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RETRACTED: Production of Hydrogen by Methane Steam Reforming Coupled with Catalytic Combustion in Integrated Microchannel Reactors

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Abstract: This paper addresses the issues related to the rapid production of hydrogen from methane steam reforming by means of process intensification. Methane steam reforming coupled with catalytic combustion in thermally integrated microchannel reactors for the production of hydrogen was investigated numerically. The effect of the catalyst, flow arrangement, and reactor dimension was assessed to optimize the design of the system. The thermal interaction between reforming and combustion was investigated for the purpose of the rapid production of hydrogen. The importance of thermal management was discussed in detail, and a theoretical analysis was made on the transport phenomena during each of the reforming and combustion processes. The results indicated that the design of a thermally integrated system operated at millisecond contact times is feasible. The design benefits from the miniaturization of the reactors, but the improvement in catalyst performance is also required to ensure the rapid production of hydrogen, especially for the reforming process. The efficiency of heat exchange can be greatly improved by decreasing the gap distance. The flow rates should be well designed on both sides of the reactor to meet the requirements of both materials and combustion stability. The flow arrangement plays a vital role in the operation of the thermally integrated reactor, and the design in a parallel-flow heat exchanger is preferred to optimize the distribution of energy in the system. The catalyst loading is an important design parameter to optimize reactor performance and must be carefully designed. Finally, engineering maps were constructed to design thermally integrated devices with desired power, and operating windows were also determined.

Keywords: hydrogen production; steam reforming; catalytic combustion; thermal management; process intensification; thermally integrated microchannel reactors; process optimization; computational fluid dynamics

1. Introduction

There has been an increasing interest in the development of synthesis gas production due to its potential applications in both fuel cells [1,2] and internal combustion engines [3,4]. The steam reforming of natural gas has become the popular synthesis gas production method in the industry [5,6]. This reaction is usually carried out in multi-tubular fixed-bed reactors inserted into large gas-fired furnaces to supply the necessary energy. The process is operated under high pressure over a commercial nickel-based catalyst with contact times exceeding one second [5,6]. In recent years, there has been an increasing interest in the production of hydrogen by nuclear-heated steam reforming of methane [7,8]. This paper aims to explore an effective approach to rapidly produce hydrogen from the steam reforming of methane by means of process intensification.

The technology of catalytic partial oxidation also offers a promising reaction pathway for the rapid production of hydrogen from methane [9,10]. In contrast, the rate of methane steam reforming reaction is usually considered to be slow [5,6]. Interestingly, millisecond kinetics for this reaction have been documented [11–14]. The rapid, efficient conversion of methane to hydrogen will be conducive to the introduction of proton exchange membrane fuel cells into automotive markets [15,16]. This technology also holds great promise in spark ignition engines [3,4] and catalytic converters [17]. There is a common feature in these processes (i.e., the rapid, efficient conversion of methane to hydrogen by means of process intensification).

Commercially valuable products can be produced at short contact times [18–20]. In particular, the steam reforming of methane on highly active catalysts is a rapid, efficient reaction pathway for the production of hydrogen for the “hydrogen economy” [11–14]. Currently, a fast reforming process has become an important topic in light of potential hydrogen utilization for fuel cell-powered automobiles [18]. Consequently, there is considerable interest in the “on-board” conversion of methane to hydrogen at short contact times [1,2]. The rapid production of hydrogen from methane steam reforming with contact times of less than 10 milliseconds have been reported, including in microchannel or microstructured reactors [11–14,21–24] and on highly active catalysts such as rhodium [25]. Careful design is necessary to further reduce the contact time, as the process has been designed to operate at sub-millisecond contact times [13], even at less than 100 microseconds at the expense of low equilibrium conversion [11]. Interestingly, recent literature has suggested that the rapid production of hydrogen from the steam reforming of methane on nickel is also feasible if the catalyst loading is properly designed [14].

To achieve millisecond reforming processes, microchannel reactors have great potentiality in this field [11,21,23,26,27]. The microreaction technology offers process intensification by using microchannel reactors in the form of enhanced transport characteristics [23,24,27,28]. This technology has the potential to reduce reaction times significantly. Fast reaction kinetics are possible in microchannel reactors, as these small-scale systems have channels with dimensions smaller than 0.3 mm [11–14,21,22,27], thus significantly improving the transport rates [21,26,28]. The net result is that the efficiency of the chemical process systems can be significantly improved by means of microreaction technology [26–29].

Process intensification through the use of microchannel reactors will yield significant investment and operating cost savings for commercial applications [30,31]. In this context, the heat exchange within the system is very efficient, and operation with high heat fluxes is allowed [32,33]. Furthermore, the resistance to heat and mass transfer can be greatly reduced. As a result, the production process of hydrogen from steam reforming can be as short as a few milliseconds, which highlights the importance of the design principles of these microchannel reactors. This is the motivation behind developing the thermally integrated microchannel reactors discussed in this paper, with an aim to understand the thermal interaction between the steam reforming and the catalytic combustion for the rapid production of hydrogen in these small-scale chemical systems.

Thermally integrated microchannel reactors show great promise for rapidly producing hydrogen for a variety of applications, and they can be further “scaled-out” or “numbered-up” to achieve the desired capacity [18]. Despite the rapid development of short-contact-time reactors over the last several decades, the design principle of these millisecond reforming processes has not yet been fully understood. This requires not only fast mass and heat transfer, but also a rapid reforming process. Therefore, a major challenge is how to implement the rapid production of hydrogen from steam reforming by means of process intensification. Methane steam reforming in small-scale chemical systems has been investigated theoretically [34–37] and experimentally [38–40] to take advantage of process intensification. Unfortunately, the design principles and optimization strategies of the steam reforming process to achieve the rapid production of hydrogen are not readily available, despite the fact that they are highly desirable for practical applications. Rapid, efficient operation requires not only novel technologies for process intensification, but also a high degree of heat integration within

a reforming system [41,42]. It is therefore necessary to explore how to achieve the rapid production of hydrogen from methane steam reforming by means of process intensification.

The development of design principles for the rapid production of hydrogen from methane steam reforming in micro-devices needed for novel fuel cell-based power sources is the motivation for this study. In order to address the challenges in realizing this vision, the primary focus of this study is on short-contact-time reaction systems and specifically on methane steam reforming coupled with catalytic combustion in thermally integrated microchannel reactors, as specific examples for illustration. Numerical simulations were performed to better understand the transfer phenomenon occurring in the system with an aim to further intensify the reforming process. The operating space allowed was determined to meet the requirements of both materials and combustion stability, and design maps for the rapid production of hydrogen were constructed. The main objective was to explore the potential to achieve the rapid production of hydrogen from methane steam reforming by means of process intensification. Special emphasis was placed on developing the design and operation strategies for the rapid production of hydrogen in integrated microchannel reactors.

2. Model Development

2.1. Description of the Reaction System

Detailed modeling is necessary to understand the interaction between kinetics and transport in reactor performance because of the small scale of the microchannel reactors involved [43–46]. The system presented in this paper is methane steam reforming coupled with catalytic combustion in thermally integrated microchannel reactors for the production of hydrogen. The catalytic combustion provides the energy required to achieve the rapid production of hydrogen on the opposite side of the dividing plate. A schematic diagram of the reactor used is given in Figure 1, where the horizontal arrows represent the direction of the flow. The two flow arrangements modeled in this paper are also given in Figure 1. In such a heat exchange design, efficient heat exchange within the small-scale system is possible [47–49]. Recent studies have demonstrated that the management of energy in a small-scale confined space is one of the great challenges in design [50,51]. Accordingly, the thermal interaction between reforming and combustion is investigated for the purpose of the rapid production of hydrogen.

Attention should be paid to the thermal management in the system to ensure the efficient operation of the integrated reactor. The reforming catalyst used is rhodium due to its excellent performance, even though the system is operated under extreme conditions [52,53], whereas the performance of nickel is not comparable to that of rhodium. However, nickel is widely used for methane steam reforming and many other catalytic processes in the industry. Therefore, one point that needs to be clarified is whether the rapid production of hydrogen from the steam reforming of methane on nickel in integrated microchannel reactors is feasible by means of process intensification.

It is quite necessary to define a reference point based on which effects of the various parameters and conditions can be easily evaluated. A “base case”—in which a typical set of design parameters and operating conditions used for the system are considered—is listed in Table 1. The characteristic length scale of the reactor modeled is 0.2 mm. In such a small dimension, high transport rates are possible, thus taking advantage of process intensification. The molar steam-to-carbon ratio at the inlet is set as 3.0 [54], and the external heat loss coefficient is set as $20 \text{ W}/(\text{m}^2 \cdot \text{K})$ [55]. For the sake of convenience, the reactor width is assumed to be 10.0 mm in this investigation when the flow rate is required. To reduce the computational cost of the numerical simulations, only the dividing plate and half of each channel are modeled in the present work. The error introduced by this simplification is small due to inherent symmetry conditions at the centerline of the channels.

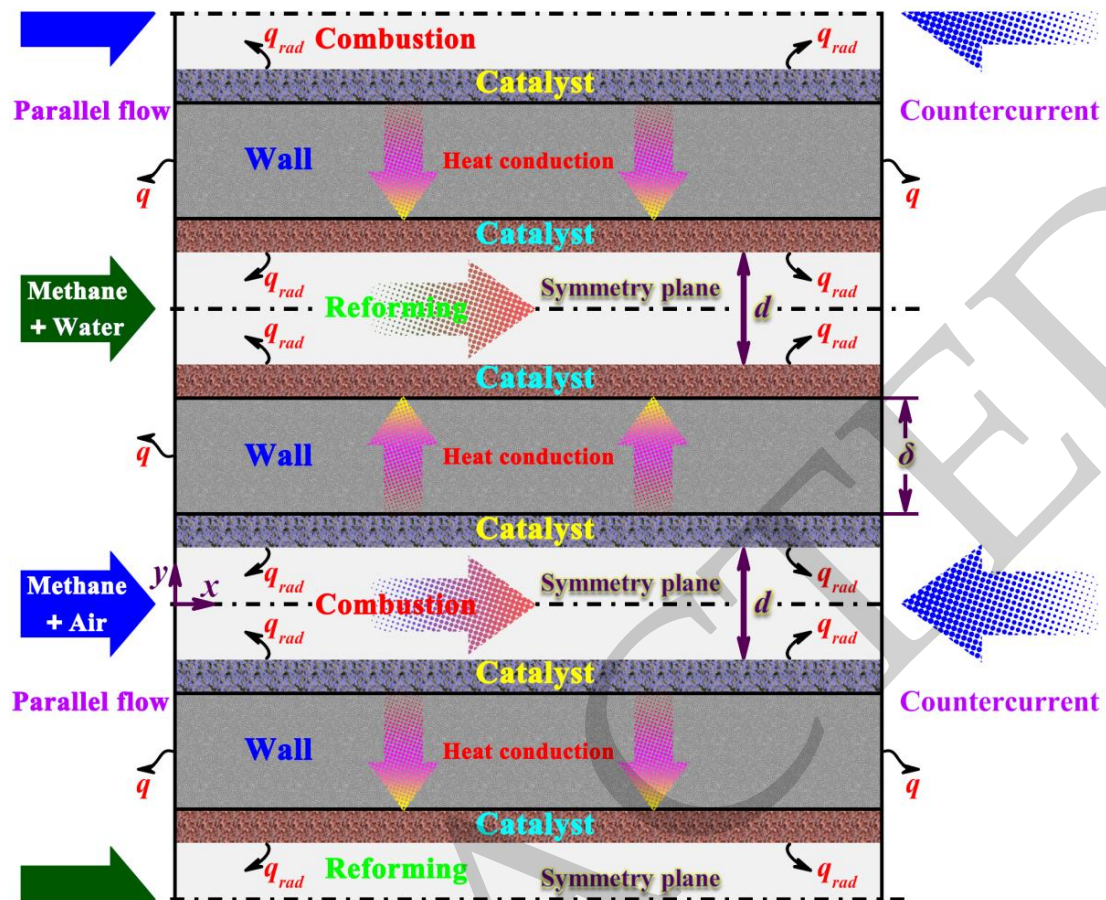


Figure 1. Schematic representation of the integrated microchannel reactor model, showing the two flow arrangements modeled in this paper. The horizontal arrows represent the direction of the flow.

