

# Distribution characteristics of temperature and species in micro-structured heat-exchanger reactors

Junjie Chen

Department of Energy and Power Engineering, School of Mechanical and Power Engineering, Henan Polytechnic University, Jiaozuo, Henan, 454000, P.R. China

\* Corresponding author, E-mail address: [cjjtpj@163.com](mailto:cjjtpj@163.com), <https://orcid.org/0000-0002-4222-1798>

## Abstract

Microchannel reactor designs suffer from a fundamental limitation resulting from the flow configuration in which a reacting stream flows parallel to a heat transfer surface through which the majority of heat is transferred perpendicular to the direction of fluid flow. The present study aims to provide a unique microchannel fluid processing system for performing chemical reactions with temperature control. The present study relates to a unique method for performing reversible endothermic, exothermic reactions, and competing reactions. The method comprises flowing reactants through a reaction channel in thermal contact with a heat exchange channel, and conducting heat in support of the reaction between the reactants and fluid flowing through the heat exchange channel to substantially raise or lower the temperature of the reactants as they travel through the reaction channel. Particular emphasis is placed upon how to provide improved conversion and selectivity in chemical reactions, provide chemical reactor systems that are compact, and provide thermally efficient chemical reactor systems. The distribution characteristics of temperature and species in micro-structured heat-exchanger reactors are investigated and the reactor performance is evaluated by performing numerical simulations using computational fluid dynamics. The results indicate that microchannel technology is capable of high heat and mass transfer coefficients between a bulk reaction fluid and the catalytic heat exchange surface. Carbon monoxide output from the fuel processor is controlled over the operating range of the processor. When the reaction in the reaction chamber is a reversible exothermic reaction, heat is generated in the reaction chamber and transferred to the heat exchange fluid. Microchannel reactors offer less resistance to heat and mass transfer thus creating the opportunity for dramatic reductions in process hardware volume. While a steam reforming catalyst in the form of a powder or pellets is appropriate in larger devices, diminished performance may result in the form of a powder or pellets in miniature devices and reactors. The steam reforming catalyst contains a suitable amount of at least one metal oxide and cerium to contribute to high methanol conversion properties. The shift reaction increases hydrogen yield while reducing carbon monoxide. Microchannel reactors offer the advantage of exceptional heat exchange integration and can be utilized for approaching optimum temperature trajectories for exothermic, reversible reactions.

**Keywords:** Distribution characteristics; Chemical kinetics; Temperature trajectories; Fluid streams; Thermal gradients; Reaction selectivity

## 1. Introduction

For some reactions, for example certain single reactions that are chemically irreversible or endothermic, maximizing the reaction temperature is often desired because both kinetics and conversion increase with increasing temperature. However, for many reactions, trade-offs exist between kinetics, equilibrium, and reaction selectivity [1, 2]. For example, reversible exothermic chemical reactions generally exhibit improved reaction kinetics but lower equilibrium conversion with increasing

temperature [3, 4]. Lowering the reaction temperature favors higher conversion but typically requires more catalyst and a larger reactor [5, 6]. Accordingly, more efficient utilization of catalyst and reactor resources for a desired conversion likely requires a non-uniform temperature trajectory for the reactants as they progress through the reaction process. For example, for a single reversible exothermic reaction, such as the water-gas-shift reaction, a theoretical optimum temperature trajectory would start at a high temperature to take advantage of fast kinetics and proceed in monotonically decreasing fashion to lower temperatures to improve conversion [7, 8]. More complex optimum temperature trajectories are possible with reaction sequences or competing reactions.

There are also reasons related to energy efficiency and energetic efficiency to control the temperature trajectory of chemical reactions. For both endothermic and exothermic chemical reactions, greater thermodynamic reversibility, and therefore greater system efficiency can theoretically be achieved with reaction temperature control [9, 10]. One conventional method for controlling the temperature trajectory for exothermic reactants as they flow through a reactor system is to employ a sequence of separate adiabatic reactors and heat exchangers [11, 12]. In this approach, the outlet stream from one adiabatic reactor is cooled in a heat exchanger prior to being fed to the next successive reactor. However, within each reactor, the temperature increases down the length due to the heat of reaction. Consequently, a plot of the temperature through the series of reactors is saw-toothed rather than monotonically decreasing. A sequence of two water-gas-shift reactors with an intervening heat exchanger is the typical approach for fuel processors being developed to produce hydrogen from liquid fuels for fuel cell power applications [13, 14]. In this application, the outlet from a fuel reformer is fed to a pair of shift reactors in series [15, 16]. The reformat is first reacted at a temperature of about 400 °C in a high temperature shift reactor, with the outlet stream of the high temperature shift reactor cooled to a temperature of around 250 °C prior to introduction in a second shift reactor [17, 18]. Overall conversion of the carbon monoxide to carbon dioxide is typically about 90 percent. Macroscale packed-bed reactors have also been employed to improve the temperature trajectory for reversible exothermic reactions [19, 20]. However, in this reactor temperature differences between the hot and cold stream at a given cross-section are on the order of 200 °C, implying large thermal gradients across the bed and high heat transfer resistance.

Accordingly, there exists a need for improvements in the reactor design to provide reactors with improved temperature control and that enable better and more precise control of reaction temperatures [21, 22]. A microreactor, or micro-structured reactor or microchannel reactor, is a device in which chemical reactions are designed to take place in confined spaces having very small lateral dimensions [23, 24]. Currently, there are major technological issues that prevent current technology from meeting the needs of micro-structured reactors for generating hydrogen, syngas, or performing specialty chemical synthesis [25, 26]. In general, gas-phase reactions for generating hydrogen and other specialty chemicals require microfabricated components that can perform under harsh operating conditions such as high temperatures, high temperature transients, or corrosive or erosive environments [27, 28]. In general, gas-phase reactions for generating hydrogen and other specialty chemicals require microfabricated components that can perform under harsh operating conditions such as high temperatures, high temperature transients, or corrosive or erosive environments.

The present study aims to provide a unique microchannel fluid processing system for performing chemical reactions with temperature control. The present study relates to a unique method for performing reversible endothermic, exothermic reactions, and competing reactions. The method comprises flowing reactants through a reaction channel in thermal contact with a heat exchange channel, and conducting heat in support of the reaction between the reactants and fluid flowing through the heat exchange channel to substantially raise or lower the temperature of the reactants as they travel through the reaction channel. The heat exchange channel may also be a reaction channel for another

chemical reaction. It is necessary to provide effective heat exchange in an endothermic reactor to add heat of reaction and to increase reaction temperature and to provide chemical reactor systems with high heat transfer power densities and reduced temperature gradients across the catalyst. It is also necessary to provide chemical reactor systems with reduced temperature gradients across the catalyst and to manage the temperature profile in a reversible exothermic reactor system to have a high initial temperature with rapid kinetics promoting an initial rapid approach to equilibrium and cooling of the reaction as it proceeds to increase conversion. Particular emphasis is placed upon how to provide improved conversion and selectivity in chemical reactions, provide chemical reactor systems that are compact, and provide thermally efficient chemical reactor systems.

