# FEDSM-ICNMM2010-30010

# PARAMETRIC STUDY OF AN AUTOTHERMAL MICRO SURFACE REACTOR FOR HYDROGEN PRODUCTION

M.H. Akbari Assistant Professor A.H. Sharafian Ardakani M.Sc. Student M. Andisheh Tadbir M.Sc. Student

Center for Fuel Cell Research, Faculty of Mechanical Engineering, Shiraz University, Shiraz, 71348-51154, Iran

# ABSTRACT

Hydrogen production through autothermal reforming (ATR) of hydrocarbons, such as methane, is one option of interest for mobile applications of hydrogen fuel cells. In the present study, a numerical investigation of catalytic autothermal reforming of methane in a surface microreactor is presented. A three-dimensional ATR reactor model is developed to simulate the flow and surface reactions in a microchannel of rectangular cross section with 340-um sides, and total length of 8.5 mm. A four-reaction mechanism is implemented to simulate the surface reactions on a Ni/Al<sub>2</sub>O<sub>3</sub> catalyst. The governing equations in the model include conservations of mass, momentum, energy and chemical species. A CFD code based on the finite-volume method has been developed in-house to solve the governing equations. Validation of the results against available data confirms the accuracy of the numerical approach. The simulation results reveal the dependency of hydrogen yield on space velocity (SV), air/fuel molar ratio (A/F), water/fuel molar ratio (W/F), and the gas feed temperature.

# **1. INTRODUCTION**

The commercial production of hydrogen for using in industries, transportable systems and electricity generation is more essential when depletion of non-renewable natural resources have been increased rapidly. Hydrogen can be used as the main fuel in all types of fuel cell, but the costs for its delivery and storage is very high at the present. In addition, hydrogen energy density is very low and hence hydrogen storage is not considered practical for many applications. If hydrogen can be produced on-demand, the problems regarding its storage or delivery will be eliminated. Currently, three major thermo-chemical reforming techniques are available to produce hydrogen from hydrocarbon fuels, i.e., steam reforming (SR), partial oxidation (POX), and autothermal reforming (ATR) [1]. SR has been used extensively in different industries for hydrogen production, but this process is strongly endothermic and the reformer needs external heat. Thus the overall configuration of SR with heat exchangers makes the reforming system very bulky and heavy, which is not suitable for a mobile fuel cell system.

One technique which is proposed to avoid heat transfer problems in SR is partial oxidation (POX). This process is exothermic and easily starts up even without the presence of a catalyst. However, high carbon monoxide concentrations are produced in POX which must be treated further otherwise will poison the membrane of PEM fuel cells.

To relegate this problem, autothermal reforming is considered in which the thermal effects of the POX and SR reactions are combined by feeding the fuel, water, and air together into the reactor. The two processes occur simultaneously in the presence of a catalyst in the reactor. The thermal energy generated from POX is absorbed by SR and, hence, the overall temperature is lowered, which is favorable to water-gas shift reaction to consume the generated carbon monoxide and produce more hydrogen. Advantages of an ATR reactor include its small size, relative simplicity, easy operation, quick response, and inexpensive material requirements [2-4].

Trimm and Lam [5] studied ATR of methane on  $Pt/Al_2O_3$ fibre catalyst. The kinetics of the reactions were measured at temperatures around 800 K. This mechanism was supported by the characterization studies. Xu and Froment [6] presented intrinsic kinetic of methane SR, methanation and water-gas shift (WGS) reaction on Ni/Al<sub>2</sub>O<sub>3</sub> catalyst for initial temperature range among 573-823 K. The kinetics they developed was implemented extensively in subsequent investigations.

Ma et al. [7] designed and tested an autothermal reactor for the conversion of light hydrocarbon to hydrogen on  $Pt/\delta$ -Al<sub>2</sub>O<sub>3</sub> catalyst, and also presented a kinetic rate of total combustion of

methane based on this catalyst for initial temperature range of 663-723 K.

Groote and Froment [8] simulated the catalytic POX of methane to synthesis gas on a Ni catalyst in an adiabatic reactor with various inlet air/fuel (A/F) and water/fuel (W/F) ratios. In this study, the kinetic rates were presented for eight reactions and a series of effectiveness factors associated with these reactions were proposed.

