**TITLE**: Hydrogen Generation for Portable Fuel Cells: Design of Reverse-Flow Catalytic Microreactors for Optimal Functionality, Manufacturability, and Low Cost

**SHORT TITLE**: Catalytic Microreactor for Hydrogen Generation

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# SUMMARY

Continuous decrease in size and enhanced performance of modern portable electronic devices put an ever-increasing demand on highly efficient, “palm” power generation. The existing battery technologies become major obstacle to the future advances of portable communication devices, and the fuel cell based energy sources appear to be the only viable candidate for battery replacement because of their potentially very high efficiency and ultra-high density of energy generation. In many cases, hydrogen is a preferred fuel for use in fuel cells because of its very high energy density (25-200 $mW/cm^2$), and this paper discusses the issue of “palm-scale” hydrogen generation in catalytic microreactors from the prospective of an innovative reactor design and optimization of surface catalyst loading that result in the optimal functionality, manufacturability, and low cost of the system.

# INTRODUCTION

During last decade, our society has witnessed spectacular progress in miniaturization and increase in processor power of portable electronic devices. The laptop computers started this revolution, the handheld computers are becoming prevalent now, and the “smart”, internet-connected mobile phones are considered to take over in the near future. Fueled by the advances in wireless communication technologies and Internet, a competitive portable electronic device must have an increased intelligence (computation), feature broad connectivity (bandwidth), and be always on. These requirements put an ever-increasing demand on development of small-scale (i.e., ranging from 0.5 W for a simple hand-held PDA to ~20 W for a notebook computer), highly efficient, “palm” power sources (Hallmark, 2002). Unfortunately, improvements in power technology have not kept up with the Moore’s Law for the rate of an increase in computation power and bandwidth (Gottesfeld, 2002). The existing battery technologies become major obstacle to the future advances of portable communication devices, and the fuel cell based energy sources appear to be the only viable candidate for battery replacement because of their potentially very high efficiency and ultra-high density of energy generation. Two main types of fuel cells are currently being actively developed for portable applications: these are the hydrogen-based fuel cells with external methanol reformation (i.e., conversion to hydrogen) and the direct-methanol fuel cells, in which methanol is reformed internally within the cell anode (Gottesfeld, 2002; Hallmark, 2002). In many cases, hydrogen is a preferred fuel for use in fuel cells because of its very high energy density (25-200 mW/cm$^2$) (Hallmark, 2002).

Conversion of methanol into hydrogen gas can be accomplished via different techniques. Among various alternatives, production of the hydrogen rich synthesis gas ($H_2$/CO mixture with some $CO_2$, $H_2O$, and $N_2$) followed by the hydrogen separation from the stream is one of the most economically plausible processes for hydrogen generation from the commonly available hydrocarbon fuels. The catalytic conversion process is based on either catalytic partial oxidation ($CH_3OH + ½ O_2 \rightarrow CO_2 + 2H_2$) or steam reforming ($CH_3OH + H_2O \rightarrow CO_2 + 3H_2$) of methanol. Each approach has its fundamental advantages and its limitations: partial oxidation is exothermic (i.e., heat is released as a result of reaction) and offers compactness, fast start-up, and rapid responses to the feed change; steam reforming is endothermic (i.e., requires external heating) but produces higher concentrations of hydrogen and results in higher system efficiencies (Edwards et al., 1998). Clearly, there is an opportunity to combine a strongly exothermic partial oxidation of the fuel with endothermic heterogeneous steam reforming to achieve much higher efficiency of the hybrid process. Further, since the overall process is slightly exothermic, it can be effectively executed in the reverse-flow catalytic reactor (Matros, 1996, Avci et al., 2001). In this transient regime, the reactor is first preheated to a uniform temperature of 600-800$^{o}$C, and then it continuously operates via autothermal heat regeneration accomplished by periodic flow reversal. In other words, as the up-stream part of the reactor is progressively cooled down by the cold reactants, the methanol partial oxidation takes off and the temperature wave propagates through the reactor in the direction of the flow. The flow is reversed before the reaction zone reaches the exit of the reactor, and this causes the high temperature wave front to move in the opposite direction. Thereby, the heat is effectively retained inside the catalytic reactor, and no additional external reheating is needed. In addition to favorable autothermal operation, the oscillatory motion of the high temperature wave in the reactor leads to gasification and removal of the carbon/soot, which is potentially deposited on the catalyst due to endothermic methane cracking and exothermic Boudouard reaction. The reverse-flow operation of the reactor makes it possible to generate and control the spatio-temporal patterns of temperature, concentrations and catalyst states that cannot be attained under the steady-state operation. The transient operation provides thermodynamically favorable conditions for reversible reactions (i.e., declining temperature profiles for exothermal reactions and increasing temperature profiles for endothermic ones) to achieve maximum reaction conversion and selectivity. It also offers opportunities for exploiting catalyst dynamic properties, and results in lower average operating temperatures, thereby reducing pressure drop and heat losses (Matros, 1996).