Table 1. Design parameters and operating conditions adopted for the base case.

Parameters and Conditions	Combustion Side	Reforming Side	Unit
Geometry			
Channel height	0.2		mm
Channel length	50.0		mm
Solid wall			
Thickness	0.2		mm
Thermal conductivity	80.0		W/(m·K)
External heat loss coefficient	20		W/(m ² ·K)
Gas phase			
Inlet molar steam-to-carbon ratio	-	3.0	-
Inlet equivalence ratio	0.8	-	-
Inlet flow velocity	6.0	2.0	m/s
Inlet pressure	0.1	0.1	MPa
Inlet temperature	300	400	K
Catalysts			
Surface site density	2.72×10^{-9} (Pt)	2.66×10^{-9} (Ni) 2.72×10^{-9} (Rh)	mol/cm ²
Porosity	0.5	0.6	-
Tortuosity factor	3	3	-
Thickness	0.08	0.08	mm
Mean pore diameter	20	20	nm
Catalyst/geometric surface area	20	20	-

2.2. Mathematical Model

The reaction system is assumed to be operated in a steady state, and ideal gas behavior is also assumed. Because all of the Reynolds numbers examined in this paper are less than 280, the flow regime is laminar on each side of the reactor, making it feasible to fully characterize the transport phenomenon occurring in the system. The radiative heat exchange is modeled between the plate surfaces, as thermal radiation is important, especially at high temperatures [51]. The modeling tool used is ANSYS® Fluent® Release 16.0 [56]. To accurately predict the thermal and chemical behaviors involved in the reforming process, detailed reaction mechanisms and transport should be accounted for. To model detailed reaction mechanisms, the Fluent software (Release 16.0, ANSYS Inc., Canonsburg, PA, USA) is coupled with module subprograms. Furthermore, detailed heat and mass transfer are also included in the model to better understand the transport characteristics in the system. The two-dimensional conservation equations are solved in the fluid. Note that all of the symbols listed in the following equations are defined in the nomenclature section.

The total mass conservation equation is as follows:

$$\frac{\partial(\rho u)}{\partial x} + \frac{\partial(\rho v)}{\partial y} = 0, \quad (1)$$

where ρ is the density of the mixture, u and v are the streamwise and transverse components of the flow velocity of a fluid, and x and y are the streamwise and transverse coordinates in the system.

The fluid phase momentum conservation equations are as follows:

$$\frac{\partial(\rho uu)}{\partial x} + \frac{\partial(\rho vu)}{\partial y} + \frac{\partial p}{\partial x} - \frac{\partial}{\partial x} \left[2\mu \frac{\partial u}{\partial x} - \frac{2}{3}\mu \left(\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} \right) \right] - \frac{\partial}{\partial y} \left[\mu \left(\frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} \right) \right] = 0, \quad (2)$$

$$\frac{\partial(\rho uv)}{\partial x} + \frac{\partial(\rho vv)}{\partial y} + \frac{\partial p}{\partial y} - \frac{\partial}{\partial x} \left[\mu \left(\frac{\partial v}{\partial x} + \frac{\partial u}{\partial y} \right) \right] - \frac{\partial}{\partial y} \left[2\mu \frac{\partial v}{\partial y} - \frac{2}{3}\mu \left(\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} \right) \right] = 0, \quad (3)$$

where p and μ are the pressure and dynamic viscosity of the mixture, respectively.

The fluid phase energy balance can be written as follows:

$$\frac{\partial(\rho uh)}{\partial x} + \frac{\partial(\rho vh)}{\partial y} + \frac{\partial}{\partial x} \left(\rho \sum_{k=1}^{K_g} Y_k h_k V_{k,x} - \lambda_g \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial y} \left(\rho \sum_{k=1}^{K_g} Y_k h_k V_{k,y} - \lambda_g \frac{\partial T}{\partial y} \right) = 0, \quad (4)$$

where h and λ_g are the specific enthalpy and thermal conductivity of the mixture, K_g is the total number of gaseous species, Y_k and h_k are the mass fraction and specific enthalpy of the k -th gaseous species, $V_{k,x}$ and $V_{k,y}$ are the streamwise and transverse components of the diffusion velocity of the k -th gaseous species, and T is the absolute temperature.

The gaseous species balance is as follows:

$$\frac{\partial(\rho u Y_k)}{\partial x} + \frac{\partial(\rho v Y_k)}{\partial y} + \frac{\partial}{\partial x} (\rho Y_k V_{k,x}) + \frac{\partial}{\partial y} (\rho Y_k V_{k,y}) - \dot{\omega}_k W_k = 0, \quad k = 1, \dots, K_g, \quad (5)$$

where $\dot{\omega}_k$ is the rate of appearance of the k -th gaseous species and W_k is the relative molecular mass of the k -th gaseous species.

The species diffusion velocities $V_{k,x}$ and $V_{k,y}$ in the above equations can be expressed as follows [57]:

$$\vec{V}_k = -D_{k,m} \nabla \left[\ln \left(\frac{Y_k \bar{W}}{W_k} \right) \right] + \left[\frac{D_k^T W}{\rho Y_k \bar{W}} \right] \nabla (\ln T), \quad (6)$$

where $D_{k,m}$ is the diffusivity for the k -th gaseous species in the mixture, $\bar{W}$ is the relative molecular mass of the mixture, D_k^T is the thermal diffusivity of the k -th gaseous species, and the symbol ∇ denotes the differential operator del.

The ideal gas and caloric equations of state are as follows:

$$p = \frac{\rho RT}{W}, \quad (7)$$

$$\text{and } h_k = h_k^o(T_o) + \int_{T_o}^T c_{p,k} dT, \quad (8)$$

where R is the ideal gas constant, h_k^o is the specific enthalpy of the k -th gaseous species at the specified temperature T_o , and $c_{p,k}$ is the specific heat capacity of the k -th gaseous species at constant pressure.

The equation of surface species coverage can be written as follows:

$$\sigma_m \frac{\dot{s}_m}{\Gamma} = 0, m = K_g + 1, \dots, K_g + K_s, \quad (9)$$

where σ_m is the site occupancy of the m -th surface species, $\dot{s}_m$ is the rate of appearance of the m -th surface species, Γ is the density of catalyst surface sites, m is the total number of gaseous and surface species, and K_s is the total number of surface species.

The two-dimensional energy equation is solved in the solid phase, as follows:

$$\frac{\partial}{\partial x} \left(\lambda_s \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial y} \left(\lambda_s \frac{\partial T}{\partial y} \right) = 0, \quad (10)$$

where λ_s is the thermal conductivity of the solid wall.

The wall thermal conductivity is set as 80.0 W/(m·K). Efficient heat exchange can be achieved by using highly conductive materials [58,59], whereas materials with low wall thermal conductivities are impractical due to the serious problem associated with the formation of hot spots [60,61].

The species transport boundary condition at the fluid-washcoat interfaces is given by the following:

$$\left(\rho Y_k V_{k,y} \right)_{interface} + \eta F_{cat/geo} W_k (\dot{s}_k)_{interface} = 0, k = 1, \dots, K_g, \quad (11)$$

where η is the effectiveness factor. The catalyst/geometric surface area (i.e., the ratio between the catalytically active surface area of the catalyst and the geometrical surface area of the wall), $F_{cat/geo}$, is defined as follows [62]:

$$F_{cat/geo} = \frac{A_{catalyst}}{A_{geometric}}, \quad (12)$$

where $A_{catalyst}$ is the catalytically active surface area of the catalyst and $A_{geometric}$ is the geometrical surface area of the wall.

The effect of the diffusion inside the washcoat is included in the model by introduction of the effectiveness factor, as follows:

$$\eta = \frac{\dot{s}_{i,eff}}{\dot{s}_i} = \frac{\tanh(\Phi)}{\Phi}, \quad (13)$$

$$\Phi = \delta_{catalyst} \left(\frac{\dot{s}_i \gamma}{D_{i,eff} C_{i,interface}} \right)^{0.5}, \quad (14)$$

where $\dot{s}_{i,eff}$ is the effective rate of appearance of the i -th species on the surface of the catalyst, Φ is the Thiele modulus, $\delta_{catalyst}$ is the thickness of the catalyst, $D_{i,eff}$ is the effective diffusivity of the i -th species inside the catalyst washcoat, $C_{i,interface}$ is the concentration of the i -th species at the gas-washcoat interface, and the solution of a one-dimensional equation of reaction–diffusion for a representative species is expressed in terms of the Thiele modulus [63,64]. This simplified effectiveness factor washcoat model is based on the assumption that the reaction rate of one target species determines overall reactivity [65]. The simplified model can significantly reduce the computational cost. Unfortunately, universal validity of the model is questionable, because it does

not account for all of the species concentration profiles [66]. Numerical simulations with a detailed reaction–diffusion model are computationally expensive but allow for discrimination between kinetics and transport effects [66], thus ensuring satisfactory solutions for the reforming process examined.

The active surface area per unit volume of the washcoat, γ , can be written as follows:

$$\gamma = \frac{F_{cat}/geo}{\delta_{catalyst}}. \quad (15)$$

The effective diffusivity, $D_{i,eff}$, can be written as follows:

$$\frac{1}{D_{i,eff}} = \frac{\tau_p}{\varepsilon_p} \left(\frac{1}{D_{i,molecular}} + \frac{1}{D_{i,Knudsen}} \right), \quad (16)$$

$$D_{i,Knudsen} = \frac{d_{pore}}{3} \sqrt{\frac{8RT}{\pi W_i}}, \quad (17)$$

where τ_p is the tortuosity factor for diffusion inside the washcoat, ε_p is the porosity of the washcoat, $D_{i,molecular}$ is the diffusivity for molecular diffusion of the i -th species in the mixture, $D_{i,Knudsen}$ is the diffusivity for Knudsen diffusion of the i -th species in the mixture, and d_{pore} is the mean pore diameter.

The heat transfer boundary condition at the fluid–washcoat interfaces can be written as follows:

$$\dot{q}_{radiation} - \lambda_g \left(\frac{\partial T}{\partial y} \right)_{interface-} + \lambda_s \left(\frac{\partial T}{\partial y} \right)_{interface+} + \sum_{k=1}^{K_g} (\dot{s}_k h_k W_k)_{interface} = 0, \quad (18)$$

where $\dot{q}_{radiation}$ is the radiative heat flux.

The washcoat is considered isothermal in the transverse direction due to its small thickness. The total heat loss to the ambient environment is given by the following:

$$q = h_o (T_{w,outer} - T_{ambient}) + \varepsilon_{s-\infty} F_{s-\infty} \sigma' (T_{w,outer}^4 - T_{ambient}^4), \quad (19)$$

where q is the heat flux, h_o is the external heat loss coefficient, $T_{w,o}$ is temperature at the outer surface of the solid wall, and $T_{ambient}$ is the ambient temperature, the effective emissivity, $\varepsilon_{s-\infty}$, is set as 0.8 [67], $F_{s-\infty}$ is the view factor from the outer surface of the solid wall to the ambient environment, and σ' is the Stefan-Boltzmann constant.

