An attempt to minimize the temperature gradient along a plug-flow methane/steam reforming reactor by adopting locally controlled heating zones

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Abstract. Plug flow reactors are very common in the chemical process industry, including methane/steam reforming applications. Their operation presents many challenges, such as a strong dependence of temperature and composition distribution on the inlet conditions. The strongly endothermic methane/steam reforming reaction might result in a temperature drop at the inlet of the reactor and consequently the occurrence of large temperature gradients. The strongly non-uniform temperature distribution due to endothermic chemical reaction can have tremendous consequences on the operation of the reactor, such as catalyst degradation, undesired side reactions and thermal stresses. To avoid such unfavorable conditions, thermal management of the reactor becomes an important issue. To carry out thermal management properly, detailed modeling and corresponding numerical analyses of the phenomena occurring inside the reforming system is required. This paper presents experimental and numerical studies on the methane/steam reforming process inside a plug-flow reactor. To optimize the reforming reactors, detailed data about the entire reforming process is required. In this study the kinetics of methane/steam reforming on the Ni/YSZ catalyst was experimentally investigated. Measurements including different thermal boundary conditions, the fuel flow rate and the steam-to-methane ratios were performed. The reforming rate equation derived from experimental data was used in the numerical model to predict gas composition and temperature distribution along the steam-reforming reactor. Finally, an attempt was made to control the temperature distribution by adopting locally controlled heating zones.

1. Introduction
Because of their high energy conversion efficiency and the low level of pollutants they emit into the environment, solid oxide fuel cells (SOFCs) have the potential to become one of the most important energy conversion devices. A solid oxide fuel cell consists of two porous ceramic electrodes (a cathode and an anode) separated by a solid ceramic electrolyte. A typical SOFC uses solid oxides such as yttria-stabilized zirconia (YSZ) for the electrolyte [1]. The operation temperature level of an SOFC is 700 °C - 1100 °C and operates at atmospheric or elevated pressures [2]. High temperature and unstechiometry in the YSZ crystal network allow the oxygen ions to be transported to the anode side. This is very important because it allows SOFC to oxidize as a fuel not only hydrogen but also carbon monoxide. The mixture of carbon monoxide and hydrogen can be produced from a wide range of hydrocarbon-based fuels via
steam reforming [3-6]. Using hydrocarbons as a fuel have a number of advantages; existing infrastructure can be used to distribute and provide fuels such as city gas to the SOFC systems. Additionally, fuel can be obtained from natural resources and enable to bypass the hydrogen source problem. For hydrocarbon-based fuel, three types of fuel conversion can be considered in the reforming reactions: an external reforming system, an indirect internal reforming system and a direct internal reforming system. High-temperature SOFC eliminates the need for an expensive external reforming system. The possibility of using internal reforming is one of the characteristics of high temperature fuel cells, SOFC. Strong endothermic fuel reforming reactions can be thermally supported by the transfer, in forms of primarily radiation and convection, of heat by exothermic electrochemical process of an SOFC as well as by the passage of electric current. However, for a high-temperature operation, thermal management of the SOFC system becomes an important issue. To carry out thermal management properly, detailed modeling and the numerical analyses of the phenomena occurring inside the SOFC system is required.

Brus and Szmyd studied a temperature distribution in an indirect internal reforming system depending on its location in the system and the distance between the stack and the reactor [7,8]. The analyzed reformer had the shape of a rectangular channel and was located above the cell stack in SOFC system. Their results indicate that, the position of the reformer in the module chamber and the emissivity of the surfaces of the reformer, cell and other elements in the SOFC module all play a key role for temperature distribution inside the internal methane/steam reforming reactor [7,8]. They present that by changing the location of the reformer or by modifying the surface property of the reactor, the thermal boundary condition can be change significantly. Further more the thermo-fluid model of heat and mass transfer inside the indirect internal methane/steam reformer was proposed to conduct parametric studies where the effect of the thermal boundary condition as well as the inlet condition on temperature distribution were investigated [9,10]. However only a uniform thermal boundary condition at the reformer walls and uniform catalyst distribution were investigated [9,10]. Additionally some systems use an internal indirect reformer that has the form of a pipe as can be found in references [11,12]. The temperature and spices distribution might be significantly different in those system and additional analyst is required.

