On reaction coupled transport phenomenon in reformer ducts

Jinliang Yuan a,*, Guogang Yang b, Bengt Sundén a

a Department of Energy Sciences, Faculty of Engineering, Lund University, Box 118, 22100 Lund, Sweden
b Marine Engineering College, Dalian Maritime University, Dalian 116026, China

1. Introduction

It is a fact that proton exchange membrane fuel cells (PEMFCs) essentially need pure hydrogen as a fuel. However, hydrogen does not appear naturally as a gaseous fuel, and it usually has to be generated from whatever fuel source is locally available. For this concern, external fuel processing components, e.g., reformers and the ones to remove CO, should be incorporated into the PEMFC systems. It is true that methane is a convenient feedstock because the existing natural gas pipeline infrastructure makes it readily available and accessible at any point along the distribution chain. Availability of highly compact hydrogen reactors is very significant for PEMFC applications at central stations, substations, or residences.

In the hydrogen reactors, methane can be converted into H2, CO and CO2, such as in steam methane reforming (SMR), partial oxidation (POX) and autothermal reforming (ATR) by employing alumina supported Ni as a catalyst.

There is an increasing interest worldwide in the development of compact fuel processing technologies for fuel cell systems. The overall idea is to catalytically activate both sides of a compact reactor, i.e., one side having combustion for supplying heat, and the other side appearing steam reforming of methane and hydrogen production. In this configuration, the thin porous layers for both sides result in small thermal conduction and species diffusion path lengths that largely eliminate heat and mass transfer restrictions associated with conventional reformers, and it is possible to have an improved utilization of the intrinsic reforming catalyst kinetics, and to achieve an efficient heat transfer. The compact design concept could lead to major applications in fuel cell systems for stationary and transportation applications, see references...
As revealed in references [3,4], most reformer literature is devoted to its steam reforming reaction kinetics, materials for the components and catalyst forming/distribution and relevant literature review shows that research on thermal management coupled by catalytic chemical reactions is very limited. In most cases, the characteristic of heat transfer has been modeled after the classical duct flow problem with either uniform wall flux or wall temperature conditions. This assumption is rather gross because the catalytic reforming reaction rates are strongly coupled with fuel gas flows and heat transfer through and over the porous layers. As a consequence, the interface boundary conditions and convective heat transfer coefficients are significantly different from the conventional ones. As expected, the thermal properties of multi-functional materials may have certain effects on the catalytic reaction and the convective heat transfer characteristics.

2. Objectives, problem statement and mathematical modeling

A three-dimensional computational procedure is applied to simulate and analyze steam reforming of methane in a composite domain consisting of a porous active layer, a gas flow duct and solid plates.

There are several transport processes (such as mass, heat and momentum transport) together with chemical reactions appearing in multi-functional reactors. It is often found that the endothermic and exothermic reactions (hydrocarbon cracking, steam reforming and dehydrogenation) are strongly coupled by heat transfer in the reactors.

A general in-house developed computational fluid dynamics (CFD) code is applied to simulate a methane reforming duct from a typical compact reformer, as shown in Fig. 1. The steam reforming, water gas-shift, and reverse methanation reactions of methane are the major ones with significant reaction rates [3,4], only the following chemical reactions are then considered in this study:

**Methane steam reforming reaction:**

\[
\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2, \quad \Delta h_{(298K)} = 226 \text{ kJ/mol (1)}
\]

**Water gas-shift reaction:**

\[
\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2, \quad \Delta h_{(298K)} = -41 \text{ kJ/mol (2)}
\]

**Reverse methanation reaction:**

\[
\text{CH}_4 + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{H}_2, \quad \Delta h_{(298K)} = 165 \text{ kJ/mol (3)}
\]

It should be mentioned that the above processes in Eqs. (1) and (3) are endothermic and the overall reactions consumes the net heat. In general, this heat is supplied depending on the thermal integration methods employed and the associated combustion processes. In this study, the solved governing

