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RETRACTED: Computational Fluid Dynamics Modeling of the Catalytic Partial Oxidation of Methane in Microchannel Reactors for Synthesis Gas Production

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Abstract: This paper addresses the issues related to the favorable operating conditions for the small-scale production of synthesis gas from the catalytic partial oxidation of methane over rhodium. Numerical simulations were performed by means of computational fluid dynamics to explore the key factors influencing the yield of synthesis gas. The effect of mixture composition, pressure, preheating temperature, and reactor dimension was evaluated to identify conditions that favor a high yield of synthesis gas. The relative importance of heterogeneous and homogenous reaction pathways in determining the distribution of reaction products was investigated. The results indicated that there is competition between the partial and total oxidation reactions occurring in the system, which is responsible for the distribution of reaction products. The contribution of heterogeneous and homogeneous reaction pathways depends upon process conditions. The temperature and pressure play an important role in determining the fuel conversion and the synthesis gas yield. Undesired homogeneous reactions are favored in large reactors, and at high temperatures and pressures, whereas desired heterogeneous reactions are favored in small reactors, and at low temperatures and pressures. At atmospheric pressure, the selectivity to synthesis gas is higher than 98% at preheating temperatures above 900 K when oxygen is used as the oxidant. At pressures below 1.0 MPa, alteration of the dimension in the range of 0.3 and 1.5 mm does not result in significant difference in reactor performance, if made at constant inlet flow velocities. Air shows great promise as the oxidant, especially at industrially relevant pressure 3.0 MPa, thereby effectively inhibiting the initiation of undesired homogeneous reactions.

Keywords: catalytic microreactors; synthesis gas production; partial oxidation; microchannel reactors; reactor design; reaction pathway; hydrogen production; computational fluid dynamics

1. Introduction

There has been an increasing interest in the production of synthesis gas through the catalytic partial oxidation of methane [1,2], due to its potential applications in many fields such as fuel cells [3,4] and gas turbines [5,6]. Currently, the primary techniques used in industry to produce synthesis gas from methane are steam reforming [7,8], autothermal reforming [9], and partial oxidation [7]. Steam reforming of methane remains the main commercial process for the production of synthesis gas [7,8]. It is important to develop new reaction routes for the production of synthesis gas from methane. A promising reaction route that has received much attention recently is the catalytic partial oxidation of methane in short contact time reactors in high temperature environment [10–12], where a high yield of synthesis gas (higher than 90%) can be achieved [13]. In comparison with other synthesis gas

production routes, this technology shows great promise because higher selectivity and better efficiency can be achieved [14].

Significant progress has been made recently in the understanding of the mechanism of this reaction [15,16]. The reaction proceeds at a lower temperature than the gas-phase partial oxidation route [17–20], thus offering many advantages such as a reduction of undesired by-products and the ability to control the process temperature [21–24]. The catalysts used for this reaction usually contain group VIII transition metals, such as rhodium [25,26], ruthenium [27,28], platinum [29,30], palladium [31,32], nickel [33,34], iridium [35,36], and cobalt [37,38]. The reaction can proceed in short contact time reactors under high-temperature conditions [39–41]. This technology provides a novel route for the production of synthesis gas from methane [1,2], since the yield of the desired products can be greatly improved under controlled conditions [42,43].

It is important to understand the mechanism of the catalytic partial oxidation reaction to improve the yield of synthesis gas [44,45]. However, the pathways for the reaction are still debated, and the prospect for industrial applications is not yet clear. In the case of noble metal catalysts, both heterogeneous and homogeneous reaction pathways may be significant [46,47]. In addition, homogeneous reactions decrease the yield of synthesis gas, thus seriously hindering reactor performance. It is therefore necessary to understand the competition phenomenon between the two reaction pathways during a catalytic partial oxidation process. Unfortunately, the relative contribution of the two reaction pathways to the formation of synthesis gas has not yet been addressed, and thus further research is needed to clarify the mechanism responsible for improving the yield of synthesis gas in a catalytic partial oxidation system.

Microreactor technology is expected to offer many advantages for process development [48,49], especially for fast, exothermic reactions such as catalytic partial oxidation. Precise temperature control is possible, thus significantly reducing the undesirable side reactions occurring during a catalytic partial oxidation process [48,49]. Furthermore, higher yields can be achieved for these processes under well-controlled conditions, by taking advantage of enhanced transport in small dimensions [50,51]. For partial oxidation micro-chemical systems, one of the engineering design challenge is to balance the gains made in heat and mass transfer by going to smaller dimensions against the increases in pressure drop [52,53]. However, microfabrication methods have the potential to realize reactor designs that combine excellent thermal uniformity, enhanced transport rates, and low-pressure drop for a catalytic partial oxidation process [54,55]. The intrinsic kinetics of these partial oxidation processes are typically very fast, and thus the realization of this process technology will require continued advances in the development of microreactors [15,16]. The small dimensions associated with these reactors can effectively inhibit the gas-phase reaction occurring during a catalytic partial oxidation process [56]. It is therefore important to determine the favorable operating conditions under which the yield of desired products can be maximized.

In addition to providing an explanation of experimental data, numerical simulations can serve as an efficiency design tool for the development of a catalytic partial oxidation system [56,57]. Iterative, costly experimental design processes can be avoided. Furthermore, numerical simulations are necessary to better understand the operating characteristics of a micro-structured device required to implement a catalytic partial oxidation process, and to evaluate the disadvantages and benefits associated with an innovative design of the process [56,57]. A number of commercial software tools are available, but, unfortunately, none of them is universally applicable. To accurately predict the operating characteristics during the process of a catalytic partial oxidation reaction occurring in microreactors and accurately reflect experimental observations, detailed mathematical modeling is often necessary [58]. Detailed computational fluid dynamics modeling can be used to evaluate design changes, such as geometric parameters, Reynolds numbers, and reaction temperature, during a catalytic partial oxidation process [57].

The main focus of this paper is on determining the favorable operating conditions for the small-scale production of synthesis gas from the catalytic partial oxidation of methane. High transport rates are possible in microchannel reactors, thus allowing the catalytic partial oxidation reaction to be

carried out under more favorable conditions. Computational fluid dynamics simulations serve as a means to understand the role of heterogeneous and homogenous reaction pathways in determining the distribution of reaction products. The effect of reactor dimension, pressure, mixture composition, and preheating temperature was investigated to better understand the operating characteristics of the partial oxidation reactor. The favorable conditions for the production of synthesis gas were determined. The major objective is to understand the relative importance of different reaction pathways in determining the distribution of reaction products. Special emphasis is placed on identifying favorable operating conditions for the production of synthesis gas in high temperature environments.

2. Model Development

2.1. Reaction System

The reaction system used in the present investigation is the catalytic partial oxidation of methane taking place in a microchannel reactor. For microchannel reactors, the width of each of the channels is about one order of magnitude larger than its height [59,60], and thus the reactor used in this paper is modeled as a two-dimensional system. A premixed methane and either air or oxygen mixture is fed to the reactor, after the reactant stream is preheated to a desired temperature. The reactor contains multiple parallel channels having sub-millimeter dimensions, thus offering advantages from enhanced heat and mass transfer [61]. The reactor modeled in this paper is shown schematically in Figure 1. Unless otherwise specified, the reactor consists of two infinitely wide parallel plates of length 8.0 mm, separated by a gap distance 0.8 mm between the two plates.
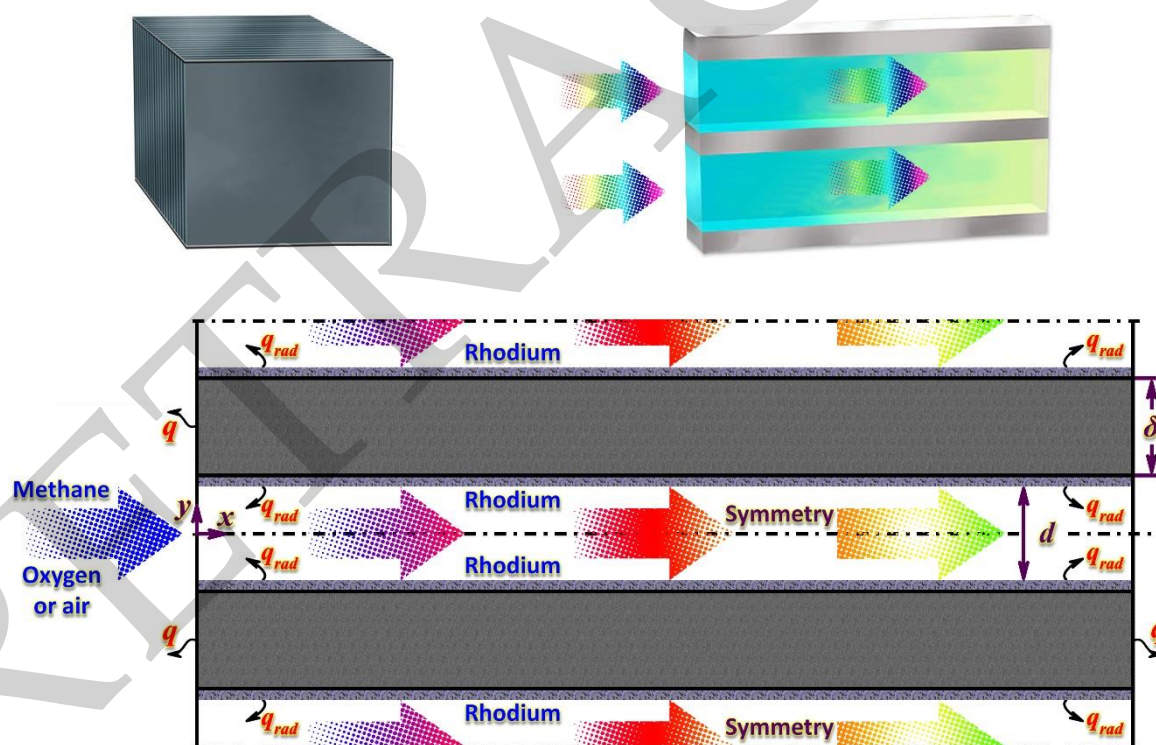

Figure 1. Two-dimensional schematic diagram of the microchannel reactor geometry used in computational fluid dynamics.

The physical properties the walls are the same as those of stainless steel. The rhodium catalyzed partial oxidation of methane is considered in the present work, since the catalyst has been reported to give a high synthesis gas yield with good long-term stability [25,26]. Additionally, a "base case",

where typical operating conditions and design parameters are considered for the catalytic partial oxidation process, is given in Table 1. In this context, the effect of various operating conditions and design parameters can be easily evaluated. Numerical simulations are carried out, and the difference between a methane–oxygen system and a methane–air system is also investigated. Note that most of the catalyst properties listed in Table 1 are taken from the works related to the reaction mechanism used; the reaction mechanism used in this paper will be described in detail in Section 2.3. *Reaction mechanisms*. The wash coat thickness is specified based on the reaction system considered.

Table 1. Nominal values of the operating conditions and design parameters used for the base case.

