A CFD model for methane autothermal reforming on Ru/γ-Al₂O₃ catalyst

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Abstract

Hydrogen is the preferred fuel for fuel cells due to high reactivity for electrochemical reaction at anode. In the present study, a three dimensional CFD (Computational Fluid Dynamics) code was developed and validated to simulate the performance of a catalytic monolith fuel processor used for hydrogen generation. Methane autothermal reforming on 5% Ru/γ-Al₂O₃ catalyst was selected as the reaction mechanism. Ruthenium catalyst is a suitable catalyst for low temperature catalytic partial oxidation (LTCPO) process. This catalyst has good reforming activity and high hydrogen yield is obtained for ruthenium/γ-alumina. This catalyst also demonstrated to be stable within the investigation time. The computational domain of the simulations was selected to be the catalytic section of the reformer. The results provided an adequate match to the experimental data from literature with respect to the outlet and maximum reactor temperature and also distribution of the products. The reactor performance was thereafter studied by numerically revealing the effects of variations of O₂/C and S/C feed molar ratios, and feed temperature on the profiles of temperature and species concentrations. Moreover, effects of using air instead of pure oxygen were also investigated. It was concluded that at higher O₂/C and S/C feed molar ratios and also at higher feed gas temperature, more hydrogen will be achieved at the reactor outlet, which is very suitable for fuel cell applications.

Keywords: Autothermal reforming; hydrogen; monolith reactor; CFD code; methane
1. Introduction

Fuel cell technology has been a subject of vital research and development recently due to the higher energy conversion efficiency and lower amounts of emission gases in comparison with internal combustion engines [1]. For polymer electrolyte membrane fuel cells (PEMFC) which are considered as the most technologically mature of the different types of fuel cells, hydrogen is the preferred fuel due to high reactivity for the electrochemical reaction at anode [2]. In addition, hydrogen is a suitable substitution for hydrocarbons for different applications including fuel cells and internal combustion engines. However, hydrogen does not exist in pure form in nature. Furthermore, high storage pressure of hydrogen and the cost of its storage along with the lack of hydrogen distribution infrastructure at the present time restrict its direct use [3]. On board reforming of other fuels is a practical option to tackle this problem at the present time. Different fuels can be used for reforming processes. Natural gas and its surrogates such as methane are considered to be among the most attractive fuels for hydrogen production due to large existing reserves and available transportation infrastructure [4].

There are three common methods for hydrogen generation. Steam reforming (SR) process is the common industrial method for hydrogen production. However, steam reforming is highly endothermic and tends to possess large heat transfer areas. As a desirable characteristic, onboard fuel processors should be compact [5]. Considering this, steam reforming is not a suitable method for onboard fuel processing. Partial oxidation (POX) is another method for hydrogen production. Although the reaction rates are much higher for POX in comparison with SR, H₂ yield per carbon in the fuel is lower than SR. In addition, POX tends to produce coke [6]. Autothermal reforming (ATR) is the combination of steam reforming and oxidation reactions [7]. The key feature of autothermal reforming is that the thermal energy generated by POX is absorbed by SR which results a thermo neutral process. Moreover, by using steam, coke formation which is occurring in partial oxidation is reduced and it also takes advantage of high hydrogen yield in steam reforming [8]. Compact size, quick response, and inexpensive material requirements are other key features of an ATR reformer [9]. Therefore, autothermal reforming is the preferred reforming method in comparison with endothermic steam reforming and exothermic partial oxidation and has been the focal point of most of the studies in recent years as a feasible technique for hydrogen production in portable fuel cell applications.

Trimm and Lam [10] studied ATR of methane on Pt/Al₂O₃ catalyst. The kinetics of the reactions was measured at temperatures around 527 °C. Numaguchi and Kikuchi [11] studied methane steam reforming on 8.7 wt% Ni/Al₂O₃ catalyst in a fixed bed reactor. The temperature was in the range of 400–890 °C. They assumed that only CO was formed from the reaction between CH₄ and H₂O. Carbon dioxide was only produced from the water gas shift reaction (WGS). Xu and Froment [12] presented intrinsic kinetics of methane steam reforming, methanation, and the WGS reactions on Ni/Al₂O₃ catalyst for initial temperature range between 300 and 550 °C. The kinetics they developed was used extensively in subsequent investigations.

Packed bed reactors have been widely used in reforming processes. Dias and Assaf [13] examined methane autothermal reforming over Ni/γ-Al₂O₃ catalyst in a packed bed reactor. The influence of addition of small amounts of noble metals to the Ni/γ-Al₂O₃ was also investigated. Temperature range in this study was between 400 and 600 °C. As reported, addition of noble metals led to hydrogen production enhancement. Zahedi Nezhad et al. [14] developed a model for methane autothermal reforming on Ni/MgAl₂O₄. The reactor they used consisted of two sections: a non-catalytic section used for partial oxidation and a catalytic packed bed section used for steam reforming. Desirable feed temperature and pressure as well as feed composition were determined to achieve higher H₂, CO, and H₂/CO ratio. Effective length of the catalyst bed was also determined.
High pressure drop of packed bed reactors limits their applications for portable devices. In contrary, the main characteristics of a monolith reformer are low pressure drop and high surface to volume ratio. These features render the monolith reactor as a suitable choice for portable applications [15]. For monolith reactors, a single channel is usually chosen as the modeled geometry [5, 16]. When single channel approach is considered as the computational domain, different boundary conditions are used among which the adiabatic boundary condition is more common [2, 17, 18]. In this boundary condition, the reactor is considered radially symmetric. Stutz et al. [5] studied catalytic partial oxidation of methane on Rh catalyst in a single channel of a monolith reformer. Effects of variations of wall heat conductivity, equivalence ratio, and wall thickness of the channel were investigated in this study. Ding et al. [17] studied catalytic partial oxidation of methane on rhodium-coated foam monolith. The reactor performance was thereafter studied by numerically revealing the effects of wall heat conduction, the channel diameter, and the catalytic surface area on the profiles of temperature and species concentrations. Chaniotis et al. [19] studied catalytic partial oxidation of methane in a single channel of a monolith reformer. The single channel was washcoated with Rh catalyst. The investigation was based on simplified reactor models and more detailed simulations (involving the Navier–Stokes equations). Parameters studied include inlet space velocity, inlet temperature, and feed gas temperature. Di Benedetto et al. [20] developed CFD models for simulation of three-channel and five-channel micro-monoliths. Catalytic oxidation of propane on platinum catalyst was selected as the reaction mechanism. Results showed that, due to the relevance of heat losses in micro-devices, it is not possible to extrapolate the behavior of the multi-channel configurations from that of the single channel. Zamaniyan et al. [21] developed a 2D numerical model of a single channel of a monolith reformer. Catalytic partial oxidation of methane on Rh catalyst was used for synthesis gas production. Gas inlet velocity, channel pressure, and fuel to air ratio (F/A) were selected as the effective parameters on the channel performance.