<table>
<thead>
<tr>
<th>Nomenclature</th>
<th>Definition</th>
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<tbody>
<tr>
<td>a</td>
<td>width of porous layer, m</td>
</tr>
<tr>
<td>b</td>
<td>width of flow duct, m</td>
</tr>
<tr>
<td>c_p</td>
<td>specific heat, J/(kg K)</td>
</tr>
<tr>
<td>D</td>
<td>molar diffusion coefficient of fuel gas species, m²/s</td>
</tr>
<tr>
<td>H</td>
<td>enthalpy, kJ/mol</td>
</tr>
<tr>
<td>h</td>
<td>overall height of the duct, m</td>
</tr>
<tr>
<td>h_d</td>
<td>height of the duct, m</td>
</tr>
<tr>
<td>h_p</td>
<td>thickness of porous layer, m</td>
</tr>
<tr>
<td>k</td>
<td>thermal conductivity, W/(m K); reaction rate constant, mol/(m³ Pa² s)</td>
</tr>
<tr>
<td>M</td>
<td>molecular weight of species, kg/mol</td>
</tr>
<tr>
<td>m</td>
<td>mass diffusion flux, kg/(m² s)</td>
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<tr>
<td>n</td>
<td>molar diffusion flux, mol/(m² s)</td>
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<tr>
<td>Nu</td>
<td>Nusselt number</td>
</tr>
<tr>
<td>n_s</td>
<td>total number of species</td>
</tr>
<tr>
<td>P</td>
<td>pressure, Pa</td>
</tr>
<tr>
<td>q</td>
<td>heat flux, W/(m²)</td>
</tr>
<tr>
<td>R</td>
<td>internal reforming reaction rate, mol/(m³ s)</td>
</tr>
<tr>
<td>g</td>
<td>gas constant, kJ/(mol K)</td>
</tr>
<tr>
<td>Re</td>
<td>Reynolds number (UD_h/n)</td>
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<tr>
<td>r_e</td>
<td>effective radius, m</td>
</tr>
<tr>
<td>S</td>
<td>source term</td>
</tr>
<tr>
<td>T</td>
<td>temperature, °C</td>
</tr>
<tr>
<td>V</td>
<td>velocity vector, m/s</td>
</tr>
<tr>
<td>V_i</td>
<td>velocity components in x, y and z directions, respectively, m/s</td>
</tr>
<tr>
<td>X</td>
<td>molar fraction of fuel species</td>
</tr>
<tr>
<td>Y</td>
<td>mass fraction of fuel species</td>
</tr>
<tr>
<td>x, y, z</td>
<td>Cartesian coordinates</td>
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<table>
<thead>
<tr>
<th>Greek symbols</th>
<th>Definition</th>
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<tr>
<td>β</td>
<td>permeability of porous layer, m²</td>
</tr>
<tr>
<td>ε</td>
<td>porosity</td>
</tr>
<tr>
<td>μ</td>
<td>dynamic viscosity, kg/(m s)</td>
</tr>
<tr>
<td>ν</td>
<td>kinematic viscosity, m²/s</td>
</tr>
<tr>
<td>ρ</td>
<td>density, kg/m³</td>
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<tr>
<td>τ</td>
<td>tortuosity</td>
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<table>
<thead>
<tr>
<th>Subscripts</th>
<th>Definition</th>
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<tr>
<td>di</td>
<td>diffusion layer</td>
</tr>
<tr>
<td>eff</td>
<td>effective parameter</td>
</tr>
<tr>
<td>f</td>
<td>fuel gas mixture</td>
</tr>
<tr>
<td>CH₄</td>
<td>methane</td>
</tr>
<tr>
<td>CO</td>
<td>carbon monoxide</td>
</tr>
<tr>
<td>CO₂</td>
<td>carbon dioxide</td>
</tr>
<tr>
<td>e</td>
<td>equilibrium</td>
</tr>
<tr>
<td>gm</td>
<td>fuel gas mixture</td>
</tr>
<tr>
<td>H₂</td>
<td>hydrogen</td>
</tr>
<tr>
<td>H₂O</td>
<td>water</td>
</tr>
<tr>
<td>in</td>
<td>inlet</td>
</tr>
<tr>
<td>k</td>
<td>Knudsen diffusion</td>
</tr>
<tr>
<td>m</td>
<td>mass transfer</td>
</tr>
<tr>
<td>p</td>
<td>permeation; porous layer</td>
</tr>
<tr>
<td>r</td>
<td>steam reforming reaction</td>
</tr>
<tr>
<td>s</td>
<td>solid wall; shift reaction; species</td>
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equations are the mass, momentum, energy and species conservation equations. A detailed discussion on the governing equations and the source terms has been reported in reference [5].

It should be mentioned that the heat source term $S_T$ in the energy equation is connected to the steam reforming, water gas-shift and reverse methanation reactions,

$$S_T = \sum_{i} R_i \Delta h_{\text{reaction},i}$$  \hspace{1cm} (4)$$

where $R_i$ is the reaction rate, and $\Delta h_{\text{reaction},i}$ is the reaction enthalpy.

