Numerical analysis of helium-heated methane/steam reformer

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Abstract. One of the most promising between many high temperature nuclear reactors applications is to produce hydrogen with heat gained. The simplest and the best examined method is steam reforming of methane. The fabricated hydrogen has wide range of use, for example can be electrochemically oxidized in fuel cells. However, heat management inside methane/steam reformer is extremely important because huge temperature gradients can cause catalyst deactivation. In this work the analysis of temperature field inside helium-heated methane/steam reformer is presented. The optimal system working conditions with respect to methane conversion rate are proposed.

1. Introduction

First high temperature gas reactor (HGTR or HTR) started its operation in 1963 \cite{1} and from that time the development of gas cooled nuclear reactor technology has been proceeding. A coolant provides amount of heat that can be used to produce electricity or to conduct endothermic chemical reactions on large scale.

The methane/steam reforming is the most important hydrogen and syngas production process for industrial scales \cite{2}. However, the process is endothermic, thus in conventional solutions provided methane is partially burned to heat up the reactor. HTR can solve the heating problem.

Numerical modeling of methane/steam reforming process gained popularity during last 30 years. In 1989 the classical analysis of methane/steam reforming kinetics has been published by Xu and Froment \cite{2}. Several researches focus on coupling methane/steam reforming with fuel cells \cite{3,4}. Mozdzierz et al. \cite{5} conducted parametric studies on methane/steam reforming reaction and shown that adaptation of heating zones and localized catalyst density can significantly help in process control. This approach can be used to combine HTR with methane/steam reforming \cite{6}. Simple model of helium-heated methane/steam reformer has been prepared by Yin et al. \cite{7}. The model is based on a helium production device installed in Chinese test reactor HTR-10.

In this work the attempt to design optimal working parameters for a methane/steam reformer heated by helium has been undertook. The mathematical model has been proposed and results of numerical calculations are presented. The crucial point is temperature field distribution inside the methane/steam reformer, because large temperature difference inside the catalyst may cause its deactivation. Temperature gradient inside the solid parts of the system results in thermal stresses and thermal cracks.
2. Numerical model

The analyzed helium production device consists of two concentric tubes. The inner tube is filled with nickel-yttria-stabilized zirconia metal foam (Ni/YSZ 40:60 % vol.), which serves as catalyst. Through the outer tube hot gaseous helium flows, which destination is to provide heat for the endothermic methane reforming reaction. Schematic sketch of the helium-heated methane/steam reformer is presented on Fig. 1.

Figure 1. Configuration of the system (working in counter-flow)

2.1. Mathematical description of methane/steam reforming process

Methane/steam reforming process can be treated as composition of two dominant reactions: the methane/steam reforming reaction Eq. (1) and the water-gas shift reaction Eq. (2).

\[
\text{CH}_4 + \text{H}_2\text{O} \rightarrow 3\text{H}_2 + \text{CO} \quad (1)
\]

\[
\text{CO} + \text{H}_2\text{O} \Leftrightarrow \text{H}_2 + \text{CO}_2 \quad (2)
\]

Standard enthalpy of the methane/steam reforming reaction is \(\Delta H_{\text{msr}}^0 = 206.1 \text{ [kJ mol}^{-1}\text{]}\), thus the reaction is strongly endothermic. Reaction (1) is slow, therefore the rate of reaction is necessary. The reaction rate can be formulated as follows:

\[
R_{\text{msr}} = w_{\text{cat}} A_{\text{msr}} \exp \left( -\frac{E_a}{RT} \right) p_a^a p_b^b \quad (3)
\]

\(w_{\text{cat}} \text{ [g m}^{-3}\text{]}\) stands for catalyst weight density and \(p_i \text{ [atm]}\) is the partial pressure of species \(i\). Arrhenius constant \(A_{\text{msr}}=6.5267 \text{ [mol min}^{-1}\text{ g}^{-1}\text{ atm}^{-0.61}]\), activation energy \(E_a=43920 \text{ [J mol}^{-1}\text{]}\) and reaction orders with respect to the methane \(a=0.39 \text{ [-]}\) and with respect to the steam \(b=0.22 \text{ [-]}\), which appear in Eq. (3) has been obtained experimentally, according to [8].