2.3. Chemical Kinetic Model

The possible occurrence of homogeneous reactions during the combustion process is discussed below. For the small-scale reaction system examined, both heterogeneous and homogeneous reactions can take place simultaneously, depending on the operation conditions [68,69]. The combustion reaction occurring in the gas phase might be important to the reactor performance [68], for example, in a high-temperature environment [69,70]. In addition, gas-phase combustion is possible in a confined space with dimensions as low as several sub-millimeters due to heating caused by the reaction occurring on the surface of the catalyst [68]. On the other hand, it has been found that the interaction between heterogeneous and homogeneous reaction pathways may be significant in catalytic combustion systems. Furthermore, a synergetic effect between the two reaction pathways has been determined in the process of catalytic combustion [71,72], and a novel catalytic combustion system based on the concept of partially-coated monoliths has been proposed recently and, subsequently, tested successfully [73–75]. Consequently, both heterogeneous and homogeneous reaction pathways should be included in the model to describe the combustion process accurately. The initiation of the oxidation reaction is possible in the gas phase at the temperatures examined in the present work.

Therefore, the reaction in the gas phase is not negligible on the combustion side, thus greatly increasing the computational cost of the numerical simulations.

For the combustion process studied, both surface and gas-phase reactions can take place simultaneously, as discussed above. To describe the gas-phase combustion process, the Leeds methane oxidation mechanism [76,77] is used. Note that 25 species involved in 105-step elementary reactions are included in the gas-phase mechanism. To describe the catalytic combustion process, the surface reaction mechanism developed by Deutschmann et al. [78] is used. Further information on this mechanism is available in the original work [78] and on the DETCHEM website [79].

For the reforming process studied, gas-phase chemistry has been found to not contribute only at temperatures lower than 950 °C [80]. Furthermore, for all of the conditions examined in the present work, the chemistry in the gas phase has no effect on the performance of the reactor. Therefore, the reforming reaction occurring in the gas phase is negligible to reduce the computational cost of the numerical simulations. For the reforming reaction on rhodium, the surface reaction mechanism developed by Karakaya et al. [81] is used. This surface reaction mechanism, which is thermodynamically consistent in the range of temperature from 273 to 1273 K, has been validated in the range of temperature from 298 to 1173 K [81]. The surface reaction mechanism can be easily implemented in CHEMKIN [82] and Surface-CHEMKIN [83]. For the reforming reaction on nickel, the reforming reaction occurring in the gas phase is negligible, as discussed above. The surface reaction mechanism developed by Maier et al. [84] is used. This mechanism is thermodynamically consistent in the range of temperatures from 273 to 1273 K and has been validated in the range of temperatures from 600 to 1300 K [84]. Further information on the surface reaction mechanisms over both catalysts can be found on the DETCHEM website [79].

Some of the catalyst properties used are listed in Table 1. The catalyst loading can be expressed by means of the surface area factor, $F_{cat/geo}$, as defined by Equation (12). It has been demonstrated that there is a linear relationship between the catalyst loading and the surface area factor [62]. In the present work, the nominal surface area factor is assumed to be 20 on each side of the reactor. Generally, the rate of a reaction increases with the increasing of the surface area factor [13]. It is therefore necessary to utilize a sufficiently high catalyst loading for realizing the rapid production of hydrogen via the steam reforming of methane. The adsorption rate constant can be written as follows:

$$k_{ad,k} = \left(\frac{2}{2 - s\theta_{free}} \right) \frac{s}{\Gamma^m} \sqrt{\frac{RT}{2\pi W_k}} \quad (20)$$

where $k_{ad,k}$ is the adsorption rate constant of the k -th species, s is the sticking coefficient, and θ_{free} is the surface coverage of free sites.

Thermochemical information is obtained from the combustion and reforming kinetic mechanisms described above. The rate of the reaction in the gas phase and on the surface of the catalyst is handled with CHEMKIN [82] and Surface-CHEMKIN [83], respectively, each of which is a plug-in chemistry solver.

2.4. Computation Scheme

Inlet temperatures, pressures, velocities, and gas compositions are specified as the feed conditions. Additionally, at each of the fluid-washcoat interfaces, detailed surface reaction mechanisms are specified. Comparisons with the results obtained from an independent model are also made, and the NASA computer program Chemical Equilibrium with Applications (CEA) [85,86] is used to obtain chemical equilibrium compositions and properties of each of the gas mixtures.

An orthogonal staggered mesh is used, with more nodes accumulated near the entrance to the reactor and within the catalyst structure. Detailed computational fluid dynamics modeling may lead to vast computational costs. In the present work, a typical mesh consisting of 200 nodes in the axial direction and 200 nodes in the transverse direction is used for the base case, whereas a mesh consisting

of 80,000 nodes in total is used in the case of the largest dimension. Furthermore, a mesh independency test is conducted by varying levels of refinement.

Figure 2 shows the profiles of the hydroxyl radical concentration along the combustion channel centerline for the meshes indicated for the base case. Refer to Table 1 for the operating conditions used in the numerical simulations performed here. As the mesh density increases, a trend toward convergence can be found for the solution. The coarsest mesh, totaling 2500 nodes, cannot accurately describe the concentration of the hydroxyl radical appearing in the reaction region and its peak position. Therefore, the coarsest mesh fails to accurately describe the chemical reaction occurring in the combustion channel. In contrast, the solution obtained from a mesh consisting of tens of thousands of nodes used for the base case can be considered to be reasonably accurate. A larger mesh density, up to 160,000 nodes in total, offers no significant advantage.

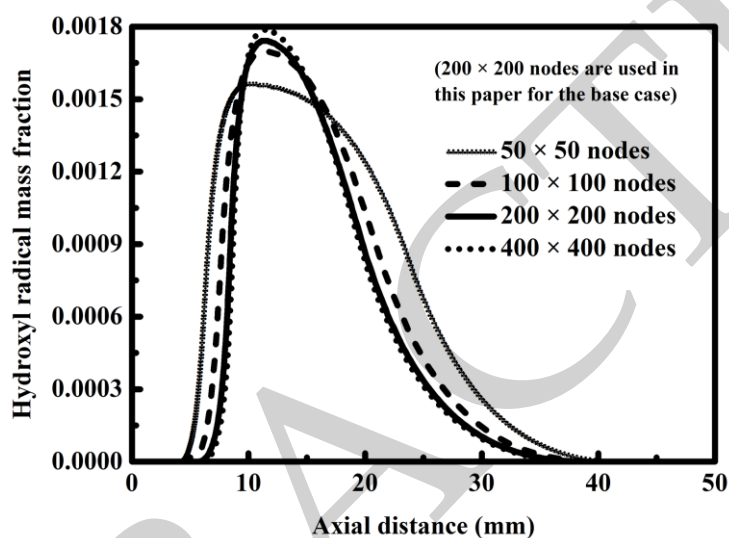


Figure 2. Profiles of the hydroxyl radical concentration along the combustion channel centerline for the meshes indicated for the base case. The operating conditions used in the numerical simulations conducted here are given in Table 1.

The solution is deemed to have converged when the residuals of the conservation equations are less than 10^{-6} . Figure 3 shows the residuals of the conservation equations after each iteration. The criterion for convergence is satisfied after about 700 iterations. In order to verify the model developed here, comparisons are needed between the results obtained from the numerical model and the experimental data measured under the same operating conditions. Furthermore, to ensure that the implementation of the numerical model is correct, the information obtained from the results of the numerical model about the combustion process, reforming process, and thermal coupling between them should also be verified and validated simultaneously. The characteristic length scale of the system examined in this paper is 0.2 mm for the base case, thus rendering spatially resolved measurements within such a small space extremely difficult. Therefore, detailed modeling is very valuable in clarifying the mechanism underlying the thermal coupling within the reaction system, as well as assisting in the design of microchannel reactors for the rapid production of hydrogen.

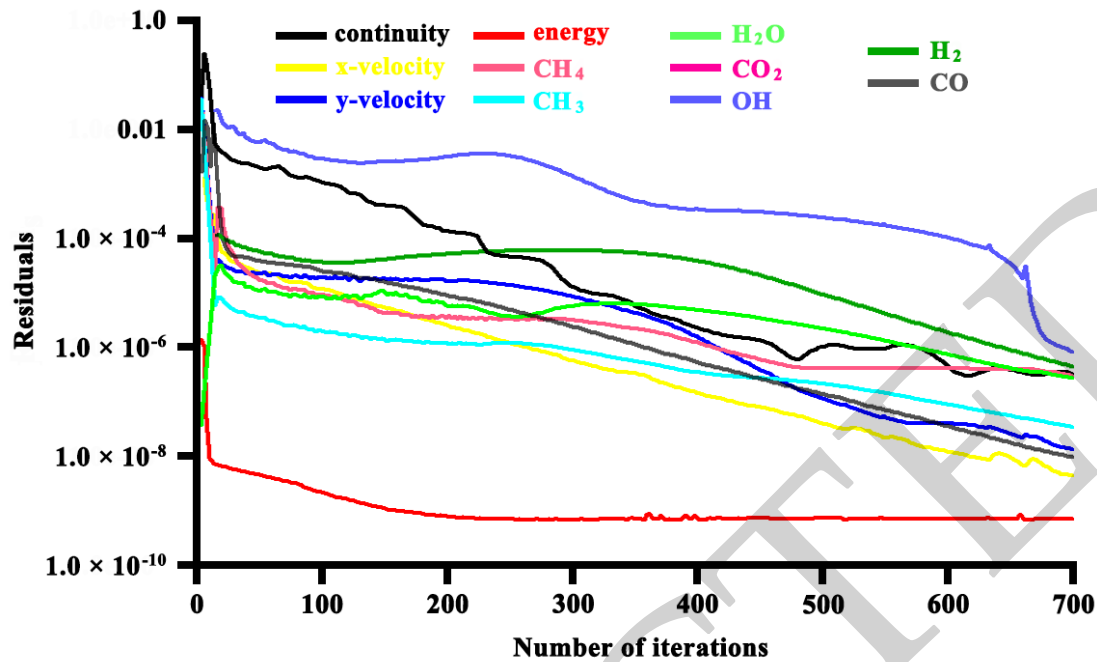


Figure 3. Residuals of the conservation equations after each iteration. The mesh used here consists of 40,000 nodes in total. The operating conditions used in the numerical simulations conducted here are listed in Table 1.

3. Results

3.1. Analysis of Transport and Reaction Time Scales

The rapid production of hydrogen can be achieved from methane steam reforming over rhodium due to both efficient transport and fast kinetics [12,13]. The role of heat and mass transfer within the small-scale system is expected to be of very great importance. To evaluate the importance of the efficient transport for process intensification, both the transport and reaction time scales involved in the system are determined. In most commercial units, the catalyst used for the production of hydrogen from methane steam reforming is based on nickel. Under typical industrial operating conditions, the rate of the methane steam reforming reaction is usually considered to be slow in the case of nickel. Therefore, it is of great interest to explore the feasibility of the rapid production of hydrogen by intensifying the steam reforming over nickel through efficient transport.

