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Enhanced heat transfer by exothermic reactions in laminar flow capillary reactors

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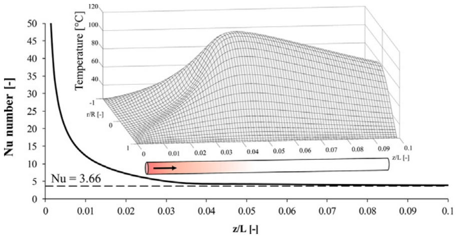
HIGHLIGHTS

- For a capillary reactor, concentration and temperature profiles are discussed.
- Exothermic reactions can significantly enhance heat transfer.
- For reactor design, commonly used plug flow models can lead to miscalculations.
- Simulating both axial and radial conversion profiles can be a key step for reactor scale-up.

GRAPHICAL ABSTRACT



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ABSTRACT

Conversion and temperature distributions in a tubular reactor with an inner diameter of 1 mm were numerically calculated for a second order exothermic reaction in laminar flow of homogeneous liquid. Based on the resulting radial temperature profiles, the local Nusselt numbers and bulk mean temperatures were determined along the reactor tube. Strong effects of the homogeneous reaction on the heat transfer can be observed in the entrance region of the reactor, where a hot spot emerges. Due to the large radial temperature gradients in vicinity of the reactor wall, heat transfer coefficients are significantly higher compared to a non-reactive system.

The consequences of this effect on the design and control of exothermic reactions in reactor/heat exchangers are demonstrated by comparison with a simple one-dimensional plug flow model. In the simplified model, neglecting thermal influence of the exothermic reaction results in a significant underestimation of the required reactor length for defined conversion. Accordingly, numerical simulation of both axial and radial transport in the hot spot region can be essential to precisely predict the bulk temperatures and conversion rates in the reaction mixture, even with the small length scales of milli- and micro-structured reactors.

1. Introduction

Milli- and micro-structured flow reactors have a high potential for process intensification. The finely adjustable reaction times and excellent heat removal in these reactors make it possible to run exothermic reactions in safe and defined conditions (Kockmann and Roberge, 2009; Taghavi-Moghadam et al., 2001; Zhang et al., 2004). To calculate the conversion profiles in microreactors, plug flow and often isothermal assumptions are widely used. Both simplifications are based on the intensified transport processes with the small channel diameters and large reactor length-to-diameter ratios: 1) With very short diffusion paths, radial mixing by molecular diffusion can be fast enough to approach plug flow behavior, even in the laminar flow regime. Further enhancement of radial mixing can be obtained by inducing a secondary flow with the specific channel design (Klutz et al., 2015). 2) Heat transfer within the reactor is very efficient as a result of the high surface-to-volume ratio and small length scale for thermal conduction. Thus, the rate of heat removal is assumed to be fast compared to the rate of heat generation and, as a result, the

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reaction mixture may be considered to be nearly isothermal. However, at a closer look, these common idealizations can significantly deviate from the actual reactor behavior: If the hydrodynamic residence time is much shorter than the characteristic time for molecular diffusion, radial concentration gradients exist, and either the convection model for laminar flow or the dispersion model are more accurate representations of the residence time distribution (Levenspiel, 1999). In the case of very fast and strongly exothermic reactions, even the superior heat transfer characteristics of microreactors might not be sufficient to avoid hot spots in the entrance region of the reactor (Barthe et al., 2008). Local temperature peaks accelerate the reaction and significantly influence the yield in the reaction system as a result.

While numerous publications describe experimental characterization and modeling of the residence time distribution in microreactors (Boskovic and Loebecke, 2008; Lohse et al., 2008; Trachsel et al., 2005; Wörner et al., 2007), less consideration is given to the temperature distribution in micro- and millireactors. Nevertheless, the formation of hot spots is a crucial concern for reactor design and control. Because temperature measurements in small spaces of microreactors are often difficult to perform in practice, precise calculation of local temperatures has additional significance.

For a rough estimation, the internal heat transfer coefficient, α, can be determined from correlations for the dimensionless Nusselt number, $\mathrm{Nu}=\frac{\alpha d}{\lambda}$, in the channel flow (Martin, 2002). For a straight tubular reactor (e.g., a stainless steel capillary in an oil bath), the internal heat transfer can be calculated by assuming a constant wall temperature and fully developed flow. With these assumptions, a constant Nusselt number, $\mathrm{Nu}=3.6568$, can be derived for laminar flow (Baehr and Stephan, 2006). However, radial temperature profiles can be strongly influenced by the reaction itself. This effect is completely neglected by using common correlations or assuming a constant Nusselt number throughout the entire channel. An intensive and comprehensive insight into the phenomena resulting from an exo- or endothermic chemical reaction with concomitant heat transfer has been published by Churchill et al. (Churchill, 2005; Churchill et al., 2008; Yu and Churchill, 2012). Churchill describes strong effects and complex behavior that significantly enhance heat transfer in the presence of a homogeneous exothermic reaction. Because additional parameters are introduced by one or several chemical reactions, he concluded that a general correlating equation cannot be derived practically. Instead, he recommends that numerical calculation of both the radial and axial transport be performed on a case-by-case basis. Radial temperature profiles in tubular reactors have been investigated for some typical gaseous reaction systems, for example, by Rothenberg and Smith (1966), or by Merrill and Hamrin (1970).