Standard enthalpy of water-gas shift reaction Eq. (2) is \(\Delta H_{\text{wgs}}^0 = -41.15 \text{ [kJ mol}^{-1}\text{]}\), which indicates that reaction is exothermic, however, in comparison with enthalpy of reaction (1), the whole process is endothermic. It is assumed that water-gas shift reaction is in equilibrium in temperature of reforming process, thus the reaction rate can be derived from equilibrium equation and partial pressures of species [5] as follows:

\[
R_{\text{wgs}} = R_{\text{msr}} y_{\text{cr}} \quad (4)
\]

where \(y_{\text{cr}} \text{ [-]}\) is the carbon oxide conversion rate during the water-gas shift reaction.

Based on reaction rates, the thermodynamic heat generation can be calculated:

\[
Q_{\text{msr}} = -R_{\text{msr}} \Delta H_{\text{msr}}^0 \quad (5)
\]
Reaction rates together with stoichiometry of chemical reactions, Eqs (1) and (2), lead to mass sources and sinks during the reforming process (shown in Table 1).

| species | mass source/sink |
|---------|-----------------|
| H₂      | 3R_{msr}M_{H₂} + R_{wgs}M_{H₂} |
| CO      | R_{msr}M_{CO} - R_{wgs}M_{CO} |
| CO₂     | R_{wgs}M_{CO₂} |
| CH₄     | -R_{msr}M_{CH₄} |
| H₂O     | -R_{msr}M_{H₂O} - R_{wgs}M_{H₂O} |

2.2. Mathematical formulation of the problem

The computational domain, shown on Fig. 1 has been divided for three parts with different governing equations adapted: porous reformer catalyst, separating wall and heating tube. The model is steady. Analyzed hydrogen producing device coupled with HTR is axisymmetric, thus equations can be formulated in two-dimensional cylindrical coordinate system. Inside the system the parallel- or counter-flow can be adopted.

For the reacting gas mixture flow inside the methane/steam reforming reactor, the governing equations for flow inside the porous media are applied. The momentum transport equations has been derived from Forchheimer extension of Darcy law [9]. The physical values are averaged locally for a representative control volume [9].

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

\[
\frac{\rho_{mix}}{\epsilon^2} \left( U_x \frac{\partial U_x}{\partial x} + U_r \frac{\partial U_r}{\partial r} \right) = -\frac{\partial P}{\partial x} + \frac{\mu_{mix}}{\epsilon} \left[ \frac{\partial^2 U_x}{\partial x^2} + \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial U_x}{\partial r} \right) \right]
- \frac{\mu_{mix}}{K_p} U_x - \frac{\rho_{mix} f}{\sqrt{K_p}} U_x \sqrt{U_x^2 + U_r^2}
\]  

\[
\frac{\rho_{mix}}{\epsilon^2} \left( U_x \frac{\partial U_x}{\partial x} + U_r \frac{\partial U_r}{\partial r} \right) = -\frac{\partial P}{\partial r} + \frac{\mu_{mix}}{\epsilon} \left[ \frac{\partial^2 U_r}{\partial x^2} + \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial U_r}{\partial r} \right) - \frac{U_r}{r^2} \right]
- \frac{\mu_{mix}}{K_p} U_r - \frac{\rho_{mix} f}{\sqrt{K_p}} U_r \sqrt{U_x^2 + U_r^2}
\]  

\[
\rho_{mix} C_{p,mix} \left( U_x \frac{\partial T}{\partial x} + U_r \frac{\partial T}{\partial r} \right) = \frac{\partial}{\partial x} \left( \lambda_{eff} \frac{\partial T}{\partial x} \right) + \frac{1}{r} \frac{\partial}{\partial r} \left( r \lambda_{eff} \frac{\partial T}{\partial r} \right) + Q_s
\]  

