

Finite Element Approach for Reactive Microfluidic Devices

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ABSTRACT

We report a finite element method (FEM) based model for simulating microfluidic devices with chemical reactions. The simulation approach incorporates a general mesh generation procedure, which allows us to explore different application-oriented designs of microfluidic devices. Simulations, which have been validated by experiments, are used to characterize temperature and species profiles of a T-shaped microreactor. Predicted results capture the observed complex temperature behavior arising from the heat generation of catalytic reactions. Simulation tools developed in this work are demonstrated to be useful in designing a silicon-membrane based microreactor with improved heat transfer characteristics.

Keywords: FEM, simulation, microreactor, microfluidic, and reaction.

INTRODUCTION

Over the past decade, advances made in the field of micro-electro-mechanical systems (MEMS) have extended the use of miniaturization technology from mechanical actuators and sensors to microfluidic devices for bio-assays. However, only recently, has the concept of miniaturized chemical processing been considered in the chemical industry. Micromachined chemical systems, specifically microreactors, offer advantages in chemical process development and operation compared to conventional chemical reactor systems. Microreactors can serve as efficient development platforms by allowing process optimization of a single unit and subsequent scale-up by replication [1]. The ability to integrate control, sensor, and reactor functionality in microreactors offers increased flexibility over the current complex, multi-unit pilot plant environment and sets them apart from passively controlled honeycomb or capillary reactors.

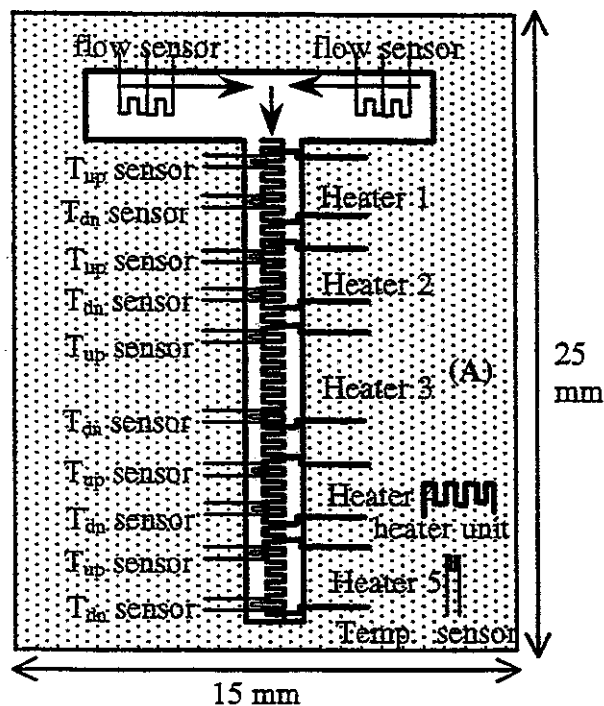
The development of microreactors is still in an early stage. To make this technology practical, several issues relating to design and device performance must be solved. Modeling tools are often used to assist design and optimization of MEMS devices. MEMS software such as MEMCAD and SOLIDIS [2-3] considers only the computation of mechanical and electrostatic domains. Interest in modeling fluid domain of microfluidic devices has increased as use of mini liquid handling systems for biological assays has grown. Finding strategies to predict pressure drops and improve thermal and mixing efficiencies are the main issues in modeling of liquid-phase microfluidic devices. Reaction chemistry modeling approaches in a

microfluidic device are not generally available and more efforts are needed. Strong coupling of fluid and thermal transport combined with chemical reactions in small dimensions is computationally more demanding compared with those non-reactive microfluidic applications.

The focus of this work is to apply our simulation methodology [4-6] to a T-shaped microreactor, to explore the reaction phenomena involved in reactors of small dimensions, and to give a framework for improving designs of new microreactors.

THE PHYSICAL SYSTEM AND COMPUTATION

A detailed description and fabrication process of the T-shaped microreactor investigated in this work has been reported by Srinivasan et al. [7]. This device consists of a 550 μm deep, 1.8 cm long T-shaped flow channel etched in a silicon wafer. The channel is capped from the top by a 1 μm thick silicon nitride membrane, and sealed from the bottom by an aluminum plate having an outlet and two inlet holes. Located on the top of the silicon nitride membrane are temperature sensors, flow sensors, and heaters, which have been patterned from 0.1 μm thick, electron-beam evaporated Pt films.