Recent advances in microfabrication have led to development of compact chemical microreactors in the USA, Europe, and Japan for various applications, especially where on-demand, small-scale production of chemicals is of interest. The chemical processing rates in heterogeneous microreactors increase significantly due to a decrease in the resistance to the species transport caused by a drastic reduction in the thickness of the boundary layer. Ideally, with a decrease in the channel size (diameter), one hopes to achieve reaction kinetics at its intrinsic rate and to maintain sufficiently large reactor throughput by using the parallel chemical processing in many small channels comprising the reactor. In addition to rapid heat and mass transport, the miniaturization of chemical reactors results in high productivity rates due to fast non-equilibrium surface chemistry as well as in opportunities for energy and chemical conversion at the optimal locations (Jensen, 2001).

Size limitations pertinent to portable electronics applications and attractive opportunities for process intensification associated with microscale stimulated several attempts to design, fabricate, and test micromachined chemical reactors for hydrogen generation for portable fuel cells. The most notable examples are the early efforts by the researchers at the Pacific Northwest National Laboratory (PNNL) and more recent efforts by the Motorola Energy Technology Labs. Despite apparent advantages of a combined partial oxidation and steam reforming approach to hydrogen generation, both groups decided to focus on a single reaction systems: the PNNL explored catalytic partial oxidation microreactor (Tonkovich et al., 1999), whereas Motorola has been developing a steam reforming microreactor (Hallmark, 2002). The major efforts of both groups went to developing the manufacturing technology for the microreactor fabrication, and unfortunately, the issues of design of MEMS chemical reactors for optimal functionality, manufacturability, and low cost have been essentially neglected. The critical importance of these issues to the future advances in the field of microchemical engineering was probably best described by Jensen (2001) in his recent review: “ The real value of the miniaturization effort, however, would be in exploring new reaction pathways and finding economical and environmentally benign solutions to chemical manufacturing. It will be important to exploit characteristics resulting from the small dimensions beyond the high transport rates…The need to develop novel structures with controlled surface characteristics suggest that microreactor fabrication must go beyond classical micromachining and silicon MEMS techniques”.

During the last two years, we have been focusing our efforts on developing and proving new design concepts and quantifying the advantages of the autothermal reverse-flow catalytic microreactors for hydrogen generation for portable fuel cells. In this paper, we summarize our experience and discuss the key design challenges faced by the developers of portable fuel processing microreactors. Major emphasis is placed on an example-based case study on the urgent need to develop simple, yet unconventional designs of the fuel-processing chemical microreactors that (1) leverage advantages offered by microscale, (2) are compatible with MEMS planar fabrication technology and (3) are low in cost, in order to indeed be able to exploit potentially enormous benefits of the chemical processing on the small scale.

