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Chemical Engineering Journal 115 (2005) 73–83

Chemical Engineering Journal

www.elsevier.com/locate/cej

Determination of the kinetic parameters of fast exothermal reactions using a novel microreactor-based calorimeter

M.-A. Schneider, F. Stoessel*

Groupe de Sécurité des Procédés Chimiques, Institut des Sciences et Ingéniérie Chimique et Biochimique,
Ecole Polytechnique Fédérale de Lausanne, Switzerland

Received 23 May 2005; received in revised form 14 September 2005; accepted 27 September 2005

Abstract

Making chemical processes safe requires a thorough knowledge of the kinetic and thermal parameters of the chemical reactions involved.

The aim of this work was to develop a calorimetric method particularly adapted to the study of fast exothermal reactions. The proposed system combines a microreactor with a commercially available microcalorimeter.

The microreactor was inserted into the cavity of the commercial calorimeter and the thermal efficiency of the system was optimized. The flow in the reaction channel of the microreactor was found to be purely laminar and the mixing time corresponded to the time for radial diffusion. Due to the small size of the channels, the mixing time was found to be adequate and not limiting for the characterization of fast reactions. First, a model reaction was studied in order to validate the results obtained with the microsystem and to avoid the risk of systematic errors. In a second stage, a previously unknown fast exothermal reaction was characterized. The heat flows measured during the reaction reached 160 000 W kg^{-1} but the conditions, however, remained completely isothermal. The global kinetics of this reaction as well as its activation energy were determined.

Keywords: Microreactor; Continuous flow; Microcalorimeter; Reaction kinetics; Exothermal reaction

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1. Introduction

The assessment of the risks linked to the industrial practice of exothermal chemical reactions requires an extensive knowledge of their thermodynamic characteristics, not only under normal operation conditions, but also in the case of deviations. Since the risk is commonly assessed in terms of severity and probability of occurrence of a failure, it is essential to be able to predict under which conditions a reaction may enter a runaway course and what the consequences would be. The consequences of a runaway reaction are directly linked to the thermal potential of the reactions, i.e. to the energy released. The probability of triggering a runaway reaction is linked to the ability of maintaining its course under control. This means that the probability depends on the reaction dynamics. Thus the determination of the macro kinetics and of the enthalpy of both the main and potential secondary reaction(s) is required for the risk assessment. The safety analysis of a process is often performed by establishing a run-away scenario of the chemical system [1].

Kinetics can be determined by various methods. However, calorimetric methods are preferred for chemical process safety analyses, since they allow measuring directly the effect that should either be avoided or controlled. Many different calorimetric systems have been developed during the last decades [2,3]. However, fast and highly exothermal reactions are still difficult to characterize in classical systems. Indeed, measuring high heat release rates under isothermal conditions or at least under strict temperature control requires extremely high heat exchange rates. Moreover, such reactions should preferably be studied on a small scale, thus involving only small amounts of very reactive compounds. The use of small quantities is also an advantage when performing safety studies at an early stage of development, when large amounts of compounds are not available or are expensive. Finally, for fast reactions, rapid mixing as well as a precise control of the reaction start are mandatory.

The use of a microreactor-based calorimeter fulfills all of these requirements [4]:

- The high surface to volume ratio provides a highly efficient heat transfer,

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[*] Corresponding author.

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doi:10.1016/j.cej.2005.09.019

- ○ The small volume of the microchannel means that only small amounts of potentially dangerous chemicals are used,
- ○ The small radius of the microchannel results in short time for radial diffusion and thus good mass transfer,
- ○ The microreactor can be designed as a plug-flow reactor operating continuously at steady state. The reactants are mixed at the beginning of the reaction microchannel. This allows a good control of the reaction start as well as a measurement of the thermal effects as soon as the reactants mix, without any perturbation due to the mixing.

The microreactor can be associated with a commercially available calorimeter with a high thermal sensitivity.

In this work, a novel microreactor-based calorimeter is described and the performances of the system are first predicted using a finite element model. The degree of mixing achieved at the end of the reaction channel of the microreactor is then assessed, and the suitability of the system for the determination of reaction kinetics is verified using a model reaction. Finally, a fast exothermal reaction is investigated.

