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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.

Keywords

Microcalorimeter; Enthalpy of reaction; Microfluidic; Coflow reactor; Nanohole array; Laminar flow interface

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 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 $Pe_T = D_{hyd}V_z/a$ 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 2D 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 the temperature field of nonreacting and reacting flows and proposed a field processing method to retrieve the source term due to the reaction. Fudym et al. [15] performed a detailed 2-D analytical study of the heat transfer between multilayered systems. This analytical model was then applied to temperature fields obtained by infrared thermography from the work by Pradere et al. [14]. In both approaches by Pradere et al. [14] and Fudym et al. [15], the temperature field used in the calculations represents temperature averaged across the depth of the microchannel and also some portion of the encapsulating materials. It was assumed that this average does not differ from the average flow field temperature. More recently, Hany et al. [16] used thermopiles to directly measure the global heat flux during the chemical reaction in a microfluidic chip for coflow and droplet flow configurations, however this device did not measure the temperature distribution within the reactor. Lee et al. [17] constructed a microscale calorimeter with thermopile sensors and thermal isolation by vacuum. Recht et al. [18] constructed thin film thermistors within microwells and used them to obtain reaction rate constants by a titration series. Our group has developed optical temperature sensors using light transmission through nanoscale apertures (nanohole arrays) [19] and we have experimentally characterized these sensors in several microreactor geometries [20–22].

This paper presents numerical analysis of the heat and mass transport, the thermal boundary characteristics, and the heat losses in all directions in a continuous coflowing reaction in a microchannel. A three-dimensional study with a diffusion-controlled reaction energy source term, dependent on the reaction kinetics, in a microchannel with a coflow configuration, and considering the boundary layer effects is a new contribution to the literature. The significance of the study is that it enables design of a novel, continuous flow, microscale calorimeter, provided that local temperature measurements can be made with adequate resolution within the reactor. Accordingly, the thermal boundary layer development in the microchannel is modeled to validate a proposed experimental measurement of temperature using optical sensors with high spatial resolution. The outline of the paper is as follows: in Section 2, the governing equations, boundary conditions, model geometry, and setup are defined. A benchmark of the solution for the flow, concentration and temperature fields is shown to confirm the accuracy of the numerical solution. In Section 3, the results from the thermal boundary and the heat transfer analysis in the simulation domain are presented. In Section 4, a formulation of the energy equation is used to perform the benchmark test and is then extended to a calorimetry relationship for measuring the enthalpy of reaction. The use of nanohole arrays as optical temperature sensors is described and shown to enable a potential microcalorimeter design.

2. Simulation methods

We constructed a numerical model corresponding to features that could be fabricated using practical techniques for a test device. A minimized channel height conserves reactant volumes. The channel width was chosen to be large enough that sidewall thermal boundary effects would have a negligible effect on the kinetics at the channel center. The channel length was chosen to be sufficiently long that equilibrium is established at the outlet. No further effort was made to optimize these dimensions. A representative base-acid reaction was used in this analysis because it is commonly used in calorimeter standardization. The boundary conditions were selected to simulate commonly used materials, compatible with sensor technologies and optical viewing.

The continuity equation, Navier–Stokes equations, energy equations, mass transport equations and reaction rate equation are solved as described below for the steady state case in 3-D space using the commercial CFD software Fluent (ANSYS, Canonsburg, PA). Fluent uses the finite volume approach by Patankar [23]. A second order upwind scheme is applied to discretize the spatial derivatives. Fluent's laminar finite-rate model which computes the chemical source terms using Arrhenius expressions. Since the flow modeled is highly laminar, temperature and pressure differences are relatively small, flow is assumed as incompressible. Heat transfer is modeled using Fourier's heat conduction law and diffusion using Fick's law for individual species. Each of these laws are linear relationships between a flux and its corresponding work conjugate. The mixture is treated as an incompressible material.

The total number of nodes used for this domain is 500,000, with Gambit software used for meshing. Simulations were performed on a PC (Intel Dual Core 1.80 GHz CPU, 3 GB RAM) and each run took approximately 48 h to complete. For the specific reaction modeled in this study, the system had 8 degrees of freedom. To study the thermal boundary layer development, a smaller portion of the domain size was used.

2.1. Model geometry and computational domain

The channel depth in the y -direction, d , is 10 μm and the channel width in the x -direction, w , is 500 μm . The length in the flow direction, L , is 5000 μm . The chamber volume is 25 nL. The fluid in the flow channel is surrounded by a glass chip on the bottom, 670 μm thick and a polydimethylsiloxane (PDMS) surface on the remaining other sides, 2 mm thick. The coordinate system used, flow direction, and the details of the layers are illustrated in Fig. 2.

We modeled a two-species reaction of the form $n_1\text{A} + n_2\text{B} \rightarrow n_3\text{AB} + n_4\text{A} + n_5\text{B}$. Aqueous solutions of compounds A and B each flow independently, at equal volumetric flow rate, and merge at the xy plane at $z = 0$, the inlet plane. The figure is not drawn to scale. Dimensions are shown in mm.

2.2. Governing equations and boundary conditions

The continuity and momentum equations solved are:

$$\nabla \times (V) = 0 \quad (1)$$

$$\vec{V} \times \nabla \vec{V} = \frac{-\nabla p}{\rho} + \mu \nabla^2 \vec{V} \quad (2)$$

where p is static pressure, μ is the molecular viscosity and $\vec{V}$ is the velocity vector of the mixture.

The energy equation is:

$$\nabla \times (V(\rho E + p)) = \nabla \times \left[k \nabla T - \sum_j h_j \vec{J}_j \right] + S_h \quad (3)$$

where $\vec{J}_j$ is the diffusion flux of species j . The first two terms on the right hand side of Eq. (3) represent the energy transfer due to conduction and species diffusion, respectively. S_h includes the energy generation from chemical reactions. Viscous dissipation is neglected due to low viscosity of the fluids and low flow rates.