## MICROREACTOR DESIGH FOR FUNCTIONALITY AND MANUFACTURABILITY

A reverse-flow microreactor for hydrogen generation must include (1) a mixing chamber where chemical reagents (methanol, water, and oxygen/air) are being mixed prior to introduction to the reaction chamber/section, (2) the flow-reversal valve(s), (3) a reaction chamber/section where the reaction(s) is being executed, and, finally, (4) the pipes and manifolds that connect the system components 1, 2, and 3 together to establish a complete, operational system. Among most desirable design characteristics of the complete system are (*i*) the flow-reversal valve needs to have the dead volume as small as possible (ideally zero) to minimize the cross-talk between the unreacted reagents and reaction products immediately after flow reversal and, thus, to eliminate the need for purging the reactor; (*ii*) the valve(s) design must be amenable for simple actuation to ensure overall system robustness and energy efficiency; (*iii*) the connecting pipes and manifolds should be reduced to a minimum or, ideally, eliminated all together, and (*iv*) it should be possible to place the mixing and reaction chambers in optimal locations to achieve additional functionality (for example, to use waste heat generated in the reaction chamber of the exothermic catalytic reactor to preheat the reagents in the mixing chamber to increase mixing and energy efficiency).

When dealing with chemical microsystems, in addition to specific functional requirements imposed on the reactor design/configuration by the process of interest (as described above), the MEMS (2-D or 2-1/2-D) fabrication technologies impose further requirements on the design and component integration of reverse-flow microreactors: that is the planar layout of individual components and stackable (layer-by-layer) integration of components are essential for low-cost fabrication and system scale-up.

To address both the functional and manufacturing challenges, we developed a unique design of the planar reverse-flow microreactor that permits efficient (i.e., without any pipes or connecting manifolds) integration of a mixing chamber, a zero-dead-volume rotating valve, and a reaction chamber within a simple and easy to manufacture reverse-flow system that could be made as small as a dime. The schematic of the design and operating principles of the proposed system is shown on Fig. 1, and Figure 2 shows the photographs of the prototype reverse-flow reactor, built out of stainless steel on the “large” scale for demonstration purposes. By inspection of Figs. 1 and 2, it should become clear that the flow reversal is accomplished by the rotation of the mixing chamber (cover plate) over a small angle about the fixed central axis/screw (also used for the system assembly), thereby making sequential connection of the flow reversal switch channels of the reaction chamber (bottom plate) to the mixing chamber/channel made in the top plate. A low-power rotary motor mounted on top of the mixing plate with a voice-coil controller can be readily integrated with a system for automatic switching of the flow direction according to an established protocol for the dynamic process. It should be noted that it is desirable to utilize the heat generated as a result of the exothermic partial oxidation reaction to preheat the feed gases as they introduced into the mixing chamber, and this is accomplished within proposed design ideology by placing the reaction chamber in the immediate vicinity but inside the mixing chamber to capture the heat escaping the reaction chamber in a radial outward direction. Also note that, although single circular channels were chosen for the mixing and reaction chambers of the prototype reactor (Figs. 1 and 2), these chambers can be made as complex as one wishes (e.g., a spiral or a Swiss roll configuration) depending on the specific design requirements of a given application (Sitzki et al., 2001).

