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Annular flow microreactor: An efficient tool for kinetic studies in gas phase at very short residence times

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ABSTRACT

This study deals with the modelling of a tubular flow microreactor and an annular flow microreactor that are used for kinetic studies of thermal reactions (873–1273 K) at very short residence times (10–100 ms). The construction of a kinetic model on the basis of experimental reaction data requires the precise characterization of the thermal behaviour and the hydrodynamics of the reactor. In kinetic studies, the reactor is usually considered as an isothermal Plug Flow Reactor. In this paper, we demonstrate that an annular flow microreactor used at very short residence time not only leads to a temperature profile which is better controlled than in a tubular flow microreactor, but also to less axial dispersion for laminar flow. The comparison between both reactors is performed on the basis of temperature measurements, RTD measurements at room temperature, dimensionless numbers calculations and Computational Fluid Dynamics in typical reaction conditions.

Keywords: Annular/tubular flow microreactor; RTD measurements; CFD simulation; Plug Flow Reactor; Thermal profile; Kinetic studies

1. Introduction

Most of the gas phase reactions at high temperature are studied in tubular flow reactors (e.g. Yarlagadda et al., 1988; Walsh et al., 1992; Chun and Anthony, 1993; Casey et al., 1994; Bromly et al., 1995, 1996; Chellappa et al., 1997; Dahm et al., 2004; Rasmussen et al., 2008; Dufour et al., 2009). The experimental results are usually used to build or to validate kinetic models. Mass balances are solved by software like CHEMKIN II (Kee et al., 1989), assuming that the reactor is isothermal, and has an ideal hydrodynamic behaviour, i.e. Plug Flow Reactor (PFR) or possibly a cascade of Continuous Stirred Tank Reactors (CSTR). The simulation results of the kinetic models are then compared with the experimental results in terms of conversion and selectivity of the products.

When reactions at very short residence time are studied (<100 ms), a flat temperature profile cannot be easily reached in a tubular flow reactor, particularly at high temperature. Moreover, in most conditions, the axial dispersion becomes important in laminar regime due to the high space velocity, which makes the assumption of a PFR erroneous. The aim of this paper is to characterize the hydrodynamics and the thermal behaviour of an annular flow microreactor, and to demonstrate that the proposed reactor leads to a rather flat temperature profile and to less axial dispersion than a tubular reactor which would operate in similar conditions. The comparison between both reactor types is made on the basis of temperature measurements, RTD measurements at room temperature, dimensionless numbers calculations and Computational Fluid Dynamics in typical reaction conditions.

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2. Experimental setup

2.1. Microreactors geometry

The studied microreactors are made of silica glass, which allows working up to 1323 K.

The first one is an annular flow microreactor (Fig. 1) (Marquaire et al., 1997; Marquaire and Al Kazzaz, 1998; Lombard and Marquaire, 2004; Zhang et al., 2011, 2012a,b) which is based on the work of Houzelot and Villermaux (1977, 1984). The annular flow microreactor is composed of three zones: the input, central and output zones. The input zone is tubular (length = 5.0 cm; inner diameter i.d. = 0.4 cm; outer diameter o.d. = 0.6 cm), the central zone presents an annular space of 50 cm length and 500 μm width (outer tube: i.d. = 1.0 cm and o.d. = 1.2 cm; inner tube: i.d. = 0.7 cm and o.d. = 0.9 cm), and the output zone has the same dimensions as the input zone. The total volume of the reactor is 8.7 cm^3. When the reactor is used at higher temperature than room temperature, the central zone is subdivided into three zones: the first one (length = 21.5 cm) stays at room temperature and allows homogenization of the gases. The second one (length = 13.5 cm) is the reaction zone and it is heated by three independent Thermocoax resistance wires. Three K-type (chromel–alumel) thermocouples, connected to the temperature controllers (Eurotherm), are respectively positioned in the centres of the three heating wires to regulate the temperature. The last zone (length = 15.0 cm) is surrounded by a heat exchanger located on the periphery of the external tube of the annular zone and cold water is used as cooling fluid in order to quench the system. The heated volume is 2.0 cm^3 and the cooled one 2.2 cm^3.

The second microreactor is very close to the first one: the only difference is the annular space which is 1 mm wide instead of 500 μm (geometry of the annular zone: length = 50 cm; outer tube: i.d. = 1.0 cm and o.d. = 1.2 cm; inner tube: i.d. = 0.6 cm and o.d. = 0.8 cm). This microreactor is used for the temperature profile measurement inside the annular space, since the annular space of the first microreactor is too thin to insert a thermocouple.

