A continuous flow microfluidic calorimeter: 3-D numerical modeling with aqueous reactants

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ABSTRACT

A computational analysis of the reacting flow field, species diffusion and heat transfer processes with thermal boundary layer effects in a microchannel reactor with a coflow configuration was performed. Two parallel adjacent streams of aqueous reactants flow along a wide, shallow, enclosed channel in contact with a substrate, which is affixed to a temperature controlled plate. The Fluent computational fluid dynamics package solved the Navier–Stokes, mass transport and energy equations. The energy model, including the enthalpy of reaction as a nonuniform heat source, was validated by calculating the energy balance at several control volumes in the microchannel. Analysis reveals that the temperature is nearly uniform across the channel thickness, in the direction normal to the substrate surface; hence, measurements made by sensors at or near the surface are representative of the average temperature. Additionally, modeling the channel with a glass substrate and a silicone cover shows that heat transfer is predominantly due to the glass substrate. Finally, using the numerical results, we suggest that a microcalorimeter could be based on this configuration, and that temperature sensors such as optical nanohole array sensors could have sufficient spatial resolution to determine enthalpy of reaction.

1. Introduction

Microfluidics has been widely used in areas such as biology, chemistry, physics and engineering to reduce sample volumes, increase reaction speed, increase measurement sensitivity, and decrease device size. A particular area where the microscale is advantageous is calorimetry. By analyzing and understanding the thermochemical heat transfer processes in the microchannels, one can obtain valuable information such as the enthalpy of reaction, entropy, Gibbs free energy, binding, and equilibrium constants. Calorimetric information is vital to the pharmaceutical and drug development industries for the decision making process [1]. Sample throughput and the amount of sample needed to execute a calorimetry experiment could be significantly decreased using microchannel reactors.

Calorimetry requires control of both mass and heat transport. One example of a microfluidic device in which mass diffusion is the main mixing mechanism is the "T-sensor" introduced by Yager and colleagues [2]. The T-sensor takes advantage of the low Reynolds number flow conditions in microfluidic channels. The interdiffusion and resulting chemical interaction of components from two or more input fluid streams are monitored optically by measuring the fluorescence intensity, which is dependent on the concentration of the reactants and products [2]. In Fig. 1, the plume of reacted compound is illustrated. Within this plume all three species coexist, and their concentrations vary in space but are constant in time after the initial transient. We have reported measurements of mass transport in the transient regime elsewhere [3]. A theoretical analysis of the molecular diffusion process in T-sensors has been published by Kamholz and Yager [4]. Using the same sensor setup, Salmon et al. [5,6] studied the diffusion dynamics and the rate constants of the reactions. Recently, an experimental and computational study was performed using surface plasmon resonance detection technology to study the diffusion kinetics of a small molecule analyte into a parallel-flowing stream containing an antibody in a T-sensor [7,8].

There have been many investigations on the mass transport properties of microreactors in the literature; however, the heat transfer has received less attention. Further information on reaction kinetics can be obtained by studying the heat transfer

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Nomenclature

A	area (m^2)
$A_{arrhenius}$	pre-exponential factor
AB	product
D	mass diffusion coefficient (m^2/s)
D_{hyd}	hydraulic diameter (m)
E_a	activation energy for the reaction (J/(kmol))
$\dot{E}$	rate of energy (W)
EOT	extraordinary optical transmission
H	heat transfer coefficient on the chip surface (W/(m^2 K))
ΔH	enthalpy (J/mol)
J	diffusion flux (mol/(m^2 s))
Kn	Knudsen number
L	channel length in z-direction (m)
L_C	characteristic length (m)
L_S	length from sensor surface
M	molar mass (kg/mol)
NHA	nanohole array
PDMS	polydimethylsiloxane
Pe_M	Peclet number for mass diffusion
Pe_T	Peclet number for thermal diffusion
Q	volumetric flow rate (nL/s)
R_{gas}	universal gas constant (J/(K mol))
R	net rate of production of species
$\hat{R}$	Arrhenius molar rate of creation/destruction of species
Re	Reynolds number
S_h	energy source term due to chemical reactions (W/m^3)
T	temperature (K)
V	velocity (m/s)
Y	mass fraction of species
c_p	specific heat at constant pressure (J/(kg K))
d	channel thickness in y-direction (m)
e	enthalpy (J/kg)
g	gravitational acceleration (m/s^2)
h	heat transfer coefficient (W/(m^2 K))
k	thermal conductivity (W/(m K))
k_f	forward reaction rate constant
l	mean free path (m)
$\dot{m}$	mass flow rate (kg/s)
m	mass fraction
n	stoichiometric coefficient
p	static pressure (Pa)
q''	heat flux (W/m^2)
w	channel width in x-direction (m)
x	coordinate in the channel width direction
y	coordinate normal the flow (chip) surface
z	coordinate in the flow direction