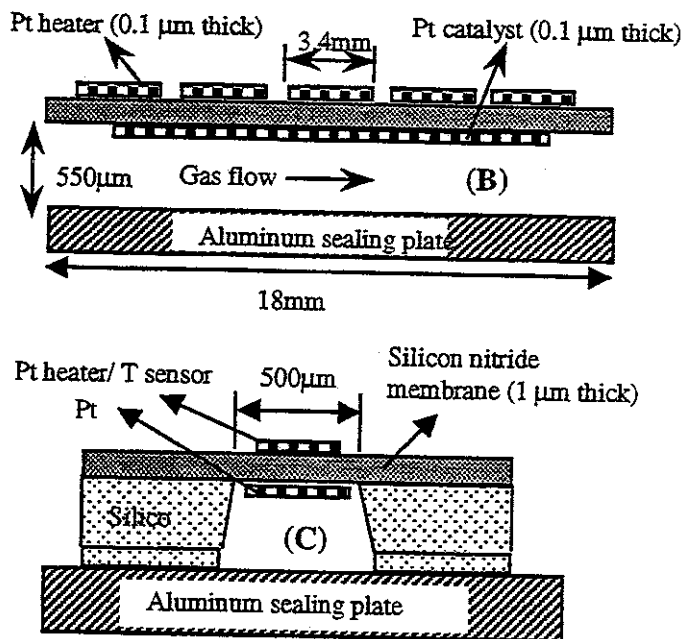


Figure 1. Schematics of the T-shaped microreactor: (A) Top view (B) Cross-section parallel to flow (C) Cross-section perpendicular to flow.

The Pt heater has five identical 3.4 mm heater units, each of which can be individually controlled. Along the flow channel, a 0.1 μm Pt film, deposited on the membrane inside the channel, defines the reaction zone for the catalyzed surface. A detailed cross-sectional view of the microreactor and the membrane layer structure are illustrated in Figure 1. Reactant gases enter the reactor from the two arms of the T, mix by diffusion at the entrance to the reaction zone, and then react on a heated Pt catalyst present on the underside of the silicon nitride membrane.

The microreactor can be modeled as two coupled computational domains; one of which is a flow channel consisting a reactive gas mixture traveling through the micro-channel towards a heated catalyst, and the other is the surrounding enclosure, which exchanges heat with the flow channel. The meandering Pt heaters are approximated as long, thin rectangular strips and only the heated section of the reactor is modeled as other areas are sufficiently cool such that reactions do not occur to any significant extent in those regions. The transport phenomena and chemical reactions within the microreactor are described by conservation equations along with appropriate boundary conditions. These equations contain properties of the gas mixture that depend on temperature, pressure, and species compositions as well as thermal properties.

The simulation approach begins with the generation of a finite element mesh of the microreactor configuration using a commercial 3D mesh generator. Particular attention is given to capturing the geometry of materials in close contact with the catalyst and membrane. Boundary conditions are assigned to surfaces and material types are assigned to the elements. Next, the equations describing transport models and chemical kinetics are discretized using Galerkin Finite Element Method (GFEM) and the resulting algebraic equations are assembled in matrix forms. Arc-length

continuation methods [8] are used to trace the ignition and extinction characteristics of a microreactor. We have developed methods for simplifying the computations. Specifically, the dimensionality of the membrane structure has been reduced from 3D to 2D by modeling heat transfer through the heater, membrane and catalyst layers as a boundary condition. Approaches for obtaining initial solutions have also been derived, which avoid regions of multiple solutions frequently encountered in ignition problems. Simulations of reaction chemistry coupled with transport phenomena are carried out in 2D. Detailed heat transfer calculations are carried out in three dimensions. A detailed description of numerical approaches used will not be reiterated here and it can be found in the papers by Hsing et al. [4,7].

CHARACTERIZATION OF MICROREACTOR

Platinum catalyzed ammonia oxidation serves as a model partial oxidation chemistry for demonstrating the microreactor technology and the associated reaction engineering analysis. This particular reaction is relatively well understood and displays competitive reaction pathways, which allow investigation of general conversion and selectivity issues in microchemical systems. Moreover, ammonia oxidation exhibits typical ignition and extinction phenomena characteristics of partial oxidation reactions. Such phenomena are useful in exploring heat transfer characteristics coupled with reaction processes. We have reported previously [4,7] that ammonia oxidation can exhibit ignition-extinction behavior in a microreactor and the simulated results demonstrated the observed upstream movement of temperature front at a low ammonia flow rate (5 std. cm^3/min). Such phenomena of temperature excursion during reactions can deteriorate integrity of the membrane, resulting in failure of the microreactor device. In this section we will use simulation tools to characterize the effects of flow rate on the T-shaped microreactor operation and suggest directions for new microreactor designs which avoid failure.