The sum of the enthalpy minus the flow work and the kinetic energy is defined as the energy carried by the flow, E . The flow work term is included in the left side of Eq. (3):

$$E = e - \frac{p}{\rho} + \frac{V^2}{2} \quad (4)$$

and for incompressible flows, e is defined as:

$$e = \sum_j Y_j e_j + \frac{p}{\rho} \quad (5)$$

where Y_j is the mass fraction of species j , and

$$e_j = c_{p,j}(T - T_{ref}) \quad (6)$$

with constant c_p the heat capacity values, and $T_{ref} = 298.15$ K.

For the species transport model the governing equations are, for each species i ,

$$\nabla \times (\rho V Y_i) = - \nabla \times \vec{J}_i + R_i \quad (7)$$

For laminar flow, mass diffusion is governed by the equation,

$$\vec{J}_i = -\rho D_{i,m} \nabla Y_i \quad (8)$$

where $D_{i,m}$ is the diffusion coefficient for species i in the mixture. R_i is the net rate of production of species i by chemical reaction and is computed using:

$$R_i = M_{w,i} \hat{R}_i \quad (9)$$

where $M_{w,i}$ is the molecular weight of species i and $\hat{R}_i$ is the Arrhenius molar rate of creation/destruction of species i . $\hat{R}_i$ is calculated using:

$$\hat{R}_i = (n_i'' - n_i') \left(k_f \prod_{j=1}^N [C_j]^{(n_j' + n_j'')} \right) \quad (10)$$

where, C_j is the molar concentration of species j , η_j' is the rate exponent for reactant species j , η_j'' is the rate exponent for product species j , and η_j' and η_j'' are stoichiometric coefficient for reactant and products respectively.

The forward reaction rate constant, k_f , is calculated using the Arrhenius expression,

$$k_f = A_{\text{arrhenius}} \exp(E_a / R_{\text{gas}} T) \quad (11)$$

where, $A_{\text{arrhenius}}$ is a pre-exponential factor, E_a is the activation energy for the reaction and R_{gas} is the universal gas constant. To simplify the analysis, as a first approximation, we neglect the reverse reaction rate constant.

The boundary conditions are as follows:

For the Navier–Stokes equations, the no slip condition is applied at the walls (channel surfaces) since the fluid is a dilute aqueous liquid. Our simulation deals with room temperature liquids at low Re number flows, the Knudsen number is in the hydrodynamic regime, and a no slip boundary condition is valid.

To accurately model the fully developed flow entering the reaction channel from two inlet channels, a uniform velocity field, V_z , is introduced normal to the xy -plane at $z = -50 \mu\text{m}$ while the wall node velocity values are kept at zero (i.e., no slip boundary condition). The following correlation was used to check if the entry length ($-50 \mu\text{m} < z < 0 \mu\text{m}$) is sufficient for the velocity profile to fully develop before reaching the inlet plane at $z = 0 \mu\text{m}$ [24]:

$$\frac{L_{\text{ent}}}{D_{\text{hyd}}} \approx \frac{0.6}{1 + 0.035 \times \text{Re}_{\text{hyd}}} + 0.056 \times \text{Re}_{\text{hyd}} \quad (12)$$

In Eq. (12), the Reynolds number is defined as the ratio of inertial forces to viscous forces and can be calculated with the relation $\text{Re}_{\text{hyd}} = D_{\text{hyd}} V_z / \nu$. D_{hyd} is the hydraulic diameter of

the flow channel ($4 A_{xy}/\text{perimeter}$), V_z is the average velocity and ν is the kinematic viscosity. Using the width value for the inlet channels ($w/2$), the entrance length was calculated as $12\mu\text{m}$ and $11\mu\text{m}$ for $V_z = 0.05\text{ m/s}$ and for $V_z = 0.005\text{ m/s}$ respectively. This calculation indicates that the inlet flow is fully developed at the $z = -38\mu\text{m}$ and $z = -39\mu\text{m}$ locations for the two velocities, i.e., well before reaching the reactor inlet.

The development of the velocity profile after the two channels merge is shown in Fig. 3. The velocity profile has a stagnation point at $x = w/2$, $z = 0\mu\text{m}$, when the two streams meet, and becomes fully developed before $z = 50\mu\text{m}$. The higher velocity near the outer walls can be attributed to the fluid acceleration that occurs due to the angled geometry of the inlet channels as they enter the reaction section of the flow cell.

For the energy boundary conditions, the upper surface of the PDMS is exposed to convection to the ambient where, $T_{\text{amb}} = 298.15\text{ K}$ and a heat transfer coefficient of $h = 18\text{ W/(m}^2\text{ K)}$. The heat transfer coefficient is based on the conduction limit of the natural convection with the characteristic length $L_{\text{PDMS}} = \text{area/perimeter}$, where area and perimeter correspond to the top surface of the PDMS facing ambient air.

$$-k \frac{\partial T(x, y=L_y, z)}{\partial y} = h[T(x, y=L_y, z) - T_{\text{amb}}] \quad (13)$$

The bottom surface of the glass chip was set to uniform temperature value, T_{set} , simulating the experimental conditions where the glass chip sits on a temperature regulated surface.

$$T(x, y = -0.670\text{ mm}, z) = T_{\text{set}} = 298.15\text{ K} \quad (14)$$

$$\frac{\partial T(x=0, y, z)}{\partial x} = 0 \quad (15)$$

$$T(x, y, z = -50\mu\text{m}) = T_{\text{inlet}} = T_{\text{amb}} \quad (16)$$

Eq. (16) establishes an upstream starting point in order to accommodate conduction effects because of the low Thermal Peclet number.