In some studies, computational domain of the simulation has been considered to be whole of the reactor [1, 7, 22]. The main feature of the full scale reactor modeling is the consideration of the heat conduction in the channel walls. Mei et al. [7] investigated methane autothermal reforming in a metal monolith reformer with two sections. Combustion reaction was taking place in the inner section and steam reforming progressed in the annular part between outer and inner pipe. Pd/Al₂O₃ and Ni/MgAl₂O₃ catalysts were used in the combustion and steam reforming sections, respectively. In this study, the performance of the reactor was numerically studied utilizing a three dimensional model based on the whole reactor. The effects of feed velocity ratios, feed gas temperature, and feed composition were investigated. Shi et al. [1] developed a CFD model to simulate the performance of a catalytic monolith reformer in which autothermal reforming of n-hexadecane was used for hydrogen production. The whole reactor was modeled as a porous media for the process of autothermal reforming. Their proprietary catalyst included cerium oxide, gadolinium oxide and 1 wt% platinum. The effects of thermal conductivity of the solid catalyst substrate were investigated. Although thermal conductivity of the solid catalyst substrate affected the temperature profile in the reactor, its effects on mole fractions of hydrogen, carbon monoxide, and carbon dioxide were negligible. It was found that the maximum temperature predicted in the reactor was decreased about 30 °C as the thermal conductivity increased from 2.76 to 202.4 W/m.K. The effects of power input on the reactor efficiency and species concentrations were also studied.

Most of the previous studies for methane autothermal reforming were carried out for packed bed reactors. In addition, in most of the studies, conventional catalysts were used. Among the noble metals, Pt and Rh have been widely used. According to Rabe et al. [23], ruthenium catalyst is also a suitable catalyst for low temperature catalytic partial oxidation (LTCPO) process. This catalyst has good reforming activity as well. This distinguished feature prevents using two different catalysts for promoting each process. Moreover, high hydrogen yield obtained for ruthenium/γ-alumina along with its stability during
the investigation time [23, 24], render this catalyst as a suitable choice for use in portable hydrogen generation systems. Investigating the reported results in literatures, the authors noticed that the number of numerical models available using ruthenium catalyst for reforming processes is much fewer than those available with conventional catalysts. Hence, in the present study, the performance of 5% Ru/γ-Al2O3 catalyst at different operating conditions was numerically investigated. Methane autothermal reforming was the reaction mechanism for hydrogen production. A monolith reformer was considered for methane ATR due to its low pressure drop and high surface to volume ratio. A CFD code was developed for simulation of the performance of the catalytic monolith reformer. Although air is usually selected as the oxidant in partial oxidation reaction, using air as the oxidant dilutes the CO2 containing products which creates problems with respect to an efficient CO2 separation. Hence, pure oxygen was used as the oxidant in this work. In order to consider the heat conduction between the channel walls, the computational domain of the simulations was selected to be the catalytic section of the reactor. However, number of the mesh elements for modeling of whole of the monolith structure is very high and solving this model is difficult. For solving this problem, it was assumed that the catalytic monolith zone is a porous media. Consequently, for each mesh element, percentage of the void space for the gas flow was defined by using the porosity concept. The method applied in the present study was similar to the approach utilized at [1].

The model was validated with the experimental measurements of Rabe et al. [24]. The effects of using air instead of pure oxygen were studied. The reactor performance was then studied by numerically revealing the effects of O2/C and S/C feed molar ratios and feed gas temperature on the profiles of temperature and species concentrations.

The other point worth mentioning is that in most of the previous works [9, 14, 25, 26, 27, 28, 29], the authors noticed the value used for the enthalpy term in the equilibrium constant expression for CO producing methane steam reforming reaction is wrong. The correct value for this parameter was calculated both mathematically and by using thermodynamic relations. This correct value was used in the simulations.

2. Numerical model

2.1. Autothermal reformer

The modeled geometry was based on the catalytic reactor used by Rabe et al. [24] for investigation of the autothermal reforming of methane. The experimental setup included a fuel delivery system, a catalytic reactor, and a reformate analysis system. The reactor length was approximately 20 cm. Their reactor consisted of four zones. The empty space considered at the reactor inlet was for mixing purpose in which a mixing plate was installed to ensure complete mixing of the reactants and establishment of a uniform flow through the monoliths. The next three zones were monolith zones. The characteristics of the monoliths used in the experiments were: 3.5 cm length, 3.5 cm diameter, 400 CPSI, and channel diameter of 0.9 mm. The first monolith was coated with 5% Ru/γ -Al2O3 (thickness: ca. 30 µm). The next two monoliths were blank. A reformate analysis system measured gas composition at the reactor outlet.