Reaction temperature

The movement of temperature front is known to be a strong function of the flow rate and reactant composition in the flow channel [4,7], thus heat transfer characteristics exhibited during reactions can be quite different at various flow rates. At small flow rates (5 sccm), the catalytic zone underneath the silicon nitride membrane is more accessible to the reactants than at high flow rates as reactants have enough time to diffuse to the catalytic surface. Reaction occurs primarily near the leading edge of the heater, causing the upstream movement of temperature. On the other hand, at high flow rates, reactants do not reach upstream catalytic surface completely because of the small residence time. As a result, reactions occur along the entire flow channel and the temperature profile of the catalytic surface is nearly uniform.

Simulated temperatures at locations of upstream and downstream sensors (Figure 2) show good agreements with measurements. Upstream temperature is much higher than

downstream at low flow rates. The downstream temperature increases with increasing flow rate. The temperature along the heater segment is uniform for flow rates higher than 30 sccm. The upstream temperature remains around 600°C regardless of the flow rate because sufficient NH_3 is available upstream, causing a constant temperature rise by the heat from surface oxidation reactions.

Simulated temperature isotherms along the flow channel at different flow rates (Figure 3) illustrate the movement of temperature from upstream to downstream at ignition. The temperature peak is broader at high flow rates than that of low flow rate (~ 5 sccm). Thus, the local thermal stress that damages the membrane structure could be eased at high flow rate conditions.

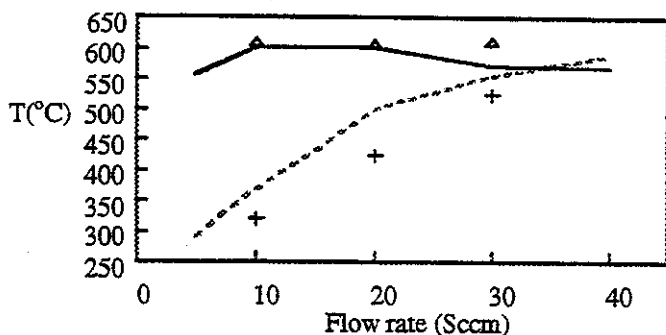


Figure 2. Simulated and measured temperature at locations of upstream and downstream sensors at different flow rates. Solid and dash lines are simulated data at locations of upstream and downstream respectively. (Δ) measured data upstream, (+) measured data downstream. Conditions: mixture of ammonia and oxygen at 1 atm pressure, mole fraction of NH_3 10% and O_2 90%, and heater power = 240 mW.

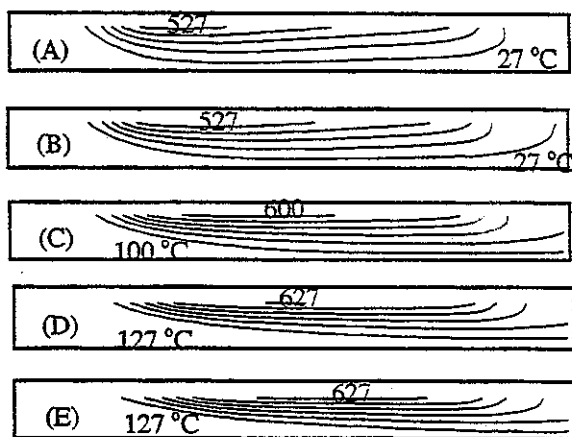


Figure 3. Temperature isotherms along the reaction flow channel of the microreactor at different flow rates. (A) 5 sccm, (B) 10 sccm, (C) 20 sccm, (D) 30 sccm, (E) 40 sccm. Temperature increment at each contour level is 100 °C. Condition, as in Figure 2.

The increase in temperature of the gas as it flows over the heated catalyst increases the flow velocity. Because the temperature front moves downstream with increasing flow rates, a similar pattern also follows for the velocity contours

(Figure 4). The large temperature gradient in the flow channel justifies the use of the equation of state to describe the temperature dependence of the mixture density.