The boundary conditions for the mass flow are as follows, the reactants are introduced from two different inlets and merge at $z = 0\mu\text{m}$, where mass diffusion starts:

$$[C_j](x, y, z = -50\mu\text{m}) = M_j \quad (17)$$

where, M is the molar concentration of species j . All of the channel walls are impermeable such that,

$$\frac{\partial [c_j](x, y, z)}{\partial x} \Big|_{x=0, w=0} = 0 \quad (18)$$

$$\frac{\partial [c_j](x, y, z)}{\partial y} \Big|_{y=0, d=0} = 0 \quad (19)$$

and the mass balance applied at the inlet and the outlet yields:

$$\dot{m}_{inlet} = \dot{m}_{outlet} \quad (20)$$

These boundary conditions correspond to a configuration where the microfluidic channel is on a nearly isothermal heat sink. The justification of adiabatic boundaries at the channel sidewalls are: (1) the thickness of the PDMS layer in x -direction is much larger than that in the y -direction; (2) since $w \gg d$ (Fig. 2), the area of the top and bottom channel walls, A_{xy} is greater than the area of the channel sidewalls, A_{yz} ($A_{xy} \gg A_{yz}$); (3) the velocity in the x -direction is zero. The preceding considerations support the assumption that the thermal resistance through the sidewalls is much greater than that in the normal direction. Hence we neglect heat flow in the x -direction at the sidewalls, but account for it in the y direction (through the top PDMS layer). The effect of gravity is neglected. The laminar flow approximation is justified by the low Reynolds numbers (Re). Using the properties of liquid water at 298.15 K, and the channel dimensions provided above, $Re_{hyd} = 0.091$ for $V_z = 0.005$ m/s and $Re_{hyd} = 0.905$ for $V_z = 0.05$ m/s. Since water is the most abundant species in the mixture and the mass fraction of the other species is small, and since the overall temperature differences are within ± 3 K, the thermophysical properties of the water at $T = 298.15$ K are used to represent the properties of the liquid solution. Using these values, the Peclet numbers were calculated as $Pe_T = 6.72$, $Pe_M = 490.20$ for $V_z = 0.05$ m/s, and $Pe_T = 0.67$, $Pe_M = 49.02$ for $V_z = 0.005$ m/s.

The above transport model can be solved for the temperature and concentration fields in the device shown in Fig. 2. As a specific test case, inlet solutions of dilute NaOH and HCl were used. This reaction provides a known energy release that is well documented, even though it is a dissociation reaction with an enthalpy of dilution rather than an enthalpy of reaction. The reaction and associated energy release are a result of the dissociated H^+/H_3O^+ ions reacting with the OH^- ions to form the product. For the purpose of the present numerical modeling and for interpretation of the resulting thermal and concentration fields, the energy released is included in the energy balance as an internal energy source. This approach equally well describes either the enthalpy of dilution or enthalpy of reaction. The equation for the reaction is,

where NaOH corresponds to reactant A and HCL corresponds to reactant B in the generalized development. Water is considered as the common solvent.

At the inlets, $z = -50 \mu\text{m}$, two different streams with different mass fractions of species enter the channel. For $0 < x < w/2$ a fixed concentration of HCl (1 M or 6M) is applied. For $w/2 < x < w$ a fixed concentration of NaOH (1 M or 6M) is applied. These values are typical of reported concentrations used to benchmark calorimeter experiments [14,16]. Concentration values of 1 M and 6M were investigated to determine the effect of molarity on the temperature and concentration fields. The 6M concentration is high for normal calorimeter applications, but it is consistent with the present purpose of determining the effect of concentration and of proof of concept. Downstream the products and excess reactants exit the channel at conditions governed by the diffusion and reaction equation. The binary diffusivity constants of HCl and NaOH are set to a constant value of $D = 2.0 \times 10^{-9} \text{ m}^2/\text{s}$. This value is reported by Leist et al. [25] for mixtures of HCl and NaOH. Our assumption is that the molecular diffusivity provides sufficient insight into the behavior of the system, though a more complete model would address each of the dissociated ionic species individually. The constants for the Arrhenius reaction rate equation and the values for the enthalpy of formation data for each species were taken from the reported values in the literature [26] and are summarized in Tables 1 and 2 for $T_{\text{ref}} = 298.15 \text{ K}$. The values of the enthalpy of formation in Table 2 are from a standard reference [27]. However, the literature does report a higher value of -64 kJ/mol for neutralizing at a concentration of 6M [28], as compared to the -56 kJ/mol in Table 2, a 14% difference. For the purpose of this initial study, we held the enthalpy of formation constant in the numerical modeling; the increase in enthalpy of formation would increase the reported temperature values while not affecting the general shape and behavior of the temperature profiles.

2.3. Validation

For validation of the flow field, numerical results for the velocity magnitude were compared with the available analytical solution for Poiseuille flow between stationary parallel plates [24]. Normalized velocity fields obtained from several x and z regions were compared with the analytical solution and found in good agreement with the analytical velocity profile as shown in Fig. 4.

Grid convergence analysis was performed at three different node spacing values. The results are presented in Fig. 5. No significant change was observed in the concentration and temperature profiles beyond 500,000 nodes. Fig. 6 presents the convergence of residual values for each calculated value in the simulation. Convergence was achieved after approximately 5500 iterations in all simulations.

3. Simulation results and discussion

The simulation was used to investigate how the thermal boundary layer affected heat transfer at the upper plate and to calculate the development of the temperature and concentration fields for different velocities and molarities. Additionally, the temperature profile across the thin dimension, the channel height, was examined to determine the difference between the temperature and concentration at the channel floor to that of the bulk of the fluid Fig. 7.

Formations of the temperature and concentration fields are presented in Figs. 7 and 8, respectively. The values shown are at $y = 0$ (the channel floor) and inlet concentrations of 1 M HCl and 1 M NaOH or 6 M HCl and 6 M NaOH. The solutions from two simulations with different flow rates ($Q = 25$ nL/s and $Q = 250$ nL/s) are shown. For comparison, a case with adiabatic boundary conditions on the upper and lower plates (y -direction) is also presented in Fig. 7f.