The transport and intrinsic reaction time scales on both sides of the reactor are shown in Figure 4. The intrinsic reaction time scale, in the absence of the effect of the transport phenomena, is given by the following:

$$\tau_{\text{reaction}} = \frac{0.5C_{\text{fuel},in}}{\left[\dot{s}_{\text{fuel}}(S/V') + \dot{\omega}_{\text{fuel}}\right]}, \quad (21)$$

where τ is the time scale, $C_{\text{fuel},in}$ is the concentration of the fuel at the inlet, S is the surface area of a channel, and V' is the volume of a channel. As discussed earlier, the reaction occurring in the gas phase is negligible on the reforming side. The intrinsic reaction time scales are evaluated under the specified conditions (i.e., 900, 1200, and 1500 K). The values obtained for the intrinsic reforming reaction time scales described for a given temperature 1500 K are adjusted by extrapolation, because each of the surface reaction mechanisms used here is thermodynamically consistent only in the range of temperatures from 273 to 1273 K.

The small dimension of the system implies that the transport processes are significantly influenced by diffusion. The time scale of the mass transfer in the transverse direction between the surface of the catalyst and the bulk fluid can be written as follows:

$$\tau_{y, \text{diffusion}} = \frac{d^2}{4D_{\text{fuel}}}, \quad (22)$$

where d is the channel height, and D_{fuel} is the diffusivity for the fuel in the mixture.

The time scale of the heat transfer in the transverse direction is given by the following.

$$\tau_{y, \text{thermal diffusion}} = \frac{d^2}{4D^T} \text{ with } D^T = \frac{\lambda_g}{\rho c_p}, \quad (23)$$

where D^T is the thermal diffusivity.

The time scale of the mass and heat transfer in the axial direction can be written as follows.

$$\tau_x \approx \frac{l}{\bar{u}}, \quad (24)$$

where l is the length of the reactor and $\bar{u}$ is the mean flow velocity of a fluid.

Typical mass and heat transfer and intrinsic reaction time scales are shown in Figure 4a for the reforming channel. The temperature can significantly affect the time scale of the intrinsic reforming reaction over either nickel or rhodium. In the temperature range examined here, the time scale changes from about 700 to 3 milliseconds for nickel, and from about 800 to 0.2 milliseconds for rhodium. The difference in the intrinsic reaction time scales between the two catalysts used in this investigation is small at low temperatures but becomes significant at high temperatures. In addition, the computations are conducted for the gas mixture with different compositions, and the results indicate that the difference can be up to 20 times in the temperature range examined in this investigation. The difference can be up to one order of magnitude under typical operating conditions (i.e., at 50% conversion and temperature 1200 K).

The time scale of the mass transfer in the transverse direction is of the order of tens of microseconds, which is far smaller than the intrinsic reaction time scale. In contrast, the time scale of the mass transfer in the axial direction is of the order of a few milliseconds. At high temperatures, the time scale of the intrinsic reforming reaction is shorter than the residence time for highly active catalysts such as rhodium. At low and moderate temperatures, however, the time scale is of the same order of magnitude as the residence time, especially for nickel. In this case, possible or even considerable incomplete conversion occurs. Overall, process intensification has been achieved through miniaturization, but catalyst improvement in activity or loading is highly desirable.

Typical mass and heat transfer and intrinsic reaction time scales are shown in Figure 4b for the combustion channel. The temperature can also significantly affect the time scale of the intrinsic combustion reaction, ranging from about 0.005 to 0.5 milliseconds. The time scale is far smaller than that of the intrinsic reforming reaction, and the difference between the two time scales becomes more pronounced when the temperature is low. On the combustion side, the difference in the time scale between the transverse transfer and the intrinsic reaction is relatively small, which is opposite to the difference obtained on the reforming side. This suggests that the combustion reaction is limited by both transport and kinetics, and it is therefore necessary to further intensify the process by reducing the dimension. The effect through the improvement of the catalyst in the activity or loading is not significant. The residence time is much higher than the other time scales, and thus complete conversion can be easily achieved for the combustion process.

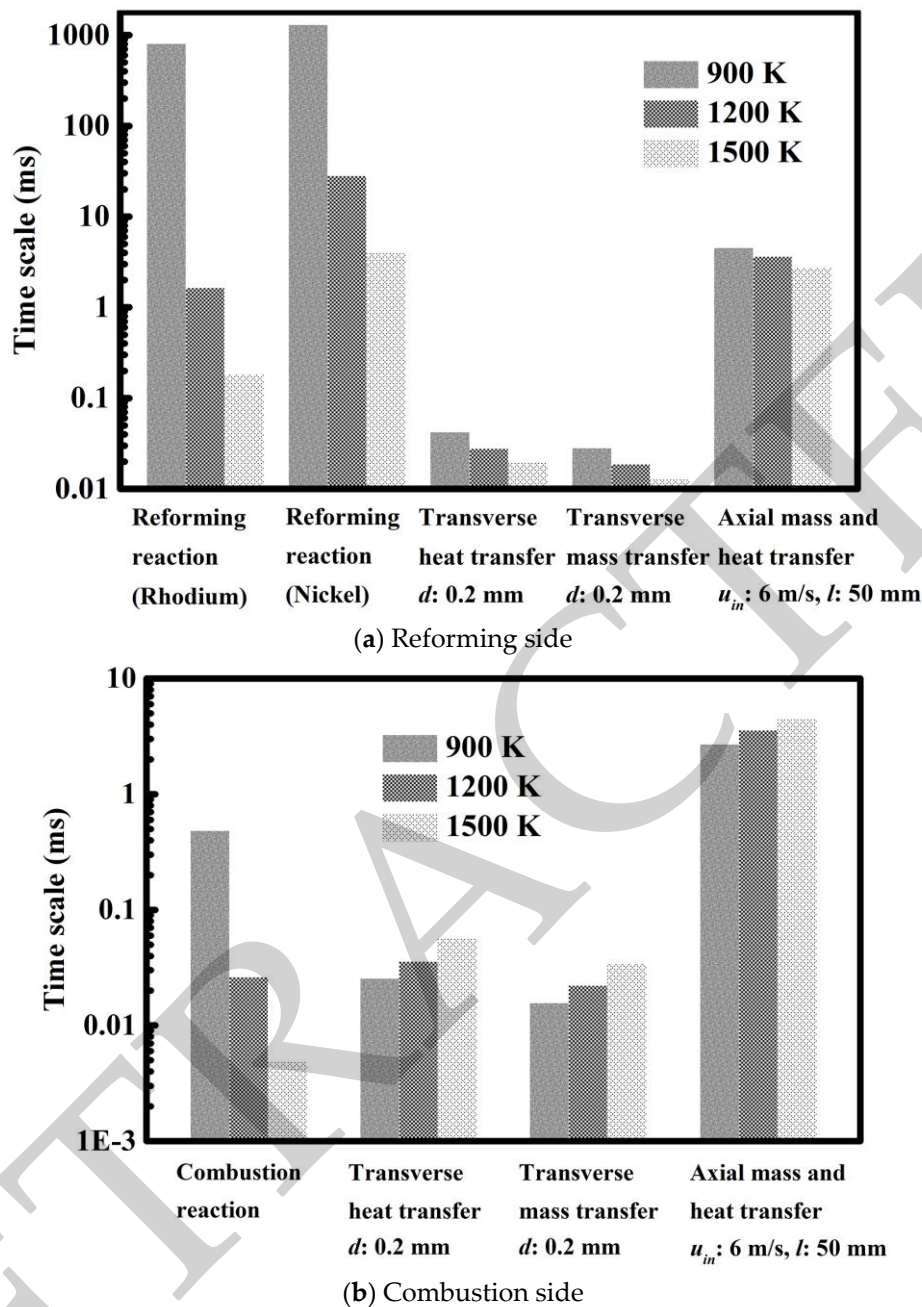
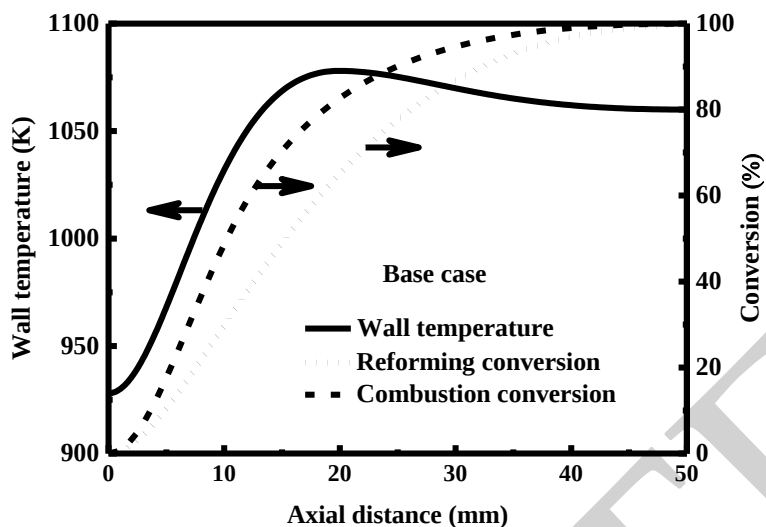


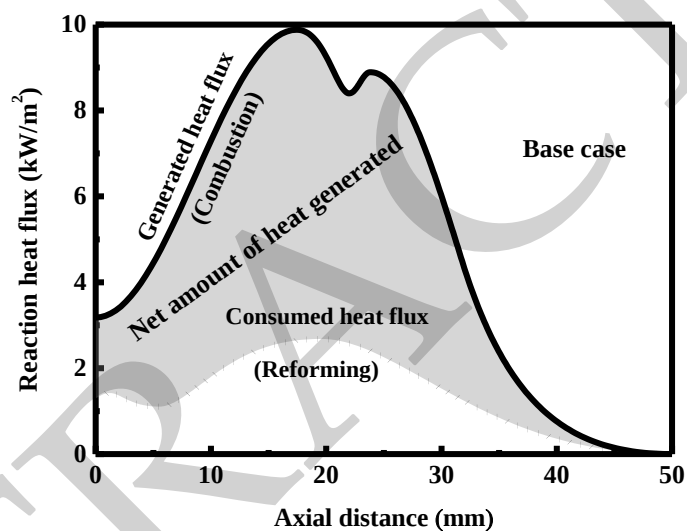
Figure 4. Transport and intrinsic reaction time scales on (a) the reforming side and (b) the combustion side under the conditions indicated.

3.2. Heat Exchange Characteristics

Because the management of energy in a small-scale confined space is very important for reactor design [51,87], the effect of the thermal coupling within the reaction system is investigated. Figure 5a shows the temperature and conversion profiles along the axial direction (i.e., along the length of the reactor). Hereafter, only rhodium is used as the catalyst employed on the reforming side; in addition, where appropriate, the reforming reaction chamber and the combustion reaction chamber will be referred to as “reformer” and “combustor”, respectively.



(a) Wall temperature and conversion profiles



(b) Heat flux (absolute values) profiles

Figure 5. (a) Wall temperature and conversion profiles and (b) heat flux (absolute values) profiles along the axial direction for the base case. The shaded region depicted in (b) represents the net amount of heat generated in the reaction system.

Figure 5a shows that the wall temperature first increases and then decreases very slowly along the axial direction. The outlet conversion is almost completed for the fuel on each side of the reactor, because the rate of each of the combustion and reforming reactions is very high under the conditions examined here. Figure 5b shows the absolute values of the consumed and generated heat fluxes, respectively, along the axial direction. The initiation of the gas-phase combustion is possible, as indicated by the sub-peak shown in the generated heat flux profile. The reaction occurring on the combustion side provides the heat energy required to heat up the gas mixtures on both sides of the reactor and to drive the reforming reaction simultaneously. The shaded region in Figure 5b represents the net amount of heat generated. The peaks shown in the generated and consumed heat flux profiles appear almost at the same axial position. The rate of the reaction on the combustion side is much higher than that on the reforming side, thus increasing the temperature at the first half of the reactor, as shown in Figure 5a. In contrast, there is a small difference between the two heat fluxes at the second

half of the reactor, and thus each of the wall and fluid temperatures is nearly uniform along the axial direction, as shown in Figure 5a.