Greek symbols

α	thermal diffusivity (m^2/s)
ε	dielectric constant
ν	kinematic viscosity (m^2/s)
ρ	density (kg/m^3)
τ	shear stress (Pa)

Subscripts

a	activation
amb	ambient
ent	entrance
gen	generated
hyd	hydrodynamic
set	set value
xy	plane normal to z-direction
xz	plane normal to y-direction
yz	plane normal to x-direction

Superscripts

T	transpose
$\rightarrow$	vector
—	averaging in one direction
=	averaging in two directions

processes in the T-sensor configuration. Though the governing equations appear similar, heat transfer, unlike mass transport, often involves flux across multiple boundaries, making it more complicated to solve. In practical applications, there is heat flow between the channel and its walls, while there is no mass flux across the boundaries of the flow channel. A simplification which is often permissible in the mass transport problem (but not in thermal transport) is that diffusive transport is negligible in the flow direction because the mass transport Peclet Number, Pe_M, is large. The Peclet number (Pe) is the ratio of the convection term to the mass or thermal diffusion term and defined as $Pe_M = D_{hyd}V_z/D$ for mass diffusion and $Pe_T = D_{hyd}V_z/\alpha$ for thermal diffusion. Due to the small values of binary mass diffusion coefficients, the Pe_M number in the flow direction is usually very large. However, for the energy equation at low Reynolds number flow, the contribution of the convective and diffusive terms must be included in the analysis because the thermal Peclet number, Pe_T, is small.

Heat transfer in rectangular microchannels has been addressed by many researchers. Tunc et al. [9] presented an analytical solution for the convective heat transfer with no source term in 2-D rectangular microchannels for fully developed flow and for a range of different Knudsen numbers with constant heat flux across the boundaries. The Knudsen number is defined as $Kn = l/L_c$, where l is the mean free path and L_c is the characteristic length. Ambatipudi et al. [10] numerically studied the conjugate heat transfer between fluid in microchannels and a silicon wafer at high Reynolds numbers in a 3-D configuration to optimize cooling of the solid region. Toh et al. [11] and Kroeker et al. [12] analyzed microchannels for convective cooling purposes in 3-D domains. The main motivation for their work was cooling of electronic devices and therefore it was directed toward convective heat transport. The heat generation source term is not included in the energy equation in these previous studies.

In recent years, the analysis of heat transfer processes in microreactors has been used to extract thermochemical information. Zhang et al. [13] used microthermopiles in a microfluidic reaction chamber to monitor the temperature change during a reaction. Pradere et al. [14] used infrared thermography to measure
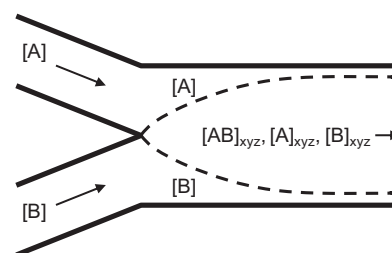

Fig. 1. Coflow configuration. Two liquids containing reactants A and B (with concentrations [A], [B]) are in continuous, laminar flow. A reaction, generating product AB, progresses according to interdiffusion of the reactants (illustrated by dashed line). The spatial distribution of reactants and products is constant in time after an initial transient but varies in space as indicated by subscripts xyz.