Fig. 7 confirms that heat transfer in y -direction changes the nature of the problem significantly. In the adiabatic case the temperature increases downstream. In contrast, for the non-adiabatic cases, the system forces the temperature field to the equilibrium temperature of the surroundings. As seen in Fig. 7f, the adiabatic case, the temperature of the fluid in the device increases to a uniform value that is above that of the surroundings. All of the energy released by the reaction leaves the system in the non-adiabatic cases. While the colored contours plots provide a good overview of the temperature field, the line plots are shown to provide clarity when the affected region is small. As seen from the combinations of Fig. 7a and b, the spatial effect of the source term is dependent on the velocity, with the lower velocity producing a smaller affected region than the higher velocity case. Comparing the results in Fig. 7e for the 6 M solution to that of Fig. 7b illustrates that higher concentrations yield more energy and higher temperatures, but the qualitative profile of the temperature profile remains the same. This is shown explicitly in Fig. 9, with temperature normalized. As discussed in Section 3, this information can be used to determine the preferable locations of sensors in an experimental device (i.e., temperature and concentration sensor spacing in z and x).

Comparing Figs. 7 and 8 shows the difference between the temperature field and the concentration field of the reaction product. The extent of diffusion in x increases in the downstream region, which would correspond to a higher concentration signal of reaction product in experimental measurements. For the temperature field, the greatest change due to the reaction occurs near the inlet region.

Fig. 8 shows the concentration distribution for the product (NaCl for this reaction). Comparing Fig. 8a and c shows that increasing the flow rate (or velocity) decreases the width of the diffusion region in x -direction. This result suggests that, for concentration measurements, resolution in the x -direction can be adjusted by adjusting the flow rate. The distinction between mass and thermal transport is seen as the concentration profiles more closely resemble the adiabatic thermal case, Fig. 7f, than the temperature profiles for the non-adiabatic cases, Fig. 7a, b and e.

To put these results into broader context, the temperature field obtained by the simulation may be qualitatively compared to existing experimental data in the literature. Pradere et al. measured the temperature field of a large substrate surrounding a laminar coflow microreactor, using an infrared camera [14]. In their system, the microchannel was approximately 1 mm wide, and the resultant temperature of the entire $4\text{ cm} \times 4\text{ cm}$ substrate was imaged. The configuration was a reaction of 0.25 M NaOH and 0.25 M HCl solutions with a flow rate of 1000 $\mu\text{L/h}$. The camera did not provide temperature measurement of sufficient resolution within the reactor for quantitative comparison, however.

The thermal boundary effects were analyzed in a smaller domain to study the temperature development in the y -direction (normal to the glass substrate surface). Since the reaction is occurring at the laminar diffusion interface, the largest temperature gradients occur along this interface, in the center of the channel with respect to the x direction (the channel width). Hence, for the thermal boundary analysis, we studied temperature profiles taken from the regions close to the half-width distances at $x = w/2$. Figs. 10–12 show the contours of the temperature development in the entrance region caused by the spatially non-uniform energy source due to the reaction. These figures plot temperature differential from bottom to top of the channel at various z locations.

Surface based temperature sensors (Section 3.2) may measure values in a region only 100–300 nm above the substrate ($y = 0$) [8], or alternately thermography measurements may record temperature through the top or bottom plate. If such sensors are to be used to measure reaction properties then the observed surface temperature values must accurately represent the respective fields in bulk of the fluid. We used the simulation results to estimate the deviation between the temperature at the surface layer, close to the channel floor, and the mean channel temperature in y -direction.

To calculate the agreement between the bottom surface temperatures and the mean channel temperature we used:

$$\text{Agreement}(\%) = \frac{1/L_s \int_0^{L_s} [T(y) - T_{\text{set}}] dy}{1/d \int_0^d [T(y) - T_{\text{set}}] dy} \times 100 \quad (22)$$

In the equation above, L_s represents the distance normal to the $y = 0$ surface where the detection occurs by surface-based sensors. This integration was done numerically for several x and z regions, using a value of $L_s = 300$ nm. The smallest agreement values were 98.61% for the low molarity case, and 98.58% for the high molarity case. This result suggests that a temperature field measured by surface sensors accurately represents the average temperature of the channel in this configuration. Further parameterized simulations are needed to determine the generality of this conclusion.

The heat transfer on the lower and upper surfaces of the channel was analyzed in order to understand the relation between these energy transfer mechanisms as compared to convective transfer due to flow. This analysis leads to simplifications which can be used for practical calculations such as determining the heat loss calibration constant. For the simulation with $V_z = 0.005$ m/s, the heat flux in the z direction, along the channel length at different x values was calculated. The laminar diffusion interface, $x = 25, 0 \mu\text{m}$, corresponds to the mid-plane of the channel. The results for both $y = 0 \mu\text{m}$ (glass chip surface) and $y = 10 \mu\text{m}$ (upper PDMS surface) are shown. Fig. 13 shows the heat fluxes on the top and bottom surfaces of the flow channel at different x -positions. The dashed line represents the heat fluxes on the top insulative PDMS surface, and the remaining curves indicate the heat flux on the bottom surface.

A quantitative comparison between two heat fluxes was performed to get a clear understanding of the contribution of each quantity. The results showed that the heat flux at the $y = 0$ surface throughout the channel is larger than that of the PDMS surface at $y = 10 \mu\text{m}$.

At any x location this ratio is calculated as:

$$\frac{\text{Heatfluxuppersurface}(x\text{line})}{\text{Heatfluxlowersurface}(x\text{line})} = \frac{\min(q''_{y=10\mu\mu})}{\min(q''_{y=0\mu\mu})} \times 100 \quad (23)$$

Using Eq. (23), the heat loss from the upper surface at $x = 250 \mu\text{m}$ equals 3.6% of the lower heat flux. The same calculation can be done by calculating the total heat flux over the entire lower and upper surface, this value is calculated from the simulation using:

$$\frac{\text{Heatfluxuppersurface(wholearea)}}{\text{Heatfluxlowersurface(wholearea)}} = \frac{q''_{y=0\mu\mu}}{q''_{y=10\mu\mu}} \times 100 \quad (24)$$

This value is calculated as 0.7% using the numerical results.