Parameter	Variable	Value
Geometry		
Channel length	l	8.0 mm
Channel height	d	0.8 mm
Solid wall		
Thickness	δ	0.8 mm
Thermal conductivity	λ_s	16 W/(m·K) (300 K)
Gas phase		
Inlet methane-to-oxygen molar ratio	ϕ	2.0
Inlet pressure	p_{in}	0.1 MPa
Inlet temperature	T_{in}	300 K
Inlet velocity	u_{in}	0.8 m/s
Catalyst		
Washcoat thickness	$\delta_{catalyst}$	0.08 mm
Mean pore diameter	d_{pore}	20 nm
Porosity	ε_p	0.5
Tortuosity factor	τ_p	3
Catalyst/geometric surface area	$F_{cat/geo}$	8
Density of rhodium surface sites	Γ	2.72×10^{-9} mol/cm^2
Other conditions		
Ambient temperature	T_{amb}	300 K
Surface emissivity	ε	0.8
External heat loss coefficient	h_o	20 W/(m^2·K)

2.2. Mathematical Model

Since the Reynolds number is less than 380, which implies laminar flow. Therefore, it is possible to fully characterize heat and mass transfer in the system. Detailed reaction mechanisms are necessary to accurately predict the partial oxidation process. A two-dimensional numerical model is developed by using the commercial software ANSYS Fluent® Release 16.0 (ANSYS Inc., Canonsburg, PA, USA) [62]. Detailed reaction mechanisms are handled with related external procedures; please refer to Section 2.3. *Reaction mechanisms* for more details. The steady-state two-dimensional conservation equations are solved in the gas phase:

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

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

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

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

$$\frac{\partial(\rho u Y_k)}{\partial x} + \frac{\partial(\rho v Y_k)}{\partial y} + \frac{\partial}{\partial x}(\rho Y_k V_{k,x}) + \frac{\partial}{\partial y}\left(\rho Y_k V_{k,y}\right) - \dot{\omega}_k W_k = 0, \; k = 1, \ldots, K_g. \qquad (5)$$

The diffusion velocity vector is given as follows [63]:

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

The ideal gas equation of state is given by

$$p = \frac{\rho R T}{\overline{W}} \qquad (7)$$

The caloric equation of state is given by

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

The coverage equation of surface species can be expressed as

$$\vartheta_m \frac{\dot{s}_m}{\Gamma} = 0, \; m = K_g + 1, \ldots, K_g + K_s. \qquad (9)$$

The steady-state energy equation in the walls is given by

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

The gaseous species equation at each of the fluid-washcoat interfaces is specified by the boundary condition taken the form

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

The catalyst/geometric surface area, $F_{cat/geo}$, is defined as follows [56]:

$$F_{cat/geo} = \frac{A'_{catalyst}}{A'_{geometric}} \qquad (12)$$

The effect of diffusional limitation in the catalyst wash coat may be significant [64], and thus included in the model

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

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

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

The effective diffusivity can be written as

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

The Knudsen diffusivity is defined as

$$D_{i,Knudsen} = \frac{d_{pore}}{3} \sqrt{\frac{8RT}{\pi W_i}}. \tag{17}$$

The energy equation at each of the fluid wash coat interfaces is specified by the boundary condition taken the form

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

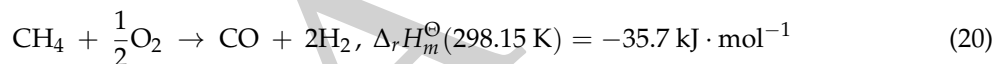For the total heat loss to the surroundings, the equation can be written as

$$q = h_o(T_{w,o} - T_{amb}) + \varepsilon F_{s-\infty} \sigma \left(T_{w,o}^4 - T_{amb}^4\right) \tag{19}$$

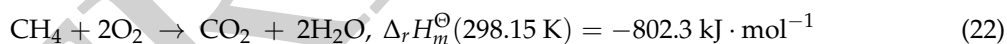The external heat loss coefficient, h_o, is assumed to be 20 W/(m$^2 \cdot$K) [65].

2.3. Reaction Mechanisms

Computational fluid dynamics modeling of the catalytic partial oxidation process is complex [15,16], especially when the role of reaction pathway needs to be determined [66]. Therefore, detailed reaction mechanisms are included in the model. The possible reactions involved in the catalytic partial oxidation process are listed as follows:
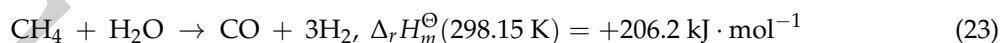
Partial oxidation

$$CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2, \; \Delta_r H_m^\Theta(298.15\,\text{K}) = -35.7\,\text{kJ} \cdot \text{mol}^{-1} \tag{20}$$

$$CH_4 + O_2 \rightarrow CO + H_2 + H_2O, \; \Delta_r H_m^\Theta(298.15\,\text{K}) = -278\,\text{kJ} \cdot \text{mol}^{-1} \tag{21}$$

Total oxidation

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O, \; \Delta_r H_m^\Theta(298.15\,\text{K}) = -802.3\,\text{kJ} \cdot \text{mol}^{-1} \tag{22}$$
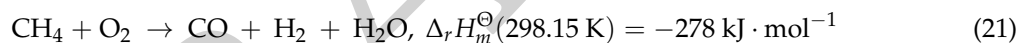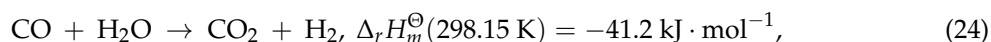
Competition between the two reaction routes is responsible for the distribution of reaction products. However, the highly exothermic total oxidation reaction serves as a heat source to ensure self-sustained operation of the system. Therefore, this reaction route can improve the selectivity towards the desired products. However, the products produced by this route decrease the selectivity. Overall, the final yield of synthesis gas is determined by this competitive effect.
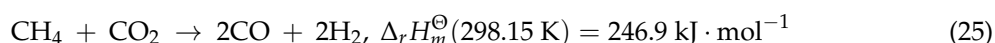
Steam reforming

$$CH_4 + H_2O \rightarrow CO + 3H_2, \; \Delta_r H_m^\Theta(298.15\,\text{K}) = +206.2\,\text{kJ} \cdot \text{mol}^{-1} \tag{23}$$

Water–gas shift reaction

$$CO + H_2O \rightarrow CO_2 + H_2, \; \Delta_r H_m^\Theta(298.15\,\text{K}) = -41.2\,\text{kJ} \cdot \text{mol}^{-1}, \tag{24}$$

Dry reforming

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2, \; \Delta_r H_m^\Theta(298.15\,\text{K}) = 246.9\,\text{kJ} \cdot \text{mol}^{-1} \tag{25}$$

The reaction mechanism has attracted increasing attention recently [15,16,67–69]. The reaction may proceed through a combination of direct partial oxidation and steam reforming [39–41]. Both partial and total oxidation products can be formed [40], and carbon dioxide has little or no role during the

process [39,41]. More importantly, both water-gas shift and carbon dioxide reforming do not contribute to the formation of synthesis gas [39,41].

The detailed heterogeneous reaction mechanism developed by Schwiedernoch et al. [70], as given in Table 2, is included in the model. The mechanism consists of 11 surface-adsorbed species and 6 gaseous species involved in 38-step elementary reactions. Since each of the reactive intermediates and elementary reaction steps involved in the catalytic partial oxidation process is included in the reaction mechanism, the global reactions such as steam and carbon dioxide reforming are automatically accounted for [70]. Note that the symbol * used in Table 2 denotes an adsorbed species or an empty site.

Table 2. Heterogeneous reaction mechanism used for the partial oxidation of methane over rhodium.

Reactions	A (cm, mol, s)	s	Ea (kJ/mol)
Adsorption			
$H_2 + * + * => H* + H*$		1.0×10^{-2}	
$O_2 + * + * => O* + O*$		1.0×10^{-2}	
$CH_4 + * => CH_4*$		8.0×10^{-3}	
$H_2O + * => H_2O*$		1.0×10^{-1}	
$CO_2 + * => CO_2*$		1.0×10^{-5}	
$CO + * => CO*$		5.0×10^{-1}	
Desorption			
$H* + H* => * + * + H_2$	3.0×10^{21}		77.8
$O* + O* => * + * + O_2$	1.3×10^{22}		$355.2–280\Theta_{O*}$
$H_2O* => H_2O + *$	3.0×10^{13}		45.0
$CO* => CO + *$	3.5×10^{13}		$133.4–15\Theta_{CO*}$
$CO_2* => CO_2 + *$	1.0×10^{13}		21.7
$CH_4* => CH_4 + *$	1.0×10^{13}		25.1
Surface reactions			
$H* + O* => OH* + *$	5.0×10^{22}		83.7
$OH* + * => H* + O*$	3.0×10^{20}		37.7
$H* + OH* => H_2O* + *$	3.0×10^{20}		33.5
$H_2O* + * => H* + OH*$	5.0×10^{22}		104.7
$OH* + OH* => H_2O* + O*$	3.0×10^{21}		100.8
$H_2O* + O* => OH* + OH*$	3.0×10^{21}		171.8
$C* + O* => CO* + *$	3.0×10^{22}		97.9
$CO* + * => C* + O*$	2.5×10^{21}		169.0
$CO* + O* => CO_2* + *$	1.4×10^{20}		121.6
$CO_2* + * => CO* + O*$	3.0×10^{21}		115.3
$CH_4* + * => CH_3* + H*$	3.7×10^{21}		61.0
$CH_3* + H* => CH_4* + *$	3.7×10^{21}		51.0
$CH_3* + * => CH_2* + H*$	3.7×10^{24}		103.0
$CH_2* + H* => CH_3* + *$	3.7×10^{21}		44.0
$CH_2* + * => CH* + H*$	3.7×10^{24}		100.0
$CH* + H* => CH_2* + *$	3.7×10^{21}		68.0
$CH* + * => C* + H*$	3.7×10^{21}		21.0
$C* + H* => CH* + *$	3.7×10^{21}		172.8
$CH_4* + O* => CH_3* + OH*$	1.7×10^{24}		80.3
$CH_3* + OH* => CH_4* + O*$	3.7×10^{21}		24.3
$CH_3* + O* => CH_2* + OH*$	3.7×10^{24}		120.3
$CH_2* + OH* => CH_3* + O*$	3.7×10^{21}		15.1
$CH_2* + O* => CH* + OH*$	3.7×10^{24}		158.4
$CH* + OH* => CH_2* + O*$	3.7×10^{21}		36.8
$CH* + O* => C* + OH*$	3.7×10^{21}		30.1
$C* + OH* => CH* + O*$	3.7×10^{21}		145.5

The Leeds methane oxidation mechanism [71,72] is included in the model to describe the reaction taking place in the gas phase. The reaction mechanism is also accounted for the free radical coupling reactions such as oxidative coupling of methane. The selectivity to C_2-hydrocarbons may be as high as 20% for the reaction proceeded under certain conditions, through a gas-phase reaction route [73,74]. These C_2-hydrocarbons are undesirable during the catalytic partial oxidation process, as they can cause the problem related to the formation of coke.

The CHEMKIN transport database [63] is used in the model. The homogeneous and heterogeneous reaction rates are handled through the CHEMKIN [75] and Surface-CHEMKIN [76] interfaces, respectively.