Within this work the authors present an attempt to minimize the temperature gradient along the plug-flow methane/steam reforming reactor by adopting a locally changed thermal boundary conditions. To realize this aim the reaction kinetics have been derived. The empirical rate was employed in the proposed numerical model. The rate and the model were verified by compering the results of the computation with experimentally obtained data. Finally a numerical analysis was used to perform parametric studies of temperature and species distributions inside the methane-steam reformer.

2. Numerical Analysis
The supplied fuel to the system is the methane (CH₄). The gaseous fluids are assumed to be Newtonian and the flow of fuel inside the fuel reformer is assumed to be laminar [13], steady and occurring in one direction. The temperature of in-flow fuel is taken to be instantly approaching the temperature of the reformer.

2.1. Heat transfer model inside the reformer
The microstructure of porous media is not to be considered directly in the present model therefore for the pores area, the governing equations derived by the volume-averaging method are applied [14]. In the adopted method physical values are locally averaged for a representative elementary volume [15,16]. The heat transfer process inside the reformer porous media is described by continuity, momentum, energy and mass transfer equations. Consequently the following transport equations of the averaged physical values for laminar flows apply:
The average temperature both over the gas and solid phase in [K]. The volume. In the above equations

\[ \frac{\partial (\rho_0 U_x)}{\partial x} + \frac{1}{r} \frac{\partial (r \rho_0 U_r)}{\partial r} = 0 \]  

\[ \frac{\rho_0}{\epsilon_0^2} \left( U_x \frac{\partial U_x}{\partial x} + U_r \frac{\partial U_r}{\partial r} \right) = - \frac{\partial P}{\partial x} + \frac{\mu}{\epsilon_0} \left[ \frac{\partial^2 U_x}{\partial x^2} + \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial U_x}{\partial r} \right) \right] 
- \frac{\mu}{K_p} U_x - \frac{\rho_0 f}{\sqrt{K_p}} U_x \sqrt{U_x^2 + U_r^2} \]  

\[ \frac{\rho_0}{\epsilon_0^2} \left( U_x \frac{\partial U_r}{\partial x} + U_r \frac{\partial U_r}{\partial r} \right) = - \frac{\partial P}{\partial r} + \frac{\mu}{\epsilon_0} \left[ \frac{\partial^2 U_r}{\partial x^2} + \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial U_r}{\partial r} \right) - \frac{U_r}{r^2} \right] 
- \frac{\mu}{K_p} U_r - \frac{\rho_0 f}{\sqrt{K_p}} U_r \sqrt{U_x^2 + U_r^2} \]  

\[ \rho_0 C_p \left( U_x \frac{\partial T}{\partial x} + U_r \frac{\partial T}{\partial r} \right) = \frac{\partial}{\partial x} \left( \lambda_{eff} \frac{\partial T}{\partial x} \right) + \frac{1}{r} \frac{\partial}{\partial r} \left( r \lambda_{eff} \frac{\partial T}{\partial r} \right) + Q \]  

\[ \rho_0 \left( U_x \frac{\partial Y_j}{\partial x} + U_r \frac{\partial Y_j}{\partial r} \right) = \frac{\partial}{\partial x} \left( \rho_0 D_{j,eff} \frac{\partial Y_j}{\partial x} \right) + \frac{1}{r} \frac{\partial}{\partial r} \left( r \rho_0 D_{j,eff} \frac{\partial Y_j}{\partial r} \right) + S_j \]  