The last microreactor is a simple tubular flow microreactor (length = 65 cm; i.d. = 0.4 cm; o.d. = 0.6 cm) in which the cross section is approximately the same (by 15% smaller) as in the first reactor, i.e. 0.15 cm^2. When the reactor is used at higher temperature than room temperature, the central zone is also subdivided into three zones, as in the first microreactor. The heating zone is heated either by three independent Thermocoax resistance wires driven by three K-type (chromel–alumel) thermocouples fitted in the centre of each wire, or by only one Thermocoax resistance wire driven by a K-type thermocouple.

2.2. Experimental RTD setup

The flow characteristics were experimentally determined by Residence Time Distributions, obtained from measurements of a pulse tracer gas concentration simultaneously measured at the inlet and the outlet of the reactor. The system used in this study was developed in our laboratory for another study by Commenge et al. (2006) and it is shown in Fig. 2. RTD were measured in the absence of reaction using a pulse of ozone in a steady flow of oxygen. Ozone was chosen as the tracer gas since it exhibits a stronger UV-light absorption peak than oxygen, and the maximum is at 253.7 nm, which corresponds to the emission wavelength of mercury. The advantage of the

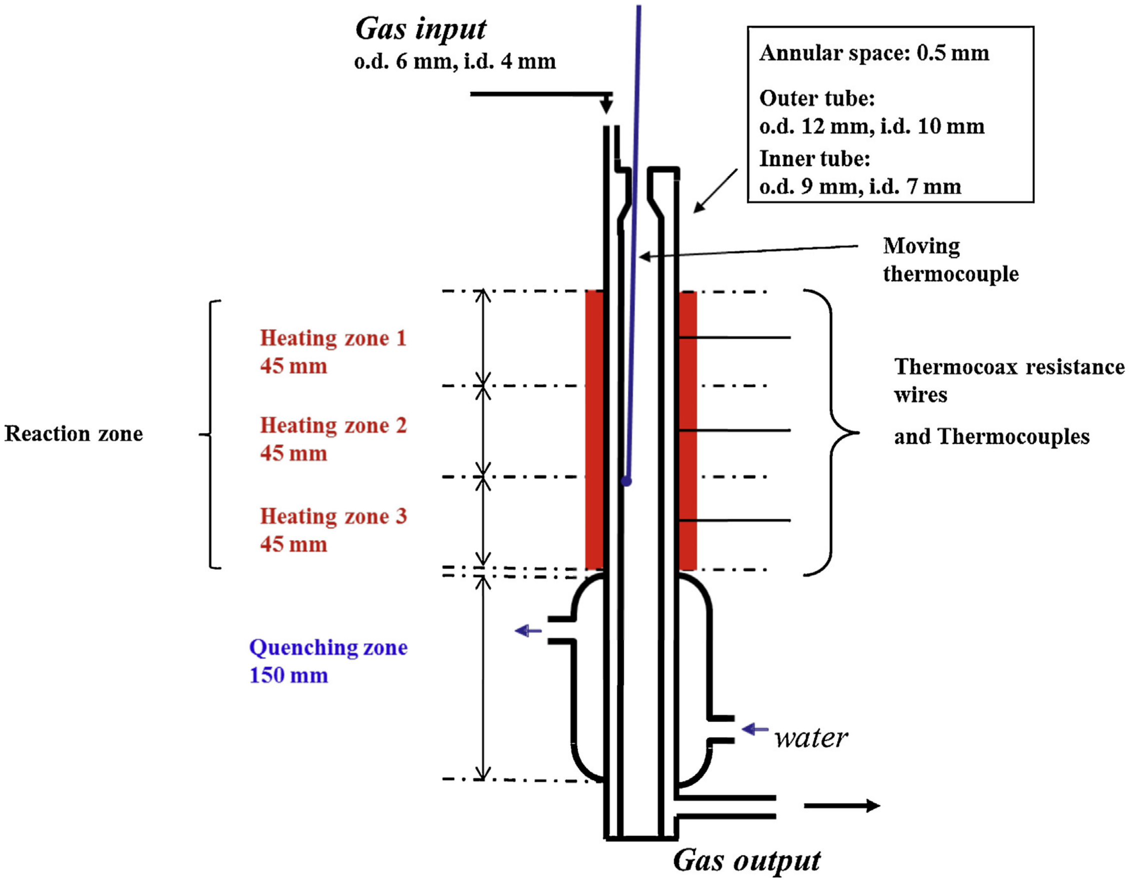

Fig. 1 – Annular flow microreactor design.