## 2. Methods

Microchannel reactors exchange heat between chemically reacting fluid streams. In this design, enclosed channels are formed by stacking plates separated by spacers, and the stack is fitted with appropriate headers so that alternating channels contain the reaction fluid with heat exchange fluid in the intermediate channels. The reaction channels can be filled with catalyst, and the heat exchange channels can have a structured packing to increase the heat exchange area. Another approach to increasing the surface area for reaction on each side of the separating plate is to add fins or other surface features. Indeed, this approach is adopted in plate-type reactor designs. Although somewhat successful, the reactor designs still add complexity and the alternating coupled reaction chambers continue to restrict the overall size of each chamber. All of these designs share the same general flow geometry where thermal energy transfers between chemically reacting fluid streams that flow parallel to and on opposite sides of a separating plate [29, 30]. These reactor designs suffer from a fundamental limitation resulting from the flow configuration in which a reacting stream flows parallel to a heat transfer surface through which the majority of heat is transferred perpendicular to the direction of fluid flow [31, 32]. Regardless of the reaction taking place in the reaction channels, its reaction rate will vary along the flow length of that channel due to changes in concentration and temperature. Balancing the heat requirements of an endothermic reaction with heat generated by an exothermic reaction flowing parallel to and on the opposite side of a separating plate is extraordinarily difficult since the endothermic reaction is likely to have a very different dependence upon concentration and temperature than the endothermic reaction. Along the flow length of the plate that divides these reactions, the heat flux through the plate that is perpendicular to fluid flow will vary due to temperature and reaction rate differences along the flow length of the plate. Since the thermally coupled reactions are so closely coupled, neither reaction can run at a significantly different reaction rate at any point along the channel length. Thus, each reaction will exhibit a peak in reaction rate at nearly the same position within the reactor with slower reaction rates before and after this peak, which leads to the need for a long reactor channel to ensure complete conversion. A specific example of this reaction rate problem encountered in the parallel flow arrangement is demonstrated by attempts to drive endothermic steam reforming with exothermic combustion in microchannel and alternating parallel plate reactors [33, 34]. A convenient way to supply heat is to couple the endothermic reaction with an exothermic combustion reaction in the heat exchange channels [35, 36]. Thus, the stacked reactor becomes an alternating series of endothermic and exothermic reactors separated by thin heat exchange walls. Unfortunately, the combustion reaction is difficult to control with convenient combustion catalysts and fuels, and most of the combustion occurs near the fuel inlet. This uneven combustion results in uneven heat transfer to the endothermic reaction and poor overall reactor performance.

Various approaches are directed to resolving the problem of uneven combustion, typically such approaches add extraordinary complexity to the stack design so as to attempt to distribute combustion along the heat exchange surface [37, 38]. The key feature of these designs is to add a fuel dispersion

channel between each unit stack consisting of combustor-reformer-combustor [39, 40]. The plate separating the combustor and dispersion channel is a porous plate that is intended to facilitate even distribution of fuel across the entire combustion chamber. Even still, the combustion reaction is somewhat uneven because air is introduced to the combustion channels at one end rather than evenly like the fuel. Moreover, the increased complexity of this design requires the addition of multiple plates and internal feed channels to keep air out of the dispersion channels, which adds to system mass, construction costs, and system limitations. A further disadvantage of the parallel flow reactor geometry is that the operating temperatures of the two reactions must be similar since the separate streams are separated only by the thin separating and heat transfer plate. For example, maintaining the temperature of methanol steam reforming at or below a temperature of 300 °C is very difficult when heat is supplied by catalytic combustion, which typically runs above a temperature of 500 °C. Thermally matching the reactions is still further complicated by the inherent temperature gradients that are present along the flow length of the reaction channel. Any solution directed to resolving this thermal matching problem in a parallel flow configuration will add significant complexity or mass to the system [41, 42]. Further disadvantages of the parallel flow reactor geometry include the complicated hindering necessary to distribute and separate flows through alternating channels and the difficulty of independently sizing the exothermic and endothermic sides of the coupled reactor [43, 44]. Since these reactors comprise an alternating stack of reformer and combustor reactor channels, it is difficult to match the size and requirements for each side. In essence, the coupled reactors cannot be separated since the alternating channel design precludes separation of reformer and combustor. The shortcomings of microchannel reactors are fundamentally related to the direct coupling of reforming and combustion reactions by performing them on opposite sides of the separating plate in a parallel flow configuration. Many of the preceding reactor examples pursue a combination of microchannel reactor technology with heat exchange in a direction perpendicular to the reacting fluid flow to achieve a compact catalytic reactor [45, 46]. This combination places several demands on the design, requiring additional complexity or mass for effective operation [47, 48]. Therefore, a new reactor design that maintains effective operation in a compact device constructed with less complexity would be greatly beneficial. Such a design has, until now, remained elusive. The present study aims to resolve the foregoing problems and concerns while providing still further advantages.

The reactor performance is evaluated by performing numerical simulations using computational fluid dynamics. Computational fluid dynamics is the study of fluid flows and the effect of fluid flows on processes such as heat transfer or chemical reactions in fluid systems. Computational fluid dynamics facilitates the analysis of systems from relatively simple fluid flows through stationary channels and pipes, to complex systems with moving boundaries such as combustible flow in internal combustion or jet engines. Physical characteristics of fluid motion are defined by fundamental governing equations, including conservation relationships such as those of mass and momentum, which may be expressed as partial differential equations. Computational fluid dynamics facilitates the determination and analysis of fluid system properties by providing for the numerical solution of these governing equations using discrete approximations. A method is provided for treating boundary cells in a computational fluid dynamic process employing a computational mesh of cells that represents a fluid system, each cell having faces, vertices and a volume, the system characterized by governing equations and having a set of boundaries. More specifically, computational fluid dynamics methods provide for the discretization of the differential forms of the governing equations over a computational mesh that represents the fluid domain. Converting partial differential equations into a system of algebraic equations allows respective solutions to be calculated through the application of numerical methods. The algebraic equations may be solved in light of specific initial conditions and boundary-condition constraints to simulate the system fluid flow and determine the values of system properties and parameters.

In the context of computational fluid dynamics analysis, arbitrary Lagrangian Eulerian methods for numerically solving the related mathematical equations incorporate advantages of Lagrangian and Eulerian solution approaches, while minimizing their disadvantages. For example, arbitrary Lagrangian Eulerian techniques provide for the precise interface definition of Lagrangian methods, while allowing displacement of a computational mesh over time, as in purely Eulerian methods, without requiring frequent remeshing. Taking advantage of the Eulerian characteristic wherein a fluid continuum under study moves relative to a fixed computational mesh facilitates accurate analysis of large distortions in the fluid motion. As a result, more accurate treatment of greater-scale distortions of the mesh is possible than would be through purely Lagrangian solution techniques, while the resolution of flow details and precision of interface definition are improved over purely Eulerian methods. Arbitrary Lagrangian Eulerian solution algorithms may be used in combination with body-fitted mesh fluid system models, where the mesh edges conform to the boundaries of a fluid system being studied. However, despite their flexibility for allowing advantageous positioning of nodes in the computational domain, disadvantages of using body-fitted meshes include difficulties of generating the mesh and automating the meshing process. Moreover, structured body-fitted meshes cannot easily be generated for systems with complex geometries, such as those that include curved walls, inlets, outlets, or moving parts. Traditional methods to overcome these difficulties, such as increasing cell density, stretching and distorting cell shapes to fit geometric irregularities of the system, or utilizing unstructured meshes are liable to reduce solution accuracy and stability, as well as to increase compute time.