The physical values in the above equations represent the local phase average of the gas control volume. In the above equations \( U \) is the gas phase average local velocity, [m s\(^{-1}\)]. \( T \) is the local average temperature both over the gas and solid phase in [K]. The \( \epsilon_0 = 0.7 \) [-] and \( K = 1.0 \times 10^{-7} \) [m\(^2\)] are the porosity and permeability of the porous medium, respectively. The \( f = 0.088 \) is the inertia coefficient which depends on the Reynolds number and the microstructure of the porous medium [16]. \( \lambda_{eff} = \epsilon_0 \lambda_f + (1 - \epsilon_0) \lambda_s \) [W m\(^{-1}\) K\(^{-1}\)] is the effective thermal conductivity, where \( \lambda_f \) represents fluid thermal conductivity and \( \lambda_s = 20.0 \) [W m\(^{-1}\)K\(^{-1}\)] is solid phase thermal conductivity [17,18]. \( D_{j,eff} \) [m\(^2\) s\(^{-1}\)] is the effective mass diffusivity of species \( j \). \( Y_j \) is the mass fraction of chemical species \( j \) and \( D_j \) is the mass diffusivity of species \( j \) in the multi-component mixture of gases respectively [19].

2.2. Mathematical model of a reforming process

The methane/steam reforming process is widely known as a conventional process for producing hydrogen [5]. In the reforming process of methane with steam, the dominant reactions are the following two [20]

fuel reforming reaction:

\[ \text{CH}_4 + \text{H}_2\text{O} \rightarrow 3\text{H}_2 + \text{CO} \]  

(6)

shift reaction:

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

(7)

The steam reforming reaction described by equation (6) is a slow, therefore a rate equation is needed. The water-gas shift reaction described by equation (7) is a fast and can be assumed to be in equilibrium at the reforming temperature [5,20,21]. The reaction rates of the two above reactions (equations (6) and (7)) \( R_{st} \) and \( R_{sh} \) are locally calculated as follows:

\[ R_{st} = w_{cat} A_{st} \exp \left( - \frac{E_a}{RT} \right) p_{\text{CH}_4}^{a} p_{\text{H}_2\text{O}}^{b} \]  

(8)
\[ R_{sh} = K_{sh}^+ p_{CO} p_{H_2O} + K_{sh}^- p_{H_2} p_{CO_2} \]  

Equation (8) is based on experimental data, where, \( a \) and \( b \) are reaction order [-], \( w_{\text{cat}} \), is the catalyst weight in a control volume of reformer [g m\(^{-3}\)], \( T \) [K] is the temperature of the fuel conversion, \( R = 8.314472 \) [J mol\(^{-1}\) K\(^{-1}\)] is the universal gas constant, \( E \) [J mol\(^{-1}\)] is the activation energy of the fuel reforming reaction, \( A_{st} \) [mol min\(^{-1}\) g\(^{-1}\) atm\(^{-(a+b)}\)] is the pre-exponential factor, \( p_{CH_4} \) is the partial pressure of methane, [atm] and \( p_{H_2O} \) is the partial pressure of steam [atm]. The water shift reaction given by equation (9) reaches equilibrium rapidly, therefore \( CO_2, H_2, CO \) and \( H_2O \) have to satisfy the equilibrium equation:

\[ K_{sh} = \frac{K_{sh}^+}{K_{sh}^-} = \exp\left(-\frac{\Delta G_{sh}^0}{RT}\right) \]  

where \( \Delta G_{sh} \) is the change of standard Gibbs free energy of shift reaction. This equilibrium constant is given by Eq. \( 10 \) is introduced into Equation (9) to calculate the rate of the shift reaction. The mass production or consumption rate of each chemical species by the fuel reforming reaction (Eq. \( 6 \)) and shift reaction (Eq. \( 7 \)) is also calculated as follows:

\[ S_{H_2} = 3R_{st} M_{H_2} + R_{sh} M_{H_2} \]  

\[ S_{CO} = R_{st} M_{CO} - R_{sh} M_{CO} \]  

\[ S_{CO_2} = R_{sh} M_{CO_2} \]  

\[ S_{CH_4} = -R_{st} M_{CH_4} \]  

\[ S_{H_2O} = -R_{st} M_{H_2O} - R_{sh} M_{H_2O} \]

The value of the mole production or consumption rate for each chemical species is introduced into the species mass transfer equation (Eq. (5)) as a part its source term. The thermodynamic heat generation rate by the reforming reactions (Eqs. \( 6 \) and \( 7 \)) are calculated based on the reaction rates, as follows:

\[ Q_{st} = -\Delta H_{st} R_{st} \]  

\[ Q_{sh} = -\Delta H_{sh} R_{sh} \]

where \( \Delta H_{st} \) and \( \Delta H_{sh} \) are the enthalpy change accompanied with each reaction, [J mol\(^{-1}\)]. The heat conduction and convection equations were solved numerically by finite volume and gauss-seidel methods \([22,23]\).