The same conclusion on heat transfer for the lower and upper surfaces can be also derived by looking at Figs. 10–12. The slope of the temperature lines are close to zero at $y = 10 \mu\text{m}$ compared to the slope of the temperature lines at $y = 0 \mu\text{m}$. This is an expected result based on the boundary conditions applied to the bottom and top surfaces, but it supports neglecting the upper heat loss as a potential simplification in an analytical model.

4. Energy balance analysis: implications for calorimetry

Having established a model for the mass transport and temperature in the reactor, an energy balance on an embedded control volume is used to benchmark the consistency of the results. In this section, we investigate the energy balance analysis and demonstrate that it provides the basis of using this device as a calorimeter. The attractiveness of such a device is further supported by the near constant concentration and temperature fields in the y -direction shown earlier. This observation from the numerical solution confirms that using discrete temperature and concentration sensors located at fixed positions at the bottom surface of the channel can provide accurate measurements for the enthalpy of reaction. As a step toward implementation in a device, we suggest nanohole array sensors and discuss the sensor positioning and how thermodynamic quantities of the reaction can be extracted from the sensor readout.

4.1. Calorimeter type calculations – enthalpy of reaction

In this section the consistency of the energy solution is benchmarked. A control volume is selected inside the computational domain and the energy balance is applied.

Starting with the three dimensional, steady state differential energy balance:

$$\sum_j (\rho c V_z)_j \frac{\partial T}{\partial z} = k \left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \right) + \dot{q}_{gen}(x, y, z) \quad (25)$$

where the heat generation term, $\dot{q}_{gen}$, represents the energy added or removed from the control volume due to the enthalpy of reaction for the species. Integrating in y-direction, from $y = 0 \mu\text{m}$ to $y = d$, and using the definition for the average temperature over the y-direction, $\bar{T} = 1/d \int T dy$, reduces the energy balance to the following form:

$$\int_0^d \sum_j (\rho c V_z)_j \frac{\partial T}{\partial z} dy = k d \left(\frac{\partial^2 \bar{T}}{\partial x^2} + \frac{\partial^2 \bar{T}}{\partial z^2} \right) + k \int_{y=0}^{y=d} \frac{\partial^2 T}{\partial y^2} dy + \dot{q}_{gen}(x, y, z) d \quad (26)$$

The y-directed conduction integral on the right hand side can be evaluated and the boundary heat flux terms introduced into the energy balance.

$$k \int_{y=0}^{y=d} \frac{\partial^2 T}{\partial y^2} dy = k \frac{\partial T}{\partial y} \Big|_{y=d} - k \frac{\partial T}{\partial y} \Big|_{y=0} = -q''_{y=d} + q''_{y=0} \quad (27)$$

Numerical results show that, $q''_{y=0} \gg q''_{y=d}$, and the heat loss on the PDMS side, $y = d$, is neglected. Next, integrating in x-direction, from $x = 0 \mu\text{m}$ to $x = w$, introduces the x-directed boundary heat flux terms into the energy balance.

$$\int_0^w \int_0^d \sum_j (\rho c V_z)_j \frac{\partial T}{\partial z} dy dx = k w d \frac{\partial^2 \bar{T}}{\partial z^2} + k d \int_{x=0}^{x=w} \frac{\partial^2 \bar{T}}{\partial x^2} dx + \int_{x=0}^{x=w} q''_{y=0}(x, z) dx + d \int_{x=0}^{x=w} \dot{q}_{gen}(x, z) dx \quad (28)$$

In the equation above, $\bar{T}$ represents average temperature over x-direction (channel width) and y and $\bar{T}$ represent averaged temperature over y-direction (channel height). As explained in the previous sections, the boundary heat transfer in x-direction is negligible,

$$k \int_{x=0}^{x=w} \frac{\partial^2 \bar{T}}{\partial x^2} dx = k \frac{\partial \bar{T}}{\partial x} \Big|_{x=w} - k \frac{\partial \bar{T}}{\partial x} \Big|_{x=0} = 0 \quad (29)$$

and the integrated energy balance is:

$$\int_0^w \int_0^d \sum_j (\rho c V_z)_j \frac{\partial T}{\partial z} dy dx = k w d \frac{\partial^2 \bar{T}}{\partial z^2} + \int_{x=0}^{x=w} q''_{y=0}(x, z) dx + d \int_{x=0}^{x=w} \dot{q}_{gen}(x, z) dx \quad (30)$$

The term, $q''_{y=0}$, represents the heat flux coming from the chip surface and can be stated in terms of the heat loss coefficient, h , using the heat sink temperature, T_{set} , on the back chip side of the device at $y = -0.670 \text{ mm}$. The heat flux term inside the integral is defined as:

$$q''_{y=0}(x, z) = h(x, z)[T_{set} - \bar{T}(x, z)] \quad (31)$$

The total heat source is evaluated by integrating along the flow direction (in $-z$), between the locations z_1 and z_2 :

$$\begin{aligned} & d \int_{z_1}^{z_2} \int_{x=0}^{x=w} \dot{q}^{gen}(x, z) dx dz \\ &= \int_{y=0}^{y=d} \int_{x=0}^{x=w} \sum_j (\rho c V_z [T(z_2) - T(z_1)]) dx dy \\ &\quad - wd \left[\frac{k \partial T}{\partial z} \Big|_{z_2} - k \frac{\partial T}{\partial z} \Big|_{z_1} \right] \\ &\quad - \int_{z_1}^{z_2} \int_{x=0}^{x=w} h(x, z) [T_{set} \\ &\quad - \bar{T}(x, z)] dx dz \end{aligned} \quad (32)$$

The total amount of energy absorbed/released is related to the enthalpy of reaction of the product, H_{AB} :

$$\Delta H_{AB} = \frac{d \int_{z_1}^{z_2} \int_{x=0}^{x=w} \dot{q}_{gen}(x, z) dx dz}{\left(\dot{m}_{AB}^{outlet} - \dot{m}_{AB}^{inlet} \right) / M_{AB}} \quad (33)$$

Each term in Eq. (32) can be calculated at the faces of the control volume using the temperature and concentration fields calculated using Fluent. A detailed sensitivity and uncertainty analysis for Eqs. (32) and (33) was performed elsewhere and included comparison against conventional ITC methods [21].