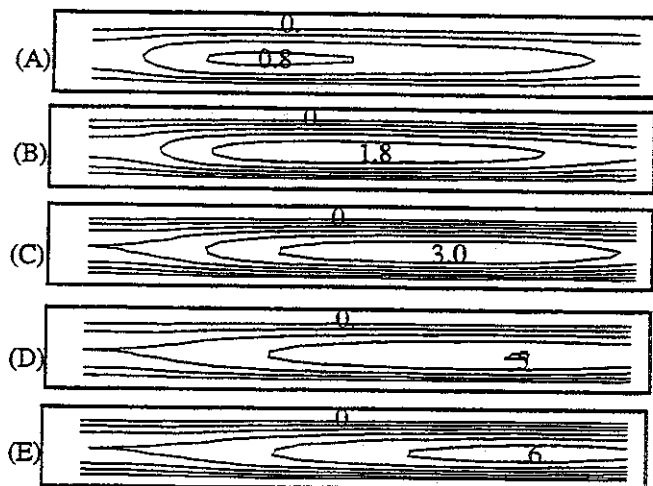


Figure 4. Velocity contours in the flow direction at different flow rates. (A) 5 sccm, Peclet number, $Pe=6$, velocity increment at each contour level: 0.2. (B) 10 sccm, $Pe=13$, velocity increment at each contour level: 0.3. (C) 20 sccm, $Pe=25$, velocity increment at each contour level: 0.5. (D) 30 sccm, $Pe=38$, velocity increment at each contour level: 1.0. (E) 40 sccm, $Pe=50$, velocity increment at each contour level: 1.0. Conditions, as in Figure 2.

For high-flow-rate convection dominated conditions (>30 sccm) we use the Streamline-Upwinding-Petrov-Galerkin (SUPG) FEM [9] to discretize the governing equations. At a flow rate of 40 sccm, the Reynolds number can be as high as 200 within the high-temperature region of the channel. For such high Re number flow, standard GFEM technique will fail and exhibit unrealistic wiggles in the velocity solutions.

Concentration and conversion

NO and N_2 are the major products from catalytic ammonia oxidation reactions. Production of N_2 is mainly from the reaction between ammonia and nitric oxide at the catalytic surface. The selectivity of NO to N_2 can be increased if NO in the bulk is deterred from readsorbing back to the catalytic surface to produce N_2 . NO concentration contours (Figure 5) reveal that at low flow rates and high residence time, significant NO is produced in the reaction channel. As the flow rate increases, i.e., reactant residence time decreases, a thin mass boundary layer develops along the catalytic surface. At high flow rates (30 and 40 sccm), NO production is only significant close to the catalytic surface, while most of the NH_3 bypasses the catalyst, remaining unreacted. Nitrogen concentration (Figure 6) reveals that nitrogen is mainly produced at the downstream catalytic zone because its production requires NO at the catalytic surface. At a very high flow rate (40 sccm), nitrogen concentration is significant at the very downstream catalytic surface. This suggests that a design improvement for a higher selectivity of NO to N_2 could be achieved if the catalytic film is only placed underneath the Pt heater area instead of covering the

whole surface underneath the silicon nitride membrane. The average conversion of ammonia increases with decreasing flow rate of reactants; i.e. increasing contact time. Simulations and experiments show a good agreement (Figure 7) and suggest that reactions are mainly mass transfer limited after the ignition.

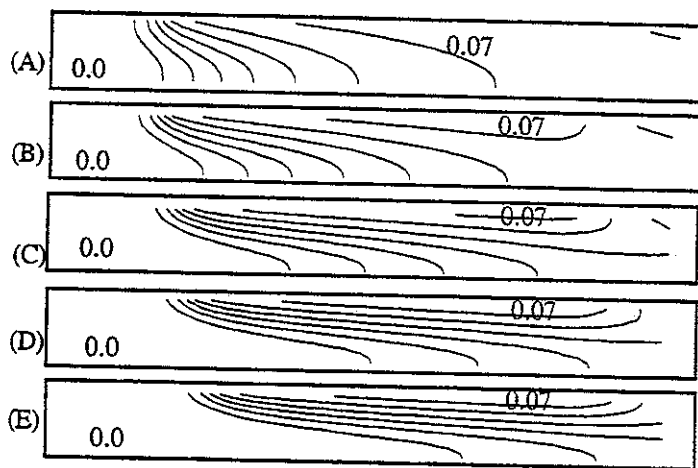


Figure 5. Nitric oxide concentration profiles in the microreactor at different flow rates. Mole fraction increment at each contour level: 0.01. Conditions as in Figure 4.