While the diffusion coefficients of species $i$ in the gas mixture for the fuel gas flow duct are evaluated by the expression based on the binary coefficients

$$D_{i,\text{gm}} = \frac{1 - X_i}{\sum_j (X_j / D_{ij})} (i \neq j)$$  \hspace{1cm} (5)$$

where $D_{i,\text{gm}}$ is the diffusion coefficient of the component $i$ in the mixture, and $X_j$ the molar fraction of the appropriate species, and $D_{ij}$ ($i \neq j$) the diffusion coefficient in the binary system, respectively. For the porous catalytic reaction layer, Knudsen diffusion occurs in porous layer with small pores or under low pressure, in these cases the mean free-path of molecules is larger than the pore size, and the molecules collide with the walls more often than between themselves. In order to calculate the Knudsen diffusion flux, the coefficient $D_{ik}$ is calculated based on the free molecule flow theory

$$D_{ik} = \frac{2}{3} r_i \bar{v}_i = \frac{2}{3} \sqrt{\frac{8kT}{\pi M_i}}$$  \hspace{1cm} (6)$$

in which $r_i$ is the effective radius and $\bar{v}_i$ the average molecular speed of the $i$th gas species. Due to the tortuous paths of real pores in the porous catalytic layer, the reduction in the cross-sectional area and the increased diffusion length are expected, the effective diffusion coefficient is then estimated by:

$$D_{\text{eff}} = \frac{\epsilon}{\tau} \left( \frac{D_{i,\text{gm}} \times D_{ik}}{D_{i,\text{gm}} + D_{ik}} \right)$$  \hspace{1cm} (7)$$

where $\epsilon$ is the porous porosity, and $\tau$ the tortuosity.

The catalytic reforming reactions are coupled with the governing equations by relevant source terms. A general rate equation based on Langmuir–Hinselwood–Hougen–Watson (LHHW) approach (see references [3–7]) describes most accurately the process for a wide range of parameters, and is applied in this study based on partial pressure, temperature and species compositions for the chemical reactions (8)–(10):

$$R_1 = \frac{k_1}{p_{CH_4}} \left( \frac{p_{CH_4} p_{H_2O}}{k_3 p_{H_2} p_{CO}} \right) \frac{m_{cl}}{(\text{Den})^2} \text{ kmol} / (\text{m}^3 \text{s})$$  \hspace{1cm} (8)$$

$$R_2 = \frac{k_2}{p_{CO}} \left( \frac{p_{CO} p_{H_2O}}{k_3 p_{H_2}} \right) \frac{m_{cl}}{(\text{Den})^2} \text{ kmol} / (\text{m}^3 \text{s})$$  \hspace{1cm} (9)$$

$$R_3 = \frac{k_3}{p_{H_2O}} \left( \frac{p_{H_2O} p_{H_2}}{k_3 p_{H_2}} \right) \frac{m_{cl}}{(\text{Den})^2} \text{ kmol} / (\text{m}^3 \text{s})$$  \hspace{1cm} (10)$$

in which, $m_{cl}$ is the catalyst loading (kg cat/m$^3$), and Den = 1 + $K_{CO} p_{CO} + K_{H_2} p_{H_2} + K_{CO} p_{CO} + K_{H_2} p_{H_2}/p_{H_2O}$.

The governing equations are blocked out and only the heat conduction equation, derived from the energy equation, is solved for the solid plates, because no gas flow is present in these domains. Based on the reforming reaction functions, the typical velocities, fuel gas mass fraction/flux boundary conditions are specified at the external walls (not at the interfaces) in this study. While for the temperature boundary conditions, the thermal insulation is put on the three walls (the top wall and the two side ones), and a constant heat flux is specified at the bottom wall.

It should be noted that the thermal conditions at the top and side interfaces are implicitly obtained by thermal coupling through the interfaces, while all the conditions at the bottom interface (between the flow duct and the porous layer in Fig. 1b) by coupling the mass, thermal and species transfer. By this way, the complex hydrodynamic and thermal transport interactions are taken into account, in terms of the catalytic reaction rates, species flux through the porous reaction layer, and the convective flows in the fuel gas duct. The thermal performance at the interfaces is evaluated by the average interface temperature and its gradient, or by the dimensionless Nusselt number. The Nusselt number $Nu_i$ at the interface is:

$$Nu_i = \frac{\overline{h_i} D_h \left( \frac{dT}{dn} \right) D_h}{k_{\text{eff}} \left( \overline{T_i} - T_{\text{bulk}} \right)}$$  \hspace{1cm} (11)$$

in which $\overline{T_i}$, is the spanwise average temperature at the interface $i$, $(dT/dn)$, the interface normal temperature gradients, $T_{\text{bulk}}$ the mean stream-wise gas flow temperature in the cross-section.
3. Numerical solution method – CFD approach