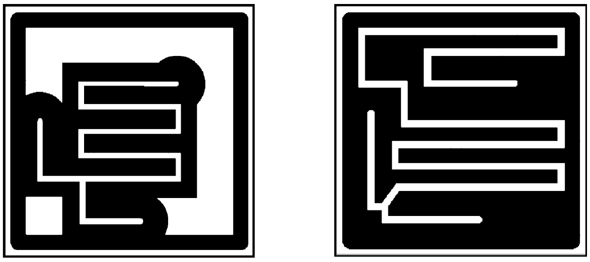
2. Experimental

2.1. Equipment

2.1.1. Layout of the system

The novel calorimetric system developed in this work uses the calorimetric measurement line of the Setline 120 microcalorimeter (Setaram, France).

Basic principle of the microcalorimeter [5,6]. In the standard measurement procedure recommended for this microcalorimeter, a crucible is introduced in the calorimetric cavity and placed on a microcalorimetric chip. The heat released or consumed by the chemical reaction induces a temperature difference between the thermocouples arranged in the center of the measurement membrane and a reference temperature outside the membrane. This temperature difference is measured by a thermopile and the resulting signal is a voltage. This voltage (V) is then converted into a thermal signal (W) by calibration with Joule effect pulses applied by a heating resistance located on the calorimetric membrane.



(a) **standard microchannel** (b) **long microchannel**

Fig. 2. Examples of reaction microchannels, width of 250 μm, depth of 100 μm and length of respectively 18.75 mm (a) and 44.00 mm (b).

In the present study, a microreactor was inserted in the calorimetric cavity replacing the crucible used in the standard procedure of the calorimeter. Fig. 1 represents a lateral section of the calorimetric cavity.

2.1.2. The reaction microchannel

The microchannel (b) was designed as a V-type or T-type mixer followed by a reaction tube of variable length.

The base of the microreactor was made of alumina (Al_2O_3) and the channel walls were built by silk-screen printing of a dielectric paste (ESL 4913, Electro-science Laboratories). The shape and the length of the reaction channel were adapted to the type of reaction. The slower the reaction rate, the longer the reaction channel.

Fig. 2 illustrates two examples of reaction microchannels.

The width of the microchannel was 250 μm and the depth 100 μm. The smaller reaction channel constructed had a length of 2.80 mm. The volume of the different microchannels constructed varied between 0.07 and 1.10 μl. The lower limit for the

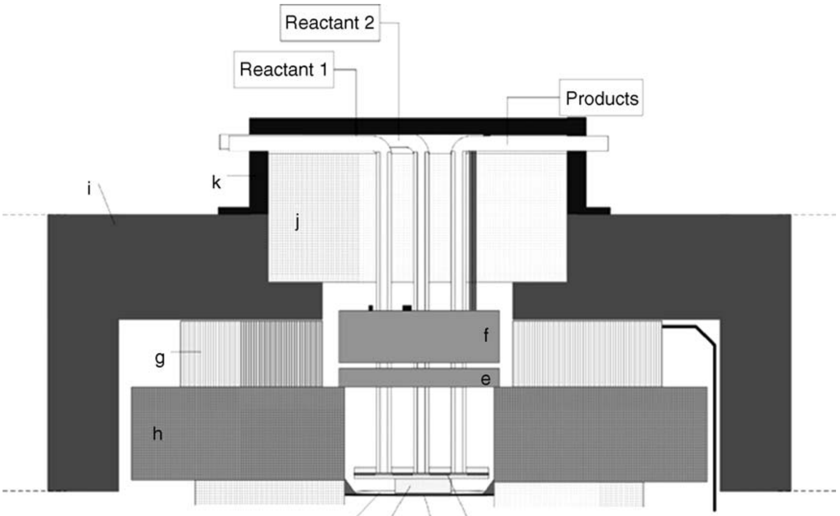


Fig. 1. Lateral section of the calorimetric cavity of the Setline 120 after insertion of the microreactor. (a) Microcalorimetric chip; (b) reaction channel; (c) heat carrier layer; (d) contact pin; (e) aluminum screen; (f) electrical preheating layer; (g) Peltier elements; (h) oven; (i) heat sink; (j) cap; (k) upper cap.