2.4. Computation Scheme

An orthogonal staggered grid is used for the base case, consisting of 200 axial nodes by 80 transverse nodes. Typical fluid node spacing near the catalyst wash coat is 40 µm in the axial direction and 5 µm in the transverse direction. For the largest reactor dimension, a grid consisting of 20,000 nodes in total is utilized. Adequate grid resolution is verified by doubling the number of grid points. Figure 2 shows the profiles of the hydroxyl radical concentration along the centerline between the two parallel plates for some of the grids used for the methane–oxygen system. The inlet pressure is 3.0 MPa. The rest of the parameters used here are listed in Table 1. As the grid density increases, there is a convergence of the solution. The numerical model with the coarsest grid, consisting of 4000 nodes in total, cannot accurately capture the hydroxyl radical concentration within the channel and its peak location, and thus fails to accurately predict the onset of gas-phase combustion within the system. In contrast, the solution obtained by the numerical model with a grid consisting of tens of thousands of nodes is reasonably accurate for the base case given in Table 1. There is little or no advantage for the largest grid density, up to 32,000 nodes in total.
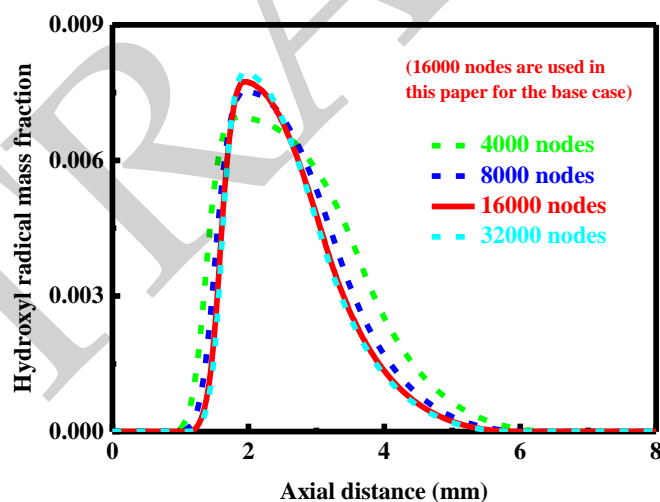

Figure 2. Profiles of the hydroxyl radical concentration along the centerline between the two parallel plates for some of the grids used for the methane–oxygen system. The inlet pressure is 3.0 MPa. The rest of the parameters used here are listed in Table 1.

The physical properties of the mixture depend on the local conditions of component and temperature. The physical properties the walls, such as the thermal conductivity and specific heat capacity, depend on the local temperature. The conservation equations are discretized by using a finite-volume method. The momentum, energy, and species equations are discretized by using a two-order upwind approximation. The pressure-velocity coupling is discretized using the "SIMPLE" method. The convergence criterion is 10^{-6} by examining the values of the residuals for all of the conservation equations. Convergence of the solution is usually difficult due to the inherent stiffness of

the detailed reaction mechanism used. Figure 3 shows the residuals for the conservation equations at the end of each solver iteration. The residual plot indicates that after approximately 800 iterations, the convergence criterion is satisfied.
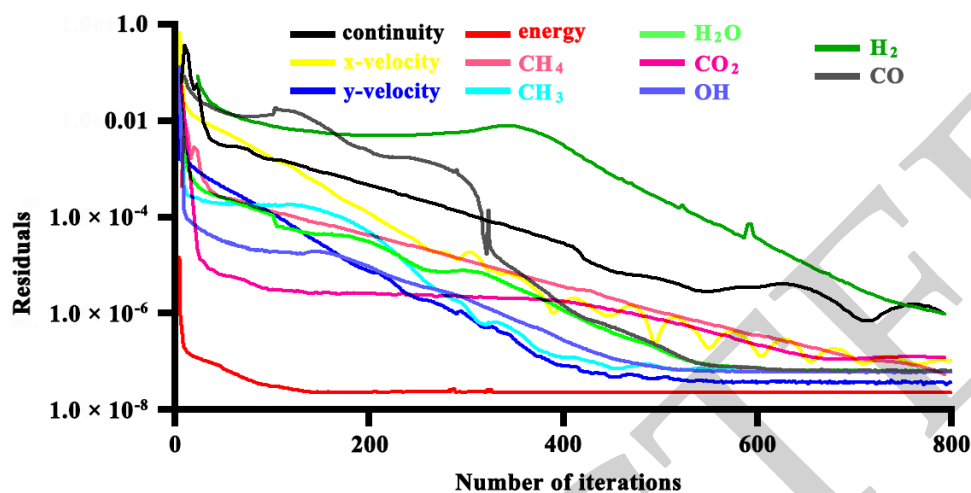

Figure 3. Residuals for the conservation equations at the end of each solver iteration. The mesh used here consists of 16,000 nodes in total. The parameters used in the numerical simulations conducted here are the same as those adopted in Figure 2.

2.5. Model Validation

In order to verify the model, the experimental results reported in the literature [77] are utilized. The reactor used is made of a quartz tube, and the inside diameter of the reactor is 18 mm, as described in the literature [77]. The inlet temperature of a methane and oxygen mixture is 20 °C, and the pressure is maintained at 0.12 MPa at the outlet. Nitrogen dilution is 30%, and the inlet flow rate is maintained at 5000 cm^3/min. A grid consisting of 36,000 nodes in total is used here. Numerical simulations are performed for the experimental case tested under the operating conditions and design parameters given in the literature [77]. The results obtained for the selectivity and the outlet conversion for the mixture with different compositions is compared to the experimental data in Figure 4. The maximum difference between the numerical results and the experimental data is about 5.6%. Therefore, the numerical results are in consistent with the experimental data.
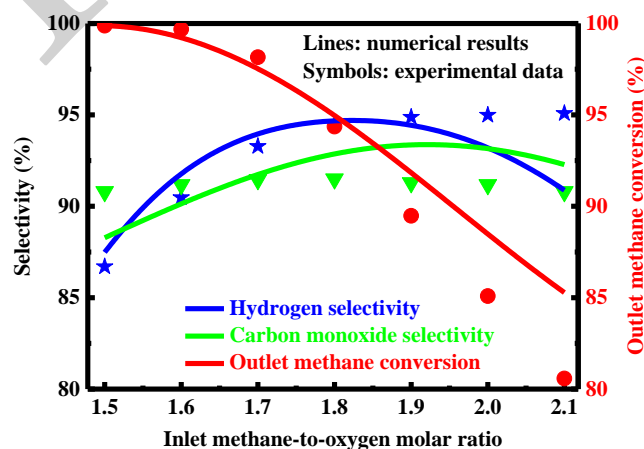

Figure 4. Comparison between the numerical results and the experimental data obtained for a methane and oxygen mixture with various compositions. The experimental data are taken from the previous work of Bodke et al. [77]. A grid consisting of 36,000 nodes in total is used here.

3. Results and Discussion

In the following sections, the reactor performance in terms of conversion, selectivity, and temperature under various operating conditions is discussed in detail, and the relative importance of different reaction pathways in determining the distribution of reaction products is investigated. Additionally, comparisons are made in terms of reactor performance between the results obtained for a methane–oxygen system and for a methane–air system.

3.1. Base Case

For the base case given in Table 1, a methane-to-oxygen molar ratio of 2.0, i.e., a stoichiometric mixture for the production of synthesis gas, is used. This ratio is ideal for the downstream processing such as in the synthesis of methanol and in the production of Fischer-Tropsch products. The temperature is set as 300 K at the inlet for the base case, thus effectively avoiding gas-phase combustion; please refer to the Section 4. *Further Discussion* for more details.

Figure 5 shows contour plots of the methane and carbon monoxide concentrations and temperature within the fluid in the methane–oxygen system. Despite the small dimension involved, the temperature and species gradients change significantly in the vicinity of reaction region. This can be attributed to the difference in the time scale between the heterogeneous reaction and the heat transfer in the transverse direction. The significant change in both temperature and species gradients may need to use a two-dimensional computational fluid dynamics model, as axial diffusion of species and energy is not negligible. Furthermore, mass-transfer limitations, typical characteristics of a catalytic partial oxidation reaction, are observed here, despite the small dimension involved. Accordingly, the effect of transport phenomena will be discussed in the following sections.
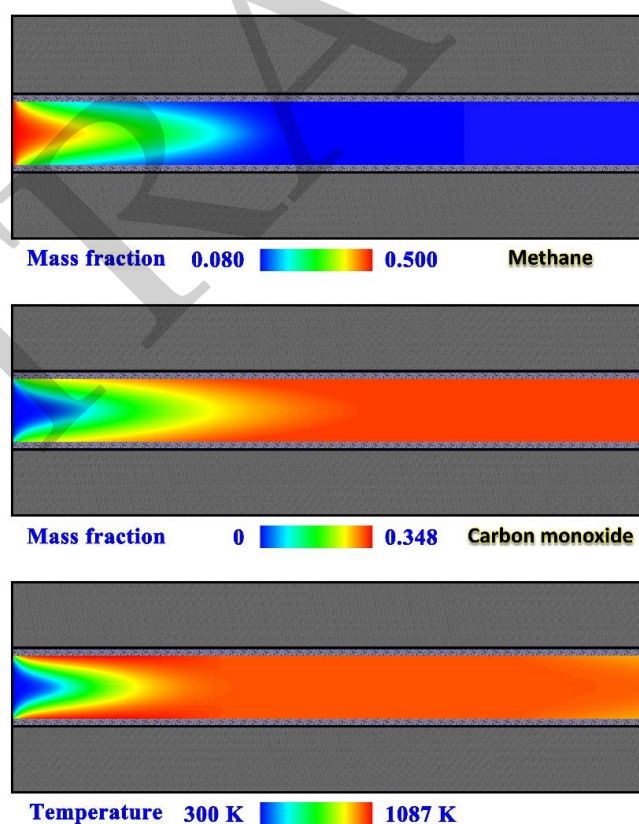

Figure 5. Contour plots of the methane and carbon monoxide concentrations and temperature within the fluid in the methane–oxygen system. The operating conditions and design parameters used are listed in Table 1.

3.2. Effect of Preheating for Oxygen Feed

Figure 6 shows the influence of preheating temperature on the performance of the methane–oxygen system. As the pressure increases, there is a sharp drop in the selectivity to synthesis gas (Figure 6a,b) and conversion (Figure 6c), but a sharp rise in wall temperature (Figure 6d). This sharp drop implies the initiation of the total oxidation reaction occurring in the gas phase. After the initiation of gas-phase combustion, the contribution of heterogeneous reactions is still considerable, as indicated by the selectivity to synthesis gas at high pressures (Figure 6a,b), but there is lack of oxygen for the catalytic partial oxidation reaction.
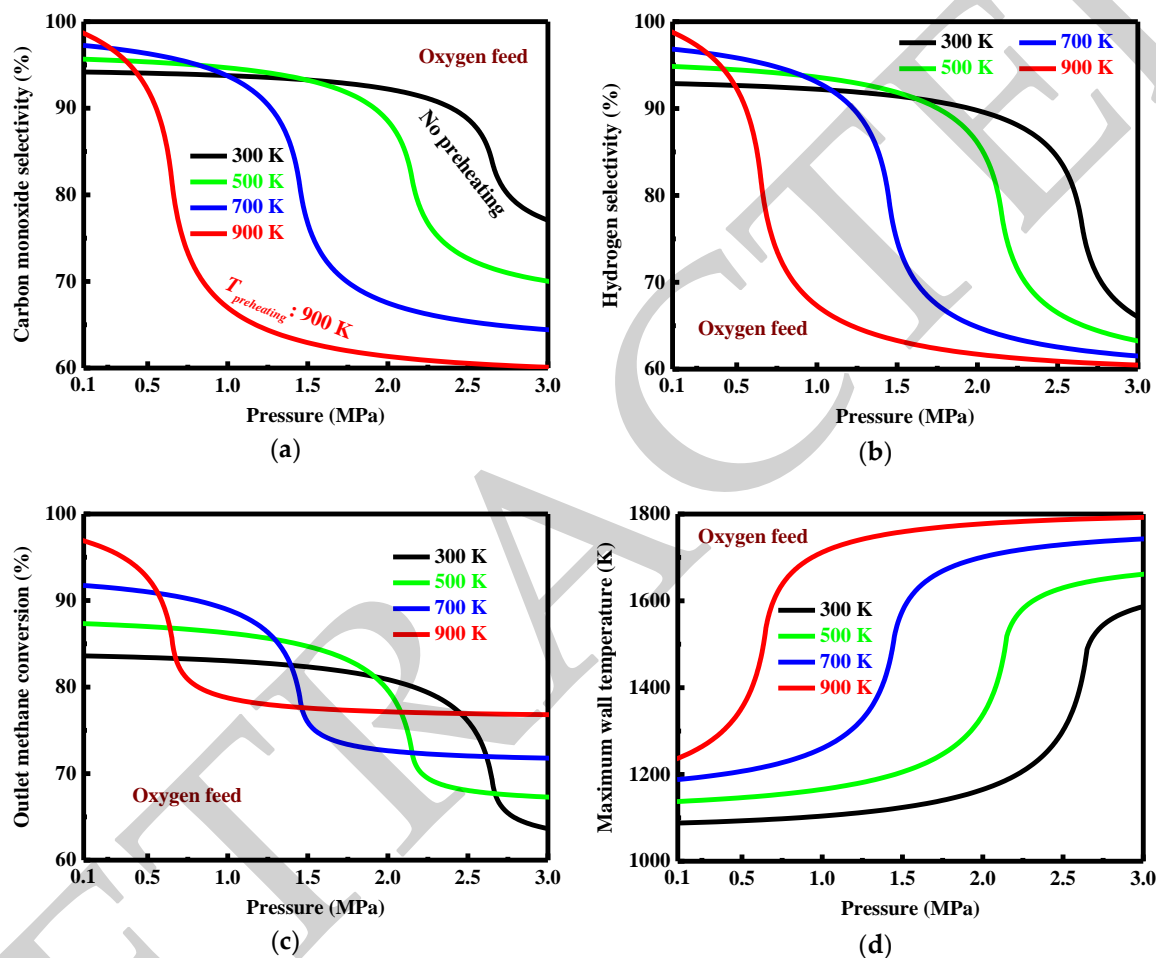