As an alternative to body-fitted methods, immersed-boundary or embedded-boundary approaches is employed in computational fluid dynamics analysis. Such methods facilitate the use of a Cartesian computational mesh throughout fluid system, with special treatment of cells near the system boundary, albeit without significant stretching and distortion of cells relative to the coordinate axes. Employing immersed or embedded boundary mesh generation techniques results in reduced mesh irregularity, as well as relative simplicity and increased speed in an automated mesh generation process. Since the sources of solution error decrease as a mesh approaches a perfect Cartesian alignment, embedded boundary approaches improve solution accuracy and stability. There are two classes of immersed boundary approaches. One immersed boundary approach involves the use of irregularly-shaped cells, at the fluid system boundaries, and the computational algorithm includes methods to account for these irregularly-shaped cells. In such approaches, cells are cut linearly along system boundary lines or surfaces that intersect the cells. An advantage of the cut cell approach is that it tracks the exact location of moving boundaries so that the computational domain conforms to the physical geometry. Thus, it is straightforward to apply a moving boundary velocity directly to let the interior fluid feel the compression and expansion effect due to the boundary motion. However, a disadvantage of the cut cell approach is that the flow transport computational algorithms need to be modified extensively to account for a large variety of irregularly-resized cells at the boundaries. The cutting or reshaping of cells to fit the system geometry may also result in a large number of relatively tiny cells near system boundaries, which may cause deterioration of solution accuracy and stability.

### **3. Results and discussion**

The temperature and oxygen mole fraction contour maps in the micro-structured heat-exchanger reactor are illustrated in Figure 1 for hydrogen production by steam methanol reforming. Chemical reactions that produce heat and those that take up heat form two very important classes of reactions. Some highly exothermic reactions, reactions with a large but negative heat of reaction, require heat to be removed from a system to prevent overheating. One example is the partial oxidation of ethylene to produce ethylene oxide, an important intermediate in the production of ethylene glycol. This reaction oxidizes ethylene over a catalyst to produce ethylene oxide and heat. If the reaction temperature is too

high, ethylene oxide will decompose to carbon dioxide and water. In order to reduce degradation into undesired products, the reaction temperature must be held under control by removing heat produced by the partial oxidation. Conversely, endothermic reactions, those with a positive heat of reaction, do not produce heat but require heat for the reaction to proceed. Steam reforming of hydrocarbons is an endothermic reaction of considerable interest for hydrogen production as a fuel for fuel cells. Steam reforming produces hydrogen and carbon monoxide when heat is added to a catalytic reactor containing steam and hydrocarbons. Although exothermic and endothermic reactions are easy to implement, to do so with a compact and simple reactor design is challenging due to the limitations of heat transfer between the reaction and the outside of the reactor. One aspect in building compact reactors with adequate thermal exchange requires a provision for high interfacial area between the reaction stream and the reactor body. Microchannel technology is capable of high heat and mass transfer coefficients between a bulk reaction fluid and the catalytic heat exchange surface. Alternating channel parallel plate designs can be employed in applications for thermally coupling endothermic steam reforming with combustion in neighboring channels. Such designs enable orders of magnitude size reduction over conventional shell-and-tube steam reformers. Enclosed parallel flow channels are typically formed by stacking plates separated by spacers, and fitting the stack with appropriate headers so that alternating channels contain the reforming reaction with exothermic combustion in the intermediate channels. Microchannel reactors exchange heat between chemically reacting fluid streams where flow is parallel to and on opposite sides of a thermally conductive separating plate.

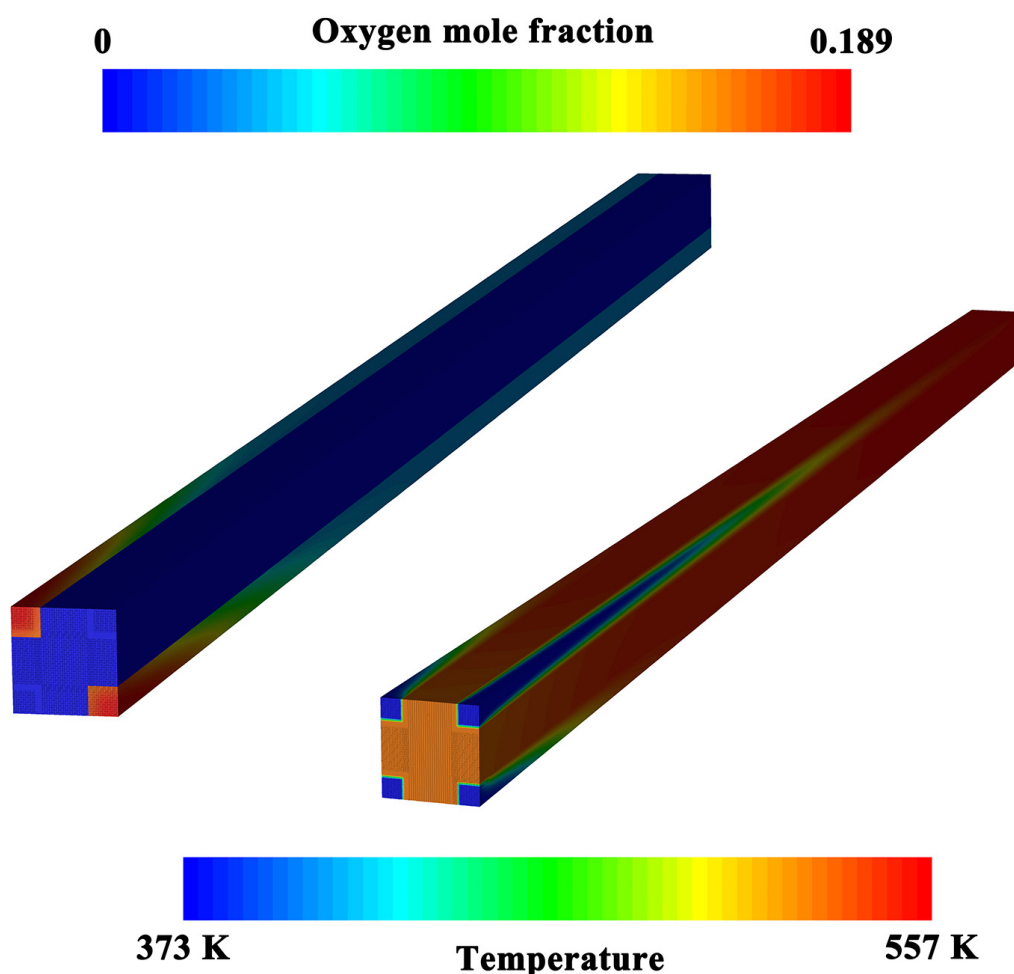


Figure 1. Temperature and oxygen mole fraction contour maps in the micro-structured heat-exchanger reactor for hydrogen production by steam methanol reforming.