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

In above equations \( U_x \) and \( U_r \) [m s\(^{-1}\)] stand for gas mixture velocity in \( x \) and \( r \) direction respectively, \( T \) [K] is the average temperature of both gas and solid phase and \( Y_j \) [-] is molar fraction of species \( j \). \( \rho_{mix} \) [kg m\(^{-3}\)] is the gas mixture density, \( C_{p,mix} \) [J kg\(^{-1}\) K\(^{-1}\)] is the constant-pressure specific heat capacity of gas mixture and \( \mu_{mix} \) [Pa s] is mixture dynamic viscosity. \( \lambda_{eff} \)
is effective thermal conductivity of both gas mixture and solid phase and it is calculated with formula \( \lambda_{\text{eff}} = \epsilon \lambda_{\text{mix}} + (1 - \epsilon) \lambda_s \), where subscript 'mix' stands for mixture thermal conductivity calculated using mixing laws [10] and 's' stands for solid phase (\( \lambda_s = 20 \text{ W m}^{-1} \text{ K}^{-1} \)). \( D_{\text{j,eff}} \text{ [m}^2 \text{ s}^{-1} \) is the effective diffusion coefficient of gas mixture calculated with correlation 
\[
D_{\text{j,eff}} = \left( 1 - \sqrt{1 - \epsilon} \right) D_j,
\]
where diffusion of species \( j \) in mixture of gases \( D_j \) is calculated with Fuller method and Blanc law [10].

\( \epsilon = 0.9 \) [-] stands for porosity and \( K = 1.0 \times 10^{-7} \text{ m}^2 \) is the permeability of porous catalyst. \( f = 0.088 \) [-] is the inertia coefficient, according to Suzuki [11].

Since flow of helium is non-reacting, the governing equations are continuity, momentum and heat transfer equations, as follows:

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

\[
\rho_{\text{He}} \left( U_x \frac{\partial U_x}{\partial x} + U_r \frac{\partial U_x}{\partial r} \right) = \frac{\partial P}{\partial x} + \mu_{\text{He}} \left( \frac{\partial^2 U_x}{\partial x^2} + \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial U_x}{\partial r} \right) \right)
\]

\[
\rho_{\text{He}} C_{p,\text{He}} \left( U_x \frac{\partial T}{\partial x} + U_r \frac{\partial T}{\partial r} \right) = \frac{\partial}{\partial x} \left( \lambda_{\text{He}} \frac{\partial T}{\partial x} \right) + \frac{1}{r} \frac{\partial}{\partial r} \left( r \lambda_{\text{He}} \frac{\partial T}{\partial r} \right)
\]

In above equations symbols has the same meaning as in governing equations for reformer, instead of \( T \) [K] - the gas temperature and subscript 'He' indicates that thermophysical properties for a hot gaseous helium are used [12].

In the solid wall the only transport phenomena is heat conduction:

\[
0 = \frac{\partial}{\partial x} \left( \lambda_w \frac{\partial T}{\partial x} \right) + \frac{1}{r} \frac{\partial}{\partial r} \left( r \lambda_w \frac{\partial T}{\partial r} \right)
\]

where \( \lambda_w = 1.1 \text{ W m}^{-1} \text{ K}^{-1} \) is the wall thermal conductivity [11].

2.3. Numerical algorithms

The computational domain can be divided for three subdomains, namely reformer, separating wall and heating tube, as shown on Fig. 2. The boundary conditions are presented on Fig. 2. The system pressure equals atmospheric pressure. Temperature field for the subdomains was conjugated with assumption of equality of a heat flux at the boundaries. The partial differential equations shown in Section 2.2 has been discretized with Finite Volume Method and the resulting systems of algebraic equations has been solved iteratively with Gauss-Seidel method.