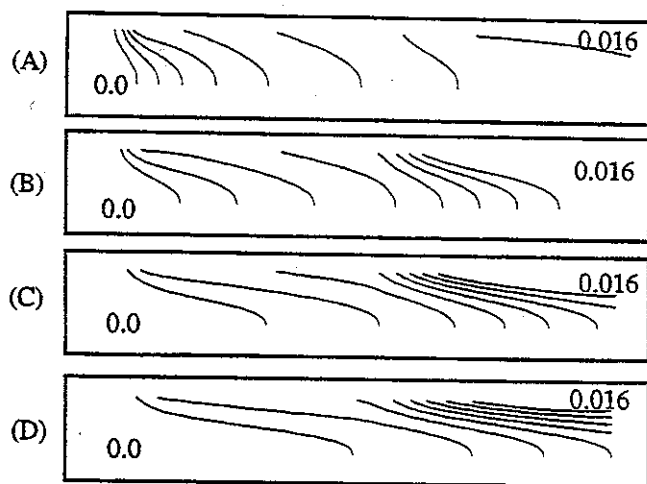


Figure 6. Nitrogen concentration profiles in the microreactor at different flow rates. Mole fraction increment at each contour level: 0.002. Conditions as in Figure 4.

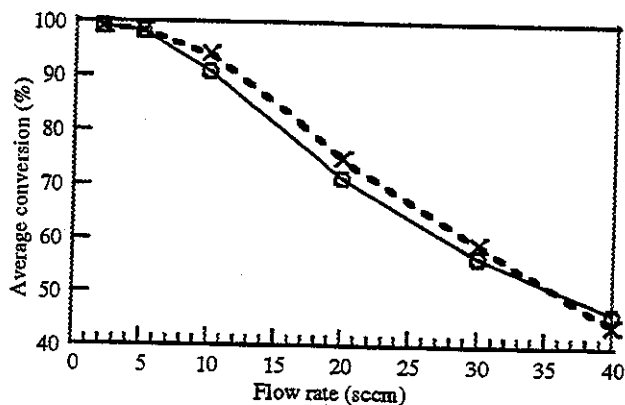


Figure 7. Average conversion of ammonia as a function of flow rate. X: simulation, O: experimental data.

SIMULATION FOR DESIGN IMPROVEMENT

We have used the detailed simulations to increase our understanding of the behavior of microreactors and to provide guidelines for the design of new microreactors. Simulation and experiment discussing in the previous section indicate that the T-shaped microreactor is efficient at removing heat from the reaction front, but suffers from a non-uniform temperature distribution over the catalyst. The T-shaped microreactor exhibits an upstream temperature movement at low flow rates. Such movement of temperature front could deteriorate the membrane integrity and damage the microreactor operation. Conversion in the T-shaped microreactor is controlled by the mass transfer rather than by catalytic surface kinetics. Therefore, at high flow rates, i.e., small residence time, reactants bypass the catalyst and conversion is reduced. As indicated above, the current design of SiN_x membrane based microreactor requires further improvements, specifically in the areas of heat removal rate and product conversion. In the following sections, we will demonstrate the use of simulations as a design vehicle to improve the performance of the T-shaped microreactor.

Heat transfer

Heat transfer rate is one of the key issues in the design of a microreactor for fast, highly exothermic reactions. To take advantage of the improved temperature control capabilities of a microreactor, it must be designed in such a way that the rate of heat removal is greater than the rate of heat generation to avoid the big temperature jump often encountered in partial oxidation reactors. However, if one blindly designs a microreactor with an extremely high heat transfer rate, this may result in a unit with an excessive power requirement. In the T-shaped microreactor design, heat provided by the Pt heater is conducted through silicon nitride layer to reach the catalyst to turn on the surface reaction. On the other hand, heat generated by reactions is removed mostly by conduction through the nitride membrane to the bulk silicon surrounding the reaction

channel. The temperature excursion behavior at low flow rates as shown by the experiment and simulation reveals that the heat removal rate of such microreactor needs to be improved.