The nitrogen and steam mole fraction contour maps in the micro-structured heat-exchanger reactor are illustrated in Figure 2 for hydrogen production by steam methanol reforming. The volume of a

reaction chamber, unless otherwise indicated, refers to the internal volume where reaction substantially occurs but not adjacent material. Where a catalyst is present, the volume includes at least the catalyst volume and catalyst void fraction. Core volume of a heat exchanger refers to the volume of the adjacent flow paths of the two fluids during the portion that they are adjacent and subject to primary heat transfer and including the volume of any intervening material, such as walls between the adjacent flow paths. The initial composition is representative of a reformat stream generated from steam reforming of isooctane at a 1.5:1 steam to carbon ratio. While a reforming outlet typically has at least these four compounds carbon monoxide, carbon dioxide, steam, and hydrogen, the ratios of the components depend on the type of reforming being performed, such as partial oxidation or steam reforming as well as the operating conditions of the reformer. In addition, additional material may be added to the reformat outlet prior to performing a water gas shift reaction. Accordingly, the inlet stream to a water gas shift reactor might have a carbon monoxide to carbon dioxide molar ratio that ranges from about 2:1 to about 1:5. Typically, the steam to gas ratio, defined as the moles of water divided by the moles of the remaining gas, is between about 0.2 and 0.6. Once the desired reactor temperatures are achieved, methanol and water injection begin and eventually generates the desired heat transfer medium which displaces the starter gas. In the meantime, the reformat exiting the first reactor, although diluted with some starter gas, can still be used in the fuel cell during system startup so long as the carbon monoxide levels are low enough. Alternatively, the diluted reformat could be diverted into the combustor for burning, or dumped to the atmosphere, if desired, until acceptable carbon monoxide levels are achieved. Once the desired operating temperatures are achieved, fresh methanol and water are again injected into the recirculating gas, and normal fuel processor operation resumes. Carbon monoxide output from the fuel processor is controlled over the operating range of the processor by varying the water-methanol ratio, the amount of air added to the reactor, and the speed of the recirculating fan to respectively drive the reaction equilibrium, oxidize the carbon monoxide and maintain the required heat transfer within the processor. Preferably, the heat exchanger is a cross flow exchanger adapted to flow the circulating heat transfer medium through the cold side second conduits in a first direction and the heating fluid through the hot side first conduits in a second direction transverse the first direction. The heating fluid will comprise combustion products exhausted from a combustor fueled by methanol and unused hydrogen exiting the anode compartments of the fuel cell that is fueled by the fuel processor. A variety of reactors can employ the steam reforming catalysts. Examples include fuel cell reactors, steam reformers, and conversion reactors. Instead of the fuel cell, the hydrogen may be transported to one of a storage tank, a refueling station, a hydrocracker, hydrotreater, or to additional hydrogen purifiers. The hydrogen may be employed as a synthesis gas, as a component in hydrogenation reactions, and the like. The alcohol reforming reactor may also be configured by placing the reaction chamber adjacent to a heat exchanger chamber that is comprised of an array of microchannels or a single microchannel. The width of the reaction chamber is dependent on the effective thermal conductivity of the catalyst insert. The higher the effective thermal conductivity of the catalyst insert, the wider the insert to enable rapid heat removal. In another configuration, the reaction chamber may be connected to a fuel tank such that alcohol from the tank can flow directly into the reaction chamber. Although a fuel tank is commonly used, any alcohol fuel source could be used. The liquid fuel stream may flow through a separate vaporizer or be vaporized within a section of the steam-reforming reactor. The alcohol is vaporized in a microchannel vaporizer and preheated in a microchannel preheater. The reformation fuel channel is disposed along the axis on a side of the reformation chamber opposite the combustion chamber. The reformation products channel is disposed outside the reformation fuel channel with respect to the axis and on the side of the reformation chamber opposite the combustion chamber, and the combustion exhaust channel is disposed outside the reformation fuel channel with respect to the axis and on the side of the reformation chamber opposite the combustion chamber.

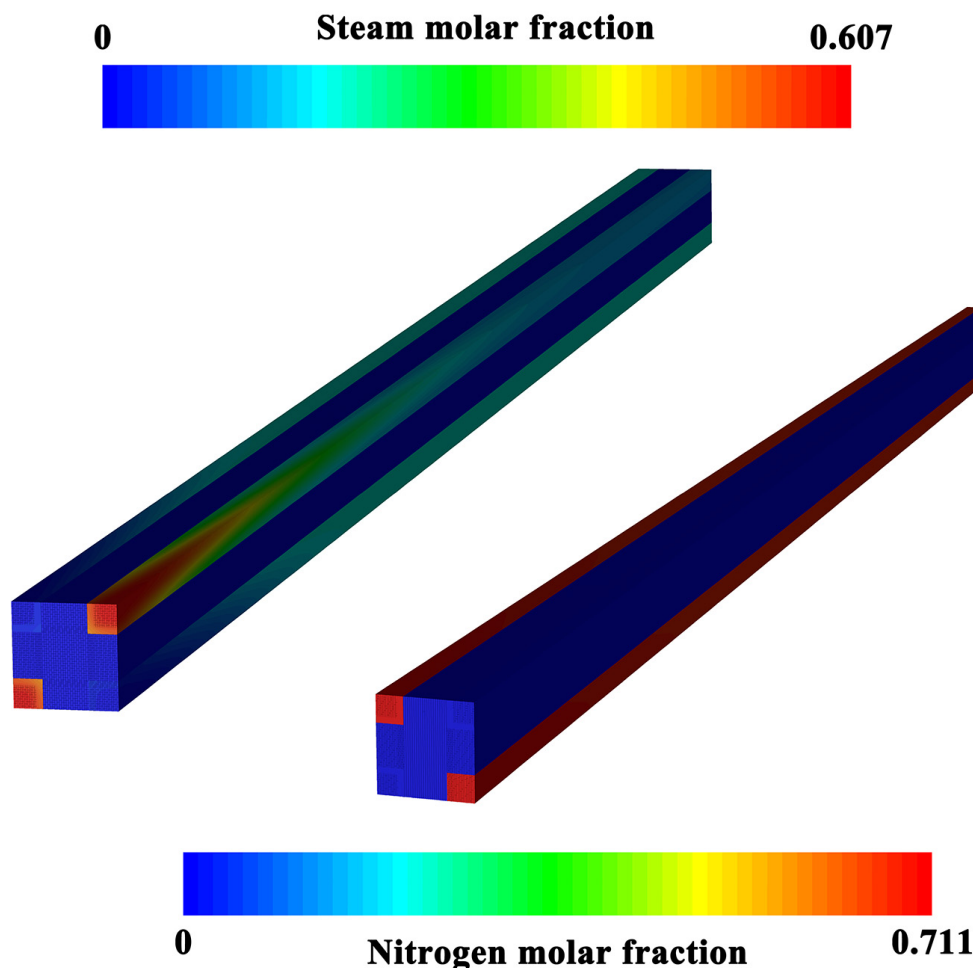


Figure 2. Nitrogen and steam mole fraction contour maps in the micro-structured heat-exchanger reactor for hydrogen production by steam methanol reforming.