Figure 6 shows the contour plots of the temperature, species concentration, flow velocity, specific heat, and molecular Prandtl number on the reforming side for the base case. The Prandtl number can be used to determine the thermal conductivity of gases at high temperatures [88]. Because the molecular Prandtl number is small, the heat diffuses quickly in comparison with the flow velocity. While the wall temperature difference is negligible in the transverse direction, there are steep species and temperature gradients in the gas phase near the reaction region, as shown in Figure 6. In this context, a two-dimensional numerical model is required, because each of the heat and mass transfer may be important in the axial direction.

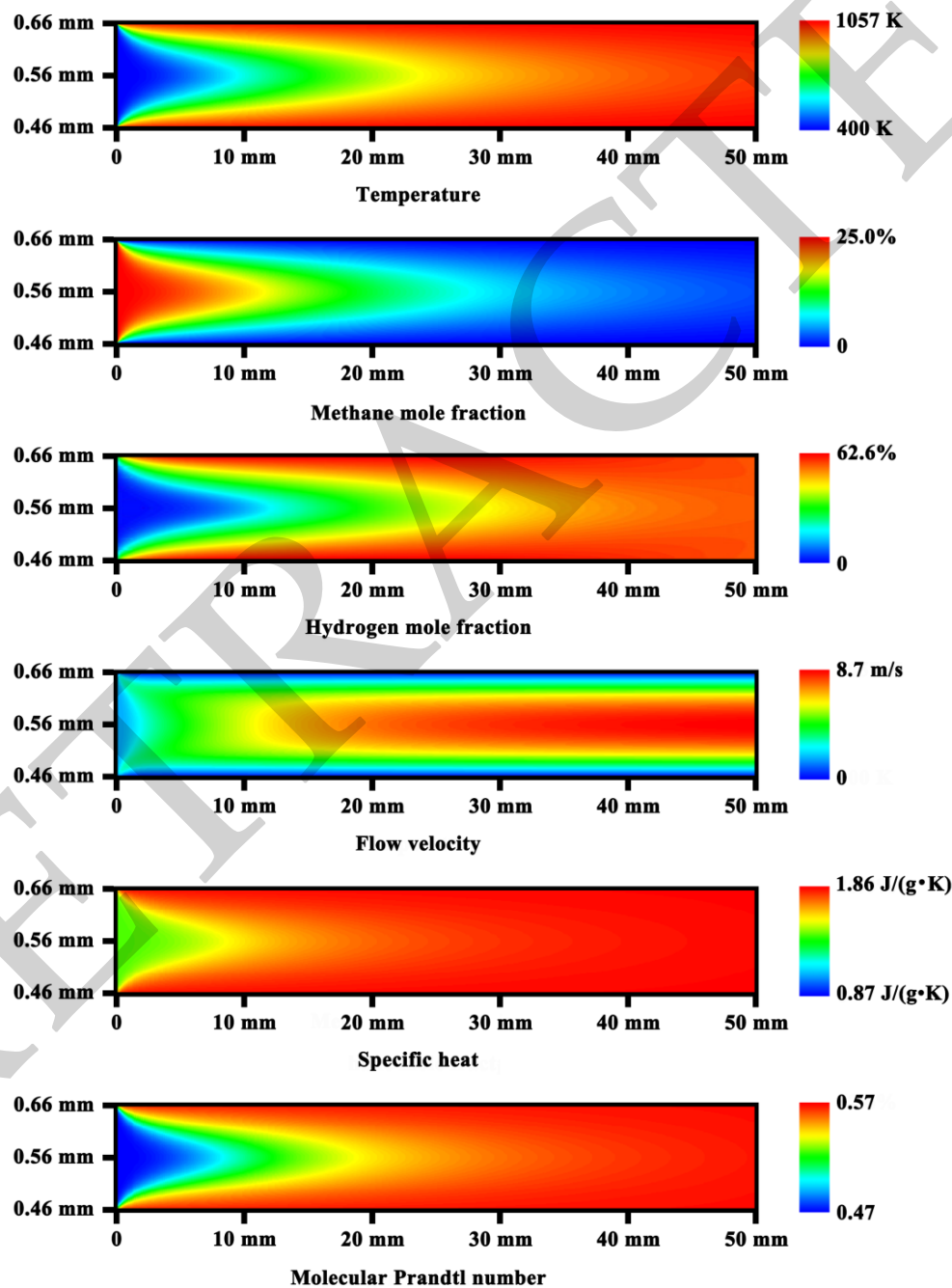


Figure 6. Contour plots of the temperature, species concentration, flow velocity, specific heat, and molecular Prandtl number on the reforming side for the base case.

The contour plots of the temperature and species concentration on the combustion side for the base case are shown in Figure 7. The results obtained demonstrate self-sustained operation within the catalytic system with nearly complete conversion of the fuel on both sides of the reactor. The highly conducting wall allows the transfer of heat toward the gas mixture near the entrance to the reactor, and the heat generated on the surface of the catalyst is transferred transversely to the fluid, thus causing the homogeneous ignition of the mixture in the vicinity of the catalytic surfaces. After the fuel has been almost completely consumed, the temperature profile in the transverse direction is fairly uniform in the post-combustion region, as shown in Figure 7. This is due to the high heat transfer rate within the system caused by the small characteristic length scale involved. Overall, the design parameters and operating conditions adopted for the base case can provide an efficient coupling of heat transfer within the system. The effects of various design parameters are discussed in the following sections to develop suitable operation strategies for the integrated small-scale system.

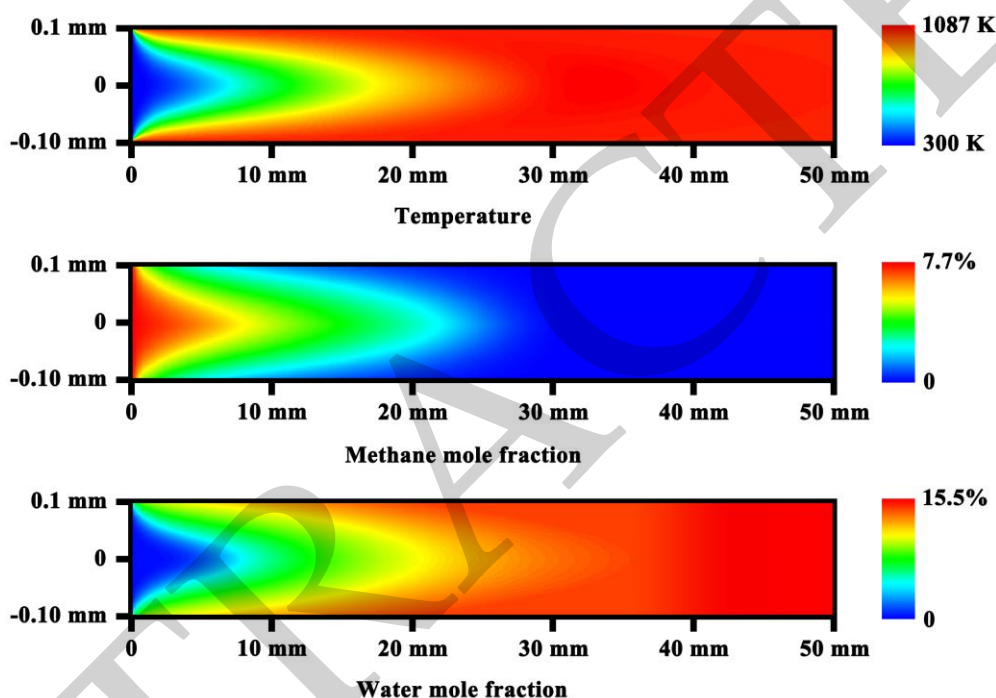
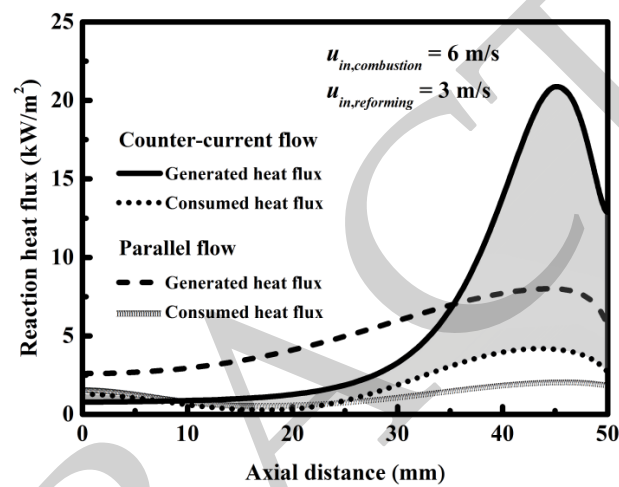


Figure 7. Contour plots of the temperature and species concentration on the combustion side for the base case.

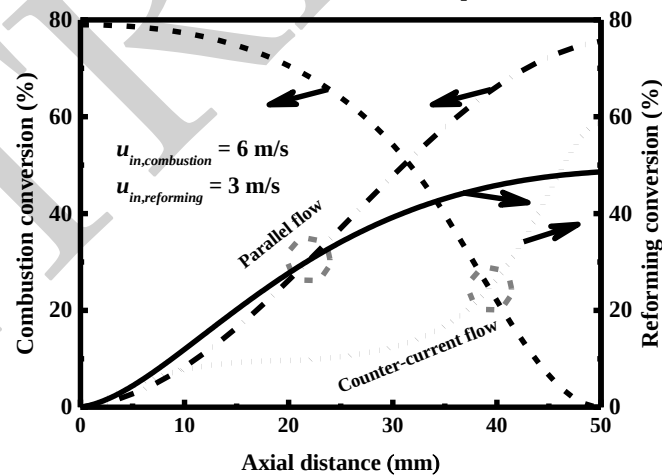
3.3. Effect of Flow Arrangement

The flows inside a heat exchanger can be arranged in various ways to meet different needs [89–91]. Some of the possibilities are parallel flow and countercurrent flow, as depicted in Figure 1; note that the horizontal dotted arrows indicate the countercurrent flow. Countercurrent flow exchange could offer significant advantages over parallel flow exchange [92,93]. However, the efficient operation of the system requires not only high operability, but also a reliable thermal management strategy. Therefore, the effect of flow arrangement on the reactor design is evaluated here with identical inlet conditions. The benefits and disadvantages associated with each of the two flow arrangements are discussed in detail based on the comparisons made between their respective results obtained. Thermal energy transport in the two heat exchange systems is also examined to achieve reasonable performance in small-scale devices. Because high hydrogen flow rates are highly desirable [12–14], the reforming stream flow rate is assumed to be high so that a direct comparison can be easily made between the two flow arrangements. In this context, a low conversion may be possible on each side of the reactor.

A direct comparison can be made between the two heat exchange systems based on the heat flux (Figure 8a) and the conversion along the length of the reactor (Figure 8b). Figure 8a shows the heat flux (absolute values) profiles for the two flow arrangements examined in this paper. In the parallel flow exchange system where the two fluids flow in the same direction, a more uniform profile can be obtained along the axial direction for each of the generated and consumed heat fluxes, as shown in Figure 8a. In contrast, in the countercurrent flow exchange system where the two fluids flow in opposite directions of each other, each of the two heat fluxes is more concentrated near the reformer outlet. The ratio of heat generation and heat consumption at the reformer entrance is 1.6 for the parallel flow exchange system and 0.6 for the countercurrent flow exchange system. Therefore, the cooling effect near the reformer entrance is more pronounced for the countercurrent flow exchange system. The ratio of heat generation and heat consumption at the reformer outlet is 2.8 for the parallel flow exchange system and 4.8 for the countercurrent flow exchange system, eventually leading to local overheating.



