**Transport Phenomena Coupled by Chemical Reactions in Methane Reforming Ducts**

J. YUAN¹*, X. LV², D. YUE² AND B. SUNDÉN¹

¹Department of Energy Sciences, Faculty of Engineering, Lund University, Box 118, 22100 Lund, SWEDEN
²Marine Engineering College, Dalian Maritime University, Dalian 116026, China

Mass, heat and momentum transport processes are strongly coupled with catalytic chemical reactions in a methane steam reforming duct. In this paper, a three-dimensional calculation method is developed to simulate and analyze reforming reactions of methane, and the effects on various transport processes in a steam reforming duct. The results show that the design and operating parameters grouped as characteristic ratios have significant effects on the transport phenomena.

Keywords: transport phenomena, chemical reactions, reformer, CFD, analysis, characteristic parameters.

**INTRODUCTION**

Methane is usually converted into \( \text{H}_2, \text{CO} \) and \( \text{CO}_2 \) by employing Ni as a catalyst supported by alumina in the reformers. Such reformers have been developed during last years. In general, technologies to produce hydrogen from methane are based on one of the following conventional processes: steam methane reforming (SMR), partial oxidation (POX), autothermal reforming (ATR) [1].

There is an increasing interest worldwide in the development of innovative fuel processing technologies for fuel cell systems, for instance, compact reformer (CR hereafter) for a variety of applications. The basic idea of the CR is, by applying thin coatings of catalyst, to catalytically activate both sides of a compact heat exchanger – one side for combustion to provide heat for the other side to sustain steam reforming of methane and produce hydrogen. In this configuration, the thin coating results in small thermal conduction and species diffusion path lengths that largely eliminate heat and mass transfer restrictions associated with conventional reformers, and an improved utilization of the intrinsic reforming catalyst kinetics is allowed to achieve an efficient transfer of thermal energy. The compact reformer concept and its

---

*Corresponding author: Jinliang.yuan@energy.lth.se
potential high power density could lead to major application in fuel cell systems for stationary and transportation applications [2–4]. For instance, coupling of steam reforming and catalytic combustion in adjacent ducts received attention recently, and an excellent review can be found in [5] regarding the CR concept application and new design development. However, literature review shows that the research on the kinetic reaction performance and effects on the transport processes are very limited.

In this study, a three-dimensional computational procedure is developed 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. The reformer conditions such as the combined thermal boundary conditions (heat flux on the active solid wall and thermal insulation on the other solid walls), mass balances associated with the reforming reactions and gas permeation to/from the porous catalyst layer are applied in the analysis. Momentum and heat transport together with fuel gas species equations have been solved by coupled source terms and variable thermo-physical properties (such as density, viscosity, specific heat, etc.) of the fuel gas mixture. It should be mentioned that various transport phenomena coupled by the chemical reactions of methane in the reformer is concentrated and presented in this paper.

**PROBLEM STATEMENT AND MATHEMATICAL MODELING**

A three-dimensional computational fluid dynamics (CFD) code is employed for a methane reforming duct from a typical compact reformer, as shown in Fig. 1. The $U$, $V$, and $W$ are the velocity components in the $x$, $y$, $z$ directions, respectively. In this study, the porous catalyst layer is assumed to be homogeneous and characterized by effective parameters and the fuel in the porous layer is in thermal equilibrium with the solid matrix. The reforming reactions are within the porous catalyst layer. A constant flow rate $U = U_{in}$ with mole fractions of the mixed fuel is specified at the inlet of the fuel flow duct, while $U = 0$ is specified at the inlet for the solid walls and the porous catalyst layer. Only half of the duct is considered by imposing symmetry conditions on the mid-plane, as shown in Fig. 1.