2.2. Model assumptions

As stated in section 2.1, a mixing plate was installed to ensure complete mixing of the reactants. However, no information was presented at [24] about the dimension and geometrical shape of the mixing plate and also the distance this plate was located from the inlet. Consequently, mixing zone and mixing plate simulation were avoided. However, the reacting gases were assumed to be completely mixed at the inlet of the first monolith zone.
In addition, the second and third monolith zones were non-catalytic. As a result, no heterogeneous reaction rate was applied in these zones. Moreover, Berman et al. [30] investigated the characteristics of the reforming reaction under homogenous conditions and the possibility to refrain from using any catalyst. Experiments were carried out at the temperature range of 900 – 1250 °C at atmospheric pressure in reactor made of alumina (D = 0.006 m). The reported methane conversions in empty reactor were 0.97%, 1.7%, and 13.7% at 1000, 1050, and 1200 °C, respectively. Therefore, we have not considered the possible occurrence of homogeneous steam reforming reaction in the non-catalytic monolith zones due to low methane conversion at the temperature range faced in these areas. Moreover, using two active ruthenium/ alumina monoliths did not improve the performance of the fuel reformer, according to Rabe et al. [24]. As a result, the authors considered the computational domain of the simulations to be the first catalytic monolith zone with a total length of 3.5 cm.

A schematic sketch of the modeled geometry is represented in figure 1. Due to symmetry, only a quarter of the reformer was modeled. The curved surface is the wall of the reformer. The mesh of the modeled geometry is shown in figure 2. The total number of elements was approximately 27000. More meshes were put near the entrance of the catalytic monolith zone because of the rapid changes in the reaction rates in this area. As the total number of mesh elements was increased from 27000 to 31000, the maximum difference in the averaged H\textsubscript{2} mole fraction along the reactor length was less than 0.1%. Therefore, the simulation results were grid independent. The catalytic monolith zone was assumed to be a porous media, as mentioned in section 1. Based on the given dimensions, porosity was calculated to be 0.4.

![Fig. 1. Sketch of the experimental setup](image-url)
The flow was considered to be compressible and the gas mixture was assumed to be an ideal gas. Steady state simulation was considered in the study. Furthermore, when the weight hourly space velocity (WHSV) was 119 h-1, the Reynolds numbers was about 320. This indicates that flow in the reactor was laminar. The mixture consisted of six species: CH$_4$, O$_2$, H$_2$O, CO$_2$, CO, and H$_2$.

2.3. Conservation equations

Assuming compressible, laminar, and steady state flow as well as considering the gas mixture to be ideal, the conservation equations for continuity, momentum, energy, and species [1, 9, 31] are given by:

$$\frac{\partial}{\partial x_j} (\rho u_j ) = 0$$  \hspace{1cm} (1)

$$\rho u_j \frac{\partial u_i}{\partial x_j} = - \frac{\partial p}{\partial x_i} + \frac{\partial \tau_{ij}}{\partial x_j} + \rho g_i + S_u$$  \hspace{1cm} (2)

$$\rho u_j \frac{\partial h}{\partial x_j} = \frac{\partial}{\partial x_j} (k_{eff} \frac{\partial T}{\partial x_j} - \sum_{i=1}^{N} h_i J_{ij} ) + u_j \frac{\partial p}{\partial x_j} + S_h$$  \hspace{1cm} (3)

$$\rho u_j \frac{\partial Y_i}{\partial x_j} = - \frac{\partial J_{ij}}{\partial x_j} + R_i$$  \hspace{1cm} (4)

where $j$ represents $x$, $y$, and $z$ direction, $u$ is the gas velocity (m/s), $\rho$ is the density of gas mixture (kg/m³), $p$ is the static pressure (Pa), $\tau_{ij}$ is the laminar stress tensor (Pa), $\mu$ is the molecular viscosity (N.s/m²), $\delta_{ij}$ is the Kronecker delta, $\rho g_i$ is the gravitational body force per unit volume (N/m³), and $S_u$
is the momentum source term. \( h \), \( k_{\text{eff}} \) and \( T \) are the sensible enthalpy (kJ/kg), effective thermal conductivity (W/m.K), and temperature (K) of the gas mixture, respectively. \( h_i \) is the sensible enthalpy of species \( i \) (kJ/kg) and \( J_{ij} \) is the diffusional flux of species \( i \) in the \( j \) direction (kg/m\(^2\).s), which was assumed to include full multi component diffusion and thermal diffusion. \( N \) is the total number of gas species and \( S_s \) is the source of energy caused by the chemical reaction (kW/m\(^3\)). \( Y_i \) is the local mass fraction of species \( i \) and \( R_i \) is the net rate of production of species \( i \) by chemical reaction (kg/m\(^3\).s).

The last term in Eq. (2) represents the resistance to fluid flow due to the presence of solid material in the monolith. In general, the source term \( (S_u) \) include the viscous loss and the inertial loss. However, the velocity was low and the inertial loss was ignored. The viscous loss was calculated by:

\[
S_u = - \eta_{ij} \mu u_j \tag{5}
\]

This loss is proportional to the velocity. The elements in the prescribed matrix \( \eta_{ij} \) are the resistance coefficients [31].

The first two terms on the right hand side of Eq. (3) account for the energy transfer due to conduction and species diffusion, respectively. The effective thermal conductivity used in the energy equation was given by:

\[
k_{\text{eff}} = \epsilon k_f + (1 - \epsilon) k_s \tag{6}
\]

where \( k_f \) and \( k_s \) are the thermal conductivity of the fluid and solid medium, respectively. \( \epsilon \) is the porosity of the monolith zone.