The effect of reactor length on the methanol and hydrogen mass fraction profiles is illustrated in Figure 3 along the length of the micro-structured heat-exchanger reactor for hydrogen production by steam methanol reforming. Channels having a dimension between one millimeter and one centimeter are sometimes referred to as meso-channels, with the term microchannels used for those less than one millimeter. However, for the purposes of the present study, a microchannel or a microchamber has at least one dimension, typically the depth, less than about one millimeter, and still more often less than about 0.8 millimeter. The width of a microchannel may be any magnitude, but typically will be constrained by the desire to control manufacturing processes or by the desire to control fluid distribution in a reactor or heat exchanger that has multiple microchannels. Length is unlimited, but as a practical matter for the overall purpose of miniaturization, the length is typically on the order of centimeters to tens of centimeters. Where the depth is the micro-dimension, microchannels will typically, though not essentially, have a large ratio of length to width, for example greater than about 8. The present design is a microchannel chemical reactor having a reaction flow path in thermal contact with a heat exchange channel. The heat exchange channel may also be a reaction channel. Either the reaction flow path or the heat transfer channel, or both, include microchannels where the smallest dimension of the microchannel is generally parallel to the direction of heat flux, which would be in a vertical direction. Reactants flow through the reaction flow path from an inlet to an outlet. Between the inlet and outlet is a reaction chamber defined by the presence of a reaction catalyst in the flow path, which can span some or substantially all of the length of the flow path. Heat exchange fluid flows through the heat exchange channel from a fluid inlet to a fluid outlet. Typically, though not essentially, at least one solid wall separates the heat exchange channel from the reaction chamber to prevent mass

transport between the fluids. An optional heater is also provided adjacent the inlet end of the reaction chamber. The heater at one end of the device can be used to help maintain a temperature gradient down the length of the reaction chamber. A cooler could be used at the other end of the reaction chamber in place of or in addition to the heater. When the reaction in the reaction chamber is a reversible exothermic reaction, heat is generated in the reaction chamber and transferred to the heat exchange fluid to cool the reactants as they proceed through the reaction chamber. Conversely, when the reaction in the reaction chamber is a reversible endothermic reaction, heat is transferred from a heating fluid in the heat exchange channel to the reacting fluid as the reactants proceed through the reaction chamber. When the heat transfer channel is also a reaction channel, heat is transferred from one reaction channel to the other, as the reactants proceed through their respective flow paths.

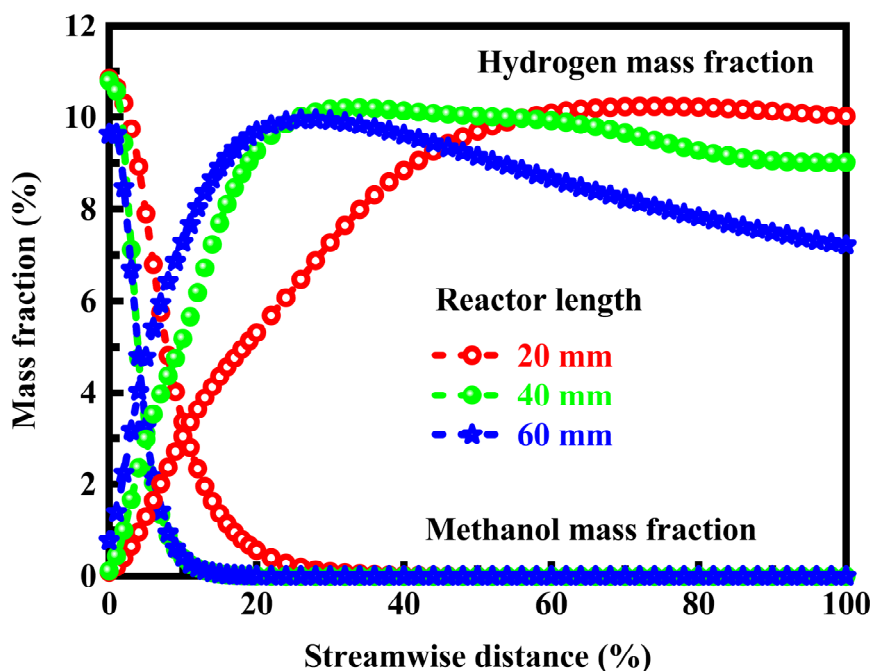


Figure 3. Effect of reactor length on the methanol and hydrogen mass fraction profiles along the length of the micro-structured heat-exchanger reactor for hydrogen production by steam methanol reforming.

The effect of reactor length on the methanol and hydrogen mole fraction profiles is illustrated in Figure 4 along the length of the micro-structured heat-exchanger reactor for hydrogen production by steam methanol reforming. A microchannel reactor is preferably designed to achieve a temperature trajectory down the length of the reaction chamber that approaches a predetermined temperature trajectory. Typically, this predetermined temperature trajectory is substantially different from the temperature trajectory that would occur if the reaction were allowed to proceed adiabatically or isothermally. In preferred forms, this predetermined temperature trajectory approaches a theoretically determined optimum temperature trajectory based on the reaction rate and design parameters specific to the particular application. Many catalytic reactions begin with gas phase reactants, for example steam reforming, partial oxidation, water gas shift and others. However, equipment, specifically reactor volume is generally large because of mass and heat transfer limitations. Microchannel reactors offer less resistance to heat and mass transfer thus creating the opportunity for dramatic reductions in process hardware volume. Further, the micro-combustor or micro-reformer can be part of an efficient integrated system, which can reform lower alcohols and even higher alcohols that require higher processing temperatures. Carbon dioxide selectivity over carbon monoxide, a poison to fuel cells, of the steam reforming process is high, so that it is possible to avoid or reduce requirements for removing carbon monoxide after reforming and before supplying the gas to the fuel cell, thereby greatly simplifying the overall system. Since catalytic combustion is used, stable low temperature performance is easily

attained for the combustor to provide uninterrupted operational heat for vaporizers and steam reformer units so they may operate in a steady optimum manner. The excess air should not be too much, since the extra air removes heat from the steam reformer. Air and methanol flows are adjusted until the steam reformer is at the desired temperature. The reformer fuel mixture flow is initiated at this point. Combustor flows are adjusted as necessary to maintain desired temperatures.

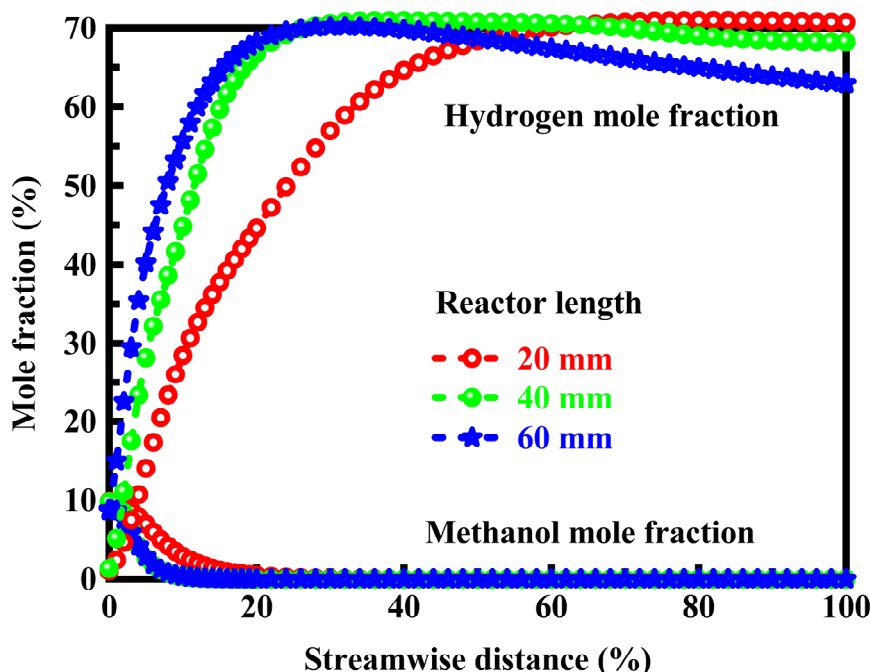


Figure 4. Effect of reactor length on the methanol and hydrogen mole fraction profiles along the length of the micro-structured heat-exchanger reactor for hydrogen production by steam methanol reforming.