Figure 6. Influence of preheating temperature on the selectivity, conversion, and maximum wall temperature in the methane–oxygen system. Hereafter, all other parameters are kept at their base case values shown in Table 1. The sharp drop in selectivity and conversion indicates the initiation of gas-phase combustion. (**a**) Selectivity to carbon monoxide; (**b**) selectivity to hydrogen; (**c**) outlet conversion; (**d**) maximum wall temperature.

At atmospheric pressure, the selectivity to synthesis gas (Figure 6a,b) and the conversion (Figure 6c) increase with increasing preheating temperature. Very high selectivity to synthesis gas (>98%) is possible at atmospheric pressure when the preheating temperature is above 900 K. At atmospheric pressure, the main product is synthesis gas, and the catalytic partial oxidation reaction is favored at high temperatures. On the other hand, gas-phase combustion is favored at high temperatures, at which the initiation of the combustion reaction is possible at lower pressures. For example, as the inlet temperature increases from 300 to 900 K, the initiation pressure decreases from about 2.5 to 0.7 MPa. At high pressures, the catalytic partial oxidation reaction is favored at low

temperatures. The situation is the reverse of the results obtained at atmospheric pressure. In all of the cases examined here, the selectivity to synthesis gas (Figure 6a,b) and the conversion (Figure 6c) decrease with increasing pressure. After the initiation of gas-phase combustion, however, the pressure has little or no effect on the conversion. Furthermore, the loss in conversion at between atmospheric pressure and the highest pressure is almost the same.

On the other hand, as the pressure increases, there is a transition of primary reaction pathway from catalytic partial oxidation to gas-phase combustion, as depicted by the inflection point in the conversion profile (Figure 6c). After the reactants have been ignited in the gas phase, there is a significant drop in conversion. This is due to lack of oxygen for the gas-phase combustion reaction, despite the fact that a stoichiometric methane–air mixture is used for the production of synthesis gas from the catalytic partial oxidation reaction. Please refer to the stoichiometric coefficients described in the chemical Equations (20)–(22) for more details.

3.3. Effect of Preheating for Air Feed

One of the major challenges during the catalytic partial oxidation process is a reduction of the cost of pure oxygen separation [15,16], since the production of pure oxygen is highly expensive. The reaction system in the presence of a catalyst can be operated at much milder conditions as compared to the gas-phase partial oxidation system, which can effectively inhibit the formation of nitrogen oxides in the gas phase, making it possible to use air instead of pure oxygen [15,16]. This shows great promise for the catalytic partial oxidation process.

Figure 7 shows the effect of preheating temperature on the performance of the methane–air system. The pressure has a small effect on the selectivity to synthesis gas, but with a tendency to shift towards a higher yield of synthesis gas as the pressure decreases, as shown in Figure 7a,b Additionally, high preheating temperatures tend to improve the yield of synthesis gas. Therefore, the production of synthesis gas is favored at low pressures and high temperatures. In this context, the outlet concentration of carbon dioxide is very low (Figure 7a), but the small amount of carbon dioxide must be removed to meet the downstream processing requirements [15,16]. The amount of the total oxidation products and C_2-hydrocarbons increases with increasing pressure, leading to a decrease in both conversion and the selectivity to synthesis gas. On the other hand, the conversion is favored at high temperatures and at low pressures, as shown in Figure 7c. In contrast, the maximum wall temperature increases with increasing pressure, especially at high preheating temperatures (Figure 7d) where the total oxidation reaction is favored. In comparison with the results obtained for the methane–oxygen system (Figure 6), the initiation of gas-phase combustion is impossible for the methane–air system, and the contribution of homogeneous reactions is small.
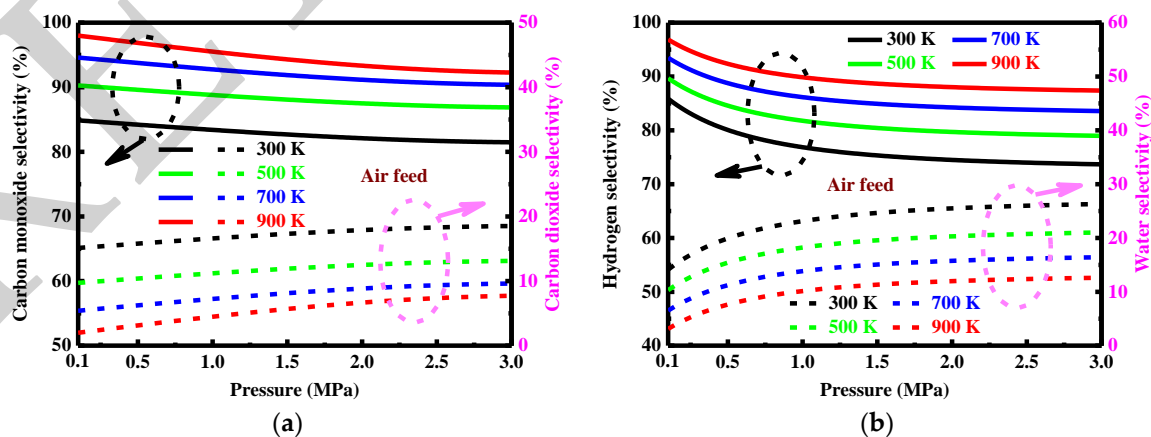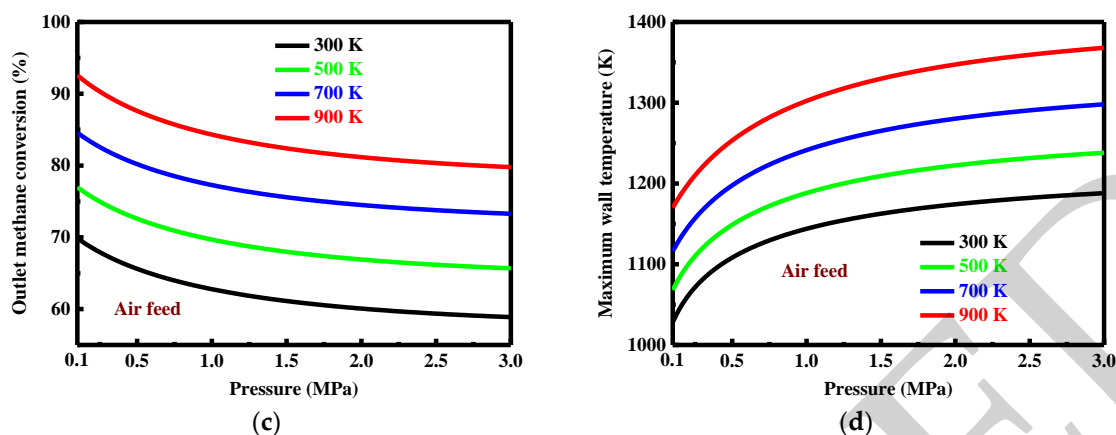

Figure 7. *Cont.*

Figure 7. Effect of preheating temperature on the selectivity, conversion, and maximum wall temperature in the methane–air system. (**a**) Selectivity to carbon monoxide and carbon dioxide; (**b**) selectivity to hydrogen and water; (**c**) outlet conversion; (**d**) maximum wall temperature.

3.4. Effect of Reactor Dimension for Oxygen Feed

The reactor dimension can significantly affect the effect of mass transfer [78]. For the system examined here, it is unclear whether there is an optimal dimension in which the yield of synthesis gas can be maximized. To provide a way to reduce the contribution of homogeneous reactions, the effect of reactor dimension is investigated.

Figure 8 presents the results obtained for the selectivity, conversion, and maximum wall temperature at different dimensions of the methane–oxygen system. The selectivity to synthesis gas is favored in smaller reactors, as shown in Figure 8a,b. The dimension has little effect on the reactor performance at low pressures, where the system is operated in a surface kinetically-controlled regime and the yield of synthesis gas is excellent. At high pressures, however, both mass-transfer limitations and homogeneous reactions become significant. For the smallest reactor studied, the dominant chemistry is heterogeneous at all of the pressures examined. At the highest pressure examined, the selectivity to synthesis gas is quite high in the smallest reactor, but drops sharply in the largest reactor. Furthermore, the yield of synthesis gas is favored in smaller reactors, in which the dominant chemistry is heterogeneous, as discussed above. Therefore, the design shows great promise for the production of synthesis gas, but only at low pressures. To achieve a high yield of synthesis gas at high pressures, the reactor dimension must be carefully designed to reduce the mass-transfer limitations.
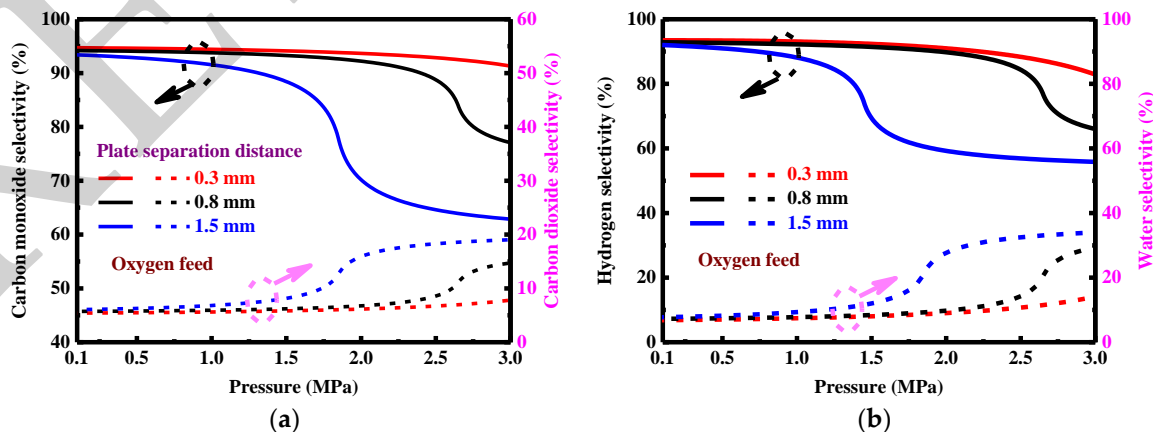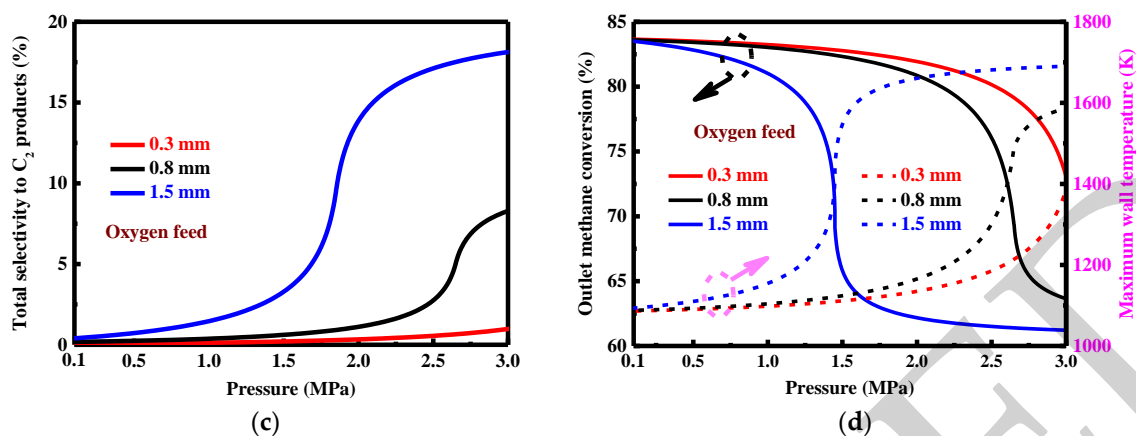