It is worth to note that the approach applied in this study is based on one set of governing equations with the extra source terms and the local transport properties’ implementation, which enables the porous reaction and pure fluid flow regions to be treated as a single domain. The local thermal–physical properties of the gas mixture depend on the position in the duct, and the species mass fraction and/or temperature as well. Fuel gas mixture density, viscosity, thermal conductivity and specific heat are then calculated and updated during the calculations.

The applied CFD code is based on the finite-volume technique with boundary fitted coordinates for solving the differential equations. The Cartesian coordinate system in the physical space is replaced by a general non-orthogonal coordinate system. The momentum equations are solved for the velocity components on a non-staggered grid arrangement. The Rhie–Chow [7–9] interpolation method is used to compute the velocity components at the control volume faces. Algorithms based on the TDMA (Tri-Diagonal Matrix Algorithm) and a modified SIP (Strongly Implicit Procedure) are employed for solving the algebraic equations. In this study, the convective terms are treated by the QUICK (Quadratic Upstream Interpolation Convective Kinematics) scheme, while the diffusive terms are treated by the central difference scheme. The SIMPLEC (Semi-Implicit Method for Pressure-Linked Equations-Consistent) algorithm handles the linkage between velocities and pressure.

4. Results and discussion

Configuration and operating parameters of a typical reformer duct are applied as a base case in this study. Table 1 shows the duct geometries. For the porous layer, the parameters are chosen as: porosity \( \epsilon = 0.5 \), permeability \( \beta = 2 \times 10^{-10} \text{m}^2 \), and catalyst loading \( m_{\text{cat}} = 1 \text{g cat/cm}^3 \). Fuel inlet temperature \( T_{\text{in}} = 650 \text{C} \); inlet mole fraction \( \text{H}_2: \text{CH}_4: \text{CO}: \text{H}_2\text{O}: \text{CO}_2 = 0.026:0.2470:0.7145:0.0125 \) with \( U_{\text{in}} = 5 \text{m/s} \). The thermal conductivities are \( k_s = 25.5 \text{W/(mK)} \) for the solid plates and \( k_p = 3.0 \text{W/(mK)} \) for the catalyst and the supporting materials in the porous layer. It should be noted that all the results presented hereafter are for the base case condition unless otherwise stated.

Fig. 2 shows temperature distribution profiles along the main flow direction and for various cross-sections of the fuel reforming duct. It is clear that the temperature increases steadily along the main flow direction. The variation in temperature distribution can also be observed in the vertical direction with a larger value at the bottom solid plate. These are created by the heat flux supplied by the catalytic combustion (modeled by a constant heat flux \( q_b = 1000 \text{J/(m}^2\text{s)} \) in this study). It is also clear that the temperature change is more sharply distributed in the solid plates compared to the ones within the porous layer and gas flow duct. It is so because the thermal conductivity of the solid plates is much bigger than those of the porous material and fuel species in this specific case.

The cross-sectional temperature distributions are plotted in Fig. 2b–d for various stations. It is found that the temperature profile has maximum values close to the bottom solid plate, which is caused by the supplied heat flux at the bottom wall. It is obvious that almost uniformly distributed temperatures can be found in the solid plates and the porous catalyst layer. However, a bigger value has been predicted in the porous layer close to the side wall. On the other side, the thermal boundary layer development can be found in the gas flow duct, in which a distortion is observed close to the bottom interfaces (between the gas flow duct and the porous layer/the solid plates) due to the gas permeation into/from the porous layer, and thermal interactions across the interfaces [6].

A noteworthy feature of the conjugate calculation and analysis in the current paper is the characterization of the thermal boundary condition development close to the interfaces between the gas flow duct and the solid plates/the porous layer. It is achieved by the coupling of the mass, momentum, heat and fuel gas species with the catalytic chemical reactions. As shown in Fig. 3a, the averaged temperature distributions at the top, side and bottom interfaces are axially increased along the main flow direction. It is clear that the interface temperatures are higher than that of the fuel gas, i.e., the fuel gas flowing in the duct is getting heated along the main stream. It is also found that the temperature at the bottom interface is lower than that at the top and side interfaces in the inlet region (when \( x \) is smaller than 0.08 m). It is so because the steam reforming reaction is strong in this region, and more heat is needed to sustain this reaction. However the temperature gradients at the interfaces display different trends (not shown in this study). The temperature difference across the top interface is getting bigger at the entrance, and decreases after a peak value until a low value reached at the middle of the duct length from the entrance. It displays monotonically an increase afterwards. However the temperature gradients at the side and bottom interfaces show more stable variations, i.e., increase sharply from the duct entrance, and maintain almost stable values until the duct outlet. The consequent impact of the altered temperatures and the interface temperature gradients on the convective heat transfer coefficient or \( \text{Nu} \) is plotted in Fig. 3b.