To solve the governing equations the in-house C++ code has been build. The working conditions, namely the temperature and the velocity of helium at the inlet, \( T_{\text{He}} \) [K] and \( U_{\text{He}} \) [m s\(^{-1}\)], the temperature of the mixture of methane and steam \( T_{\text{mix}} \) [K], velocity \( U_{\text{mix}} \) [m s\(^{-1}\)] and the composition of gases at the inlet (calculated from \( SC \) [-], which is the ratio of the steam to the methane) and the amount of catalyst, given as catalyst weight density \( w_{\text{cat}} \) [g m\(^{-3}\)], can be manipulated. The results of the computations are molar concentrations of species inside the reformer and temperature field in the system.
3. Results

The analysis to chose optimal system configuration has been performed. Some trends, e.g.,
strong influence of catalyst density and fuel inlet velocity on temperature gradient and methane
conversion rate, come from earlier works [5], thus current study focuses on influence of hot
helium thermophysical parameters. The nondimensionalized geometry is adopted:

- the ratio of length to reformer radius $L/R_{ref} = 6.0$ [-];
- the ratio of length to wall radius $L/R_{wall} = 5.0$ [-];
- the ratio of length to system radius $L/R = 2.73$ [-].

3.1. Optimal flow direction

As mentioned above, the helium-heated methane/steam reforming reactor may work in parallel-
or counter-flow configuration. Generally, the counter-flow heat exchanger layout leads to higher
efficiency than the parallel-flow heat exchanger when the same value of heat capacity ratio and
number of transferred units are adopted [13]. However, at the reactor inlet the heat demand is
the highest, because of endothermic nature of the process.

The numerical calculations to check which configuration is preferable and the results are
presented on Figs 3 and 4. The working conditions are the same in both tests and the only
difference is the system configuration direction.

As can be seen on Fig. 3, the amount of produced hydrogen and carbon oxides is almost the
same in both cases. However, the heat is transported more effectively and the reaction is in inlet
part of the reformer in case of parallel-flow system, which results in stronger concave of function
that represent methane molar fraction, as shown on Fig. 3(a). The temperature difference inside
the reformer, Figs 4(a) and 4(b), is similar in both configurations, in counter-flow case at the
reformer outlet small zone of high temperature appears, Fig. 4(b). However, the temperature
distribution inside the wall in case with the counter-flow can destroy the separating wall because
of huge temperature gradient in the longitudinal direction.

Because of methane/steam reforming specification, the parallel- and counter-flow performance
is similar, but the temperature difference in the wall is dangerous in the case of counter-flow.
Thus in further analyses the parallel-flow is adhibited.
3.2. Effect of helium inlet velocity

The set of numerical calculations to test the influence of helium inlet velocity has been conducted. The results are shown on Figs 5 and 6, and the inlet velocity varies from 1 [m s\(^{-1}\)] to 3 [m s\(^{-1}\)].

As can be seen on Fig. 3.2, the amount of produced hydrogen is a little bit higher when higher helium inlet velocity is adopted. It is consequence of large zone of high temperature when the inlet velocity equals 3 [m s\(^{-1}\)] (see Fig. 6(b)). The zone of the lowest temperature inside the reformer is shorter when higher helium velocity is adopted, however, the temperature at the reformer wall is higher. Nevertheless, the difference is not significant, thus the higher helium inlet velocity has positive impact on process.

3.3. Optimal system configuration

Based on analyses presented here and on conclusions of earlier works [8, 5], the conditions for optimal system configuration are proposed. The aim is to get methane conversion rate as high as
Figure 5. Average gas composition along the reformer for different helium inlet velocities; \( T_{\text{He}}=1200 \, [\text{K}] \), \( T_{\text{mix}}=500 \, [\text{K}] \), \( U_{\text{mix}}=0.25 \, [\text{m s}^{-1}] \), \( SC=2.0 \, [-] \), \( w_{\text{cat}}=2 \cdot 10^5 \, [\text{g m}^{-3}] \).

Figure 6. Distribution of temperature for different helium inlet velocities; \( T_{\text{He}}=1150 \, [\text{K}] \), \( T_{\text{He}}=1200 \, [\text{K}] \), \( T_{\text{mix}}=500 \, [\text{K}] \), \( U_{\text{mix}}=0.25 \, [\text{m s}^{-1}] \), \( SC=2.0 \, [-] \), \( w_{\text{cat}}=2 \cdot 10^5 \, [\text{g m}^{-3}] \).

possible and to process reaction in whole volume of catalyst. The strong temperature difference in the reformer and in the wall should be avoided. The results are shown on Fig. 7.