(a) Heat flux (absolute values) profiles



(b) Conversion profiles

Figure 8. (a) Heat flux profiles along the axial direction in different flow arrangements. (b) Conversion profiles along the axial direction in different flow arrangements. The shaded regions presented in (a) represent the net heat generated from the combustion and reforming reactions occurring in the countercurrent flow exchange system. The heat in the gray area is accounted for as positive, and the heat in the pink area is accounted for as negative.

Figure 8b shows the conversion profiles for the two flow arrangements examined in this paper. At the outlet of the combustor, a higher conversion can be achieved for the countercurrent flow exchange system (79.0%) than for the parallel flow exchange system (75.6%). On the combustion side, most of the fuel is converted near the reformer outlet for the countercurrent flow exchange system; in this context, the heat released by the catalytic combustion is more concentrated near the reformer outlet. For the countercurrent flow exchange system, the gradual disappearance of the reactants along their flow direction can decrease the rate of the reaction occurring on the combustion side and subsequently the capability of the gas mixture on the reforming side to consume the heat released by the catalytic combustion. Therefore, a high imbalance of energy flow can be found within the countercurrent flow exchange system under the conditions examined here; in addition, the excess heat released by the catalytic combustion near the outlet of the reformer overheats the gas mixture on each side of the reactor, thus increasing the possibility of the reaction occurring in the gas phase on the combustion side. On the other hand, the conversion is higher on the reforming side for the parallel flow exchange system than for the countercurrent flow exchange system along the whole length of the reactor, except at the outlet of the reformer due to the increased temperature for the countercurrent flow exchange system.

Several characteristics for each of the two flow arrangements examined in this paper are summarized in Table 2. A comparison is conducted between the results obtained for the two flow configurations based on criteria for reactor performance (e.g., conversion, temperature, and thermal balance) listed in Table 2. The reactor in a parallel flow arrangement is better balanced thermally between the exothermic process and the endothermic process, which can eliminate hot spots and thus may offer potential advantages for practical applications. When the reactor is in a countercurrent flow arrangement, the utilization of the overall heat released by the catalytic combustion can be better achieved, and a higher conversion can also be achieved on each side of the reactor. In this flow arrangement, however, the difference in temperature is significant within the wall and within the fluid in the transverse direction. This situation is undesirable, because it may significantly increase the possibility of extinction occurring in the small-scale system or may lead to loss of control over the combustion or reforming process. Furthermore, localized hot spots may occur within the wall, causing damage to the wall materials and the catalysts used.

Table 2. Comparisons of the parallel and countercurrent flow arrangements used for the reactor.

Reactor Performance	Parallel	Countercurrent
Flow velocity at the inlet of the reformer	3.0 m/s	3.0 m/s
Flow velocity at the inlet of the combustor	6.0 m/s	6.0 m/s
Conversion at the outlet of the reformer	48.6	58.7
Conversion at the outlet of the combustor	75.6	79.0
Maximum wall temperature	1047 K	1160 K
Minimum wall temperature	870 K	848 K
Fluid temperature difference		
Maximal value appeared in the transverse direction	570 K	687 K
Minimum value appeared in the transverse direction	−66 K	−180 K
Ratio of overall generated and consumed heat	3.78	3.26
Ratio of local generated and consumed heat		
At the reformer entrance	1.6	0.6
At the reformer outlet	2.8	4.8

3.4. Effect of Reactor Dimension

The micro-chemical system studied here is expected to have many advantages for chemical production and process development. It is of importance to exploit the enhanced transport characteristics resulting from the small dimension of the system. The channel height should be properly designed, as small channels can reduce diffusional resistance. The influence of channel height on the performance of the integrated reactor is evaluated when each of the two inlet flow velocities

is kept constant. In addition, the time scales involved in the small-scale system are determined, and several dimensionless quantities are computed.

Figure 9a shows the some of the dimensionless quantities obtained at different reformer dimensions at the inlet flow velocities indicated. The shaded region in Figure 9a indicates a kinetically-controlled regime ($Da_y < 0.1$), where the formation of products from the steam reforming reaction is much slower than the diffusion of reactants in different phases. Some of the dimensionless quantities, such as the transverse Damköhler number (Da_y), Péclet number (Pe), and Fourier number (Fo) are defined as follows [94]:

$$Da_y = \frac{\tau_{y, \text{diffusion}}}{\tau_{\text{reaction}}} = \frac{d^2 \dot{s}_{\text{fuel}} (S/V')}{2D_{\text{fuel}} C_{\text{fuel}, \text{in}}}, \quad (25)$$

$$Pe = \frac{\tau_{y, \text{diffusion}}}{\tau_x} = \frac{d^2 \bar{u}}{4D_{\text{fuel}} l'}, \quad (26)$$

$$Fo = \frac{\tau_x}{\tau_{y, \text{thermal diffusion}}} = \frac{4\lambda_g l}{d^2 \bar{u} \rho c_p}. \quad (27)$$

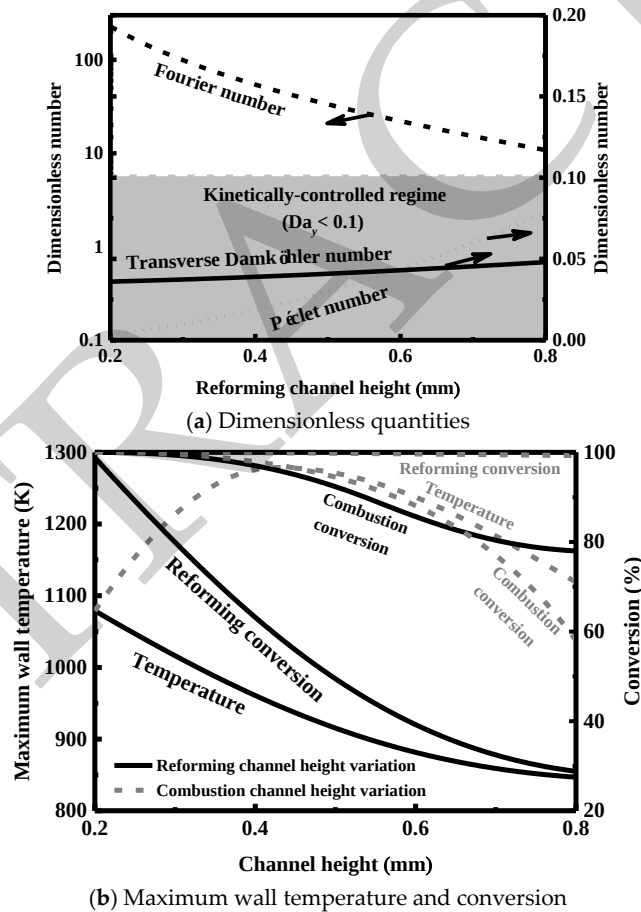


Figure 9. (a) Effect of channel height on the Péclet, Fourier, and transverse Damköhler numbers. (b) Effect of channel height on the conversion and maximum wall temperature. The solid lines represent a change in reformer dimension, and the dashed lines represent a change in combustor dimension. In (a), the shaded region indicates a kinetically-controlled regime ($Da_y < 0.1$). The inlet flow velocity is kept constant at 6.0 (combustible stream) and 2.0 m/s (reforming stream), respectively. The dimensionless quantities are computed at the axial position of 10.0 mm for simplicity. The kinetically-controlled regime depicted in (a) is only demarcated by the transverse Damköhler number.

The above dimensionless quantities depend upon the local position. In the present work, these dimensionless quantities are computed at the axial position of 10.0 mm for simplicity. Figure 9a shows that there is little change in the transverse Damköhler number when the reformer dimension varies from 0.2 to 0.8 mm. This is because increasing the height not only results in slower diffusion in the transverse direction, but also leads to a lower reforming reaction rate due to the decreased wall temperatures caused by a higher reforming stream flow rate. Overall, the reforming reaction is limited by kinetics for the system examined in this paper, as discussed previously in Figure 4a. Figure 9a also determines the relative importance of the transfer time scales in both the transverse and axial directions. The transfer time scale in the transverse direction is always one order of magnitude smaller than that in the axial direction, as illustrated previously in Figure 4a.

Figure 9b shows the conversion and maximum wall temperature at different channel heights when the inlet flow velocities are kept constant on both sides of the reactor. Each of the combustion and reforming channel heights varies from 0.2 to 0.8 mm; note that for the small-scale catalytic system considered here, the combustion reaction cannot be self-sustained in channels with heights lower than 0.17 mm due to thermal quenching. Each of the two channel heights can significantly influence the performance of the reactor, as shown in Figure 9b. When the reforming channel height is increased, three effects result in the reduction of the conversion at the outlet of the reformer: (a) the diffusion resistance becomes significant between the surface of the catalyst and the bulk fluid, (b) a sufficient amount of catalysts are not available for the reforming reaction, and (c) there is a certain amount of the sensible heat used to heat up a larger amount of reactants. Interestingly, as the reforming channel height increases, the temperature decreases along the length of the reactor. This is because of the increased amount of the reactants on the reforming side.

Figure 9b shows that the conversion on the reforming side is almost complete when the combustor dimension increases from 0.2 to 0.8 mm. Although the decrease in conversion may be more or less unavoidable on the combustion side, the catalytic combustion can always provide enough energy for the reforming reaction. Both the energy input on the combustion side and the diffusion resistance in the transverse direction can directly affect the temperature and conversion. At higher combustion channel heights, the conversion in the combustion channel decreases due to the increased diffusion resistance, although there is an increase in the energy input on the combustion side. Interestingly, the temperature increases firstly and then decreases with increasing the combustor dimension, as shown in Figure 9b. At lower combustion channel heights, conversion is nearly complete on the combustion side; in this context, a larger combustion channel increases the energy input and thus the temperature. At higher combustion channel heights, the energy input plays a less important role than the diffusion resistance; in this context, the temperature decreases with increasing the combustor dimension.

Overall, the reactor dimension can significantly influence the performance of the system for a given inlet flow velocity. Both conversion and temperature change significantly. The use of a larger reforming channel might be practical at a constant inlet flow rate [13], but this conflicts with the rapid production of hydrogen as the residence time increases.

3.5. Effect of Catalyst Loading

The effect of the catalyst loading is evaluated in this section. The catalyst loading is adjusted by means of the catalytically active surface area (e.g., the noble metal loading in the catalysts used), while keeping all the other parameters at their base case values quoted in Table 1. The ratio of the catalyst loadings K , which is used to evaluate the effect of the catalyst loading, is defined as follows:

$$K = \frac{F_{cat/geo}}{\left(F_{cat/geo}\right)_{basecase}}. \quad (28)$$

Figure 10 shows the effect of the combustion catalyst loading on the performance of the reactor. Figure 10a shows the wall temperature profiles along the axial direction for the ratios of the combustion

catalyst loadings indicated, and Figure 10b shows the outlet conversions on each side of the reactor as a function of the ratio of the combustion catalyst loadings.