It is obvious that the classical duct thermal boundary conditions (constant heat flux or wall temperature or the combined ones on the walls) are not rigorously applicable in the chemical reaction coupled gas flow and heat transfer, such as in this study, in which the heat source/sink in the porous materials and the heat conduction in the solid plates are involved. It is revealed that the real thermal interface represents axial variations in both the wall heat flux (or the interface temperature gradient) and surface temperature due to

<table>
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<tr>
<th>Table 1 – Geometries of the reaction duct (cm).</th>
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<tbody>
<tr>
<td>Length (x)</td>
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<tr>
<td>Overall duct</td>
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<tr>
<td>Fuel flow duct</td>
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<tr>
<td>Porous layer</td>
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the involved chemical reactions and heat supply, which requires a conjugate treatment of the mass transfer, gas flow, heat transport and chemical reactions in various functional components.

Special attention is then paid to evaluate the influence of thermal conductivity on the convective heat transfer in the fuel gas flow duct and temperature distribution within the functional components in this study. The simulations are done under the same standard conditions except the thermal conductivities of the porous layer and the solid plates. For the case of low thermal conductivities, \( k_p = 0.6 \) and \( k_s = 5 \) W/(mK) for the porous layer and the solid plates, respectively, the maximum temperature (691°C vs. 655°C reached in the bottom solid plate close to the exit) is bigger compared to that of high thermal conductivities, \( k_p = 15 \) and \( k_s = 125 \) W/(mK) (not shown in this paper). Moreover, the porous layer and the

![Fig. 2 – Temperature contours: (a) along main flow direction; at the cross-sections of: (b) entrance; (c) half length; (d) outlet of the fuel reforming duct.](image)

**Table 2 – Methane conversion rate.**

<table>
<thead>
<tr>
<th>Thermal conductivity, W/(mK)</th>
<th>Methane conversion rate, %</th>
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<tbody>
<tr>
<td>( k_p = 0.6 ) and ( k_s = 5 )</td>
<td>77.3</td>
</tr>
<tr>
<td>( k_p = 3 ) and ( k_s = 25.5 )</td>
<td>69.5</td>
</tr>
<tr>
<td>( k_p = 15 ) and ( k_s = 125 )</td>
<td>68.7</td>
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![Fig. 3 – (a) Temperature distribution and (b) Nu at the interfaces along the main flow reformer duct.](image)
bottom solid plate with higher temperatures can be found with small thermal conductivities. This is mainly due to the fact that the heat supply to compensate the steam reforming reactions cannot be effectively transported by thermal conduction in the bottom solid plate and further heat transfer in the porous layer due to small thermal conductivities. That implies a slow cooling process by the reaction related heat consumption in the porous layer. For the case of big thermal conductivities, the heat conduction becomes quick enough to balance the heat supply and the heat consumption, the maximum temperature then decreases.

As a consequence, more significant impacts on the reforming reaction performance are expected for the case of the low thermal conductivities, \( k_p = 0.1 \) and \( k_s = 5 \text{ W/(mK)} \). As revealed in the previous studies, the methane conversion rates are affected by various design and operating parameters, such as high temperature promotes big methane conversion rate. This trend is reflected in Table 2 as well. The convective heat transfer or \( Nu \) varies more significantly for the case of the small thermal conductivities, as seen in Fig. 4.

5. Conclusions

A fully three-dimensional CFD code was applied to simulate and analyze gas flow and heat transfer processes coupled by the chemical reactions in a composite duct relevant for a compact fuel reformer. The model offers the possibilities of determining temperature and convective heat transfer by taking into account the methane steam reforming, water gas-shift and reverse methanation reactions. It is found that either the averaged temperature gradient (heat flux) or the surface temperature distributions at the top-, side- and bottom interface are axially varied along the main flow direction. The small thermal conductivities of the functional materials promote this variation when the other design and operating parameters are kept the same.

Acknowledgements

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References