3. Experimental investigation

3.1. Experimental set-up

A schematic view of the experimental setup is shown in Figure 1. A stainless steel reformer was located in an electrical furnace, which can be heated up to 1000 [°C]. High purity methane was the fuel used in the experiment. It was supplied to the reformer via a flow controller and evaporator, which was also used as a pre-heater. Water was fed to the system with a pump. The gas composition after the reforming process was analyzed by gas chromatography prior to which the steam had been separated by cooling down the gas mixture to 2 [°C]. The reforming reaction tube was filled by nickel supported on yttria stabilized zirconia coming from a crushed anode (see Table 1 to check the properties). To control the thermal condition of the experiment, four thermocouples were placed in the experimental set-up as shown in Figure 1 (marked as \( T \)). To derive correct kinetics data, the reaction has to occur in a whole volume of catalyst. This can be accomplished by keeping the reforming conversion rate low. To achieve a low level of methane conversion, the fuel was additionally mixed with nitrogen. Nitrogen does not directly influence
the reforming reaction but the partial pressure of the components changed, which decreases both the reaction rate and methane conversion rate. All measurements presented in this paper have been performed at atmospheric pressure. The geometrical properties of the reactor have been summarized in Table 2.

![Diagram](image-url)

**Figure 1.** Schematic view on experimental setup

| **Table 1. Catalyst properties** |
|----------------------------------|
| **Type** | **Ni contain** | **Particle size** | **Mass** |
| Ni/YSZ   | 60vol%         | 1 [µm]            | 0.3 [g]  |

| **Table 2. Reactor properties** |
|----------------------------------|
| **Type** | **Bed height** | **Diameter** | **Length** |
| stainless steel | ~ 1 [mm] | 25.4 [mm] | 450 [mm] |

### 3.2. Reaction rate equation

The mathematical forms of expression describing the kinetics of the methane/steam reforming process can be categorized by three basic concepts [6,10,21,24-27]: i) General Langmuir-Hinshelwood kinetics [5], ii) first order reaction with respect to methane [21,24] and iii) power law expressions derived from data fitting [10,25-27]. In this study, the primarily assumed form of the equation describing the steam reforming kinetic is the power law expression with respect to the partial pressures of methane and steam. This form of kinetic equation is commonly used in thermo-fluid models of the methane/steam reactors [17,18,28,29]. Therefore, the rate equation in the presented research takes the following form:
Equation (18) has been determine using the method described in references [25,30-32]. In this method, the effects of the supply gas composition are first examined by varying the values of SC (steam-carbon ratio) and NC (nitrogen-carbon ratio) at a constant temperature to determine the values of the exponential indexes \( a \) and \( b \) from Equation (8). Then, experiments are conducted varying the temperature while keeping the supply gas composition unchanged. The reaction constant \( k \) is constant for the given temperature, therefore \( A \) and \( E \) can be determined from the Arrhenius plot. The water-gas shift reaction (2) is assumed to be in equilibrium because of the high temperature.

3.3. Verification of the numerical model
In the numerical model presented in this section, the gas composition at the outlet of the reformer can be predicted based on the inlet conditions. Examples of numerical results and their comparison with the experimental data are shown in Figure 2. In the present results, the effect of the temperature on the steam reforming reaction was studied by increasing the reaction temperature from 773 [K] to 973 [K]. The data shows the outlet dry gas composition to be a function of the reaction temperature. Predictably, the outlet molar fraction of methane decreases with increasing reaction temperature and the amount of carbon monoxide increases as the reaction temperature increases. This observation is significant because in contrast to the low-temperature fuel cell, the carbon monoxide does no poison the high temperature solid oxide fuel cell anode but can be electrochemically converted as a fuel [21].