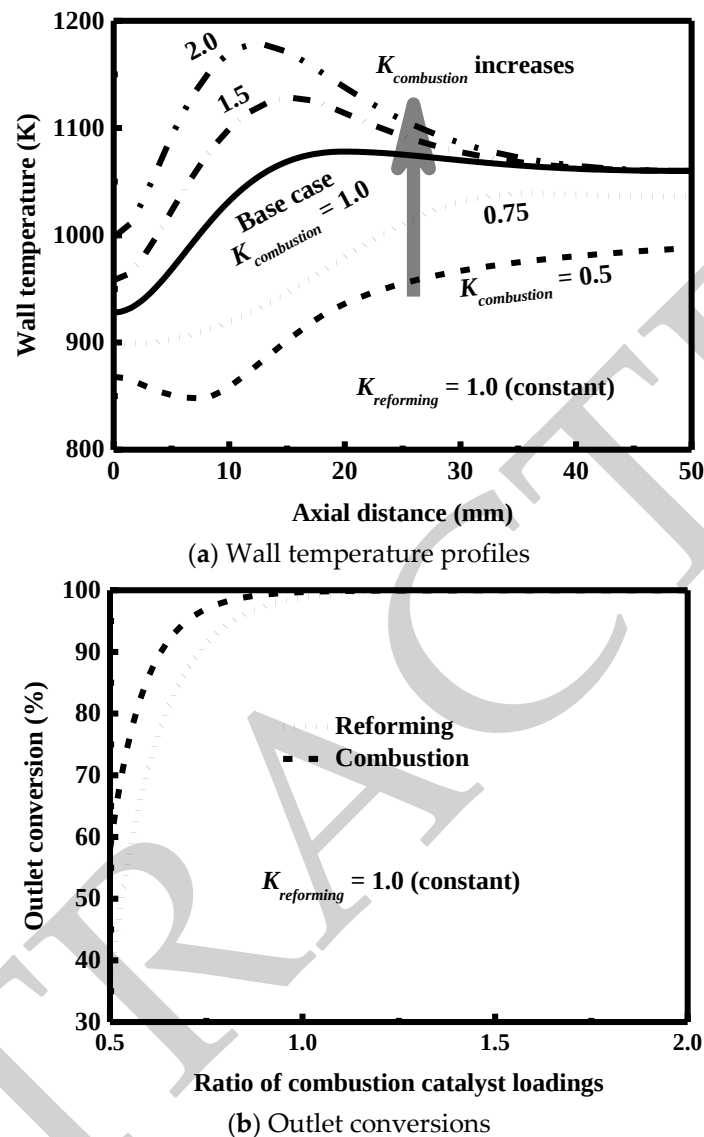
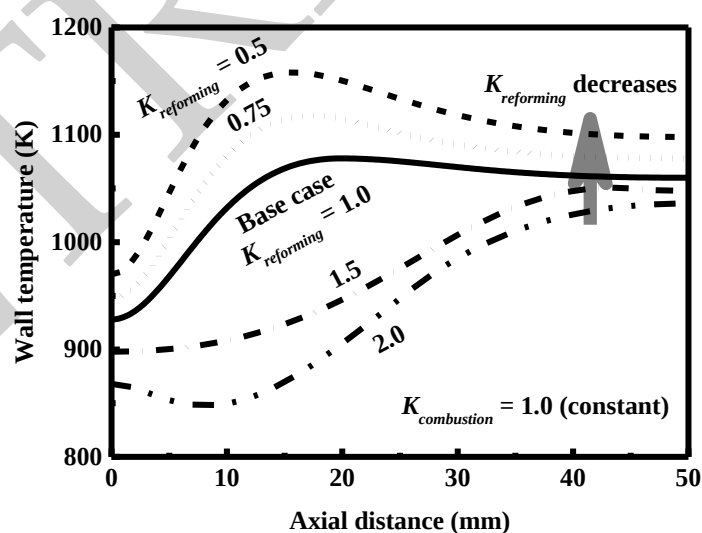


Figure 10. (a) The wall temperature profiles along the length of the reactor for the ratios of the combustion catalyst loadings indicated. (b) The outlet conversions as a function of the ratio of the combustion catalyst loadings.

As the ratio of the combustion catalyst loadings decreases from its base case value to a lower value, the rate of the reaction on the combustion side decreases gradually, eventually leading to lower outlet conversions on each side of the reactor, as shown in Figure 10b. Consequently, in comparison with the results obtained for the base case, there is a smaller amount of the heat released during the catalytic combustion, resulting in a decrease in the wall temperature, as shown in Figure 10a. In addition, the rate of the reaction on the reforming side, as well as the equilibrium conversion, also decrease, resulting in a decrease in the conversion at the outlet of the reformer, as shown in Figure 10b. As the ratio of the combustion catalyst loadings decreases further to a minimum value, $K_{\text{combustion}} = 0.5$, the amount of the heat released during the catalytic combustion is so small that the steam reforming reaction takes place by the utilization of the sensible heat absorbed by the gas mixture, eventually leading to the formation of a cold spot, as shown in Figure 10a for the case with $K_{\text{combustion}} = 0.5$.

The wall temperature decreases until the axial position at about 8 mm and then increases. In contrast, as the ratio of the combustion catalyst loadings increases from its base case value to a higher value, there is an increase in both the amount of heat released by the catalytic combustion and the outlet conversion on each side of the reactor, as shown in Figure 10b. Additionally, a hot spot is formed within the wall, because the reaction rate is much higher in the combustion channel than in the reforming channel (as discussed previously in Figure 4). In this case, the amount of heat released is much larger than that of heat consumed; therefore, each of the gas mixtures is heated rapidly to a higher temperature. As a result, there is an increase in the rate of the reaction in the reforming channel and thus the amount of heat consumed within the system. The wall temperature eventually decreases, as shown in Figure 10a for the cases with $K_{\text{combustion}} = 1.5$ and 2.0. The situation is undesirable, because hot spots formed in the wall may eventually lead to rapid catalyst deactivation.

Figure 11 shows the effect of reforming the catalyst loading on the performance of the reactor in terms of the wall temperature profile along the length of the reactor, as well as the outlet conversion on each side of the reactor. Figure 11a shows the wall temperature profiles along the axial direction for the ratios of the reforming catalyst loadings indicated, and Figure 11b shows the outlet conversions on each side of the reactor as a function of the ratio of the reforming catalyst loadings. Interestingly, a higher loading of the reforming catalyst does not improve the performance of the reactor under the conditions examined here. As the ratio of the reforming catalyst loadings increases from its base case value to a higher value, there is an increase in both the rate of the reforming reaction and the amount of heat consumed, eventually leading to lower wall temperatures, as shown in Figure 11a. For the cases with $K_{\text{reforming}}$ equal to or greater than 2.0, this cooling effect is so significant that a cold spot is formed within the wall, as shown in Figure 11a. Therefore, as the ratio of the reforming catalyst loadings increases from its base case value to a higher value, there exists a decrease in both the wall temperature as shown in Figure 11a, and the conversion on each side of the reactor as shown in Figure 11b. In contrast, as the ratio of the reforming catalyst loadings decreases from its base case value to a lower value, the conversion on the combustion side is almost complete, but there exists a decrease in the conversion in the reforming channel because of the decreased activity of the reforming catalyst, as shown in Figure 11b.



(a) Wall temperature profiles

Figure 11. Cont.

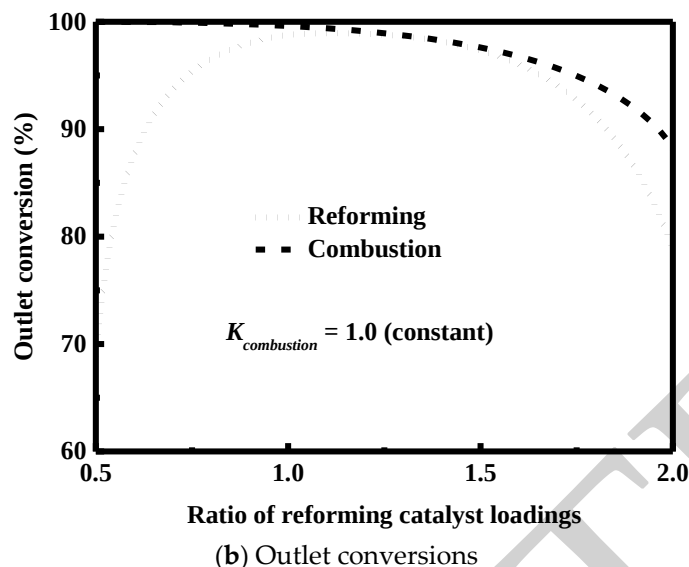
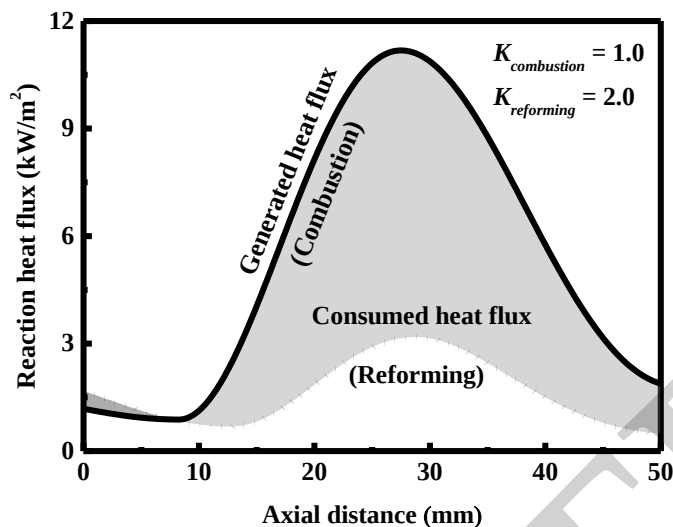
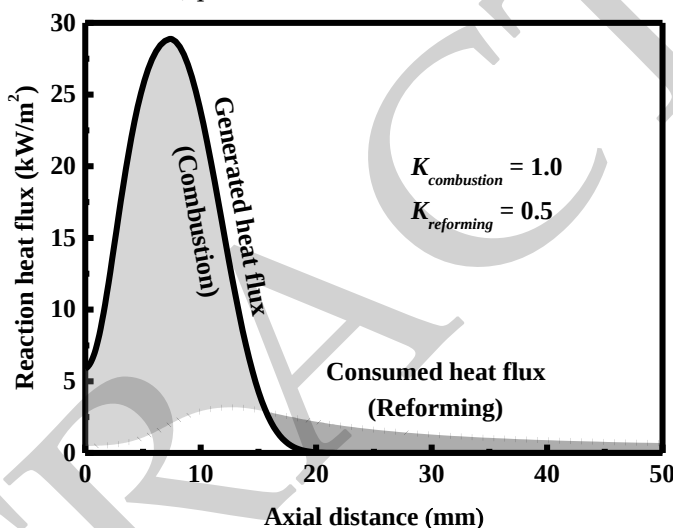


Figure 11. (a) The wall temperature profiles along the length of the reactor for the ratios of the reforming catalyst loadings indicated. (b) The outlet conversions as a function of the ratio of the reforming catalyst loadings.