Since, in the present system a non-dilute mixture existed, the diffusional flux of species \( i \) in the species \( j \), \( J_{ij} \) was solved using the full multi component diffusion method which is based on the Maxwell-Stephan equation. For more details about methods of calculating \( J_{ij} \) and other physical properties of the mixture, reference shall be made to [9, 31].

### 2.4. Chemical kinetics

As the amount of CO\(_2\) produced in the experimental work of Rabe et al. [24] was higher than that of CO (18.5\% vs. 5.2\% dry composition, respectively, for input power of 1.09 kW\(_{th}\)), in this study ATR of methane was defined as the combination of steam reforming and total combustion. Although many reactions take place during methane autothermal reforming, four reactions are proven to have higher rates in comparison with others [25]. Therefore, only four major reactions were considered in the present model.

\[
\text{CH}_4 + 2\text{O}_2 \rightleftharpoons \text{CO}_2 + 2\text{H}_2\text{O} \tag{7}
\]

\[
\text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons \text{CO} + 3\text{H}_2 \tag{8}
\]

\[
\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2 \tag{9}
\]

\[
\text{CH}_4 + 2\text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + 4\text{H}_2 \tag{10}
\]
Adopted reaction rates for total oxidation and steam reforming were based on Ma et al. [32] and Xu
and Froment [12], respectively. The catalyst used in Ma et al. experiments was Pt based and a Ni based
catalyst was used in that of Xu and Froment;

\[
\begin{align*}
r_1 &= \frac{k_1}{(1 + K_{\text{CH}_4} p_{\text{CH}_4} + K_{\text{O}_2} p_{\text{O}_2})^{1/2}} P_{\text{CH}_4} P_{\text{O}_2}^{1/2} \\
r_2 &= \frac{k_2}{P_{\text{H}_2}^{2/5}} (p_{\text{CH}_4} p_{\text{H}_2} - \frac{p_{\text{H}_2}^3 p_{\text{CO}}}{K_{\text{e}}^3}) \cdot \frac{1}{\text{den}^2} \\
r_3 &= \frac{k_3}{p_{\text{H}_2}} (p_{\text{CO}} p_{\text{H}_2} - \frac{p_{\text{H}_2}^3 p_{\text{CO}_2}}{K_{\text{e}}^3}) \cdot \frac{1}{\text{den}^2} \\
r_4 &= \frac{k_4}{P_{\text{H}_2}^{3/5}} (p_{\text{CH}_4}^2 p_{\text{H}_2} - \frac{p_{\text{H}_2}^4 p_{\text{CO}_2}}{K_{\text{e}}^4}) \cdot \frac{1}{\text{den}^2}
\end{align*}
\]

(11)  
\hspace{1cm} (12)  
\hspace{1cm} (13)  
\hspace{1cm} (14)

where \( r_j \) is in \( \text{kmol/kgcat.hr} \) and \( \text{den} \) is defined as:

\[
den = 1 + K_{\text{CO}} p_{\text{CO}} + K_{\text{H}_2} p_{\text{H}_2} + K_{\text{CH}_4} p_{\text{CH}_4} + K_{\text{H}_2 \text{O}} p_{\text{H}_2 \text{O}} / p_{\text{H}_2}
\]

The kinetics rate constants used are: \( k_j = A_j \exp( -E_j / RT) \) and the modified values for 5% Ru/\( \gamma \)-
Al\(_2\)O\(_3\) catalyst are represented in Table 1 (index \( j \): 1-4) [26]. Modified adsorption constants,
\( K_k = A_k \exp( -\Delta H_k / RT) \) with \( k = \text{CH}_4, \text{O}_2, \text{CO}, \text{H}_2, \) and \( \text{H}_2 \text{O} \) for the four reactions are given in Table
2 [26]. Finally, the modified equilibrium constants, \( K_i^e = K_{ij} \exp( -H_i / T) \), for the second, third, and
fourth reactions \( (i=2,3,4) \) are represented in Table 3 [26]. In most of the previous works [9, 14, 25, 26, 27,
28, 29], \( H_i \) for the second reaction have been considered to be 11476 K; however, the authors tried to
verify the validity of this widely used value for \( H_i \) \( (i=2) \) using the relation of \( K_2 = K_4 / K_3 \), which is true for
the \( K_i \) factors and it was concluded that 11476 K is not a correct value for the \( H_i \) for the second reaction;
the correct value for the \( H_i \) \( (i=2) \) is 26285 K. This value was further examined using the thermodynamic
relations given at [33]. In this investigation, equilibrium constant for the second reaction was calculated at
different temperatures by using the relations given at [33]. Then, the values of the calculated equilibrium
constant were compared with the values of the equilibrium constant which were calculated from Table 3
at the same temperatures (with \( H_i \) for the second reaction equals to 26285 K). Maximum error in the value
of the equilibrium constants calculated from both methods was less than 4%. Therefore, the authors
considered the \( H_i \) for the second reaction to be equal to 26285 K and all of the simulations were
implemented based on this value.
Table 1. Modified parameters for the rate laws [26]

<table>
<thead>
<tr>
<th>Kinetic parameters</th>
<th>Ru parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r_1$</td>
<td>$A_1 = 5.60 \times 10^{17} \text{ (kmol.bar}^{-1.5}/\text{kg cat.hr})$</td>
</tr>
<tr>
<td></td>
<td>$E_1 = 1.89 \times 10^5 \text{ (kJ/kmol)}$</td>
</tr>
<tr>
<td>$r_2$</td>
<td>$A_2 = 4.27 \times 10^{15} \text{ (kmol.bar}^{0.5}/\text{kg cat.hr})$</td>
</tr>
<tr>
<td></td>
<td>$E_2 = 3.25 \times 10^5 \text{ (kJ/kmol)}$</td>
</tr>
<tr>
<td>$r_3$</td>
<td>$A_3 = 2.20 \times 10^6 \text{ (kmol.bar}^{-1}/\text{kg cat.hr})$</td>
</tr>
<tr>
<td></td>
<td>$E_3 = 5.81 \times 10^4 \text{ (kJ/kmol)}$</td>
</tr>
<tr>
<td>$r_4$</td>
<td>$A_4 = 7.90 \times 10^{14} \text{ (kmol.bar}^{0.5}/\text{kg cat.hr})$</td>
</tr>
<tr>
<td></td>
<td>$E_4 = 2.69 \times 10^5 \text{ (kJ/kmol)}$</td>
</tr>
</tbody>
</table>