4. Results
Figures 3 and 4 present the results for different heat flux at the reformer wall. In each case the wall was divided into four heating zones. Figures (a) and (c) present results where heat flux increases gradually \( Q_1=0.5 \) [kW m\(^{-2}\)], \( Q_2=1 \) [kW m\(^{-2}\)], \( Q_3=10 \) [kW m\(^{-2}\)], \( Q_4=20 \) [kW m\(^{-2}\)] for each heating zone respectively. Figures (b) and (d) present result where heat flux decreases gradually \( Q_1=20 \) [kW m\(^{-2}\)], \( Q_2=10 \) [kW m\(^{-2}\)], \( Q_3=1 \) [kW m\(^{-2}\)], \( Q_4=0.5 \) [kW m\(^{-2}\)] for each heating zone respectively. As can be seen in figures 3 and 4, the conversion rate of methane is higher in the case where heat flux decreases gradually. Also, the difference between the highest and lowest temperature was reduced from 235 [K] to 141 [K] when heat flux decrease gradually.
The results indicate that even when the same amount of heat is supplied to the reactor, the results might be significantly different depending on the location of the heating zone along the reactor. The results indicate that it is more efficient to heat up the reactor stronger at the beginning. Such approach leads to a higher conversion rate of methane and a lower temperature gradient inside the reactor.

![Image](image1)

(a) $Q_1 = 0.5 \ [\text{kW m}^{-2}]$, $Q_2 = 1 \ [\text{kW m}^{-2}]$, $Q_3 = 10 \ [\text{kW m}^{-2}]$, $Q_4 = 20 \ [\text{kW m}^{-2}]$

(b) $Q_1 = 20 \ [\text{kW m}^{-2}]$, $Q_2 = 10 \ [\text{kW m}^{-2}]$, $Q_3 = 1 \ [\text{kW m}^{-2}]$, $Q_4 = 0.5 \ [\text{kW m}^{-2}]$

![Image](image2)

(c) $Q_1 = 0.5 \ [\text{kW m}^{-2}]$, $Q_2 = 1 \ [\text{kW m}^{-2}]$, $Q_3 = 10 \ [\text{kW m}^{-2}]$, $Q_4 = 20 \ [\text{kW m}^{-2}]$

(d) $Q_1 = 20 \ [\text{kW m}^{-2}]$, $Q_2 = 10 \ [\text{kW m}^{-2}]$, $Q_3 = 1 \ [\text{kW m}^{-2}]$, $Q_4 = 0.5 \ [\text{kW m}^{-2}]$

**Figure 3.** Distribution of temperature (a-b) and the mole fraction of methane (c-d) for different thermal boundary conditions.

![Image](image3)

(a) $Q_1 = 0.5 \ [\text{kW m}^{-2}]$, $Q_2 = 1 \ [\text{kW m}^{-2}]$, $Q_3 = 10 \ [\text{kW m}^{-2}]$, $Q_4 = 20 \ [\text{kW m}^{-2}]$

(b) $Q_1 = 20 \ [\text{kW m}^{-2}]$, $Q_2 = 10 \ [\text{kW m}^{-2}]$, $Q_3 = 1 \ [\text{kW m}^{-2}]$, $Q_4 = 0.5 \ [\text{kW m}^{-2}]$

**Figure 4.** Average gas composition along the reformer.

5. **General conclusions**

This paper has presented experimental and numerical studies on the methane/steam reforming process on Ni/YSZ catalyst. The gas mixture composition was measured at the outlet of the reformer to establish the methane reforming rate and the kinetics of the reforming reaction. The reforming rate equation derived from the experimental data was used in the mathematical model to predict gas composition at the outlet of the reformer and to verify the reforming
reaction model. The temperature and species distribution in the longitudinal direction of the cylindrical plug-flow reformer has been presented. Local heating was implemented in numerical computations to discuss the possibility of reducing the temperature gradients along the reformer. It was shown that the location of heating zones plays a key role and might help to not only decrease temperature gradients but also to increase the conversion rate of the methane.

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