The hydrogen and carbon dioxide mole fraction contour maps in the micro-structured heat-exchanger reactor are illustrated in Figure 5 for hydrogen production by steam methanol reforming. The steam reforming catalyst is involved in the production of hydrogen, typically hydrogen gas. Most often, the steam reforming catalyst is involved in the production of hydrogen from methanol and water. In some instances, the methanol steam reforming reaction can be represented by two reactions, namely, a first cracking reaction followed by a water gas shift reaction. When the steam reforming catalyst is coated on a monolith substrate, a suitable amount is provided to produce hydrogen. While the steam reforming catalyst may be in the form of a powder or pressed into pellets, in small-scale applications involving miniature devices and reactors with mesoscale and microscale features, including channels and other miniature device structures, pellets are not feasible due to their size. And both pellets and powders are not often mechanically stable in smaller configurations. In this connection, concerns over attrition, clogging of channels, sufficient adherence to the substrate, and stability during vibration are raised. Thus, while a steam reforming catalyst in the form of a powder or pellets is appropriate in larger devices, diminished performance may result when using the steam reforming catalyst in the form of a powder or pellets in miniature devices and reactors. The steam reforming catalyst is formed on or in a ceramic monolith substrate to provide for a miniaturized chemical reactor including a porous ceramic material having a catalyst immobilized within or upon the porous ceramic material. In miniature devices and reactors, it may be more desirable to have an immobilized support that retains the high porosity and surface area possible with bulk powders. When the steam reforming catalyst is formed on or in a ceramic monolith substrate, the immobilized catalyst is positioned in such a way as to allow reactants to intimately contact the immobilized catalyst, while not degrading the catalytic activity of the catalyst. When fabricating a monolithic steam reforming catalyst system using multilayer ceramic structures, the reactors that constitute the system which typically include a post fire deposition of a

catalyst, do not provide for selective deposition of the catalyst material post firing. This is because, in part, it is difficult to deposit catalyst into small channels. In many instances, since the structure is fired prior to introduction of the steam reforming catalyst, the steam reforming catalyst is not able to be positioned where it is needed so as to provide optimum temperature profiles as desired. In order to make steam reforming catalyst system containing multilayer ceramic structures, a green multilayer ceramic structure is coated with the steam reforming catalyst described herein containing yttrium, palladium, a metal oxide and cerium, and optionally zinc, and then the coated green multilayer ceramic structure is fired to provide a steam reforming catalyst system. This steam reforming catalyst system may have a honeycomb structure, and may or may not contain spacers between individual reactors. The ceramic substrate may be porous ceramic substrate.

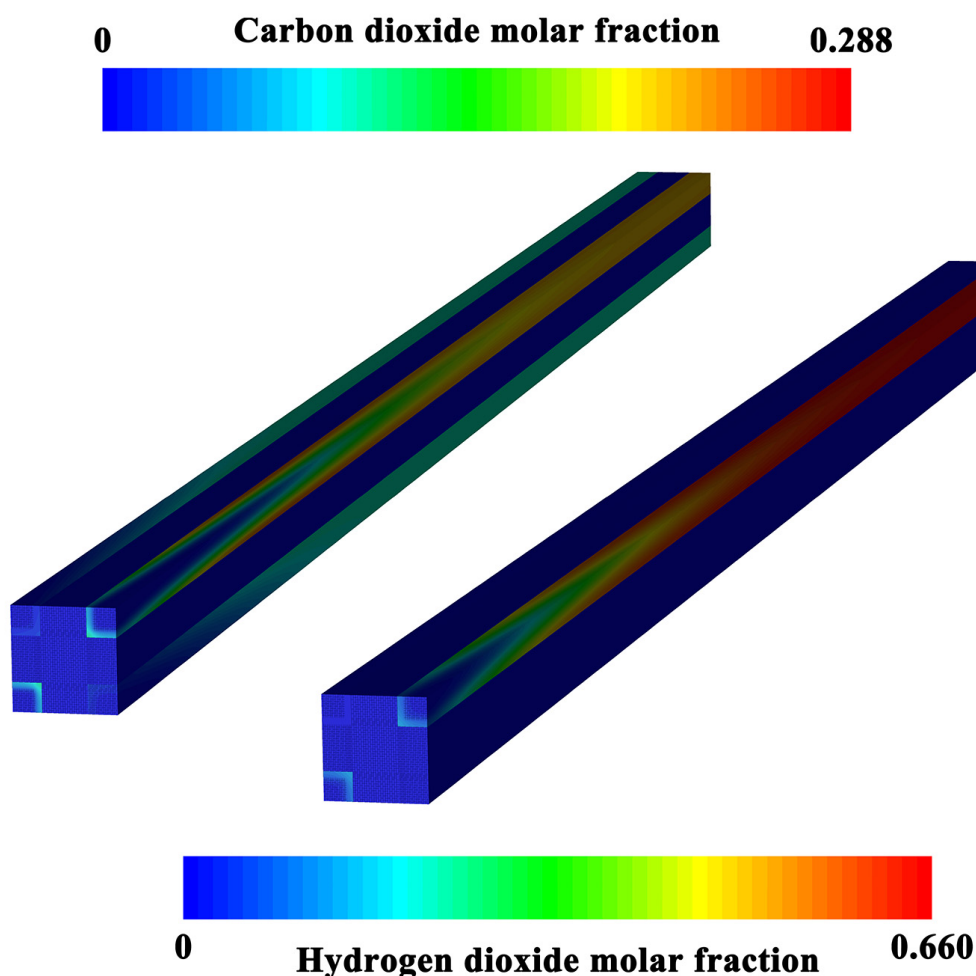


Figure 5. Hydrogen and carbon dioxide mole fraction contour maps in the micro-structured heat-exchanger reactor for hydrogen production by steam methanol reforming.

The mesh and methanol mole fraction contour maps in the micro-structured heat-exchanger reactor are illustrated in Figure 6 for hydrogen production by steam methanol reforming. The alcohol steam reforming catalyst converts a lower alcohol such as methanol into hydrogen and carbon oxides. In the specific case where the lower alcohol is methanol, the alcohol steam reforming catalyst may be called a methanol steam reforming catalyst. The generation of carbon monoxide is undesired as carbon monoxide is a poison to the fuel cell electrode [49, 50]. Even generating small amounts of carbon monoxide can cause significant degradation [51, 52]. Consequently, any decrease in generating carbon monoxide is a positive advance in the steam reforming catalyst field. The alcohol steam reforming catalysts containing yttrium, palladium, a metal oxide and cerium, and optionally zinc generally display high carbon dioxide selectivity and thus have reduced or mitigated generation of carbon monoxide. It is also difficult to improve both good methanol activity and good carbon dioxide selectivity in alcohol