Table 2. Modified adsorption constants for the four reaction rates [26]

<table>
<thead>
<tr>
<th>For $r_1$</th>
<th>For $r_2, r_3, r_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{\text{CH}_4}^1$</td>
<td>$A_{\text{CH}_4}$</td>
</tr>
<tr>
<td>$4.02 \times 10^5 \text{ bar}^{-1}$</td>
<td>$6.65 \times 10^4 \text{ bar}^{-1}$</td>
</tr>
<tr>
<td>$103.5 \text{ kJ/mol}$</td>
<td>$-38.28 \text{ kJ/mol}$</td>
</tr>
<tr>
<td>$A_{\text{O}_2}^1$</td>
<td>$A_{\text{H}_2}^1$</td>
</tr>
<tr>
<td>$5.08 \times 10^9 \text{ bar}^{-0.5}$</td>
<td>$1.77 \times 10^5 \text{ bar}^{-1}$</td>
</tr>
<tr>
<td>$66.2 \text{ kJ/mol}$</td>
<td>$88.68 \text{ kJ/mol}$</td>
</tr>
<tr>
<td>$A_{\text{H}_2\text{O}}$</td>
<td>$A_{\text{CO}}$</td>
</tr>
<tr>
<td>$6.12 \times 10^9 \text{ bar}^{-1}$</td>
<td>$8.23 \times 10^5 \text{ bar}^{-1}$</td>
</tr>
<tr>
<td>$-82.90 \text{ kJ/mol}$</td>
<td>$-70.65 \text{ kJ/mol}$</td>
</tr>
</tbody>
</table>

Table 3. Modified equilibrium parameters for the rate laws (with T in Kelvin) [26]

<table>
<thead>
<tr>
<th>$K_{2}^{e}$ (bar$^2$)</th>
<th>$K_{4}^{e}$ (bar$^2$)</th>
<th>$H_{4}^{e}$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$5.75 \times 10^{12}$</td>
<td>$7.24 \times 10^{10}$</td>
<td>$26285$</td>
</tr>
<tr>
<td>$1.26 \times 10^{-2}$</td>
<td>$-4639$</td>
<td>$21646$</td>
</tr>
</tbody>
</table>

2.5. Boundary conditions

The boundary conditions applied to solve the model are discussed in this section. Parameters specified at the inlet of the considered computational domain were temperature, velocity, pressure, and the composition of the inlet gas mixture. No slip condition was used at the reactor wall. Adiabatic boundary condition was applied at the wall of the reactor. The outflow mixture was discharged to atmospheric
pressure, and the gradients of all other dependent variables were set to zero at the outlet of the reactor. In summary;

Inlet: \[ u_x = u_0, \ u_y = u_z = 0, \ c_i = c_{i0}, \ T_s = T_0 \] (16)

Outlet: \[ \frac{\partial u_x}{\partial z} = \frac{\partial u_y}{\partial z} = \frac{\partial u_z}{\partial z} = \frac{\partial c_i}{\partial z} = \frac{\partial T_s}{\partial z} = 0 \] (17)

Wall: \[ u_x = u_y = u_z = \nabla T = 0 \] (18)

In order to solve the coupled governing equations, a CFD code was applied based on the finite volume method using the COUPLED algorithm for the coupling of pressure and velocity domains. The under relaxation factors for pressure, density, momentum, energy, and species were 0.6, 0.4, 0.6, 0.5, and 0.2, respectively.

3. Results

3.1. Model validation

The validation of the model was implemented using experimental data in literature [24]. As stated in section 2.2, it was assumed that reacting gases were completely mixed before entering the first monolith zone. Hence, simulation of the mixing zone was not considered. However, temperature at the inlet of the catalytic zone should be determined. According to Noguchi et al. [34], the mixing zone temperature should be higher than a minimum partial oxidation temperature and lower than a self ignition temperature, where the self ignition temperature is the temperature at which the mixed gas self ignites and the minimum partial oxidation temperature is the minimum temperature at which the catalyst undergoes the partial oxidation reaction. Considering the above mentioned temperature setting, the reactions are properly brought about at the catalytic zone (not at the mixing zone). This issue prevents soot formation at the mixing zone. According to Rabe et al. [24], the catalytic ignition temperature of the feed mixture is approximately 450 °C. Hence, the lower limit of the mixing zone temperature is 450 °C. Moreover, auto ignition temperature of methane in the presence of oxygen is 556 °C, according to Glassman et al. [35]. The presence of steam in the feed will further increase this auto ignition temperature. As a result, the higher limit of the mixing zone temperature is at least 556 °C. Therefore, the temperature of the feed at the inlet of the catalytic zone should be between these two margins. This temperature was estimated to be 550 °C according to the temperature measurements in the experimental setup for input powers of 0.97 and 1.09 kWth. Other experimental conditions used for model validation are summarized in Table 4.