The objective of the present study is the detailed investigation and discussion of heat transfer in a liquid phase reaction, based on exemplary process specifications that closely approximate the typical operating conditions in milli- and microstructured flow reactors. A fast, exothermic, second-order reaction in a circular duct with 1 mm diameter was simulated using two different models: 1) A simple one-dimensional plug flow model assuming a constant Nusselt number (heat transfer in thermally developed flow) and 2) a two-dimensional model of the rotationally symmetric geometry that accounts for the axial and radial heat and mass transport. Visualization and discussion of radial temperature and concentration profiles in the investigated capillary reactor provide the basis for an improved understanding of the effects previously described by Churchill and coworkers. By comparing results of both models, the applicability of the simplified model can be evaluated with regard to practical aspects in the design and control of reactor/heat exchangers. Furthermore, the influence of the exothermic reaction is demonstrated by comparing the reactor/heat exchanger with a corresponding heat exchanger without chemical reaction.

2. Basic model assumptions

The exothermic reaction is assumed to be second order and irreversible and to take place in a homogeneous liquid phase (Table 1). The temperature dependence of the reaction rate was described by the Arrhenius equation, in which the activation energy was varied to ascertain the thermal effects.

The material properties used were based on toluene and assumed to be constant for all temperatures and conversions. For the purpose of this study, a reaction medium with a density of 867 kg m^{-3}, heat capacity of 1707 J kg^{-1} K^{-1}, thermal conductivity of 0.134 W m^{-1} K^{-1}, and a mass diffusivity of 10^{-9} m^2 s^{-1} for the reactant was considered.

The considered reactor is a tubular flow reactor (Table 2). Due to its rotational symmetry, the three-dimensional problem can be reduced to a two-dimensional axisymmetric problem. A constant wall temperature, T_w, was defined and for all simulations with an exothermic reaction, the inlet temperature of the reactor was defined as $T_0=T_w$.

The partial differential equations resulting from the mass and energy balance in the tube flow are

$$\frac{\partial X_A}{\partial z}-\frac{D}{u}\left[\frac{1}{r}\frac{\partial X_A}{\partial r}+\frac{\partial^2 X_A}{\partial r^2}+\frac{\partial^2 X_A}{\partial z^2}\right]-\frac{r_A}{u c_{A,0}}=0 \tag{1}$$

$$\frac{\partial T}{\partial z}-\frac{\lambda}{u\rho c_p}\left[\frac{1}{r}\frac{\partial T}{\partial r}+\frac{\partial^2 T}{\partial r^2}+\frac{\partial^2 T}{\partial z^2}\right]+\frac{r_A \Delta H_R}{u\rho c_p}=0 \tag{2}$$

The following boundary conditions that were used in this study:

$$T(r,z=0)=T_0 \quad X_A(r,z=0)=0$$

$$T(r=R,z)=T_w \quad \frac{dX_A}{dr}(r=R,z)=0$$

$$\frac{dT}{dr}(r=0,z)=0 \quad \frac{dX_A}{dr}(r=0,z)=0$$

For all z, the velocity profile in laminar Hagen–Poiseuille flow is defined as

$$u(r)=2u_m\left(1-\left(\frac{r}{R}\right)^2\right) \tag{3}$$

With these definitions, it was assumed that the reaction was initiated in a hydrodynamic fully developed flow with a homogeneous radial reactant distribution.

Table 1
Reaction parameters used for the simulations.

Rate constant	0.0004	m^3 mol^{-1} s^{-1}
Reference temperature	30	°C
Initial reactant concentration	4	mol L^{-1}
Reaction enthalpy	−40	kJ mol^{-1}

Table 2
Reactor parameters used for the simulations.

Reactor diameter	1	mm
Reactor length	1	m
Mean flow velocity	0.1	m s^{-1}
Wall temperature	25	°C
Reactor pressure[a]	5	bar

[a] The reactor pressure was chosen in order to avoid exceeding the boiling temperature in the reactor tube for the reference material toluene.