steam reforming catalysts [53, 54]. Often, improvement in one of these properties results in a decrease in the other property [55, 56]. Consequently, merely combining two catalyst components, one that improves methanol activity and the other that improves carbon dioxide selectivity, does not typically result in a material that has both good methanol activity and good carbon dioxide selectivity. Even small increases in carbon monoxide generation are disfavored because of the large resultant poisoning effect [57, 58]. The fuel combustion and steam reforming processes can be stably and efficiently operated at lower temperatures, without the need for energy input to sustain or even to start the micro-combustion process. In some instances, the micro-combustor is started with hydrogen or vapors such as methanol. Heat losses can be effectively controlled and reduced. Another advantage is that the simplicity of the design and the materials used enable mass production at competitive costs. Another advantage is an extremely fast response time. When a suitable amount of yttrium is included in a steam methanol reforming catalyst based on palladium, a metal oxide and cerium, and optionally zinc, a steam reforming catalyst that departs from the undesired trade-off relationship results. Specifically, steam reforming catalysts containing yttrium, palladium, a metal oxide and cerium, and optionally zinc display both desirable properties of a high methanol conversion rate and high carbon dioxide selectivity. The steam reforming catalyst contains a suitable amount of at least one metal oxide and cerium to contribute to high methanol conversion properties. The cerium may or may not act as a support. In instances where the steam methanol reforming catalyst is subjected to high temperatures, such as during firing of a green ceramic substrate coated with the steam reforming catalyst, two or more metals of the steam reforming catalyst may form an alloy. If the steam methanol reforming catalyst does not contain cerium, then the steam reforming catalyst contains at least one metal oxide.

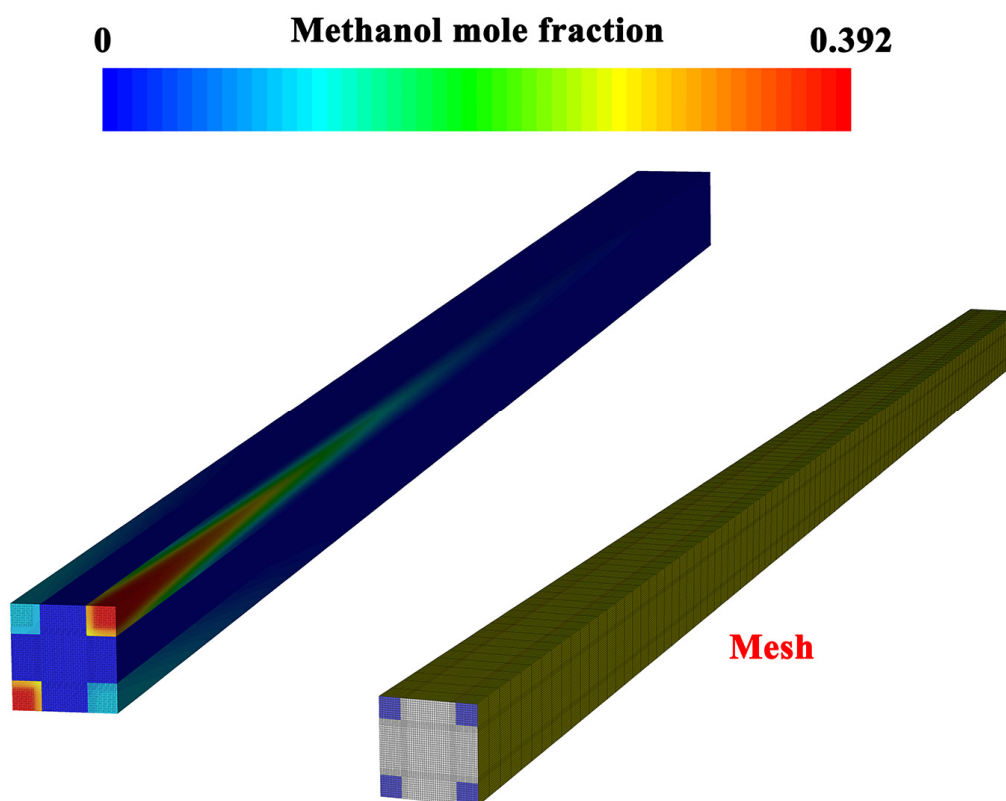


Figure 6. Mesh and methanol mole fraction contour maps in the micro-structured heat-exchanger reactor for hydrogen production by steam methanol reforming.

The oxidation channel and wall centerline temperature profiles are presented in Figure 7 along the length of the micro-structured heat-exchanger reactor for hydrogen production by steam methanol reforming. The reaction rate for a single reaction with a given catalyst is a function of the composition and the temperature. The temperature corresponding to the maximum reaction rate at a given

composition is determined by setting the partial derivative of the reaction rate with respect to temperature equal to zero. Assuming an ideal plug flow reactor, a theoretical optimum temperature trajectory is determined from the mass balance equation. Integrating this equation gives the minimum reactor length required to achieve a given level of conversion. The appropriate catalyst loading is also calculated from the reaction rate equation. An exemplary reaction useful in the present design is the water-gas-shift reaction. The water-gas-shift reaction is employed in fuel processors that reform liquid fuels to produce hydrogen for fuel cells. The shift reaction increases hydrogen yield while reducing carbon monoxide, which is a poison for the proton-exchange membrane fuel cell anode. The water-gas-shift reaction is exothermic and reversible. The initial composition is representative of a reformat stream generated from steam reforming of isooctane at a 3:1 steam to carbon ratio and contains. The initial maximum reaction rate occurs at a temperature of about 280 °C. As the reaction proceeds, the peak reaction rate rapidly drops. The temperature at which the peak rate occurs also drops with increasing carbon monoxide conversion. The size of a reactor to accomplish high conversion and the amount of catalyst required is dependent on the temperature trajectory through the reactor. For a reactor operating with this temperature trajectory, most of the conversion would occur in the first third of the reactor, and the remaining two-thirds of the reactor would be required for the remaining percent of conversion, a direct result of much lower activity as the temperature decreases. For a variety of reasons, however, it may not be practical or desirable to follow a theoretically optimum temperature profile during the entire length of the reactor. For example, concerns over methane formation, coking, or catalyst sintering may place constraints on the inlet temperature to the reactor or the maximum temperature in the reactor. Likewise, cost constraints can become manifest if following the ideal temperature trajectory would require that the reactor system be manufactured in more expensive materials than would otherwise be practical. An alternative temperature trajectory is to enter the reactor at a temperature near an upper limit temperature and operate substantially isothermally through the initial stage of the reactor. Once the reaction has proceeded to a point where the optimum temperature drops below an upper constraint, then the theoretically optimum temperature profile can be followed.

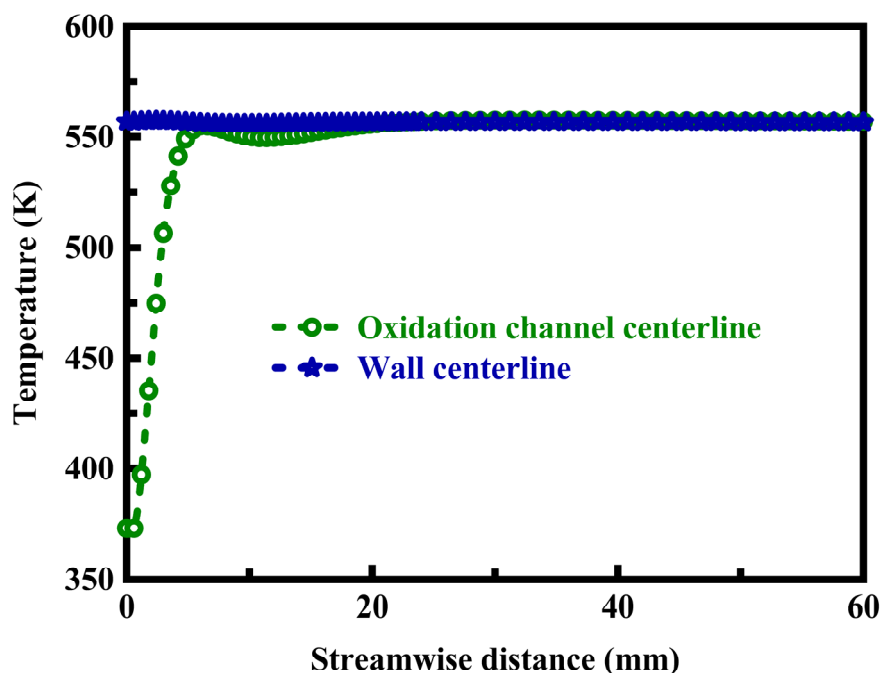


Figure 7. Oxidation channel and wall centerline temperature profiles along the length of the micro-structured heat-exchanger reactor for hydrogen production by steam methanol reforming.