In the experimental setup of Rabe et al. [24], a good heat conductor thermocouple was used and, as the authors indicated, this thermocouple could not reflect the real gas temperature. In addition, it was stated that temperature profile was broadened due to good heat conductivity of the thermocouple. Hence, due to limitations in the experimental setup the authors could not exactly compare the temperature profile predicted by the CFD model with the measured temperature profile in the experimental setup [24]. For model validation, maximum temperature and the temperature and species concentration at the reactor outlet were compared with the results in the experimental setup.
Table 4. Experimental conditions used for model validation

<table>
<thead>
<tr>
<th></th>
<th>Exp. 1</th>
<th>Exp. 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power input (kW)</td>
<td>1.09</td>
<td>0.97</td>
</tr>
<tr>
<td>O₂/C molar ratio</td>
<td>0.445</td>
<td>0.445</td>
</tr>
<tr>
<td>S/C molar ratio</td>
<td>2.9</td>
<td>2.9</td>
</tr>
<tr>
<td>Standard gas flow (Sm³/min)</td>
<td>1.32 E -5</td>
<td>1.18 E -5</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>550</td>
<td>550</td>
</tr>
<tr>
<td>Pressure (bar)</td>
<td>2.1</td>
<td>2.1</td>
</tr>
</tbody>
</table>

Table 5 shows the comparison between the predicted and experimentally measured maximum temperature for input powers of 1.09 and 0.97 kWth. As mentioned in section 2.2, only the catalytic section of the reactor was used in the simulations. Table 5 also compares the predicted temperature at the end of the catalytic section with the experimental results. As can be observed, the temperatures predicted by the simulation were slightly higher than the experimental results. Maximum temperature faced in the simulations was approximately 120 °C higher than experiments for both input powers of 1.09 and 0.97 kWth. At reactor rear face in which endothermic methane steam reforming reactions occur, temperature predicted by the model was approximately 90 °C higher for the corresponding points (in both experiments and simulations) for input powers of 1.09 and 0.97 kWth. As the combustion reaction is highly exothermic, this deviation was comparatively greater for the maximum temperature faced in the reactor.

Table 5. Temperature comparison between model predictions and literature data

<table>
<thead>
<tr>
<th>Component</th>
<th>Experiment (°C)</th>
<th>Model (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Max. Temp.</td>
<td>710 a</td>
<td>828 a</td>
</tr>
<tr>
<td>Outlet Temp.</td>
<td>704 b</td>
<td>825 b</td>
</tr>
<tr>
<td></td>
<td>640 a</td>
<td>733 a</td>
</tr>
<tr>
<td></td>
<td>635 b</td>
<td>726 b</td>
</tr>
</tbody>
</table>

(a) 1.09 kWth power input
(b) 0.97 kWth power input

One of the main important causes of such deviation is the uncertainty in the measurement of temperature in the experimental setup which prohibits a correct comparison between the predicted and measured temperature data. In addition, simulation of the mixing zone was avoided in this study due to lack of information about the shape and location of the mixing plate. Although temperature of the mixing zone was set in a way that the reactions mainly occur at the catalytic section (not at the mixing zone), there is the potential for methane self ignition near the outlet of the mixing zone, according to Noguchi et al. [35]. This is mainly due to the high heat release of the exothermic combustion reaction that occurs at the inlet of the catalytic section. As the mixing zone is linked to the inlet of the catalytic zone, temperature at the outlet portion of the mixing zone can rise quite high. This issue can also be observed
from the measured temperature profile in the experimental setup [24]. As stated at [24], for the start of the experiments, the reactor was heated to the catalytic ignition temperature of the feed mixture (approximately 450 °C [24]). Then, after ignition of the reactions, the external reactor heating was turned off. But, the approximate gas temperature of 550 °C at the inlet of the catalytic monolith zone (with respect to the experimental temperature profiles [24]) suggests that part of the methane self ignited in the mixing zone, causing the temperature at the outlet portion of the mixing zone rise. As a result, part of the methane and oxygen fed to the reactor inlet was consumed in the mixing zone of the experimental setup and less oxygen was available at the inlet of the catalytic monolith zone in the experiments. However, no analysis system was available at the inlet of this zone in the experimental setup to measure gas composition. Therefore, for simulating the reactor, the amount of oxygen at the inlet of the catalytic monolith zone (the inlet of the computational domain) was assumed to be the same as the oxygen fed to the reactor inlet in the experimental setup. More oxygen available in the simulations (which is due to ignoring the mixing zone and the reactions which probably occur in the mixing zone), caused the combustion reaction take place with a higher rate in the catalytic monolith zone. This effect led to higher temperatures in the simulations in comparison with the experiments.

Predicted temperatures were further studied, considering the adiabatic flame temperature. Adiabatic flame temperature for the feed mixture, for both input powers of 1.09 and 0.97 kW\textsubscript{th}, was calculated to be 1354 °C. As the maximum temperature predicted in the simulation was approximately 830 °C, the simulation temperature prediction is reasonable.

Considering the limitations in measuring temperature in the experimental setup and the lack of information about the mixing zone which prohibits a correct investigation of whole of the reactor, it was concluded that the present model is acceptable for temperature prediction in the reactor.

In the experimental setup [24], species compositions were measured at the reactor outlet. However, only the catalytic section was considered in the simulations, as mentioned in section 2.2. Hence, dry compositions of H\textsubscript{2}, CO, and CO\textsubscript{2} were predicted at the end of the catalytic section. Table 6 represents the simulation results for dry compositions of the species at this area. These results are compared with the experimental data [24] which were measured at the reactor outlet. Maximum error faced in prediction of the outlet dry composition was for CO which was about 30% for input power of 1.09 kW\textsubscript{th}. This error is mainly due to the deviation in the temperature prediction mentioned above. Higher temperature predicted by the model demoted the exothermic WGS reaction. Consequently, less CO was consumed in the WGS reaction and the CO content in the reactor outlet was higher in the simulations. However, errors in prediction of the outlet dry compositions of H\textsubscript{2} and CO\textsubscript{2} (in both powers input of 1.09 and 0.97 kW\textsubscript{th}) were less than 5%. It is worth mentioning that difference in location of measurement of the species composition in the model and experiment also makes error; in the simulations, the species compositions were measured at the end of the catalytic section; but, in the experiments, the species compositions were measured at the reactor outlet. In fact, steam reforming reactions may occur in the non-catalytic section due to relatively high temperature in the reactor; however, the authors did not simulate the non-catalytic section of the reactor due to negligible or slow non-catalyzed steam reforming reaction rate in the temperature range of 550 to 1000 °C. However, this error was unavoidable due to the lack of analysis system at the end of the catalytic section in the experimental setup.
Table 6. Species dry composition at reactor outlet, model predictions and literature data