## MICROREACTOR DESIGN FOR LOW COST

To minimize the cost of heterogeneous catalytic systems, which is primarily determined by the amount of the chemically active catalyst, usually highly expensive noble metals or alloys, we developed a unique approach for significant reduction of the catalyst loading by optimal structuring of active catalyst surfaces in the heterogeneous chemical reactors and fuel cells (Phillips et al., 2002). Intuition tells us that any decrease in the active (i.e., loaded with catalyst) surface area should result in an equivalent decrease in the reaction yield and efficiency. However, our theoretical analysis based on solving coupled mass and momentum conservation equations for the reacting mixture over the heterogeneous catalytically active surface (Phillips et al., 2002) shows that the active surface and hence the catalyst loading can be reduced drastically in the diffusion-limited heterogeneous reaction systems, while the conversion rate remains essentially unchanged by using fractals for spatial distribution of the catalyst load. Mathematically, this result owes to optimal placement of singularities in the boundary conditions at the points where the active surface meets the inactive surface. The local mass flux goes asymptotically to infinity near the singularities, thereby establishing a mechanism for conserving the total rate of chemical conversion despite significant reduction in the catalytically active surface area.  The pertinent question is then how can the singularity be manipulated in order to minimize the active surface area while maintaining the total rate of chemical conversion unchanged? We demonstrate that the answer to this question is in using fractal structuring of the active surface. Essentially, the procedure is the following: a given portion from the center of each segment of active surface is removed repeatedly, thus reducing the surface towards zero and consistently adding more singularities to maintain the total rate of chemical conversion. This configuration is known as a Cantor set, and the first four fractal iterations are shown in Fig. 3. The simulation results indicate (Fig. 4) that introduction of periodic singularities into the boundary conditions through fractal structuring of the active surface allows a 76% reduction in the catalyst loading while losing only 2.25% of the original rate of chemical conversion when only transport by diffusion is considered. We also found that the effect of fractal structuring of the active surface is the most profound to the design of micro/nano scale chemical systems, for which the Peclet number is intrinsically small due to the small characteristic length scale. Specifically, a 76% reduction in the active surface area by fractal structuring corresponds to only approximately a 4% decrease in the total mass transfer rate when Pe=1, whereas the total rate of mass transfer decreases by as much as 20% and 40% for Pe=1000 and $Pe=10^6$, respectively. Thus, introduction of periodic singularities into the mass transfer boundary condition is ideally suited for drastically lowering the cost of chemical microreactors and micro/nanoporous electrodes of fuel cells, and this phenomenon can be exploited to its fullest extent by utilizing the advances in our abilities to manipulate matter on the micro/nano scale (Kenis et al., 1999; Jensen, 2001).

## CONCLUDING REMARKS

This paper discusses the issues of “palm-scale” hydrogen generation in catalytic microreactors from the prospective of innovative and highly integrated design aimed at optimal functionality, manufacturability and low cost. The importance and opportunities for innovative approaches to design of microchemical systems are demonstrated on the example of reverse-flow catalytic microreactor for highly efficient, autothermal hydrogen production via combined partial oxidation and steam reforming of methanol. We also present an approach for drastically lowering the cost of catalytic microreactors through minimization of the catalyst loading achieved by fractal structuring of chemically active surfaces. Finally, although the focus of the paper on chemical microreactors for hydrogen production, the design approaches and recommendations presented here are of the fundamental nature and applicable to microchemical systems in general.