There are several transport processes (such as mass, heat and momentum transport) together with chemical reactions appearing in multifunctional reactors. It is often found that endothermic and exothermic reactions are strongly coupled by heat exchange in the reactors, such as hydrocarbon cracking, steam reforming and dehydrogenation. In a catalytic reformer, there are many reactions taking place. It is a fact that [1, 5–6] the

![FIGURE 1](image-url) Scheme of an investigated duct of steam reforming reactors.
steam reforming, water gas-shift, and reverse methanation reactions of methane are the major ones with significant reaction rates, while other side reactions include cracking of methane and carbon monoxide to carbon deposition, and gasifying carbon by steam with very low reaction rates. The above mentioned side reactions can then be ignored and only the following major chemical reactions are included in this study:

Methane steam reforming:

\[
CH_4 + H_2O \rightarrow CO + 3H_2, \Delta h_{(298K)} = 226000 \text{kJ/kmol}
\]  

(1)

Water gas-shift:

\[
CO + H_2O \rightarrow CO_2 + H_2, \Delta h_{(298K)} = -41000 \text{kJ/kmol}
\]  

(2)

Reverse methanation:

\[
CH_4 + 2H_2O \rightarrow CO_2 + 4H_2, \Delta h_{(298K)} = 165000 \text{kJ/kmol}
\]  

(3)

It is clear that the above processes in Eqs. (1) and (3) are endothermic and the overall balance of the reactions requires net heat input by the catalytic combustion in the adjacent ducts. This heat supply is represented by a heat flux \( q_b \) in this study.

The governing equations to be solved are the general ones including continuity, momentum, energy and species equations. These equations together with specific source terms have been documented in, e.g., [7], and are not repeated here. It should be mentioned that the inclusion of the source term in the momentum equation allows it to be valid for both the porous catalytic layer and the fuel gas flow duct. This heat supply is represented by a heat flux \( q_b \) in this study.

The Stefan-Maxwell model is more commonly used in multi-component system, as in this study. The diffusion coefficients of species \( i \) in the fuel gas flow duct are calculated by the expression based on the binary coefficients [10]

\[
D_{A,B} = \frac{1 - X_A}{X_B/D_{AB} + X_C/D_{AC} + ...}
\]  

(5)

where \( D_{A,B} \) is the diffusion coefficient of the component \( A \) in the mixture with \( B, C, \ldots, X_A, X_B, X_C \) are the molar fraction of the appropriate species, and \( D_{AB} \) and \( D_{AC} \) are the diffusion coefficients in the \( AB \) and \( AC \) binary system, respectively. It is clear that for an \( n \) component system, \( n(n-1)/2 \) binary diffusivities are required.

There exist various reaction kinetics and rate/equilibrium constants reported in the literature for the reactions. In this study, the following reaction rates are employed to express the kinetic rates of absorption or
production of the gas species, based on partial pressure, temperature and species compositions for the chemical reactions (1)-(3):

\[ R_i = \frac{k_i p_i^{n_i}}{(\text{Den})^2} m_i, \text{kmol/(m}^3\text{s)} \]  

(6)

\[ R_2 = \frac{k_2 p_i^{n_i}}{p_i^{n_i}} m_i, \text{kmol/(m}^3\text{s)} \]  

(7)

\[ R_3 = \frac{k_3 p_i^{n_i}}{p_i^{n_i}} m_i, \text{kmol/(m}^3\text{s)} \]  

(8)

in which, \( m_i \) is the catalyst loading (kg cat/m\(^3\)), and \( \text{Den} = 1 + K_{CO} p_{CO} + K_{H_2} p_{H_2} + K_{CH_4} p_{CH_4} + K_{H_2O} p_{H_2O} / p_i \). The values of the pre-exponential factors, activation energies, equilibrium constants, and heat of adsorption are given in Table 1 and Table 2, respectively.

In the species mass conservation equations, the source terms \( S_{i} \), read:

\[ S_{i} = (3R_i + R_2 + 4R_3)M_{H_2} ; \]  

\[ S_{i} = (-R_1 - R_2)M_{CH_4} ; \]  

\[ S_{i} = (-R_1 - R_2 - 2R_3)M_{H_2O} ; \]  

\[ S_{i} = (R_1 - R_2)M_{CO} \]  

(9)

Based on the reforming reaction function, the thermal and fuel gas mass concentration/flux boundary conditions at the walls are specified as follows. At the bottom wall \((y = 0)\):

\[ U = V = W = 0, q = -k_{eff} \frac{\partial T}{\partial y} ; J_i = -\rho_{eff} D_{i, eff} \frac{\partial Y_i}{\partial y} (i = H_2, CO, H_2O \text{ and } CH_4) \]  