<table>
<thead>
<tr>
<th>Component</th>
<th>Experiment (%)</th>
<th>Model (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>65.4 a</td>
<td>67.65 a</td>
</tr>
<tr>
<td></td>
<td>65 b</td>
<td>67.63 b</td>
</tr>
<tr>
<td>CO</td>
<td>5.2 a</td>
<td>6.8 a</td>
</tr>
<tr>
<td></td>
<td>5.2 b</td>
<td>6.7 b</td>
</tr>
<tr>
<td>CO₂</td>
<td>18.5 a</td>
<td>17.54 a</td>
</tr>
<tr>
<td></td>
<td>18.6 b</td>
<td>17.69 b</td>
</tr>
</tbody>
</table>

(a) 1.09 kW th power input  
(b) 0.97 kW th power input

Considering the predicted maximum and outlet temperatures along with the satisfactorily consistency of the dry compositions of the species at the reactor outlet, this model can satisfactorily predict the behavior of the reactor used by Rabe et al. [24]. The same model setup was used for studying the effects of using air instead of pure oxygen, O₂/C and S/C feed molar ratios, and feed temperature on the reactor performance.

3.2. Using air as the oxidant

The model was first used to examine the effects of using air as the oxidant. The input power in this study was 1.09 kW th. The O₂/C and S/C feed molar ratios were 0.445 and 2.9, respectively. However, air was used as the oxidant and nitrogen was added to the feed, considering the desirable O₂/C feed molar ratio. Temperature of the feed mixture was 550 °C. Figures 3 and 4 show the comparison between H₂ and CO concentration profiles in two cases; using pure oxygen as the oxidant and using air. As shown in figure 3, addition of nitrogen decreased the hydrogen concentration up to 10%. Nitrogen addition also diluted the CO concentration. Dilution of the products, especially hydrogen, is not desirable for fuel cell applications. Moreover, dilution of the CO₂ containing products creates problems with respect to an efficient CO₂ separation [24]. Therefore, pure oxygen was used as the oxidant in the subsequent investigations.
3.3. Influence of O$_2$/C and S/C ratio

The oxygen to methane feed molar ratio was varied between 0.295 and 0.5. Steam to methane feed molar ratio was used as a parameter. Three S/C feed molar ratios were used: 2.9, 3.8, and 4.5. Power input was selected to be 1.09 kW$_{th}$ and feed temperature was 550 °C. CH$_4$, H$_2$, and CO concentration profiles and the relevant temperature profiles along the reformer are shown in figures 5 through 8.
As shown in figure 5, methane concentration was decreased by the increase in oxygen concentration in the reactor inlet as it provides more oxygen for combustion reaction to occur; as a result, more methane was consumed. Consequently, temperature was increased in the reformer (figure 8) due to the higher heat release in the reformer. Higher heat release at greater O₂/C ratio promoted endothermic steam reforming reactions which produce higher hydrogen (figure 6). However, increasing the inlet O₂/C ratio to around 0.5 would consume more methane by the combustion reaction, leaving less methane available for H₂ production in the steam reforming reactions. Consequently, H₂ concentration at the end of the catalytic zone for O₂/C ratio of 0.5 was very close to that of 0.445. Increased CO concentration in the reactor at higher O₂/C ratio (figure 7) was mainly due to the increased steam reforming reaction rate.

Fig. 5. O₂/C effect on methane concentration (S/C=2.9, feed temperature of 550 °C)

Fig. 6. O₂/C effect on hydrogen concentration (S/C=2.9, feed temperature of 550 °C)
Fig. 7. O₂/C effect on carbon monoxide concentration (S/C=2.9, feed temperature of 550 °C)

Fig. 8. O₂/C effect on temperature profile along the reactor (S/C=2.9, feed temperature of 550 °C)
The same trend for species and temperature profile was observed for higher S/C feed molar ratio. For achieving better insight of the influence of S/C feed molar ratio on the reactor performance, H₂ and CO yields, defined below, were compared. In this study, O₂/C was varied between 0.295 and 0.5 for three cases in which S/C were 2.9, 3.8, and 4.5.

\[
Y_{H_2} = \frac{H_{2\text{out}}}{3CH_{4\text{in}}} \tag{19}
\]

\[
Y_{CO} = \frac{CO_{\text{out}}}{CH_{4\text{in}}} \tag{20}
\]

in which species names refer to molar flow rates. Tables 7 and 8 represent hydrogen and carbon monoxide yields for different O₂/C and S/C ratios, respectively.