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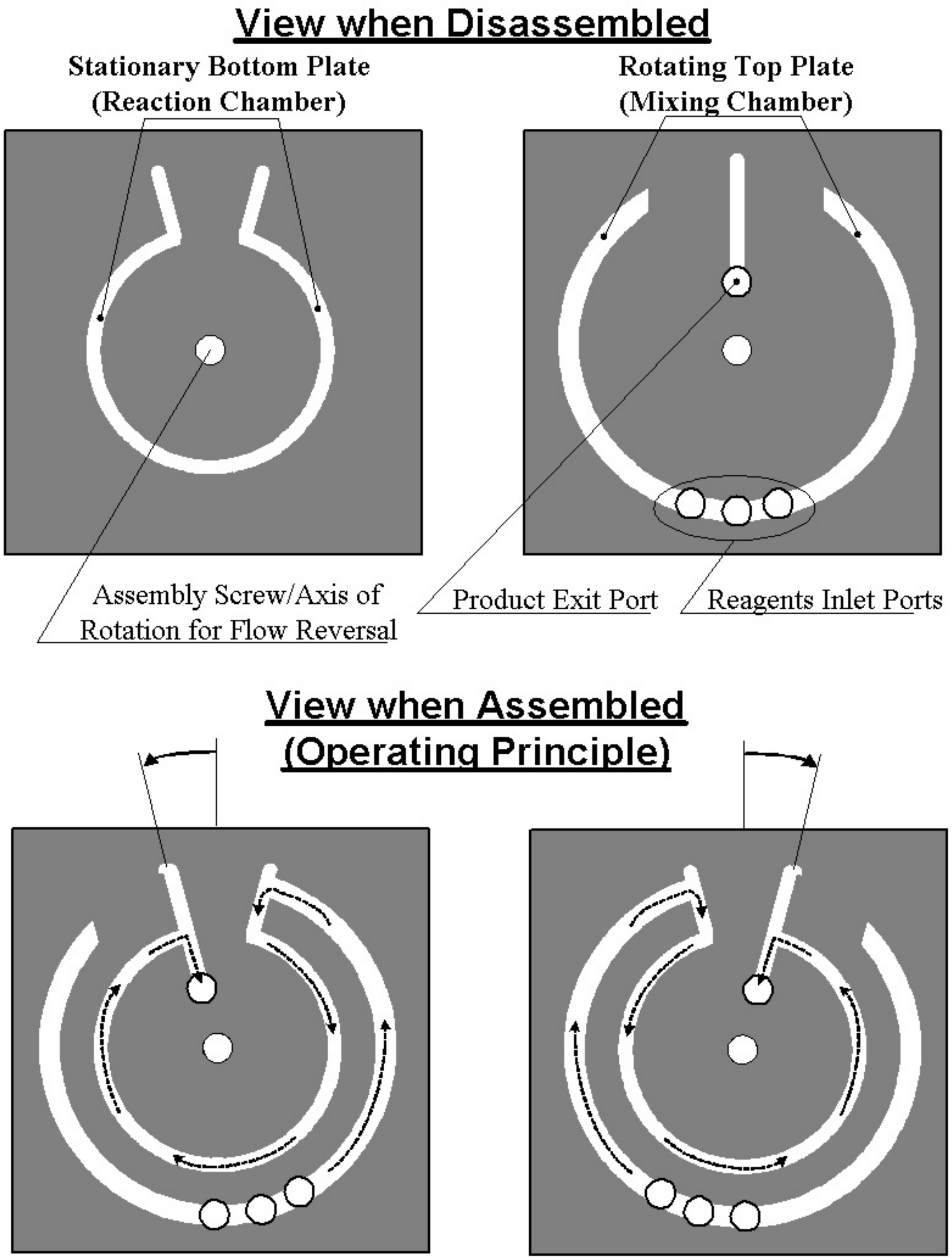
# FIGURE CAPTIONS

**Fig. 1**: Design and operating principle of planar catalytic microreactor with zero dead volume switching valve for flow reversal (patent pending).

**Fig. 2**: Fabricated reverse-flow microreactor with zero dead-volume flow switching valve (patent pending): (a) photograph when assembled; (b) photograph when disassembled.

**Fig. 3**: Schematic of the fractal structuring of the catalytically active surface.

**Fig. 4**: Effect of the fractal-based reduction of the catalyst loading on the rate of mass transfer (pure diffusion case): (A) Dimensionless total mass transfer rate to the active surface (equivalent to the rate of chemical conversion) as a function of fractal iterations; (B) Loss of the total mass transfer rate (relative to the nominal rate when the entire surface is catalytically active) as a function of the reduction in the catalytically active surface area.