Figure 8. *Cont.*

Figure 8. Effect of reactor dimension on the selectivity, conversion, and maximum wall temperature in the methane–oxygen system. (**a**) Selectivity to carbon monoxide and carbon dioxide; (**b**) selectivity to hydrogen and water; (**c**) total selectivity to C_2 products; (**d**) outlet conversion and maximum wall temperature.

Figure 8a,b also shows the selectivity to the total oxidation products. For the largest dimension examined here, the amount of the total oxidation products is considerable, especially at high pressures, as shown in Figure 8a,b. In this context, there is an increases in temperature due to the heat released by the total oxidation reaction Figure 8d, thus increasing the amount of undesired by-products such as C_2-hydrocarbons (Figure 8c). Therefore, the contribution of homogeneous reactions at high pressures is considerable for the largest dimension examined. After the initiation of gas-phase combustion, there is a sharp drop in conversion for the moderate to large reactors studied, as shown in Figure 8d. The inflection point of the pressure decreases with increasing the reactor dimension. The maximum wall temperature increases with increasing pressure. This is mainly due to the increased amount of the reactants. A sharp rise in temperature represents the initiation of gas-phase combustion, as shown in Figure 8d. Finally, the maximum wall temperature levels off at high pressures. Overall, the yield of synthesis gas is favored at low pressures for the methane–oxygen system.

3.5. Effect of Reactor Dimension for Air Feed

As discussed above, the dimension can significantly affect the performance of the methane–oxygen system operated at high pressures. To gain a better understanding of the design described in this paper, the effect of reactor dimension is investigated for the methane–air system operated at various pressures.

Figure 9 presents the results obtained for the selectivity, conversion, and maximum wall temperature at different reactor dimensions. The reactor dimension has little or no effect on the selectivity to synthesis gas (Figure 9a,b) under the conditions studied here. The production of C_2-hydrocarbons is favored in lager reactors (Figure 9c). On the other hand, the reactor dimension has little effect on the conversion (left vertical axis, Figure 9d), and the maximum wall temperature (right vertical axis, Figure 9d). As expected, the dominant chemistry is heterogeneous in all of the cases under the conditions studied here, and the initiation of gas-phase combustion is impossible in the methane–air system examined.
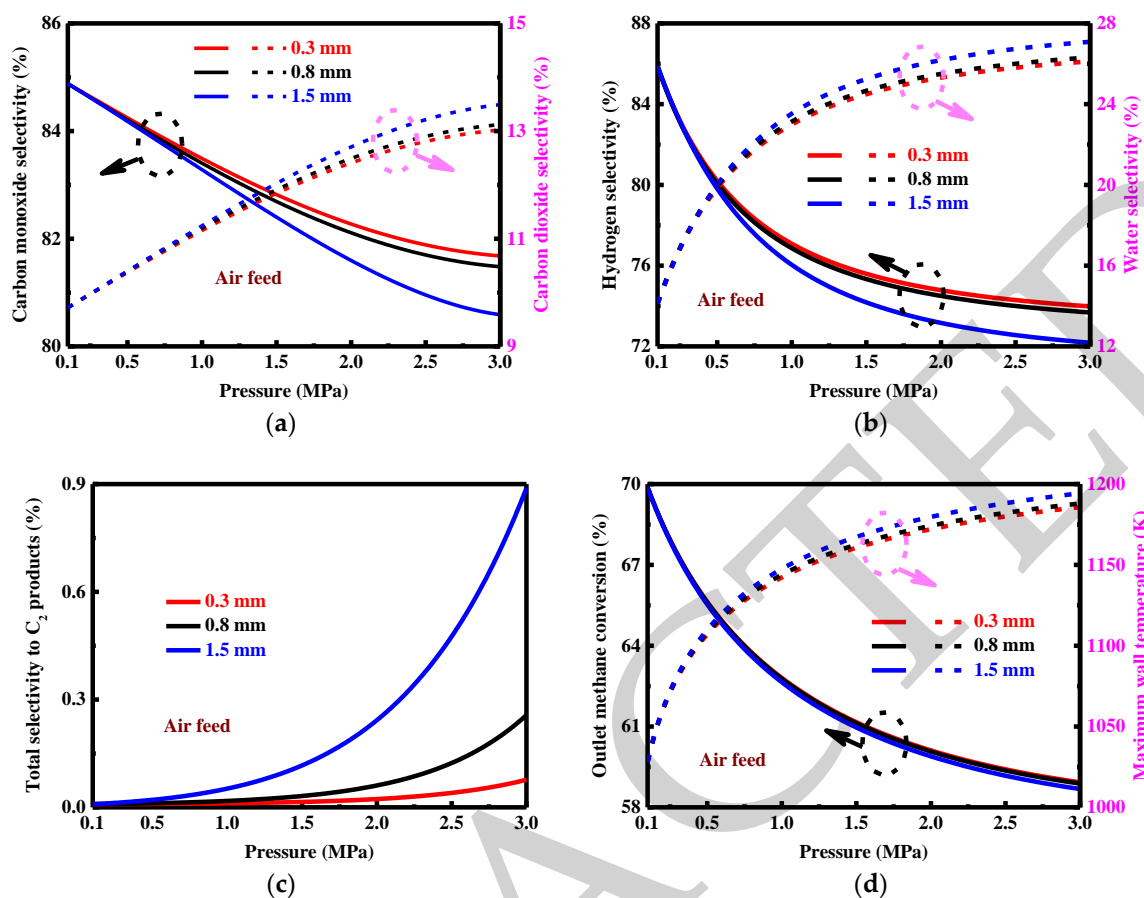
Figure 9. Effect of dimension on the performance of the methane–air system operated at various pressures. (**a**) Selectivity to carbon monoxide and carbon dioxide; (**b**) selectivity to hydrogen and water; (**c**) total selectivity to C_2 products; (**d**) outlet conversion and maximum wall temperature.

3.6. Effect of Nitrogen Diluent

For the design examined, the onset of gas-phase combustion can be inhibited by utilizing a methane–air system (Figures 7 and 9), while a methane–oxygen system (Figures 6 and 8) will allow the gas mixture to be ignited at a certain pressure, as discussed above. It is therefore important to determine the critical dilution to reduce the contribution of the reaction occurring in the gas phase.

Figure 10 shows the influence of nitrogen diluent on the performance of the reactor operated at preheating temperature 700 K. The contribution of homogeneous reactions is small, but considerable under certain conditions. At high pressures, the methane–air system has the advantage of reducing undesired by-products and improving the selectivity to synthesis gas, as shown in Figure 10a,b. At the highest pressure examined, there appears to be an optimal dilution ratio, of about 38% nitrogen in the mixture, which exhibits the maximum yield of synthesis gas. The methane–air system suffers a slight drop in conversion (Figure 10d), but offers an economical solution to the production of synthesis gas (Figure 10a,b). At moderate pressure 1.5 MPa, only 8% nitrogen diluent is needed to avoid the initiation of the combustion reaction occurring in the gas phase. At atmospheric pressure, the contribution of homogeneous reactions is rather small, and thus nitrogen dilution has little or no effect on the yield of synthesis gas. At moderate to high pressures, there exists a sharp rise in the yield of synthesis gas, as shown in Figure 10. The inflection point of the nitrogen diluent increases with increasing pressure. For the methane–air system, the yield of synthesis gas also increases with increasing pressure. For the system operated at moderate to high pressures with a low dilution, the initiation of gas-phase

combustion is possible, and both the amount of C_2-hydrocarbons and the maximum wall temperature increases with increasing pressure, as shown in Figure 10c,d.
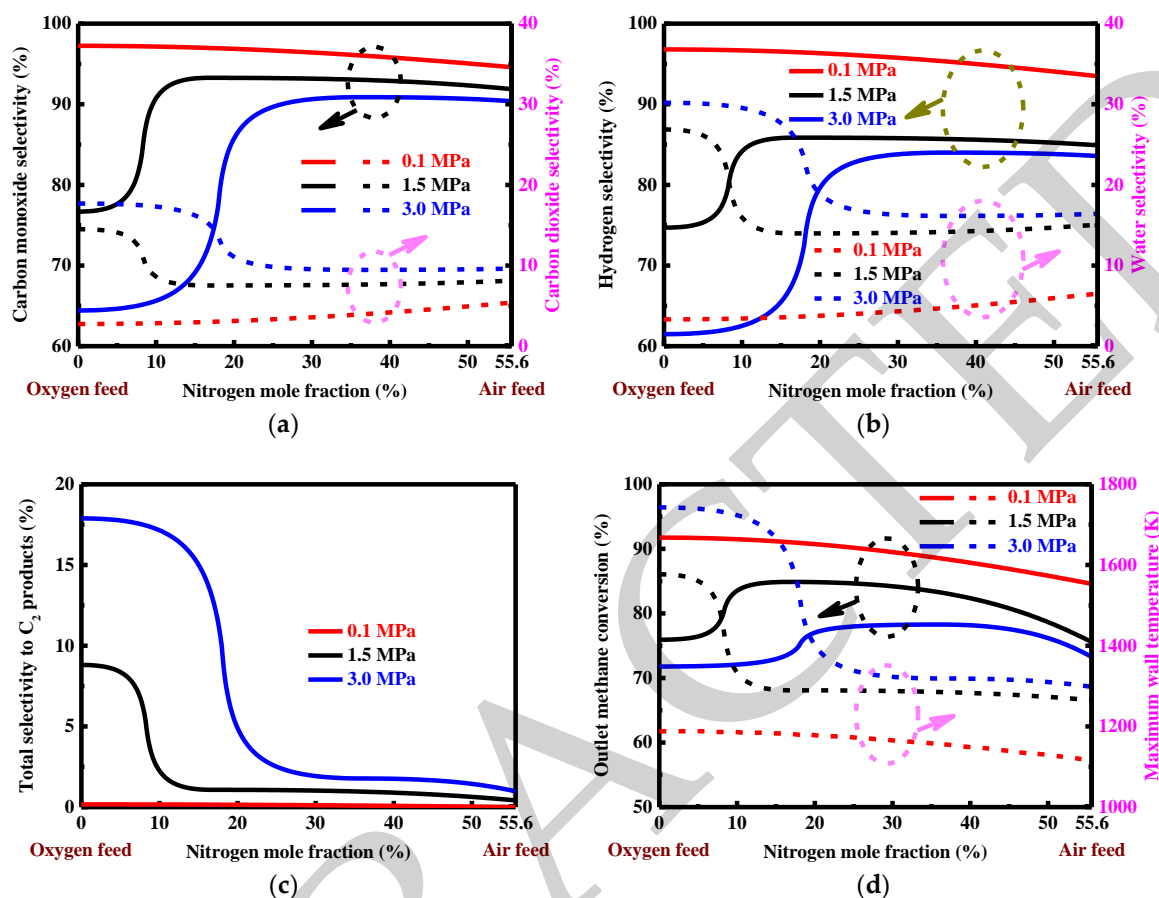

Figure 10. Effect of nitrogen diluent on the selectivity, conversion, and maximum wall temperature at different pressures when the reactor is operated at preheating temperature 700 K. (**a**) Selectivity to carbon monoxide and carbon dioxide; (**b**) selectivity to hydrogen and water; (**c**) total selectivity to C_2 products; (**d**) outlet conversion and maximum wall temperature.