We have used simulation tools that were developed for the SiN_x -membrane based microreactor [4-6] to simulate a silicon-membrane based microreactor prior to its fabrication and to evaluate its performance and power requirements for reaction ignition. Unlike the SiN_x microreactor, the silicon microreactor has a $3\ \mu\text{m}$ silicon instead of a $1\ \mu\text{m}$ SiN_x as the catalyst-support membrane. Because the high thermal conductivity of Si ($146\ \text{W/m-K}$), the silicon microreactor provides better heat transfer characteristics and thus the movement of temperature front arising from the heat of reaction can be better controlled. In contrast to the SiN_x microreactor [7], the silicon microreactor exhibit no ignition-extinction behavior in the ammonia oxidation process. The reactor can therefore be operated in a continuous temperature regime often infeasible in conventional catalytic reactors. However, the improved heat transfer also implies that silicon microreactor requires higher heater power to initiate the reactions. 3D heat transfer simulations reveal that an order of magnitude higher electric power than for the SiN_x microreactor is needed to increase the catalyst temperature from room temperature to around 200°C , the temperature required to ignite ammonia oxidation. Simulations have been useful in predicting the range of power requirement needed ($\sim 1\text{-}2\ \text{W}$) and predicted results show a good agreement with experimental data (Figure 8).

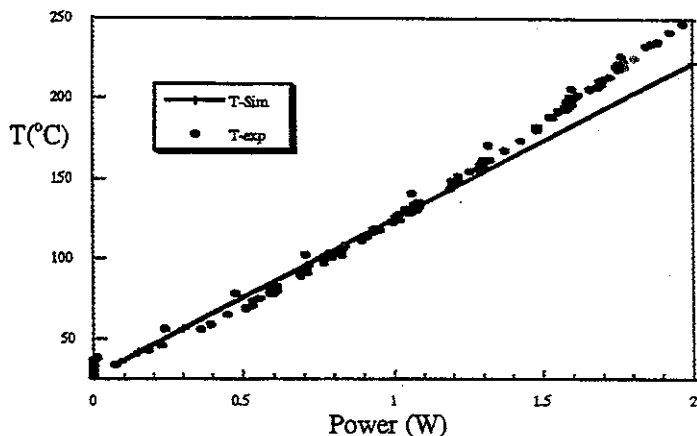


Figure 8. Simulated and measured temperature as a function of heater power for the silicon-membrane microreactor.

Mass transfer

Mass transfer to the catalytic surface governs the overall product conversion. As illustrated in the previous section, although the T-shaped microreactor has a very large surface-to-volume ratio, a relatively small fraction of the reactants diffuses to the catalytic surface. At high flow rate conditions, reactants are swept out of the reactor before they can reach the catalytic surface. It has been shown that the conversion efficiency is related to the ratio of the thickness of the mass boundary layer to the channel height [6]. Thus, the conversion can be increased with reducing the channel

height and this design modification can be done experimentally by molding a ceramic insert that is placed inside the reaction channel. Simulations show that this solution is effective and the average conversion can be increased about 20% even at high flow rates (Figure 9). More simulation studies are needed to find an optimum design parameter because the narrow channel could cause too high gas velocities, which may impose a kinetic limitations on the conversion.

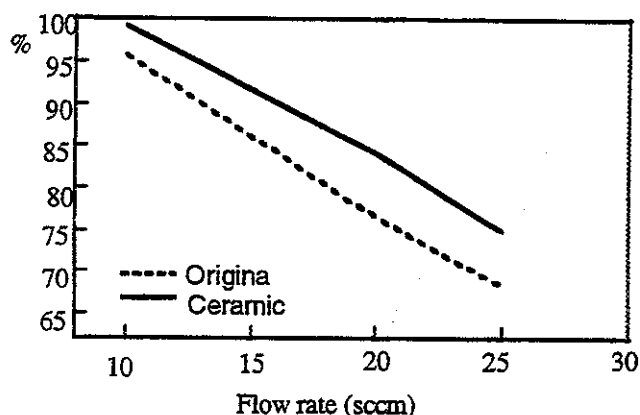


Figure 9. Comparison of reactant conversion as a function of flowrate for the original microreactor and the microreactor with the ceramic insert.

CONCLUSIONS

As the development and understanding of catalytic microreactors increases, these systems will likely find growing applications in industry. To successfully design, implement, and optimize microfabricated systems, a thorough understanding of the underlying physics and chemistry is necessary. This work demonstrates that detailed FEM analysis can be used to simulate heat transfer and reaction processes in microchemical systems. Using knowledge acquired from simulations, new, improved microreactors may be fabricated. The simulation methodology developed here could provide a framework for the evaluation of transport and reaction processes in more complex microreactor designs and scale-up. Ultimately, the reaction engineering simulations should become design tools along side standard MEMS tools for layout and fabrication.

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