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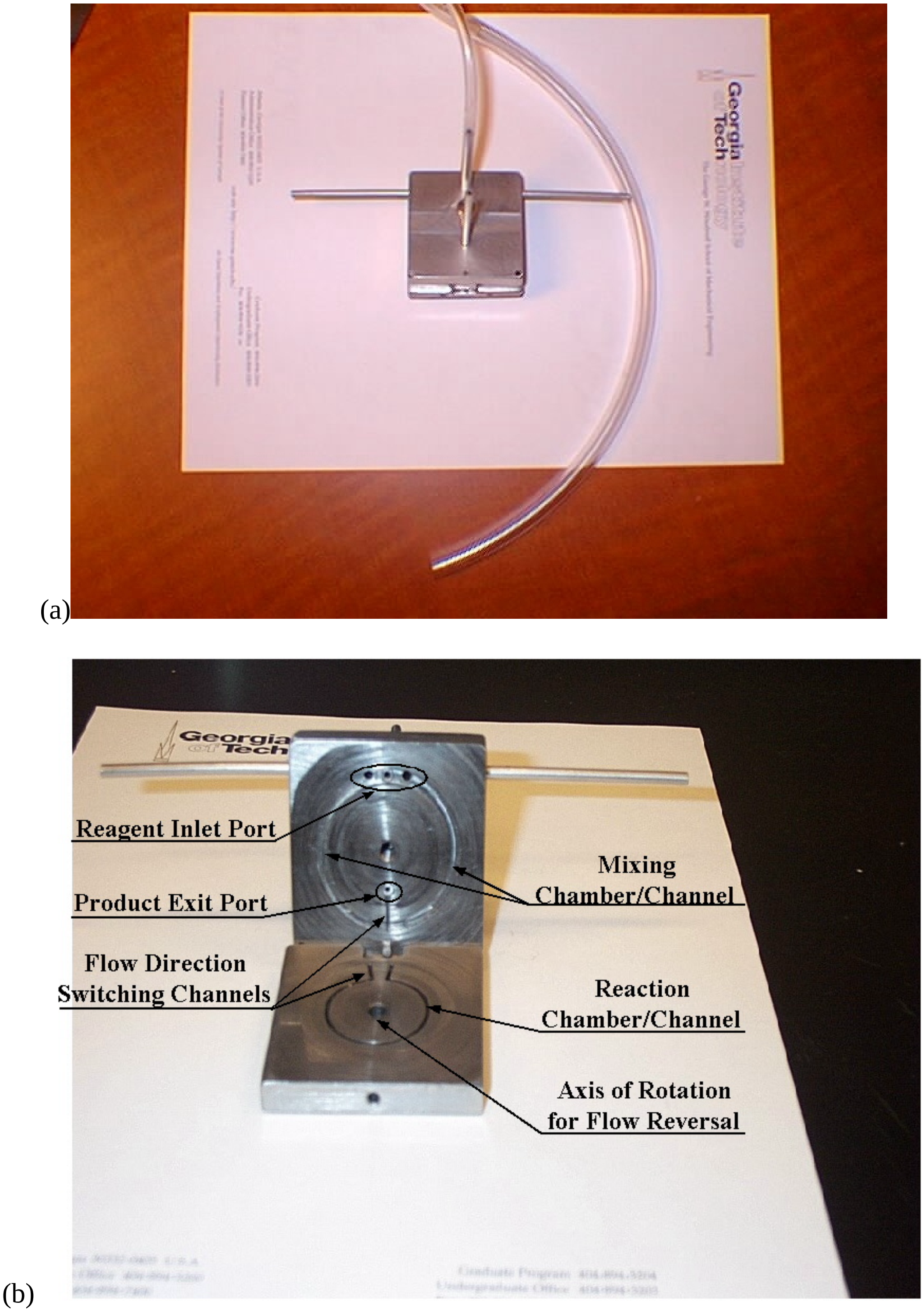
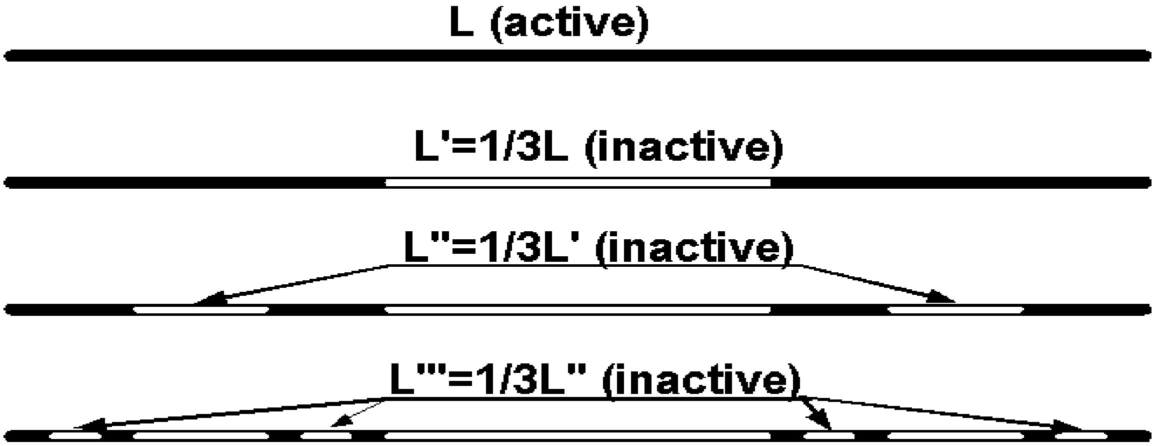


Fig. 2: Fabricated reverse-flow microreactor with zero dead-volume flow switching valve (patent pending): (a) photograph when assembled; (b) photograph when disassembled.