3.7. Air Feed Versus Oxygen Feed

Comparisons are made between the results obtained for the two systems operated at atmospheric pressure. Figure 11 shows the influence of preheating temperature on the performance of the two systems operated at atmospheric pressure. Both the selectivity to synthesis gas (Figure 11a,b) and the outlet conversion (Figure 11c) are higher for the methane–oxygen system than for the methane–air system, especially at lower temperatures. For both systems, the production of synthesis gas is favored at high preheating temperatures, but the methane–air system can benefit more from preheating, as shown in Figure 11. Therefore, the effect of preheating is more pronounced for the methane–air system. For each of the two systems, the maximum wall temperature increases with increasing preheating temperature under the conditions examined here (Figure 11c). As expected, the maximum temperature within the walls is higher for the methane–oxygen system than for the methane–air system.
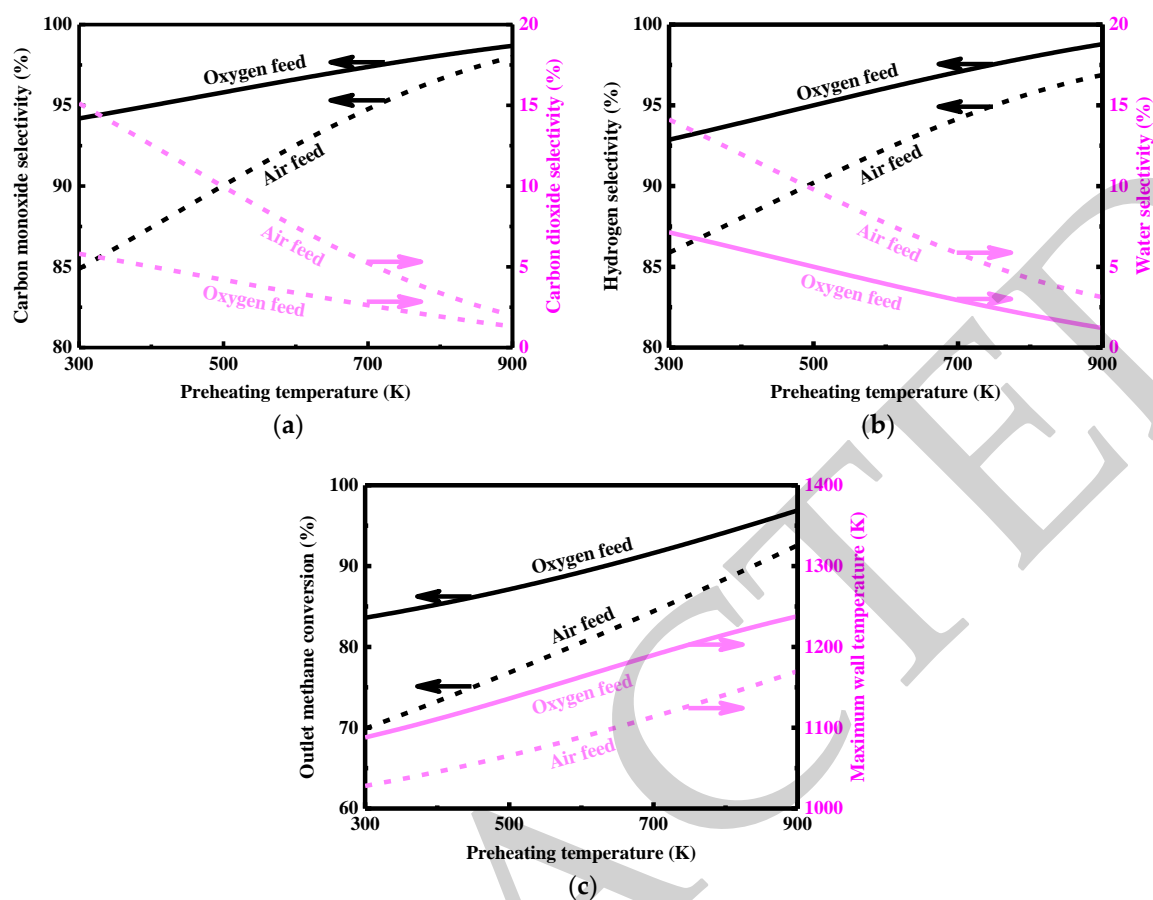
Figure 11. Comparisons between the methane–oxygen system and the methane–air system operated at atmospheric pressure. (**a**) Selectivity to carbon monoxide and carbon dioxide; (**b**) selectivity to hydrogen and water; (**c**) outlet conversion and maximum wall temperature.

4. Further Discussion

The results presented above indicate that the design shows great promise for the production of synthesis gas from methane. When the dominant chemistry is heterogeneous, the effect of pressure is small. In contrast, when the gas-phase chemistry is considerable, the pressure can significantly affect the reactor performance such as the yield of synthesis gas. In this context, the initiation of gas-phase combustion is possible, the temperature is high, the amount of undesired by-products is relatively large, and the out conversion is low, as shown in Figure 8. For the base case, a stoichiometric mixture for the production of synthesis gas is utilized. In this context, homogeneous reactions can lead to a lower outlet conversion, because they tend to consume more amount of oxygen than heterogeneous reactions, which leads to lack of oxygen.

At the highest pressure examined, it may be difficult to optimize operating conditions of the methane–oxygen system. This is because high preheating temperatures increase the outlet conversion, but decrease the selectivity to synthesis gas, as shown in Figure 6. Furthermore, the selectivity to synthesis gas is not high enough, at all of the preheating temperatures examined for the methane–oxygen system. The selectivity to synthesis gas decreases with increasing the preheating temperature, as shown in Figure 6. However, smaller reactors show great promise, since they can delay the initiation of gas-phase combustion, as shown in Figure 8.

At high pressures, the methane–air system has the advantage of reducing the contribution of homogeneous reactions, as shown in Figures 6 and 7. At low pressures, the dimension has little or no effect on the performance of each of the two systems, as shown in Figures 8 and 9. At all of the

pressures examined here, the dimension has little effect on the performance of the methane–air system, and the contribution of homogeneous reactions is negligible, as illustrated in Figure 9. For the mixture of methane and oxygen diluted with a large amount of nitrogen, the collision between the reactant molecules becomes less frequent, which can greatly reduce the contribution of homogeneous reactions, as shown in Figure 10. However, the contribution may still be considerable at high pressures, as shown in Figure 10, because mass-transfer limitations are significant under the conditions examined here.

At the highest pressure examined here, the methane–air system can offer a good yield of synthesis gas, especially at high preheating temperatures, as shown in Figure 7. For each of the two systems, the yield of synthesis gas decreases with increasing pressure, as shown in Figures 6 and 7. At high pressures, the production of synthesis gas is favored at low preheating temperatures for the methane–oxygen system (Figure 6), but at high preheating temperatures for the methane–air system (Figure 7). At atmospheric pressure, the use of oxygen and the use of preheated air have the similar effect on the reactor performance, due to the negligible contribution of homogeneous reactions (Figure 11). At high pressures, however, the effect played by the above two feeding methods is quite different from each other, because in this context the contribution of homogeneous reactions is considerable. For each of the two systems, the outlet conversion decreases with increasing pressure due to the mass-transfer limitations and the possible occurrence of gas-phase combustion, especially in larger dimensions. The mass-transfer effect is more pronounced at high pressures, as shown in Figures 7 and 8. As the dimension of the methane–oxygen system increases, the outlet conversion drops sharply (Figure 8), because in this context the mass-transfer effect may be important [79,80] and the initiation of gas-phase combustion is possible.

5. Conclusions

Catalytic partial oxidation of methane in microchannel reactors in high temperature environments was studied numerically. This investigation provided knowledge on how reaction conditions affect the operating characteristics and the distribution of reaction products in the reactor. Comparisons were made with published results, suggesting that the model developed in this paper is reliable and helpful to the design of the system. Furthermore, the catalytic partial oxidation process under extremely short contact time conditions can be accurately described by the model via the combination of detailed heterogeneous and homogenous reaction mechanisms.

The results have shown that the relative role of heterogeneous and homogeneous reaction pathways depends strongly upon the operating conditions. The distribution of reaction products depends upon a number of factors, such as the reactor dimension, pressure, temperature, and feed composition. The operating temperature can significantly affect the yield of synthesis gas. Undesired homogeneous reactions are favored in large reactors, and at high temperatures and pressures. It is more economical to utilize air instead of oxygen as the oxidant. Such an arrangement is particularly beneficial, since the onset of homogeneous reactions can thereby be inhibited or avoided. It is necessary to use the reactant mixture diluted with a sufficient amount of nitrogen to avoid homogenous reactions at high pressures. When air is used as the oxidant, preheating is needed, and the production of synthesis gas is practically favored at high pressures. The use of air as the oxidant is preferred at industrially relevant pressure 3 MPa, at which the contribution of undesired homogeneous reactions is usually small.

Further research is needed on the principles underlying the catalytic partial oxidation process. Catalyst deactivation may be an important risk factor, which is not addressed in this paper. This deactivation can significantly decrease the yield of synthesis gas, thus reducing the performance of the system. There are potential solutions to this issue, such as process control to maintain the temperature below a certain damaging threshold, non-uniform catalyst distribution, and thicker catalyst layers. Furthermore, the success of microchannel reactors is highly dependent on the robust catalysts suitable for the operating conditions of these small-scale chemical systems. On the other hand, high temperatures obtained within the system may destroy the catalyst wash coat employed

and impose severe constraints on the materials used. Lower reactor temperatures are essential for the stability of the catalyst and materials used. The problem related to the materials stability limit is also not addressed in this paper. A temperature threshold should be well defined in the practical design, which will be the subject of future work.