The reforming channel and wall centerline temperature profiles are presented in Figure 8 along the length of the micro-structured heat-exchanger reactor for hydrogen production by steam methanol

reforming. Advantages can be realized by using one or more reactors with controlled temperature trajectories as compared to two adiabatic reactors with intercooling, which is the typical approach used in fuel steam reforming processes [59, 60]. In the case of adiabatic reactors with intercooling, reactor productivity is maximized for a given total conversion by optimizing the two inlet temperatures and the amount of conversion in the first reactor [61, 62]. When comparing this three-component configuration to the optimum temperature trajectory for the steam reformat stream and using the same kinetic rate expression, approximately double or more catalyst is required for 80 percent conversion in the optimized two-stage adiabatic reactor system than is required if the optimized temperature trajectory is achieved [63, 64]. Of course, the actual size of a single reactor operating with the temperature trajectory would likely be larger than any single component of the three-component system [65, 66]. However, if the entire system of two reactors plus the intervening heat exchanger is considered, the overall size and mass will likely be smaller with the optimum temperature profile [67, 68]. The optimum temperature system is also simplified by combining three components into one. In addition, the steam reforming catalyst may be an important cost element, so improving catalyst productivity may be sufficient alone for pursuing an optimized profile. Microchannel reactors offer the advantage of exceptional heat exchange integration and can be utilized for approaching optimum temperature trajectories for exothermic, reversible reactions. Catalytic monoliths are located at the center of each of an array of reaction flow channels such that reactants flow by both sides of the catalyst structures. Reactants from the reaction flow channel diffuse into pores in the catalyst structure to react, generating heat. Reaction products then diffuse out of the steam reforming catalyst structure and into the bulk reactant flow path. Diffusion into and out of the steam reforming catalyst is in a direction generally transverse to the bulk flow direction. The reaction flow channel arrays are interleaved with heat exchange channels, and a heat exchange fluid flowing co-current or counter-current to the reaction flow removes the heat of reaction and cools the gas, thereby establishing a desired temperature trajectory for the reaction. The choice of coolant, the temperature and flow of the coolant, and the geometry and relative orientation of the flow channels are among the design variables that can be modified for achieving a desired temperature profile for a given reaction and catalyst. In a preferred form, design variables are selected to substantially maximize catalyst productivity.

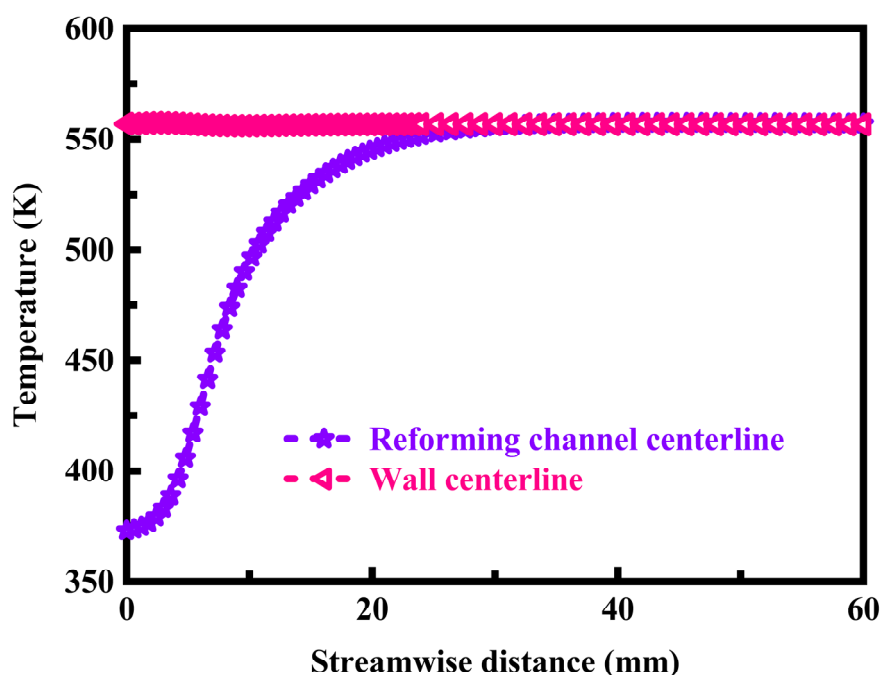


Figure 8. Reforming channel and wall centerline temperature profiles along the length of the micro-structured heat-exchanger reactor for hydrogen production by steam methanol reforming.

## 4. Conclusions

The present study relates to a unique method for performing reversible endothermic, exothermic reactions, and competing reactions. The method comprises flowing reactants through a reaction channel in thermal contact with a heat exchange channel, and conducting heat in support of the reaction between the reactants and fluid flowing through the heat exchange channel to substantially raise or lower the temperature of the reactants as they travel through the reaction channel. Particular emphasis is placed upon how to provide improved conversion and selectivity in chemical reactions, provide chemical reactor systems that are compact, and provide thermally efficient chemical reactor systems. The major conclusions are summarized as follows:

- Microchannel technology is capable of high heat and mass transfer coefficients between a bulk reaction fluid and the catalytic heat exchange surface.
- Carbon monoxide output from the fuel processor is controlled over the operating range of the processor by varying the water-methanol ratio, the amount of air added to the reactor, and the speed of the recirculating fan to respectively drive the reaction equilibrium, oxidize the carbon monoxide and maintain the required heat transfer within the processor.
- When the reaction in the reaction chamber is a reversible exothermic reaction, heat is generated in the reaction chamber and transferred to the heat exchange fluid to cool the reactants as they proceed through the reaction chamber.
- Microchannel reactors offer less resistance to heat and mass transfer thus creating the opportunity for dramatic reductions in process hardware volume.
- While a steam reforming catalyst in the form of a powder or pellets is appropriate in larger devices, diminished performance may result when using the steam reforming catalyst in the form of a powder or pellets in miniature devices and reactors.
- The steam reforming catalyst contains a suitable amount of at least one metal oxide and cerium to contribute to high methanol conversion properties.
- The shift reaction increases hydrogen yield while reducing carbon monoxide, which is a poison for the proton-exchange membrane fuel cell anode.
- Microchannel reactors offer the advantage of exceptional heat exchange integration and can be utilized for approaching optimum temperature trajectories for exothermic, reversible reactions.

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