The energy balance validation presented in Appendix A can be inverted to obtain a measure of the enthalpy of reaction by measuring temperature and concentration at the boundaries of a control volume and by applying calibrations for the heat loss coefficients as developed above. This use of the preceding analysis with the flow cell device is the basis of a small scale calorimeter. In this case, Eq. (32) was solved for the heat generation term and combined with Eq. (33) to develop an expression for the enthalpy of reaction in terms of the calibrated heat loss coefficient and temperature and concentration field measured at $y = 0$, the defined chip interface.

$$d \int_{x=0}^{x=w} \dot{q}_{gen}(x, z) dx = \int_0^{x=w} \int_0^{y=d} \sum_j (\rho c V_z)_j \frac{\partial T}{\partial z} dy dx - kwd \frac{\partial^2 \bar{T}}{\partial z^2} - \int_{x=0}^{x=w} q''_{y=0}(x, z) dx \quad (34)$$

This analysis can be performed on a control volume comprising a segment of the channel between two z locations. The temperature and concentration field information is taken from the numerical simulation at the indicated z -locations and the error term is neglected. This calculation was repeated for the z intervals that are summarized in, along with the input quantities and resulting error terms. The error terms are based on the tabulated values of the enthalpy of reaction, Table 1. The z increment in these intervals (200 μm in this case) is

dependent on the grid resolution of the numerical domain. In practice, this value is limited by the spatial resolution of the sensors, which we discuss further below. The error in these estimated values are less than 1.25%, compared with reference values. The difference in the accuracy stated in Table 3 compared to that for the example based on the Table 1 values is that it includes the assumptions discussed in the above development; furthermore Table 3 reflects the method of using measurements only at $y = 0$ and neglecting the x -directed heat loss.

4.2. Nanohole array sensors

Nanohole array (NHA) sensing technology allows one to measure temperature and concentration in a region within 100–300 nm of the fluid boundary and at many sampling points across the channel length and width. NHA sensing is based on monitoring changes in transmitted light intensity through periodic nanoscale apertures in a metal film on a transparent substrate [29,30]. Because the transmission exceeds that predicted by classical analysis, the effect is called extraordinary optical transmission (EOT). Fundamentally a surface plasmon phenomenon, the changes in EOT are caused by the change in the dielectric constant of the medium adjacent to the NHA surface and are dependent on temperature, pressure, and concentration in the sensing layer. The effect of concentration change on the EOT signal was shown by Stark et al. [31], and the effect of temperature change on the EOT signal was demonstrated by Kowalski et al. [19], expressing the generalized change in the dielectric constant as,

$$d\varepsilon = \left. \frac{\partial \varepsilon}{\partial T} \right|_{P,C} dT + \left. \frac{\partial \varepsilon}{\partial P} \right|_{T,C} dP + \left. \frac{\partial \varepsilon}{\partial [C]} \right|_{P,T} d[C] \quad (35)$$

Estimates of the resolution of these measurement are 0.001 K and 0.001 M, respectively [19,32]. Hence, Eq. (35) suggests that at a constant pressure, EOT is capable of measuring the temperature and concentration in the sensing region. During steady state continuous flow, the pressure gradient over each sensor in the flowcell is expected to be constant.

NHA sensing is a promising candidate for realizing the calorimeter proposed here, not only because of its sensitivity but also because of its spatial resolution. Ji et al. [33] used nanohole array sensors spaced every 56 μm . In this configuration, each sensor consisted of a 10×10 array of 150 nm diameter holes fabricated at a pitch of 350 nm. With these dimensions, the size of a single NHA sensor is 3.3 μm . The minimum distance between the sensing arrays is restricted by the propagation of surface plasmon waves and the width of the collimated light emitted at the each sensor site [34]. Use of Bragg mirrors can reduce the center to center distance between sensing arrays to as low as 5 μm leading to higher spatial resolution and higher density of sensing regions, as reported by Lindquist et al. [35]. These sensor sizes, pitch requirements and resolution, combined with the analysis of Eqs. (33)–(35) suggest that a small scale calorimeter could be designed and constructed using this technology.

To be successful, this device would have to employ a method to deconvolve the measured EOT into the temperature and concentration information required in Eq. (33). Deconvolution

is a signal processing technique to find a solution of a convolution equation in the form [36], $F = SC + \gamma$, where, F is a recorded signal, S is the signal which needs to be recovered (temperature in our case) but has been convolved with a signal source C (concentration in our case). γ represents the experimental noise in the measurements. This process is based on a multivariate curve resolution alternating least squares (MCR-ALS) algorithm and has been successfully used in pharmaceutical and agricultural problems [37], to monitor chemical reaction processes [38,39], to investigate temperature dependent protein structural transitions [40], chemical interactions of ions with acids [41], and to analyze voltametric data acquired from differential pulse polarography [42].

4.3. Sensor positioning in the flow channel

In this section, positioning of an array of many sensors is discussed using the information from the temperature and concentration fields obtained from simulation. Interference of light and surface plasmons between two neighboring NHA sites imposes a restriction on the minimum spacing between two sensors. On the other hand, maximum spacing results in less number of NHA sites, leading to easier fabrication. We show that an array of small, local sensors, such as nanohole array sensors, could have sufficient resolution to provide calorimetric measurements. Elsewhere, we have presented a detailed analysis on the optimization of sensor positioning in these configurations [20]. The optimization analysis constituted estimation of enthalpy of reaction at different sensor spacing values and different sensor placement patterns with respect to the channel walls.

