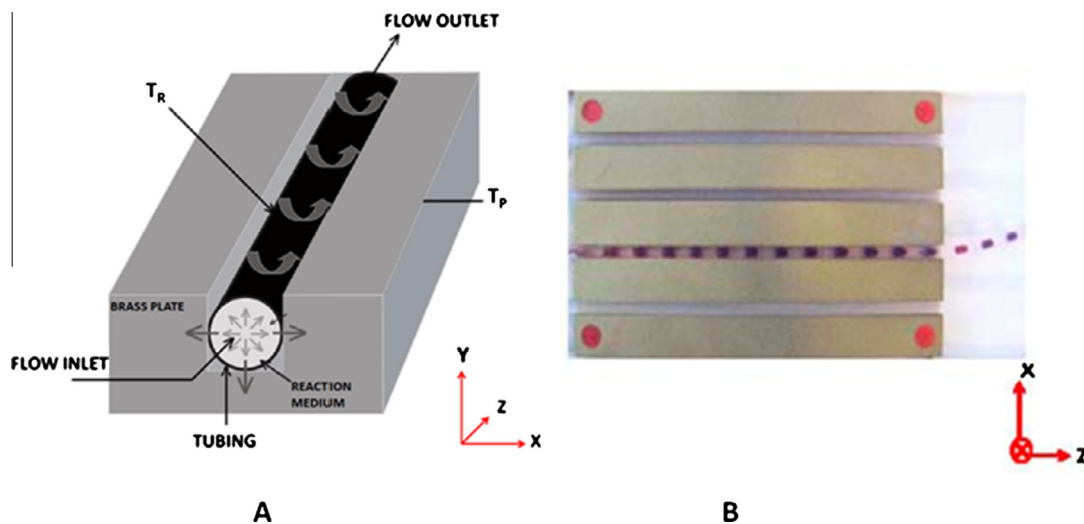
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**Table 1**  
Experimental droplet-oil flow rate ratios.

$R = Q_O/Q_D$	Oil flow $Q_O$ , (mL h <sup>-1</sup> )	Droplet flow $Q_D$ , (mL h <sup>-1</sup> )
0.5	3.33	6.66
2	6.67	3.33
4	8	2
8	8.89	1.11
10	9.09	0.91

250  $\mu\text{m}$ , respectively. This design allows to master the initial and boundary conditions. The brass bulk is thermally regulated by a Peltier module from  $-5$  to  $90$   $^{\circ}\text{C}$  for accurate control of the cooling or heating of the tubes. The boundary condition of the external diameter of the tubing is isoperibolic (i.e., imposed temperature). As a result, measurement of the temperature inside the tubing (reaction media) yields the heat transfer coefficient between the imposed temperature of the brass bulk and the inner diameter of the tube. Fig. 1A shows a cross-sectional representation of the isoperibolic system, from which it can be noted that 3/4 of the tube is in contact with the brass plate. Additionally, heat sink paste was added between the tube and the brass plate to ensure that the heat transfer acts as a thermal conductance, a method that was also previously employed [3]. Inside the reactor (tubing), the biphasic flow is performed using a NEMESYS high precision syringe pump (Cetoni), which is suitable for the high precision delivery of micro volumes. The droplets are generated by the injection of fluorinated IKV oil (continuous phase, viscosity of 32 cSt at  $25$   $^{\circ}\text{C}$ ) and the reactive phase at different flow rate ratios. With this configuration, the hydrodynamic parameters such as the total flow rate (i.e., droplet velocity), the droplet size, and the volume fraction of oil and droplets are all controlled [4]. In this study, a chemical reaction between hydrochloric acid (HCl, Sigma Aldrich) and sodium hydroxide base (NaOH, Sigma Aldrich) was performed at a total flow rate of  $Q_T = 10$  mL h<sup>-1</sup>. The two reagents were added into the droplets at the same initial concentration of  $C_0 = 0.5$  M. The total flow rate of the droplet is equal to the sum of both reagents flows:  $Q_D = Q_{acid} + Q_{base}$ . The oil flow ( $Q_O$ ) was carried out at different flow rate ratios ( $R = Q_O/Q_D$ ) that are summarized in Table 1.

An infrared FLIR camera (model SC7000) was used for the temperature field measurements. The camera detector contains 76,800 individual InSb detectors, has an optimum detection wavelength between 2.5 and 5.2  $\mu\text{m}$ , and has a pitch of 30  $\mu\text{m}$ . A MWIR F/2 objective lens with a focal length of 25 mm was used in this study.



**Fig. 1.** (A) Schematic representation of the isoperibolic system. (B) Millifluidic droplet-based system composed of a brass chip and Teflon tubing.

The spatial resolution of the temperature measured by each pixel of the sensor is approximately 250  $\mu\text{m}$ , and a scanning frequency of up to 1 kHz can be used.

### 3. Principle of the proposed method

A chemical reaction was performed inside the droplet, each of which can be considered an isolated chemical reactor, and the biphasic flow was analyzed using infrared thermal measurements. In Fig. 2, different temperature fields are reported to demonstrate that the spatial evolution of the temperature is periodic. Note that the temperature was measured in the arbitrary Digital Level (DL) unit. Fig. 2 illustrates that the thermal phenomena can be managed according to different orders, as described by Eq. (1). The observation of the IR raw temperature profile ( $T(z, t_i)$ ) shown in Fig. 2A demonstrates that the signal is composed of a continuous contribution ( $\bar{T}$ , Fig. 2B) and a fluctuating contribution ( $\tilde{T}(z, t_i)$ , Fig. 2C):

$$T(z, t_i) = \bar{T}(z) + \tilde{T}(z, t_i) \quad (1)$$

It is important to ensure that the continuous contribution (CC) schematized in Fig. 2B represents almost 90% of the signal. While the fluctuating component highlights the presence of the biphasic flow shown in Fig. 2C, it represents less than 10% of the temperature profile at a time  $i$ . The Biot number of the droplets is lower than 1, so the temperature homogeneity in the  $r$  direction allowed us to neglect the heat transfer along this direction. Moreover, it is important to note that the velocity field within the droplet shows evidence of recirculation, while the velocity field within the oil phase indicated a plug flow (or piston flow) [5]. Therefore, recirculation inside the droplet enhances the temperature homogeneity. Finally, combining all of these assumptions a thin body media model can be used to approximate the global heat transfer in such millifluidic and isoperibolic systems. More precisely, in this approximation only the parietal heat exchange between the equivalent homogeneous medium and the brass bulk were taken into account. The model is expressed as follows:

$$(\rho C_p V)^* \frac{d\bar{T}_{CC}(t)}{dt} = \frac{\phi(t)}{(1+R)} - h_p S (\bar{T}_{CC}(t) - T_p) \quad (2)$$

where  $\phi(t)$  represents the heat source (unit: W),  $R$  is the flow rate ratio (dimensionless),  $h_p$  is the parietal heat exchange coefficient between the tubing and the isoperibolic boundary (unit:  $\text{W m}^{-2} \text{K}^{-1}$ ),  $S$  is the heat exchange surface ( $S = \pi d L_T$ , unit:  $\text{m}^2$ ),  $\bar{T}_{CC}$  is the

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