(10)

at the top and side walls:

\[ U = V = W = 0, q = 0, J_i = 0 \]  

(11)

at the mid-plane \((z = a/2)\):

\[ \frac{\partial U}{\partial z} = \frac{\partial V}{\partial z} = W = \frac{\partial T}{\partial z} = \frac{\partial Y_i}{\partial z} = 0 \]  

(12)

**NUMERICAL SOLUTION METHODOLOGY**

A three-dimensional computation fluid dynamics (CFD) code is applied to solve the governing equations together with the boundary conditions (10–12). The employed code is a general purpose one and 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 interpolation method is used to compute the velocity components at the control volume faces. Algorithms based on the TDMA and a modified SIP are employed for solving the algebraic equations. In this study, the convective terms are treated by the QUICK scheme, while the diffusive terms are treated by the central difference scheme. The SIMPLEC algorithm handles the linkage between velocities and pressure. More details can be found in, e.g., [7].
As shown in [7], the equations to be calculated are coupled by temperature, partial pressure/concentration of gas species via source terms and thermal-physical properties. It should be mentioned that no gas flow is present in the solid plates. Only the heat conduction equation, derived from the energy equation, is solved for this domain. The thermal-physical properties of the gas mixture are variables. These parameters depend on the position in the duct, and the species mass fraction and/or temperature as well. Fuel gas mixture density, viscosity and specific heat are then calculated and updated during the calculations. In this investigation, a uniform grid point distribution in the cross section is applied. To obtain finer meshes in the entrance region of the duct, a non-uniform distribution of grid points with an expansion factor is implemented for the main flow direction. Various values of the expansion factor have been checked and 1.01 was found to be sufficient to achieve grid independent solutions.

RESULTS AND DISCUSSION

Parameters of a typical reforming duct are applied as a base case in this study, while the parameter studies are conducted for various duct configuration and operating conditions to compare with. The base geometry parameters are shown in Table 3. For the porous layer, the parameters are chosen as: porosity $\varepsilon = 0.5$, permeability $\beta = 2 \times 10^{-10} \text{m}^2$, and catalyst loading $m_{cl} = 0.1 \text{gcat/cm}^3$. The binary diffusion coefficients of the fuel species are shown in Table 4 [11]. Fuel inlet temperature $T_{in} = 650^\circ \text{C}$; inlet mole concentration $H_2$: $\text{CH}_4: \text{CO}: \text{H}_2\text{O}: \text{CO}_2 = 0.026:0.2470:0:0.7145:0.0125$ with $U_{in} = 5 \text{m/s}$. It should be noted that all the results for the base case was presented in [7], and are not repeated in this paper.

| TABLE 3 | Geometries of the reforming reaction duct (cm) |
|-----------------|-----------------|-----------------|
|                | Length ($x$)    | Depth ($y$)     | Width ($z$)     |
| Overall Duct   | 20              | 1               | 1               |
| Fuel Flow Duct | 20              | 0.4             | 0.8             |
| Porous Catalytic Layer | 20 | 0.4 | 1 |

Three characteristic ratios, having significant effects on various transport processes and chemical reactions as discussed later in this paper, are defined in this study. These are the hydraulic diameter ratio $D_{hr}$ (ratio of the porous layer diameter to the flow duct diameter), the permeation length ratio $PL_{r}$ (ratio of the fuel flow duct width to the porous catalyst layer width), and the permeation rate ratio $PR_{r}$ (ratio of the entrance pressure gradient to permeation resistance).

\[
D_{hr} = D_{hp} / D_{hd} \quad (13)
\]

\[
PL_{r} = a / b \quad (14)
\]

\[
PR_{r} = (\rho U_{in}^2 / 2h_p) / (\mu U_{in} / \beta) = (\rho \beta U_{in}) / (2\mu h_p) \quad (15)
\]