To improve the performance of the reactor, it is important to achieve a thermal balance within the small-scale system. Figure 12 shows the heat flux profiles along the axial direction for the two cases indicated. For the case with $K_{reforming} = 2.0$, a cold spot is formed at the axial position of about 8.2 mm, as shown in Figure 12a. For the case with $K_{reforming} = 0.5$, a hot spot is formed at the axial position of about 15.8 mm, as shown in Figure 12b. When the rate of heat release is lower than the rate of heat consumption, the temperature of the gas mixture decreases on each side of the reactor, eventually leading to a lower rate of each of the combustion and reforming reactions until the axial position of about 8 mm, as shown in Figure 12a. Over this axial distance, the rate of heat consumption becomes smaller than the rate of heat release, thus increasing the temperature of the gas mixture on each side of the reactor. In this context, a cold spot is formed within the wall, as shown in Figure 11a for the case with $K_{reforming} = 2.0$. Additionally, the initiation of the gas-phase combustion is impossible because of the low temperatures caused by the higher reforming catalyst loading used. Figure 12b shows that near the entrance to the reactor, the rate of heat release is higher than the rate of heat consumption, thus increasing both the temperature of the gas mixture and the rate of the reaction on each side of the reactor. Most of the heat generated by the catalytic combustion is released at the first half of the reactor, and thus, there exists a peak appearing in each of the heat flux profiles. After almost complete conversion in the combustion channel, the rate of heat release decreases rapidly, resulting in a decrease in both the reforming reaction rate and the rate of heat consumption. Over an axial distance of about 15.6 mm (Figure 12b), the rate of heat release becomes lower than the rate of heat consumption, eventually leading to the formation of a hot spot, as shown in Figure 11a for the case with $K_{reforming} = 0.5$. Therefore, a thermal balance within the system is required to avoid the formation of hot spots within the wall.



(a) Heat flux (absolute values) profiles for the case with $K_{\text{combustion}} = 1.0$ and $K_{\text{reforming}} = 2.0$



(b) Heat flux (absolute values) profiles for the case with $K_{\text{combustion}} = 1.0$ and $K_{\text{reforming}} = 0.5$

Figure 12. Heat flux profiles along the axial direction for the two cases indicated. (a) A cold spot is formed. (b) A hot spot is formed. The shaded regions represent the net heat generated within the system. The heat in the gray area is accounted for as positive, and the heat in the pink area is accounted for as negative.

4. Engineering Maps

Process intensification may significantly reduce the cost associated with hydrogen production through the use of microchannel reactors [95]. Furthermore, energy reduction can be achieved by integrating the combustion and reforming processes within a single reactor vessel, resulting in a reduction in overall utility requirements [96]. Engineering maps are presented and operating windows are identified to meet the power requirements for practical applications.

Figure 13a shows the operation diagram, where the power based on the hydrogen produced is expressed as a function of residence time of the gas mixture on the combustion side. The shaded region represents the operation space allowed. The flow rate on each side of the reactor should be properly designed to ensure the efficient operation of the system. Figure 13a shows that only a relatively narrow range of the power generated is allowed for a fixed residence time of the gas mixture on the combustion side. The minimum of the power generated is determined by the limit of the stability of the materials used in the case of low flow rates used for the gas mixture on the reforming side. The limit depends

solely on the maximum wall temperature allowed for the system [12–14]. The threshold temperature is assumed to be 1500 K [12–14], which is typically lower than the melting points of the typical materials and catalysts used in the integrated micro-chemical systems. The flow rate on the combustion side must be carefully designed in terms of the threshold temperature so as to avoid the problem of catalyst deactivation. The maximum of the power generated is determined by the maximum flow rate of the hydrogen produced. Extinction may take place in the combustion channel when a high flow rate is employed on the reforming side. Powers outside the operation space are impossible for a fixed residence time of the gas mixture on the combustion side.

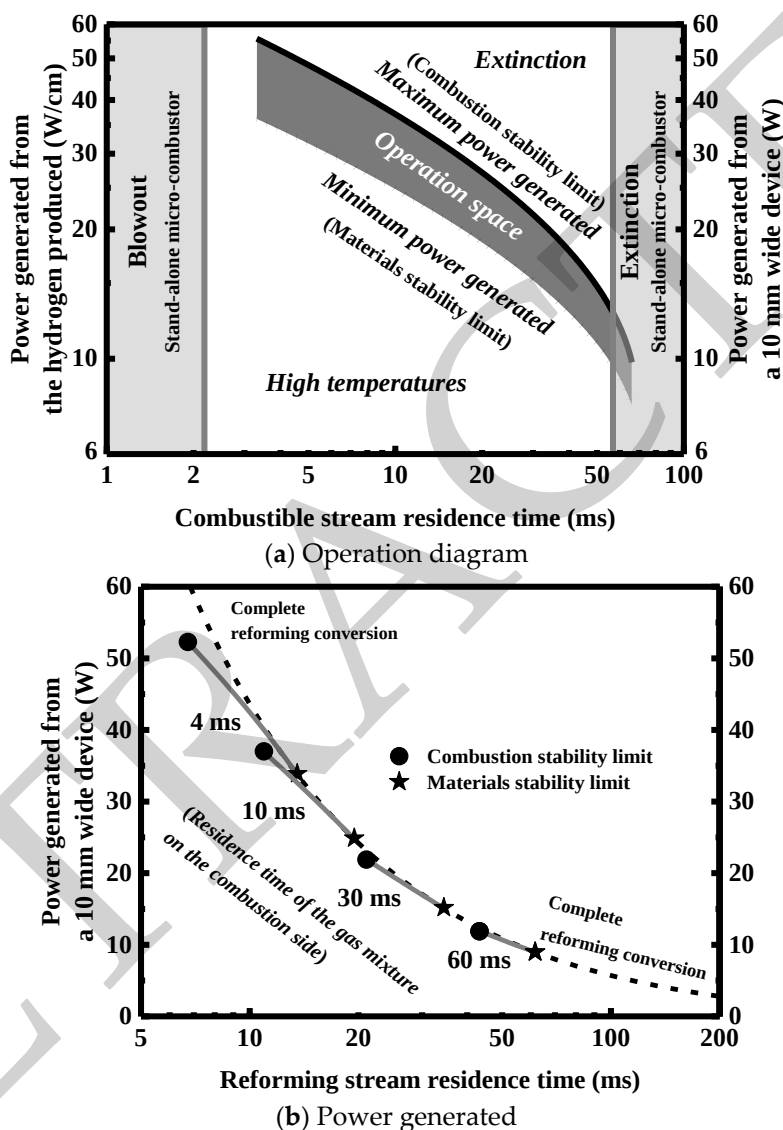


Figure 13. (a) The operation diagram based on an assumption of full utilization of the hydrogen produced by the reforming reaction at different residence times of the gas mixture on the combustion side. (b) The power generated from the small-scale system with a width of 10.0 mm as at different residence times of the gas mixture on the reforming side at the residence times indicated for the gas mixture on the combustion side.

The operation space in terms of the power generated is dependent on the fuel used. However, for a thermally integrated microchannel reactor with fixed dimensions, operation outside the power regime depicted in Figure 13a can be achieved by changing the fuel used. There is also a limit of the maximum flow rate allowed on the combustion side, determined by the stability of combustion,

because the residence time of the gas mixture in a small-scale combustion system is restricted to a rather narrow regime to ensure stability operation [97]. Extinction may occur at a low flow rate because of the insufficient heat generated, and blowout may occur at a high flow rate due to insufficient residence time. The prohibited operation space, determined by the critical flow velocities obtained from an individual, small-scale combustion system, is depicted in Figure 13a as the two vertical shaded regions to better understand the residence times allowed on the combustion side.

The power generated is determined by implementing a two-parameter continuation from the flow rate used on the reforming side at the residence times allowed on the combustion side. Figure 13b shows the power generated from the small-scale system with a width of 10.0 mm at different residence times of the gas mixture on the reforming side. The dashed line shown in Figure 13b represents the complete conversion obtained at the outlet of the reformer, and the circles and pentagrams denoted in Figure 13b represent the limits determined by either combustion stability or materials stability for each of the residence times indicated for the gas mixture on the combustion side. Under the conditions examined here, high outlet conversions can be achieved on the reforming side, thus ensuring the efficient operation of the system, as shown in Figure 13b.

The engineering maps presented above can be used to guide the design of integrated microreactors. To obtain the desired power, the residence time allowed for the gas mixture on the combustion side can be determined based on the operation space depicted in Figure 13a. Then, the residence time allowed for the gas mixture on the reforming side can be determined by the plot of power generated, as illustrated in detail in Figure 13b. Unfortunately, only a rather narrow regime is allowed for the flow rates used. A combination of a flow rate in the middle range of the combustible stream residence times allowed (Figure 13a) and a flow rate near the minimum reforming stream residence times allowed (Figure 13b) should be preferred in order to ensure nearly complete conversion on the reforming side and higher fuel utilization.

5. Conclusions

Methane steam reforming thermally coupled with catalytic combustion in micro-chemical systems was investigated to address the requirements for the design of the rapid production of hydrogen by means of process intensification. The main points are summarized as follows:

- The production of hydrogen can be achieved at millisecond contact times from methane steam reforming, but the flows, catalysts, and dimensions must be properly designed.
- The improvement in catalyst performance is necessary for the reforming process. High transport rates and a rapid reforming process must be symbiotic for achieving the efficient production of hydrogen.
- The dimension of the reactor is an important design parameter. Small dimensions are required to enable both fast transport rates and a rapid reforming process.
- The catalyst loading is an important variable to optimize the performance of the reactor and must be carefully designed to avoid the formation of hot spots and low outlet conversions.
- Countercurrent heat exchange can achieve slightly better reactor performance, but parallel heat exchange is recommended to ensure stable and reliable operation of the system.
- Thermal management is an effective way to improve the performance of the reactor. The flow rates should be carefully designed to meet the requirements of the materials and combustion stability.

Because microchannel reactors may offer many significant advantages, further research is needed. One interesting topic is catalyst deactivation, which can lead to degradation in reactor performance. Further exploration on the use of alternative solutions is also needed to broaden the operation window and to achieve a better thermal balance within the system. Focusing on the integration of the development of new catalysts and the advance in micro-process engineering may eventually result in the development of improved microchannel reactors for hydrogen production.

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Nomenclature

A	surface area
C	concentration
c	specific heat capacity
d	gap distance
d_{pore}	mean pore diameter
D	diffusivity
D^T	thermal diffusivity
D_m	mixture-averaged diffusivity
Da_y	transverse Damköhler number
$F_{cat/geo}$	catalyst/geometric surface area
Fo	Fourier number
F	view factor
h	specific enthalpy
k_{ad}	adsorption rate constant
h_o	external heat loss coefficient
K	ratio of catalyst loadings
K_g	number of gaseous species
K_s	number of surface species
l	length
m	total number of gaseous and surface species
p	pressure
Pe	Péclet number
q	heat flux
R	ideal gas constant
s	sticking coefficient
$\dot{s}_m$	rate of appearance of surface species m
S	surface area
T	absolute temperature
u	streamwise velocity component
$\bar{u}$	average flow velocity
u_m	inlet flow velocity
V	diffusion velocity
v	transverse velocity component
V'	volume
W	relative molecular mass
x, y	streamwise and transverse reactor coordinates
Y	mass fraction

Greek Variables

γ	active surface area per unit volume of the washcoat
δ	thickness
ε	emissivity
ε_p	catalyst porosity
η	effectiveness factor
θ_{free}	surface coverage of free sites

λ	thermal conductivity
ρ	density of the gas mixture
σ	Stefan–Boltzmann constant
σ	site occupancy
μ	dynamic viscosity
τ	time scale
τ_p	catalyst tortuosity factor
$\tau_{reaction}$	intrinsic reaction time scale
τ_x	axial transfer time scale
τ_y	transverse transfer time scale
$\dot{\omega}_k$	rate of appearance of gaseous species k
Γ	density of catalyst surface sites
Φ	Thiele modulus

Subscripts

g	gas
i, k, m	indexes of species, gaseous species, and surface species
s, w	solid and wall
x, y	streamwise and transverse components

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