In order to perform this calculation, Eqs. (32) and (33) were employed using the temperature, concentration and heat flux values at the channel surface. The derivative term in z was calculated using equally spaced discrete points (sensor locations). The integrals were estimated by calculating the averages along x at each desired z location. The integral terms in Eq. (33) were estimated using MATLAB.

For design purposes, first the spacing in the x -direction is analyzed to ensure that average temperature in x at any z location is represented by the available discretely spaced sensors. Sensors are placed on the channel floor ($y = 0$), 30 μm apart in x and z directions and starting 10 μm away from the side wall and 20 μm downstream of the beginning of the reaction chamber. The sensors are positioned in the patterns illustrated in Table 4.

The integral in the first term in the right hand side of Eq. (32) can be approximated averaging over x -direction (channel width) using the available sensor locations. The integrated mean temperature in the x -direction is calculated first using the entire x field and then using only the temperature information from the discrete sensor locations 30 μm apart. The maximum deviation from the actual mean based on the temperature field to that based on the discrete locations is 1.42%. This result indicates that the temperature information from the idealized sensors can be used to estimate the average temperature in x -direction in the flow channel.

In Eq. (32), $T(z)$ represents the x direction integrated mean temperature obtained from the sensors at a z -location (integrated over x -direction). Derivative terms on the right hand side of the Eq. (32) can be numerically calculated from the sensor data. The derivative of

temperature with respect to z was calculated using all the all points in z from the numerical simulation data. The result was compared with a calculation using the data from the discrete sensors locations spaced $30\text{ }\mu\text{m}$ apart from each other. The maximum deviation between the two derivative approximations is less than 5%.

According to the method of Eq. (33) and using the approximations based on measurements at $30\text{ }\mu\text{m}$ spacing, we obtain a value for the enthalpy of reaction that is within 9% of the reference value. This value reduces to 4% for $20\text{ }\mu\text{m}$ spacing.

5. Conclusion

A three dimensional numerical model of a coflow continuous microreactor was performed using Fluent software to solve for the temperature and concentration fields using the conservation of mass, momentum and energy relationships. The implications of results were discussed in terms of developing a microcalorimeter and how measurements could be taken to obtain enthalpy of reaction.

The thermal analysis for the microchannel reactor includes a non-uniform heat source due to reaction in the channel and flow over a constant temperature surface (glass chip). This setup and its dimensions were chosen to correspond to a device that can be fabricated with conventional techniques [3]. Thermal boundary analysis revealed that the temperature sensed in the vicinity of the channel floor represents the average temperature in y -direction (normal to the glass surface) (over 98.58%) for a wide shallow channel. The results are useful and significant for surface measurement sensors such as nanohole array sensors, where the sensed region is only the $100\text{--}300\text{ nm}$ normal to the sensor substrate. This result shows that measurement from the NHA sensor could provide a good approximation of the channel temperature.

The heat losses were analyzed for the same configuration. The results show that heat loss from upper insulative PDMS surface is less than 3% of the total heat loss from the system and that in the x -direction the heat loss is negligible. The analysis used to benchmark the energy flows was then inverted to analyze the response of the device as a calorimeter. Using the numerical results it was demonstrated that the described device could determine the enthalpy of reaction to within 1.25% of the tabulated value using the approximations justified by the numerical analysis. The effect of using discrete sensors to measure the temperature gradients used in the calorimetric analysis was also investigated and found to differ from the case of ideal continuous temperature measurement by between 0.15% and 5%. Using discrete sensors $30\text{ }\mu\text{m}$ and $20\text{ }\mu\text{m}$ apart on the lower surface of the channel, enthalpy of formation can be estimated within 9% and 4% respectively.

Our analysis suggests that a practical microcalorimeter could be developed according to this design, provided that the case studied here can be generalized to other reactants and operating conditions. Our model incorporates a number of assumptions, and further analysis is needed to assess how these assumptions would limit its applicability to the variety of reactants and operating conditions that might be encountered. Specifically, for example, the model considers only incompressible Newtonian fluids flowing at low number, no slip boundary conditions at the channel walls, low fluid shearing rate, and negligible viscous

dissipation. Additionally, the heat transfer is taken to obey Fourier's law, and the reaction is simplified by neglecting a reverse rate constant. Moreover, to achieve useful measurements, the temperature sensors would have to provide sufficient signal-to-noise in the proposed configuration to detect the relatively low energy signal due to the small quantity of reactants.

Should these conditions be met, in the device we envision a microfluidic flow channel with an optically transparent cover could define a flow path across nanohole array sensors arranged at spacing on the order of tens of microns. Measurement of the EOT from sensor sites, along with temperature and concentration calibration would permit an enthalpy calculation. Such a device could in principle provide calorimetric measurements on the time scale of tens of seconds and could require much lower amounts of reagent because of its small size (25 nL reactor) and sensitivity, thereby enabling new applications for calorimetry in drug discovery and in fundamental research.