Nomenclature

A	pre-exponential factor
A'	surface area
C	concentration
c	specific heat capacity
D	diffusivity
D^T	thermal diffusivity
D_{eff}	effective diffusivity
D_m	mixture-averaged diffusivity
d	channel height
d_{pore}	mean pore diameter
Ea	activation energy
$F_{cat/geo}$	catalyst/geometric surface area
F	view factor
$\Delta_r H_m^\ominus$	standard molar enthalpy of reaction
h	specific enthalpy
h_o	external heat loss coefficient
K_g, K_s	number of gaseous species and number of surface species
l	length
m	total number of gaseous and surface species
p	pressure
q	heat flux
R	ideal gas constant
$\dot{s}$	rate of appearance of a heterogeneous product
s	sticking coefficient
T, T_o	absolute temperature and reference temperature
u, v	streamwise and transverse velocity components
$V, \overrightarrow{V}$	diffusion velocity and diffusion velocity vector
$W, \overrightarrow{W}$	relative molecular mass and relative molecular mass of the mixture
x	streamwise coordinate
Y	mass fraction
y	transverse coordinate

Greek variables

γ	surface area per unit catalyst volume
ε	emissivity
δ	thickness
ε_p	catalyst porosity
λ	thermal conductivity
η	effectiveness factor
μ	dynamic viscosity
ρ	density
σ	Stefan-Boltzmann constant
ϑ	site occupancy
τ_p	catalyst tortuosity factor
ϕ	inlet molar ratio
$\dot{\omega}$	rate of appearance of a homogeneous product
Γ	site density
Θ	surface coverage
Φ	Thiele modulus

Subscripts

amb	ambient
eff	effective
g	gas
i, k, m	species index, gaseous species index, and surface species index
in	inlet
o	outer
rad	radiation
s	solid
w	wall
x, y	streamwise and transverse components

References

1. Guo, S.; Wang, J.; Ding, C.; Duan, Q.; Ma, Q.; Zhang, K.; Liu, P. Confining Ni nanoparticles in honeycomb-like silica for coking and sintering resistant partial oxidation of methane. *Int. J. Hydrogen Energy* **2018**, *43*, 6603–6613. [CrossRef]

2. Grundner, S.; Luo, W.; Sanchez-Sanchez, M.; Lercher, J.A. Synthesis of single-site copper catalysts for methane partial oxidation. *Chem. Commun.* **2016**, *52*, 2553–2556. [CrossRef] [PubMed]

3. Kee, R.J.; Zhu, H.; Sukeshini, A.M.; Jackson, G.S. Solid oxide fuel cells: Operating principles, current challenges, and the role of syngas. *Combust. Sci. Technol.* **2008**, *180*, 1207–1244. [CrossRef]

4. Baldinelli, A.; Barelli, L.; Bidini, G. Performance characterization and modelling of syngas-fed SOFCs (solid oxide fuel cells) varying fuel composition. *Energy* **2015**, *90*, 2070–2084. [CrossRef]

5. Pramanik, S.; Ravikrishna, R.V. Numerical study of rich catalytic combustion of syngas. *Int. J. Hydrogen Energy* **2017**, *42*, 16514–16528. [CrossRef]

6. Zheng, X.; Mantzaras, J.; Bombach, R. Homogeneous combustion of fuel-lean syngas mixtures over platinum at elevated pressures and preheats. *Combust. Flame* **2013**, *160*, 155–169. [CrossRef]

7. Sengodan, S.; Lan, R.; Humphreys, J.; Du, D.; Xu, W.; Wang, H.; Tao, S. Advances in reforming and partial oxidation of hydrocarbons for hydrogen production and fuel cell applications. *Renew. Sustain. Energy Rev.* **2018**, *82*, 761–780. [CrossRef]

8. Tran, A.; Pont, M.; Crose, M.; Christofides, P.D. Real-time furnace balancing of steam methane reforming furnaces. *Chem. Eng. Res. Des.* **2018**, *134*, 238–256. [CrossRef]

9. Lu, N.; Gallucci, F.; Melchiori, T.; Xie, D.; Van Sint Annaland, M. Modeling of autothermal reforming of methane in a fluidized bed reactor with perovskite membranes. *Chem. Eng. Process* **2018**, *124*, 308–318. [CrossRef]

10. Goralski, C.T.; O'Connor, R.P.; Schmidt, L.D. Modeling homogeneous and heterogeneous chemistry in the production of syngas from methane. *Chem. Eng. Sci.* **2000**, *55*, 1357–1370. [CrossRef]

11. Shelepova, E.; Vedyagin, A.; Sadykov, V.; Mezentseva, N.; Fedorova, Y.; Smorygo, O.; Klenov, O.; Mishakov, I. Theoretical and experimental study of methane partial oxidation to syngas in catalytic membrane reactor with asymmetric oxygen-permeable membrane. *Catal. Today* **2016**, *268*, 103–110. [CrossRef]

12. Zhang, Q.; Liu, Y.; Chen, T.; Yu, X.; Wang, J.; Wang, T. Simulations of methane partial oxidation by CFD coupled with detailed chemistry at industrial operating conditions. *Chem. Eng. Sci.* **2016**, *142*, 126–136. [CrossRef]

13. Chakrabarti, R.; Kruger, J.S.; Hermann, R.J.; Blass, S.D.; Schmidt, L.D. Spatial profiles in partial oxidation of methane and dimethyl ether in an autothermal reactor over rhodium catalysts. *Appl. Catal. A* **2014**, *483*, 97–102. [CrossRef]

14. Chen, W.-H.; Lin, S.-C. Characterization of catalytic partial oxidation of methane with carbon dioxide utilization and excess enthalpy recovery. *Appl. Energy* **2016**, *162*, 1141–1152. [CrossRef]

15. York, A.P.E.; Xiao, T.C.; Green, M.L.H. Brief overview of the partial oxidation of methane to synthesis gas. *Top. Catal.* **2003**, *22*, 345–358. [CrossRef]

16. Christian Enger, B.; Lødeng, R.; Holmen, A. A review of catalytic partial oxidation of methane to synthesis gas with emphasis on reaction mechanisms over transition metal catalysts. *Appl. Catal. A* **2008**, *346*, 1–27. [CrossRef]

17. Guo, D.; Wang, G.-C. Partial oxidation of methane on anatase and rutile defective TiO_2 supported Rh_4 cluster: A density functional theory study. *J. Phys. Chem. C* **2017**, *121*, 26308–26320. [CrossRef]

18. Kraus, P.; Lindstedt, R.P. Microkinetic mechanisms for partial oxidation of methane over platinum and rhodium. *J. Phys. Chem. C* **2017**, *121*, 9442–9453. [CrossRef]

19. Urasaki, K.; Kado, S.; Kiryu, A.; Imagawa, K.-i.; Tomishige, K.; Horn, R.; Korup, O.; Suehiro, Y. Synthesis gas production by catalytic partial oxidation of natural gas using ceramic foam catalyst. *Catal. Today* **2018**, *299*, 219–228. [CrossRef]

20. Gil-Calvo, M.; Jiménez-González, C.; de Rivas, B.; Gutiérrez-Ortiz, J.I.; López-Fonseca, R. Effect of Ni/Al molar ratio on the performance of substoichiometric $NiAl_2O_4$ spinel-based catalysts for partial oxidation of methane. *Appl. Catal. B* **2017**, *209*, 128–138. [CrossRef]

21. Kumar Singha, R.; Shukla, A.; Yadav, A.; Sain, S.; Pendem, C.; Kumar Konathala, L.N.S.; Bal, R. Synthesis effects on activity and stability of Pt-CeO_2 catalysts for partial oxidation of methane. *Mol. Catal.* **2017**, *432*, 131–143. [CrossRef]

22. Osman, A.I.; Meudal, J.; Laffir, F.; Thompson, J.; Rooney, D. Enhanced catalytic activity of Ni on η-Al_2O_3 and ZSM-5 on addition of ceria zirconia for the partial oxidation of methane. *Appl. Catal. B* **2017**, *212*, 68–79. [CrossRef]

23. Singha, R.K.; Ghosh, S.; Acharyya, S.S.; Yadav, A.; Shukla, A.; Sasaki, T.; Venezia, A.M.; Pendem, C.; Bal, R. Partial oxidation of methane to synthesis gas over Pt nanoparticles supported on nanocrystalline CeO_2 catalyst. *Catal. Sci. Technol.* **2016**, *6*, 4601–4615. [CrossRef]

24. Luo, Z.; Kriz, D.A.; Miao, R.; Kuo, C.-H.; Zhong, W.; Guild, C.; He, J.; Willis, B.; Dang, Y.; Suib, S.L.; et al. TiO_2 Supported gold-palladium catalyst for effective syngas production from methane partial oxidation. *Appl. Catal. A* **2018**, *554*, 54–63. [CrossRef]

25. Boukha, Z.; Gil-Calvo, M.; de Rivas, B.; González-Velasco, J.R.; Gutiérrez-Ortiz, J.I.; López-Fonseca, R. Behaviour of Rh supported on hydroxyapatite catalysts in partial oxidation and steam reforming of methane: On the role of the speciation of the Rh particles. *Appl. Catal. A* **2018**, *556*, 191–203. [CrossRef]

26. Scarabello, A.; Dalle Nogare, D.; Canu, P.; Lanza, R. Partial oxidation of methane on Rh/ZrO_2 and Rh/Ce-ZrO_2 on monoliths: Catalyst restructuring at reaction conditions. *Appl. Catal. B* **2015**, *174–175*, 308–322. [CrossRef]

27. Figen, H.E.; Baykara, S.Z. Effect of ruthenium addition on molybdenum catalysts for syngas production via catalytic partial oxidation of methane in a monolithic reactor. *Int. J. Hydrogen Energy* **2018**, *43*, 1129–1138. [CrossRef]

28. Zhu, Y.; Barat, R. Partial oxidation of methane over a ruthenium phthalocyanine catalyst. *Chem. Eng. Sci.* **2014**, *116*, 71–76. [CrossRef]

29. Wang, F.; Li, W.-Z.; Lin, J.-D.; Chen, Z.-Q.; Wang, Y. Crucial support effect on the durability of $Pt/MgAl_2O_4$ for partial oxidation of methane to syngas. *Appl. Catal. B* **2018**, *231*, 292–298. [CrossRef]

30. Singha, R.K.; Shukla, A.; Yadav, A.; Sasaki, T.; Sandupatla, A.; Deo, G.; Bal, R. Pt-CeO$_2$ nanoporous spheres - an excellent catalyst for partial oxidation of methane: Effect of the bimodal pore structure. *Catal. Sci. Technol.* **2017**, *7*, 4720–4735. [CrossRef]

31. Li, B.; Li, H.; Weng, W.-Z.; Zhang, Q.; Huang, C.-J.; Wan, H.-L. Synthesis gas production from partial oxidation of methane over highly dispersed Pd/SiO$_2$ catalyst. *Fuel* **2013**, *103*, 1032–1038. [CrossRef]

32. Yashnik, S.A.; Chesalov, Y.A.; Ishchenko, A.V.; Kaichev, V.V.; Ismagilov, Z.R. Effect of Pt addition on sulfur dioxide and water vapor tolerance of Pd-Mn-hexaaluminate catalysts for high-temperature oxidation of methane. *Appl. Catal. B* **2017**, *204*, 89–106. [CrossRef]

33. Singha, R.K.; Shukla, A.; Yadav, A.; Sivakumar Konathala, L.N.; Bal, R. Effect of metal-support interaction on activity and stability of Ni-CeO$_2$ catalyst for partial oxidation of methane. *Appl. Catal. B* **2017**, *202*, 473–488. [CrossRef]

34. Kaddeche, D.; Djaidja, A.; Barama, A. Partial oxidation of methane on co-precipitated Ni-Mg/Al catalysts modified with copper or iron. *Int. J. Hydrogen Energy* **2017**, *42*, 15002–15009. [CrossRef]

35. Nakagawa, K.; Ikenaga, N.; Suzuki, T.; Kobayashi, T.; Haruta, M. Partial oxidation of methane to synthesis gas over supported iridium catalysts. *Appl. Catal. A* **1998**, *169*, 281–290. [CrossRef]

36. Nakagawa, K.; Ikenaga, N.; Teng, Y.; Kobayashi, T.; Suzuki, T. Partial oxidation of methane to synthesis gas over iridium-nickel bimetallic catalysts. *Appl. Catal. A* **1999**, *180*, 183–193. [CrossRef]