The results indicate that the methane completely reacted inside the reformer and the reaction rate is the highest at the reactor inlet (see Fig. 7(a)). The high energy of mixture of methane and steam is sufficient to start methane/steam reforming reaction immediately after gases reach catalyst, thus the zone of low temperature due to endothermic reaction is shifted, Fig. 7(b).

4. General conclusions

The paper presents numerical analyses of methane/steam reforming process on Ni/YSZ catalyst heated by hot helium from high temperature reactor. The proper numerical model has been developed and parametric studies has been conducted to propose working conditions, namely inlet temperatures and velocities, amount of catalyst and \( SC \) ratio in order to react whole provided methane and to use whole volume of the reactor.

The studies lead to the following conclusions:
Figure 7. Average gas composition along the reformer (a) and distribution of temperature (b) for optimal configuration; \( T_{\text{He}}=1200 \ [\text{K}] \), \( U_{\text{He}}=3 \ [\text{m s}^{-1}] \), \( T_{\text{mix}}=800 \ [\text{K}] \), \( U_{\text{mix}}=0.25 \ [\text{m s}^{-1}] \), \( SC=2.0 \ [-] \), \( w_{\text{cat}}=2.5 \cdot 10^6 \ [\text{g m}^{-3}] \).

- the order of magnitude of catalyst density should be \( 10^6 \ [\text{g m}^{-3}] \);
- inlet temperatures should be as high as possible, the heat regeneration to raise temperature of methane and steam mixture is significant;
- the helium-heated system contains of two pipes should work in parallel-flow and the helium inlet velocity should be around \( 3 \ [\text{m s}^{-1}] \).

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References

[1] Yan X L, Hino R and Ohashi K 2011 Nuclear Hydrogen Production Handbook ed Yan X L and Hino R (Boca Raton: CRC Press) chapter 10 pp 211-292
[2] Xu J and Froment G F 1989 AIChE Journal 35 pp 88-96
[3] Brus G, Kimijima S and Szmyd J S 2012 Journal of Physics: Conference Series 395 012159
[4] Sciakzo A, Komatsu Y, Brus G, Kimijima S and Szmyd J S 2014 Journal of Power Sources 262 245-254
[5] Mozdzierz M, Brus G, Sciakzo A, Komatsu Y, Kimijima S and Szmyd J S 2016 Flow, Turbulence and Combustion pp 1-19 (in press, DOI: 10.1007/s10494-015-9693-2)
[6] Mozdzierz M, Brus G, Kimijima S and Szmyd J S 2015 NHT 2015: Numerical Heat Transfer 2015 Eurotherm seminar no. 109: 27-30 September, 2015, Warsaw, Poland ed Nowak A J et al. pp 115-124
[7] Yin H, Jiang S, Zhang Y and Ju H 2007 Journal of Nuclear Science and Technology 44 pp 977-984
[8] Mozdzierz M, Brus G, Sciakzo A, Komatsu Y, Kimijima S and Szmyd J S 2014 Journal of Physics: Conference Series 530 012040
[9] Nield D A and Bejan A 2006 Convection in Porous Media (New York: Springer Science+Business Media Inc.)
[10] Poling B E, Prausnitz J M and O’Connell J P 2001 The Properties of Gases and Liquids (New York: McGraw-Hill)
[11] Suzuki K, Iwai H and Nishino T 2005 Transport Phenomena in Fuel Cells ed Sunden B and Faghri M (Southampton: WIT Press) chapter 3 pp 83-131
[12] Gierszewski P, Mikie B and Todreas N 1980 Property Correlations for Lithium, Sodium, Helium, FLiBe and Water in Fusion Reactor Applications (Cambridge: Massachusetts Institute of Technology) PFC-RR-80-12
[13] Kraus A D 2003 Heat Transfer Handbook ed Bejan A and Kraus A D (Hoboken: John Wiley & Sons Inc.) chapter 11 pp 797-911