<table>
<thead>
<tr>
<th>S/C = 2.9</th>
<th>S/C = 3.8</th>
<th>S/C = 4.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂/C = 0.295</td>
<td>70.04 %</td>
<td>72.96 %</td>
</tr>
<tr>
<td>O₂/C = 0.345</td>
<td>78.42 %</td>
<td>85.71 %</td>
</tr>
<tr>
<td>O₂/C = 0.395</td>
<td>87.27 %</td>
<td>90.68 %</td>
</tr>
<tr>
<td>O₂/C = 0.445</td>
<td>93.81 %</td>
<td>98.83 %</td>
</tr>
<tr>
<td>O₂/C = 0.5</td>
<td>98.59 %</td>
<td>100.00 %</td>
</tr>
</tbody>
</table>

Table 8. Carbon monoxide yields at S/C ratios of 2.9, 3.8, and 4.5

<table>
<thead>
<tr>
<th>S/C = 2.9</th>
<th>S/C = 3.8</th>
<th>S/C = 4.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂/C = 0.295</td>
<td>22.15 %</td>
<td>16.43 %</td>
</tr>
<tr>
<td>O₂/C = 0.345</td>
<td>29.87 %</td>
<td>23.61 %</td>
</tr>
<tr>
<td>O₂/C = 0.395</td>
<td>38.89 %</td>
<td>29.87 %</td>
</tr>
<tr>
<td>O₂/C = 0.445</td>
<td>49.17 %</td>
<td>38.60 %</td>
</tr>
<tr>
<td>O₂/C = 0.5</td>
<td>60.92 %</td>
<td>49.30 %</td>
</tr>
</tbody>
</table>

Figure 9 represents methane mole fraction at reactor outlet at different O₂/C ratios for S/C ratios of 2.9, 3.8, and 4.5. Figure 10 shows the influence of S/C ratio on temperature profile along the reformer at O₂/C ratio of 2.9. Increasing the inlet water content promoted steam reforming reactions, both of which also consumed methane (figure 9). At higher O₂/C ratio, it was also observed that methane outlet fraction was almost independent of S/C ratio. At higher O₂/C ratio, combustion reaction progressed with a higher rate and most of the methane was consumed in the combustion. In this case, water content of the mixture would have an insignificant effect on the overall reactor product, since steam reforming and water gas shift reactions were demoted. Moreover, hydrogen yield increased and carbon monoxide yield decreased at higher S/C ratio. Enhancement in hydrogen yield at higher S/C ratio was due to the promotion of steam reforming reactions, both of which produce hydrogen. In addition, by increasing S/C ratio, water gas shift reaction was also promoted. However, water gas shift reaction was more sensitive to this increase, which caused a reduction in the outlet CO content which is very desirable for fuel cell applications. A cooling
effect can be observed due to the higher water partial pressure which increased the endothermic steam reforming activity (figure 10).

Fig. 9. CH₄ wet mole fraction at reactor outlet at different O₂/C ratios for S/C ratios of 2.9, 3.8, and 4.5 (feed temperature of 550 °C)

Fig. 10. Temperature comparison for S/C molar ratios of 2.9, 3.8, and 4.5 (O₂/C ratio of 0.445, feed temperature of 550 °C)
3.4. Influence of feed gas temperature

Influence of variations of feed gas temperature on outlet mole fraction of H₂, CO, CH₄ and temperature profile along the reformer are represented in figures 11 through 14. Feed gas temperature was varied between 450 and 700 °C. O₂/C and S/C feed molar ratios in this investigation were 0.445 and 2.9, respectively. Power input was kept constant (1.09 kWth).

![H₂ mole fraction at different feed temperatures, O₂/C=0.445, S/C=2.9](image1)

![CO mole fraction at different inlet temperatures, O₂/C=0.445, S/C=2.9](image2)
Fig. 13. CH₄ wet mole fraction at different inlet temperatures, O₂/C=0.445, S/C=2.9

Fig. 14. Temperature profile along the reformer at different inlet temperatures, O₂/C=0.445, S/C=2.9
The results showed that mole fractions of hydrogen and carbon monoxide increased as the inlet temperature was increased in the range of 450–700 °C (figures 11 and 12). This is mainly due to the increase in the activity of steam reforming reactions at higher inlet temperature. Higher inlet temperature also demoted water gas shift reaction. This led to more increase in CO concentration. Increasing the inlet temperature also increased methane consumption in the reformer (figure 13). As expected, increasing feed gas temperature resulted higher temperatures in the reactor (figure 14).

4. Conclusion

In this study, a CFD code was developed for simulation of a catalytic monolith reformer. To ensure an overall high concentration of hydrogen, an appropriate catalyst should be selected. Ruthenium catalyst is a suitable catalyst for low temperature catalytic partial oxidation (LTCPO) process which has good reforming activity as well. This distinguished feature prevents using two different catalysts for promoting each process. These features along with high hydrogen yield and its stability render this catalyst as a suitable choice for use in portable hydrogen generation systems. Investigating the reported results in literatures, the authors noticed that the number of numerical models available using ruthenium catalyst for reforming processes is much fewer than those available with conventional catalysts. Hence, in the present study, the performance of 5% Ru/γ-Al2O3 catalyst at different operating conditions was numerically investigated. Methane autothermal reforming was the reaction mechanism for hydrogen production. Due to symmetry, only a quarter of the catalytic section of the reformer was selected as the computational domain. Pure oxygen was used as the oxidant in this study. The catalytic monolith zone was assumed to be a porous media. The results provided an adequate consistency with the experimental data from literature with respect to the distribution of products. Agreement adequate for engineering design purposes was also found between the CFD predictions and experimental measurements with respect to the maximum and outlet temperature. The reactor performance was then studied for other operating conditions. Investigated parameters include O2/C and S/C feed molar ratios and feed temperature. The effects of using air as the oxidant were also studied. It was concluded that at higher O2/C and S/C feed molar ratios and at higher feed gas temperature, more hydrogen will be achieved at the reactor outlet, which is very suitable for fuel cell applications. High concentration of hydrogen and low CO content in the CFD predictions can be attributed to high hydrogen selectivity of ruthenium catalyst and high S/C ratio used in the model. Extra purification units such as water gas shift (WGS) unit and preferential oxidation unit (PROX) might be required for to deliver pure hydrogen for fuel cell.

References


[31] Shi L, Computational fluid dynamics simulation of steam reforming and autothermal reforming for fuel cell applications, Ohio University; 2009.