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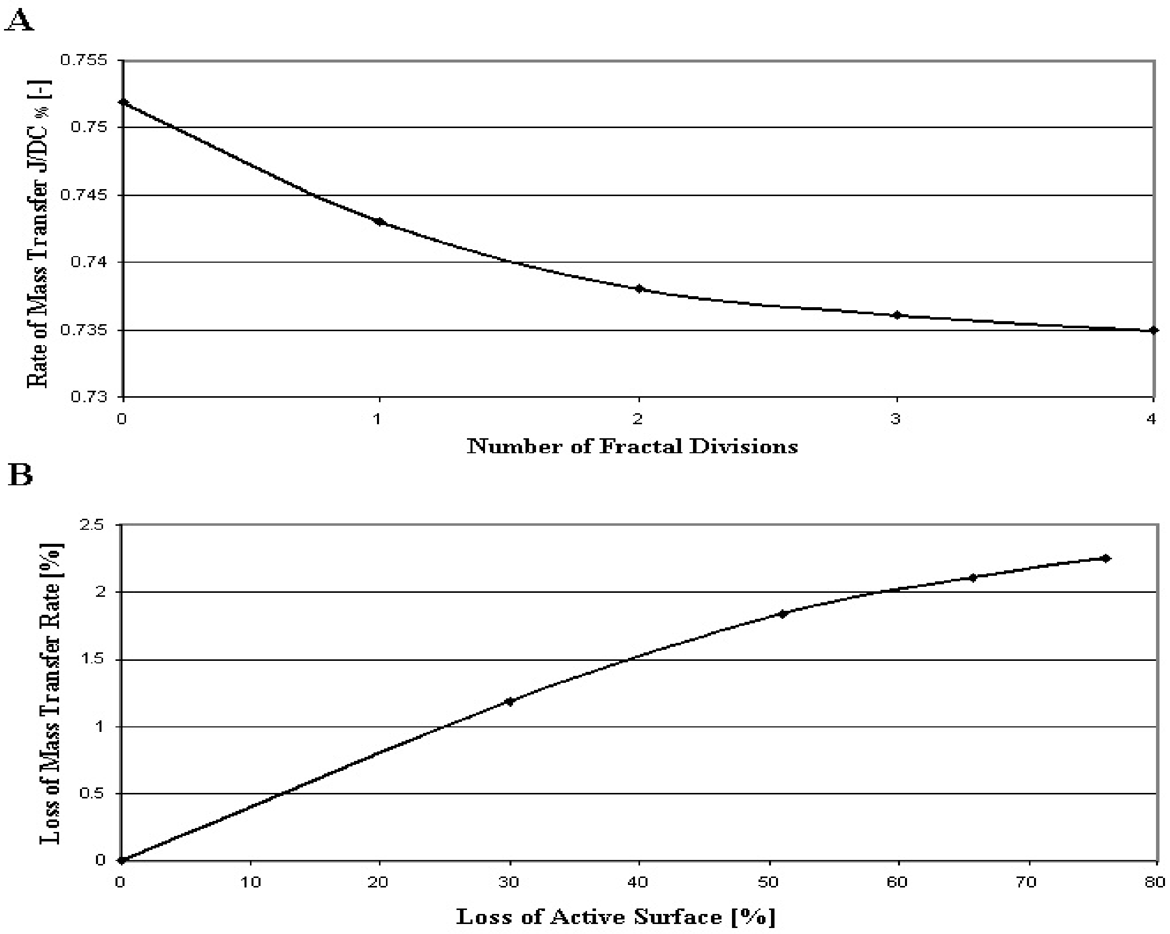

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