37. De SantanaSantos, M.; Neto, R.C.R.; Noronha, F.B.; Bargiela, P.; da Graça Carneiro da Rocha, M.; Resini, C.; Carbó-Argibay, E.; Frétya, R.; Brandão, S.T. Perovskite as catalyst precursors in the partial oxidation of methane: The effect of cobalt, nickel and pretreatment. *Catal. Today* **2018**, *299*, 229–241. [CrossRef]

38. López-Ortiz, A.; González-Vargas, P.E.; Meléndez-Zaragoza, M.J.; Collins-Martínez, V. Thermodynamic analysis and process simulation of syngas production from methane using CoWO$_4$ as oxygen carrier. *Int. J. Hydrogen Energy* **2017**, *42*, 30223–30236. [CrossRef]

39. Horn, R.; Williams, K.A.; Degenstein, N.J.; Schmidt, L.D. Syngas by catalytic partial oxidation of methane on rhodium: Mechanistic conclusions from spatially resolved measurements and numerical simulations. *J. Catal.* **2006**, *242*, 92–102. [CrossRef]

40. Nogare, D.D.; Degenstein, N.J.; Horn, R.; Canu, P.; Schmidt, L.D. Modeling spatially resolved data of methane catalytic partial oxidation on Rh foam catalyst at different inlet compositions and flowrates. *J. Catal.* **2011**, *277*, 134–148. [CrossRef]

41. Horn, R.; Williams, K.A.; Degenstein, N.J.; Bitsch-Larsen, A.; Dalle Nogare, D.; Tupy, S.A.; Schmidt, L.D. Methane catalytic partial oxidation on autothermal Rh and Pt foam catalysts: Oxidation and reforming zones, transport effects, and approach to thermodynamic equilibrium. *J. Catal.* **2007**, *249*, 380–393. [CrossRef]

42. Zhan, Z.; Lin, Y.; Pillai, M.; Kim, I.; Barnett, S.A. High-rate electrochemical partial oxidation of methane in solid oxide fuel cells. *J. Power Sources* **2006**, *161*, 460–465. [CrossRef]

43. Lee, D.; Myung, J.; Tan, J.; Hyun, S.-H.; Irvine, J.T.S.; Kim, J.; Moon, J. Direct methane solid oxide fuel cells based on catalytic partial oxidation enabling complete coking tolerance of Ni-based anodes. *J. Power Sources* **2017**, *345*, 30–40. [CrossRef]

44. Wang, B.; Albarracín-Suazo, S.; Pagán-Torres, Y.; Nikolla, E. Advances in methane conversion processes. *Catal. Today* **2017**, *285*, 147–158. [CrossRef]

45. Taifan, W.; Baltrusaitis, J. CH$_4$ conversion to value added products: Potential, limitations and extensions of a single step heterogeneous catalysis. *Appl. Catal. B* **2016**, *198*, 525–547. [CrossRef]

46. Védrine, J.C.; Fechete, I. Heterogeneous partial oxidation catalysis on metal oxides. *C. R. Chim.* **2016**, *19*, 1203–1225. [CrossRef]

47. Arutyunov, V.S.; Strekova, L.N. The interplay of catalytic and gas-phase stages at oxidative conversion of methane: A review. *J. Mol. Catal. A Chem.* **2017**, *426*, 326–342. [CrossRef]

48. Tanimu, A.; Jaenicke, S.; Alhooshani, K. Heterogeneous catalysis in continuous flow microreactors: A review of methods and applications. *Chem. Eng. J.* **2017**, *327*, 792–821. [CrossRef]

49. Yao, X.; Zhang, Y.; Du, L.; Liu, J.; Yao, J. Review of the applications of microreactors. *Renew. Sustain. Energy Rev.* **2015**, *47*, 519–539. [CrossRef]

50. Geyer, K.; Codée, J.D.C.; Seeberger, P.H. Microreactors as tools for synthetic chemists—The chemists' round-bottomed flask of the 21st century? *Chem. Eur. J.* **2006**, *12*, 8434–8442. [CrossRef] [PubMed]

51. Kashid, M.N.; Kiwi-Minsker, L. Microstructured reactors for multiphase reactions: State of the art. *Ind. Eng. Chem. Res.* **2009**, *48*, 6465–6485. [CrossRef]

52. Kiwi-Minsker, L.; Renken, A. Microstructured reactors for catalytic reactions. *Catal. Today* **2005**, *110*, 2–14. [CrossRef]

53. Kolb, G.; Hessel, V. Micro-structured reactors for gas phase reactions. *Chem. Eng. Sci.* **2004**, *98*, 1–38. [CrossRef]

54. Jensen, K.F. Microreaction engineering—Is small better? *Chem. Eng. Sci.* **2001**, *56*, 293–303. [CrossRef]

55. Jähnisch, K.; Hessel, V.; Löwe, H.; Baerns, M. Chemistry in microstructured reactors. *Angew. Chem. Int. Ed.* **2004**, *43*, 406–446. [CrossRef] [PubMed]

56. Deutschmann, O. Modeling of the interactions between catalytic surfaces and gas-phase. *Catal. Lett.* **2015**, *145*, 272–289. [CrossRef]

57. Bawornruttanaboonya, K.; Devahastin, S.; Mujumdar, A.S.; Laosiripojana, N. A computational fluid dynamic evaluation of a new microreactor design for catalytic partial oxidation of methane. *Int. J. Heat Mass Transf.* **2017**, *115*, 174–185. [CrossRef]

58. Navalho, J.E.P.; Pereira, J.M.C.; Pereira, J.C.F. Multiscale modeling of methane catalytic partial oxidation: From the mesopore to the full-scale reactor operation. *AIChE J.* **2018**, *64*, 578–594. [CrossRef]

59. Tonkovich, A.; Kuhlmann, D.; Rogers, A.; McDaniel, J.; Fitzgerald, S.; Arora, R.; Yuschak, T. Microchannel technology scale-up to commercial capacity. *Chem. Eng. Res. Des.* **2005**, *83*, 634–639. [CrossRef]

60. Tonkovich, A.Y.; Perry, S.; Wang, Y.; Qiu, D.; LaPlante, T.; Rogers, W.A. Microchannel process technology for compact methane steam reforming. *Chem. Eng. Sci.* **2004**, *59*, 4819–4824. [CrossRef]

61. Suryawanshi, P.L.; Gumfekar, S.P.; Bhanvase, B.A.; Sonawane, S.H.; Pimplapure, M.S. A review on microreactors: Reactor fabrication, design, and cutting-edge applications. *Chem. Eng. Sci.* **2018**. [CrossRef]

62. *ANSYS Fluent User's Guide*; Release 16.0; ANSYS Inc.: Canonsburg, PA, USA, 2014.

63. Kee, R.J.; Dixon-lewis, G.; Warnatz, J.; Coltrin, M.E.; Miller, J.A.; Moffat, H.K. *A Fortran Computer Code Package for the Evaluation of Gas-Phase, Multicomponent Transport Properties*; Report No. SAND86-8246B; Sandia National Laboratories: Livermore, CA, USA, 1998.

64. Von Rickenbach, J.; Lucci, F.; Narayanan, C.; Dimopoulos Eggenschwiler, P.; Poulikakos, D. Effect of washcoat diffusion resistance in foam based catalytic reactors. *Chem. Eng. J.* **2015**, *276*, 388–397. [CrossRef]

65. Bergman, T.L.; Lavine, A.S.; Incropera, F.P.; DeWitt, D.P. *Fundamentals of Heat and Mass Transfer*, 8th ed.; John Wiley & Sons, Inc.: Hoboken, NJ, USA, 2017; ISBN 978-1-119-32042-5.

66. Glarborg, P.; Miller, J.A.; Ruscic, B.; Klippenstein, S.J. Modeling nitrogen chemistry in combustion. *Prog. Energy Combust. Sci.* **2018**, *67*, 31–68. [CrossRef]

67. Messaoudi, H.; Thomas, S.; Djaidja, A.; Slyemi, S.; Chebout, R.; Barama, S.; Barama, A.; Benaliouche, F. Hydrogen production over partial oxidation of methane using NiMgAl spinel catalysts: A kinetic approach. *C. R. Chim.* **2017**, *20*, 738–746. [CrossRef]

68. Pruksawan, S.; Kitiyanan, B.; Ziff, R.M. Partial oxidation of methane on a nickel catalyst: Kinetic Monte-Carlo simulation study. *Chem. Eng. Sci.* **2016**, *147*, 128–136. [CrossRef]

69. Neagoe, C.; Boffito, D.C.; Ma, Z.; Trevisanut, C.; Patience, G.S. Pt on Fecralloy catalyses methane partial oxidation to syngas at high pressure. *Catal. Today* **2016**, *270*, 43–50. [CrossRef]

70. Schwiedernoch, R.; Tischer, S.; Correa, C.; Deutschmann, O. Experimental and numerical study on the transient behavior of partial oxidation of methane in a catalytic monolith. *Chem. Eng. Sci.* **2003**, *58*, 633–642. [CrossRef]

71. Hughes, K.J.; Turányi, T.; Clague, A.R.; Pilling, M.J. Development and testing of a comprehensive chemical mechanism for the oxidation of methane. *Int. J. Chem. Kinet.* **2001**, *33*, 513–538. [CrossRef]

72. Turanyi, T.; Zalotai, L.; Dobe, S.; Berces, T. Effect of the uncertainty of kinetic and thermodynamic data on methane flame simulation results. *Phys. Chem. Chem. Phys.* **2002**, *4*, 2568–2578. [CrossRef]

73. Aseem, A.; Harold, M.P. C_2 yield enhancement during oxidative coupling of methane in a nonpermselective porous membrane reactor. *Chem. Eng. Sci.* **2018**, *175*, 199–207. [CrossRef]

74. Gambo, Y.; Jalil, A.A.; Triwahyono, S.; Abdulrasheed, A.A. Recent advances and future prospect in catalysts for oxidative coupling of methane to ethylene: A review. *J. Ind. Eng. Chem.* **2018**, *59*, 218–229. [CrossRef]

75. Kee, R.J.; Rupley, F.M.; Meeks, E.; Miller, J.A. *CHEMKIN-III: A Fortran Chemical Kinetics Package for the Analysis of Gasphase Chemical and Plasma Kinetics*; Report No. SAND96-8216; Sandia National Laboratories: Livermore, CA, USA, 1996. [CrossRef]

76.　Coltrin, M.E.; Kee, R.J.; Rupley, F.M.; Meeks, E. *SURFACE CHEMKIN-III: A Fortran Package for Analyzing Heterogeneous Chemical Kinetics at a Solid-Surface-Gas-Phase Interface*; Report No. SAND96-8217; Sandia National Laboratories: Livermore, CA, USA, 1996. [CrossRef]

77.　Bodke, A.S.; Bharadwaj, S.S.; Schmidt, L.D. The effect of ceramic supports on partial oxidation of hydrocarbons over noble metal coated monoliths. *J. Catal.* **1998**, *179*, 138–149. [CrossRef]

78.　Hunt, G.; Karimi, N.; Torabi, M. Two-dimensional analytical investigation of coupled heat and mass transfer and entropy generation in a porous, catalytic microreactor. *Int. J. Heat Mass Transf.* **2018**, *119*, 372–391. [CrossRef]

79.　Venvik, H.J.; Yang, J. Catalysis in microstructured reactors: Short review on small-scale syngas production and further conversion into methanol, DME and Fischer-Tropsch products. *Catal. Today* **2017**, *285*, 135–146. [CrossRef]

80.　Faridkhou, A.; Tourvieille, J.-N.; Larachi, F. Reactions, hydrodynamics and mass transfer in micro-packed beds—Overview and new mass transfer data. *Chem. Eng. Process* **2016**, *110*, 80–96. [CrossRef]