$D_{hr}$ in Eq. (13) is the hydraulic diameter of the porous catalyst layer ($D_{hp} = 4bh/(2(b + h_p))$), $D_{hd}$ the hydraulic diameter of the fuel flow duct ($D_{hd} = 4ah/(2(a + h_p))$); $a$ in Eq. (14) is the width of gas flow duct, $b$ the width of the porous catalyst layer; $h_p$ in Eq. (15) is the thickness of the porous layer. It is clear that both diameter ratio $D_{hr}$ and permeation length ratio $PL_{r}$ are related to the fuel flow duct and catalytic porous layer configurations, to account for the characteristics of the permeation area and length, respectively. The permeation rate ratio $PR_{r}$ considers the characteristics of the catalytic porous material (such as the permeability $\beta$) and duct operation parameter (such as the inlet velocity $U_{in}$).

To investigate effects of the diameter ratio on the transport phenomena and reformer performance, the
height of fuel flow duct \(h_d\) was varied. Figure 2 shows velocity contours for the cases of \(D_{hw} = 1.17\) (\(h_d = 3.5\) mm) and \(D_{hw} = 0.99\) (\(h_d = 4.5\) mm). As shown by dashed lines, the base case (\(D_{hw} = 1.07, h_d = 4\) mm) is present as well in Fig. 2. It should be noted that the height of the upper solid plate was changed accordingly to keep the total height of the upper solid plate and the fuel flow duct constant.

As shown in Fig. 2, the velocity contours for big or small \(D_{hw}\) have a similar trend as that of the base case, i.e., there is no symmetry of the axial velocity and the position of the maximum values shifts away from the physically central plane. This effect is more significant for the big \(D_{hw}\) case (Fig. 2a), if compared to the one with small \(D_{hw}\) (Fig. 2b). More critically, more fuel is permeated to and kept in the porous reaction region, as shown in Fig. 2a with smaller velocity contours than those in Fig. 2b. This may be due to the fact that the fuel flow duct in Fig. 2a is small if compared to the porous catalyst layer.

Effects of the permeation length ratio have been investigated as well by varying the width of the fuel flow duct \(a\), while other ratios were kept constant. Permeation length ratios \(PL_r = 0.6\) (\(a = 3\) mm) and \(PL_r = 0.9\) (\(a = 4.5\) mm) were employed, and the predicted performance is compared with that of the base case (\(PL_r = 0.8, a = 4\) mm). From Fig. 3, it is found that the cross-section velocity profiles are similar to each other for different permeation length ratios. Moreover, the steam reforming reaction rate for the case with small permeation length ratio (Fig. 4a) is almost in the same order as that achieved in the case with big permeation length ratio (Fig. 4b).

The effects of the permeation rate ratio on the fuel gas flow are shown and discussed in the following section. It is noted from Fig. 5a that, by increasing the permeability, fuel gas permeation to the porous layer is big, i.e., the length having a axial velocity in the porous layer close to the fuel flow duct is longer, if compared to the case with a small permeability shown in Fig. 5b. This is so because the permeability is a term used for the conductivity of the porous medium with respect to permeation by a fluid. It is known that a big permeability of a porous layer allows more gas to pass at the same pressure gradient. Consequently, more fuel gas is permeated from the fuel flow duct, and the gas convection can be found with bigger velocities in the porous layer close to the fuel flow duct at the entrance region. Certain impacts on the change of the axial velocity distribution are expected.

![Figure 2](image1.png)

**FIGURE 2**
Velocity contours for the cases of: a) \(D_{hw} = 1.17\); b) \(D_{hw} = 0.99\).
for both the fuel flow duct and the porous catalytic layer, when the permeability is large.

Effects of inlet velocity on the reforming performance are shown in Figs. 6 and 7. Permeation rate ratios $PR_r = 0.021$ ($U_{in} = 2.5$ m/s) and $PR_r = 0.084$ ($U_{in} = 10$ m/s) have been employed to compare with each other, i.e., $PR_r = 0.042$ and $U_{in} = 5$ m/s. It is revealed that, in the entrance region, small $PR_r$ has a

---

FIGURE 3
Distribution of velocity contours at the inlet cross section for the cases of: a) $PL_r = 0.6$; b) $PL_r = 0.9$.