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Appendix A

The energy balance equation is used as a benchmark check by introducing an error term, δ . This benchmark check is simplified by expressing Eq. (28) in terms of energy in and out of the control volume.

$$\dot{E}_{in} + d \int_{z_1}^{z_2} \int_{x=0}^{x=w} \dot{q}_{gen}(x, z) dx dz - \dot{E}_{out} + \dot{E}_{loss} = \delta \quad (A1)$$

with δ representing the simulation error, which is 0 in the exact case. Here:

$$E_{in} = \rho A_{xy} V \left[\sum_i c_{p,i} \times m_i^{\text{inlet}} \times (T_i^{\text{inlet}} - T_{\text{ref}}) \right] \quad (A2)$$

$$E_{out} = \rho A_{xy} V \left[\sum_i c_{p,i} \times m_i^{\text{outlet}} \times (T_i^{\text{outlet}} - T_{\text{ref}}) \right] \quad (A3)$$

$$\dot{E}_{loss} = q''_{y1} A_{xy} + q''_{y2} A_{xy} + q''_{x1} A_{yz} + q''_{x2} A_{yz} + wd \left[k \frac{\partial T}{\partial z} \Big|_{z_2} - k \frac{\partial T}{\partial z} \Big|_{z_1} \right] \quad (A5)$$

This energy balance calculation was applied to a control volume that includes the region in which the reaction is complete for the example compound of NaOH, HCL and NaCl, $(x_1, y_1, z_1) = (200, 0, 40) \mu\text{m}$ and $(x_2, y_2, z_2) = (300, 10, 300) \mu\text{m}$. Surface averaged heat fluxes crossing each face and mass fractions at the inlet and the outlet planes are taken from the Fluent solution. Enthalpy of formation for each species is taken from reference values [26]. Table A1 reports the area averaged values passing through the inlet and outlet planes. Solving Eq. (A1) for the error term, δ , resulted in a net energy balance error of 0.418% of

the input energy rate. This result is consistent with the accuracy of the Fluent solution and is to be expected.

Table A1

Values obtained from the simulation for the benchmark calculations.

	$T-T_{\text{ref}} \text{ (K)}$	m_{NaOH}	m_{HCl}	m_{NaCl}	$m_{\text{H}_2\text{O}}$	$V \text{ (m/s)}$
z_1	1.85×10^{-1}	1.81×10^{-2}	1.83×10^{-2}	2.75×10^{-2}	9.61×10^{-1}	5×10^{-3}
z_2	4.09×10^{-2}	6.99×10^{-3}	8.14×10^{-3}	1.90×10^{-2}	9.66×10^{-1}	5×10^{-3}

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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))
	rate of energy (W)
EOT	extraordinary optical transmission
H	heat transfer coefficient on the chip surface (W/(m ² K))
H	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/(Kmol))
R	net rate of production of species
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

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 .

Fig. 2.
Flow geometry of the CFD model and the coordinate system.

Fig. 3. Velocity profile development after the two developed flows merge at the mid-plane, $y = d/2$ for the case $V_z = 0.005 \text{ m/s}$.

Fig. 4.
Comparison of velocity profiles computed by Fluent with the analytical solution [24].

Fig. 5. Concentration and temperature profiles along the channel width at $z = 300 \mu\text{m}$ for different grid spacing values.

Fig. 6.
Residuals of each calculated value for the simulation with $V_z = 0.005$ m/s.

Fig. 7.

(a) Temperature contours for 1M concentration, $Q = 25$ nL/min, (b) Temperature contours for 1M concentration, $Q = 250$ nL/min, (c) corresponding line plot for (a), (d) corresponding line plot for (b) at six downstream positions in z , (e) Temperature contours for 6M concentration, $Q = 250$ nL/min, (f) Temperature contours for 6M concentration, $Q = 250$ nL/min, adiabatic case.

Fig. 8. Molarity of reaction product, contour plots for (a) 1 M inlet concentration, $Q = 25$ nL/s, (b) 6 M inlet concentration, $Q = 25$ nL/s, (c) 1 M inlet concentration, $Q = 250$ nL/s.

Fig. 9.

Normalized temperature profiles for $V_z = 0.5$ m/s at 1M concentration and 6 M concentration at three z locations along the reactor.

Fig. 10.
Development of the temperature profiles at $x = w/2$ ($M = 1.0$).

Fig. 11.
Development of the temperature profiles at $x = w/2$ ($M = 6.0$).

Fig. 12.

Development of the temperature profiles at $x = w/4$ ($M = 6.0$).

Fig. 13.

Heat flux values at different x values along the z direction at the lower and upper surfaces. The inset shows detail along the first 200 μm . There is sufficiently low heat flux through the PDMS surface that the traces are nearly indistinguishable for all positions across the channel (dashed lines, top of the plot).

Table 1

The constants used for the Arrhenius reaction rate equation.

<i>A</i>	<i>E_a</i> (J/kmol)
1.69×10^{11}	3.33×10^6

Table 2

Enthalpy of formation and molecular weight values of the species.

	NaOH	HCl	NaCl	H ₂ O
ΔH_f^0 (J/mol)	-4.07×10^5	-1.67×10^5	-4.07×10^5	-2.86×10^5
M (kg/mol)	40.00×10^{-3}	36.46×10^{-3}	58.44×10^{-3}	18.02×10^{-3}

Table 3

Tabulated values for the energy balance benchmark calculations.

	$z = 200\text{--}400\mu\text{m}$ interval	$z = 400\text{--}600\mu\text{m}$ interval	$z = 600\text{--}800\mu\text{m}$ interval
$T_{\text{inlet}} - T_{\text{set}}$ (K)	4.07×10^{-1}	3.27×10^{-1}	2.39×10^{-1}
$T_{\text{outlet}} - T_{\text{set}}$ (K)	3.27×10^{-1}	2.77×10^{-1}	2.44×10^{-1}
$\dot{Q}_{\text{loss}}$ [W]	-8.60×10^{-5}	-6.46×10^{-5}	-5.32×10^{-5}
$\rho A_{xy} c V (T_{\text{inlet}} - T_{\text{outlet}})$ [W]	8.33×10^{-6}	5.22×10^{-6}	3.52×10^{-6}
Error (%)	1.25	0.95	0.70

Table 4

Tabulated values for the sensor position patterns.

Pattern	$x, \mu\text{m}$	$y, \mu\text{m}$	$z, \mu\text{m}$
1	10	0	20
1	10	0	50
1	10	0	Continues to exit
2	40	0	20
2	40	0	50
2	40	0	80
2	40	0	Continues to exit
3	70	0	20
3	70	0	50
3	70	0	80
3	70	0	Continues to exit
Pattern continues			