FIGURE 4
Distribution of steam reforming reaction at the inlet cross section for the cases of: a) $PL_r = 0.6$; b) $PL_r = 0.9$. 
small steam reforming reaction rate in Fig. 6a compared to the case in Fig. 6b with a big inlet velocity case. It is because the fuel gas permeation to the porous catalyst layer is small as revealed in [9]. Big inlet velocity on the other hand has more significant effects not only on the fuel gases permeation to the porous catalyst layer for the reactions, but also on the convection (the fuel flow rate) in the gas flow duct. It is then
TRANSPORT PHENOMENA COUPLED BY CHEMICAL REACTIONS IN METHANE REFORMING DUCTS

FIGURE 7
Effects of the permeation rate ratio (inlet velocity) on the H2 distribution at inlet velocity of: a) \( PR_r = 0.021 \) \( (U_{in} = 2.5 \text{ m/s}) \); b) \( PR_r = 0.084 \) \( (U_{in} = 10 \text{ m/s}) \).

FIGURE 8
Effects of the permeation rate ratio (thickness of the porous layer) on the H2 distribution. a) \( PR_r = 0.084 \) \( (h_p = 2.0 \text{ mm}) \); b) \( PR_r = 0.168 \) \( (h_p = 1.0 \text{ mm}) \).

noted from Fig. 7a that the exit H2 mole fraction is high even the reforming reaction rate is small compared to the case in Fig. 7b. It means that the H2 yield is controlled by the combined effects of the reforming reactions in the porous catalyst layer and convective flow (the fuel flow rate) along the flow direction downstream the fuel gas flow duct.

As expected, thickness of the porous catalyst layer is one of the most important parameters. To investigate effects of the porous layer thickness on the gas
flow and the reformer reactions, the height of porous layer \( h_p \) was varied while other parameter ratios were kept constant. It should be mentioned that the thickness of the lower solid plate was changed accordingly to keep the total height of the porous catalyst layer and the lower solid plate constant. It is noted that the ducts employing thin porous layers (thickness \( h_p \) = 2.0 and 1.0 mm, respectively, vs. 4.0 mm) predict very similar \( \text{H}_2 \) mole fraction profiles, as shown in Fig. 8. However for the case of the thinner porous catalyst layer (Fig. 8b), a smaller \( \text{H}_2 \) mole fraction is found in the corner of the porous catalyst layer close to the exit and the bottom solid plate.

It is clear that the distribution of steam reforming reaction rates in Fig. 9 holds a similar trend, i.e., strong steam reforming reaction appears in the interface region of the porous catalyst layer close to the fuel flow duct. On the other hand, weak reaction (with small reaction rate value) can be found in the remaining areas as well for the thin porous catalyst layers shown in Fig. 9. The reforming reaction performance achieved in the case of \( PR_r = 0.084 \) (\( h_p = 2.0 \)mm) is smaller than the one for the case \( PR_r = 0.168 \) (\( h_p = 1.0 \)mm) (Fig. 9b).

Figure 10 shows the temperature distribution to reveal the porous layer thickness effects. It is found that the reforming ducts employing thin porous layers have high temperatures in both the fuel flow duct and the porous catalyst layers. For instance, the maximum temperatures appearing in the active plate corner (the bottom plate in Fig. 1) at the exit are 779°C and 769°C for thin porous layers, compared to 758.6°C for the base condition (not shown). It is so because the thin porous catalytic layers are employed to have reforming reactions, where the less heat is consumed.

As discussed above, it is clear that the thickness of the porous catalytic layer has various roles in the chemical reaction rates and the transport processes. It is due to the fact that the thickness of the porous catalyst layer is involved in both the diameter ratio and permeation rate ratio, i.e., a thin porous layer generates a smaller diameter ratio \( D_{hr} \), however a bigger permeation rate ratio. Further study is needed to find an optimal thickness of the porous catalytic layer, in conjunction with the catalyst loading and distribution.

**CONCLUSIONS**

In this paper, a fully three-dimensional calculation method has been further developed to study the design
and operating parameter effects on transport phenomena coupled by the chemical reactions in a composite duct relevant for a compact reformer. The model offers the possibilities of determining temperature and fuel gas fraction/velocity profiles by taking into account the methane steam reforming, water gas-shift and reverse methanation reactions. The important variables based on reformer duct configurations and operations are grouped into three characteristic ratios. The transport processes are then evaluated based on these ratios. Big diameter ratio and the permeation length ratio have significant effects to yield high methane reforming efficiencies at the exit of the duct. For big permeation rate ratio (high inlet velocity and permeability, and small thickness of the porous catalyst layer) induces big steam reforming and reverse methanation reaction rates. The porous layer thickness has complex effects and no simple conclusion can be drawn for the effects on the transport phenomena and overall reforming reaction performance.

ACKNOWLEDGMENT

The Swedish Research Council (VR) financially supports the current research.

NOMENCLATURE

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>width of fuel flow duct, m</td>
</tr>
<tr>
<td>b</td>
<td>width of porous catalyst layer, m</td>
</tr>
<tr>
<td>c_p</td>
<td>specific heat, J/(kg K)</td>
</tr>
<tr>
<td>D</td>
<td>diffusion coefficient of species, m²/s</td>
</tr>
<tr>
<td>D_h</td>
<td>hydraulic diameter, m</td>
</tr>
<tr>
<td>D_hr</td>
<td>hydraulic diameter ratio</td>
</tr>
<tr>
<td>h</td>
<td>overall height of the duct, m; enthalpy, kJ/mole</td>
</tr>
<tr>
<td>h_a</td>
<td>height of the fuel flow duct, m</td>
</tr>
<tr>
<td>h_p</td>
<td>thickness of porous catalyst layer, m</td>
</tr>
<tr>
<td>h_t</td>
<td>thickness ratio (h_p/h)</td>
</tr>
<tr>
<td>J</td>
<td>reaction related molar flux, mol/(m² s)</td>
</tr>
<tr>
<td>k</td>
<td>thermal conductivity, W/(m K); kinetic rate constant, kmol/(kgcat h)</td>
</tr>
<tr>
<td>K_e</td>
<td>equilibrium constants, Pa²</td>
</tr>
<tr>
<td>L</td>
<td>reformer length, m</td>
</tr>
<tr>
<td>m_cl</td>
<td>catalyst loading, kgcat/m³</td>
</tr>
<tr>
<td>m</td>
<td>mass diffusion flux, kg/(m² s)</td>
</tr>
<tr>
<td>n</td>
<td>molar diffusion flux, mol/(m² s)</td>
</tr>
<tr>
<td>M</td>
<td>molecular weight of species, kg/mol</td>
</tr>
<tr>
<td>P</td>
<td>pressure, Pa</td>
</tr>
<tr>
<td>PL_r</td>
<td>permeation length ratio</td>
</tr>
<tr>
<td>PR_r</td>
<td>permeation rate ratio</td>
</tr>
<tr>
<td>q</td>
<td>heat flux, W/(m²)</td>
</tr>
</tbody>
</table>
R  reaction rate, kmol/(m$^3$s)
R  gas constant, kJ/(mol K)
s  effective radius, m
Re  Reynolds number (UD$_h$/ν)
S  source term
T  temperature, °C
V  velocity vector, m/s
Vi  velocity components in x, y and z directions, respectively, m/s
x, y, z  Cartesian coordinates
X  molar fraction of fuel species
Y  mass fraction of fuel species

Greek Symbols
β  permeability of porous layer, m$^2$
ed  porosity
µ  dynamic viscosity, kg/(m s)
ν  kinematic viscosity, m$^2$/s
ρ  density, kg/m$^3$
τ  tortuosity

Superscripts
+  forward reaction
−  reverse reaction

Subscripts
di  diffusion
eff  effective parameter
f  fuel gas mixture
form  formation
gm  fuel gas mixture
CH$_4$  methane
CO  carbon monoxide
CO$_2$  carbon dioxide
H$_2$  hydrogen
H$_2$O  water
in  inlet
k  Knudsen diffusion
m  mass transfer
p  permeation

r  steam reforming reaction
re  reverse methanation reaction
s  solid wall; shift reaction

REFERENCES