Halabi et al. [9] modeled and analyzed a one-dimensional heterogeneous autothermal reactor of methane to hydrogen with gas feed temperature and pressure of 773 K and 1.5 bar in a Ni/Al<sub>2</sub>O<sub>3</sub> fixed-bed reformer. The influence of different parameters such as oxygen/carbon and steam/carbon was investigated.

Most of the previous investigations were carried out for packed-bed reactors (with volumetric reactions). This type of reactor causes high pressure losses which prohibit their application for mobile devices. In the present study, catalytic ATR of methane in a surface microchannel reactor at the presence of a Ni-based catalyst is numerically simulated. A three-dimensional, steady-state, adiabatic model is developed. Steady state performance of the reactor is examined with respect to major parameters including gas feed temperature, air/methane and water/methane molar ratios and space velocity. The microchannel reactor is of a square cross section with 340µm sides, and a total length of 8.5 mm. The synthesis gas generated by an assembly of such ATR microreactors would be fed to WGS and preferential oxidation (PROX) reactors downstream. Ultimately, the generated hydrogen-rich stream would be fed to a PEM fuel cell for a portable electronic device.

Our simulation results indicate that a total number of 10,000 of these microreactors (an array of  $100 \times 100$  microchannels) would be required to provide enough power for a 100 W portable device, for instance. Such assembly will take up an overall space of about  $35 \times 35 \times 10$  mm as part of a complete micro-fuel processor device. One advantage of a microchannel surface reactor of this type is its negligible pressure loss, in addition to its small size and weight.

## 2. NUMERICAL MODEL

#### 2.1. Model Assumptions

The flow regime is assumed to be steady, incompressible and laminar. The gas mixture is treated as an ideal gas with variable properties based on the local composition. The gas flow mixture consists of 7 species:  $CH_4$ ,  $O_2$ , CO,  $CO_2$ ,  $H_2$ ,  $H_2O$ and  $N_2$ . Furthermore, Dufour and Soret effects are neglected in the species mass diffusion.

The schematic of microreactor is indicated in Fig. 1 which is made from a simple microchannel with catalyst layer on its inside walls.



Fig. 1. Schematics and dimensions of the microchannel reactor.

## 2.2. Governing Equations

Governing equations include conservations of mass, momentum, energy and chemical species, as well as the ideal gas mixture equation. The continuity equation for a steady-state flow in a Cartesian coordinate is given by Eq. 1.

$$\nabla \left(\rho \vec{V}\right) = 0 \tag{1}$$

The conservation of momentum is stated by the Navier-Stokes equation, given below.

$$\vec{V}.\nabla(\rho \,\vec{V}) = -\nabla p + \nabla \cdot \left(\mu \,\nabla \vec{V}\right) \tag{2}$$

Chemical species conservation for the  $i^{\text{th}}$  species is given by Eq. 3, with the molar production rate given by Eq. 4.

$$\nabla (\rho \vec{V} Y_i) = \nabla (D_{eff,i} \rho \nabla Y_i) + \omega_i M W_i$$
(3)

$$\omega_i = \rho_{cat} \sum_{j=1}^{4} \left( \xi_{ij} R_j \eta_j \right)$$
(4)

Nitrogen does not participate in any reaction, therefore, Eqs. 3 and 4 are applied only for 6 species. Nitrogen mass fraction is obtained from Eq. 5.

$$Y_{N_2} = 1 - \sum_{i, i \neq N_2} Y_i$$
 (5)

It is necessary to note that the source term,  $\omega_i M W_i$ , in Eq. 3 is zero for the internal cells of the computational domain, because reactions occur only on the walls.

Conservation of energy is implemented to calculate the temperature, as given by Eq. 6.

$$\nabla \cdot \left(\rho c_p \vec{V} T\right) = \nabla \cdot \left(k \nabla T\right) + \rho_{cat} \sum_{i=1}^{4} \left(\Delta H_i R_i \eta_i\right)$$
(6)

For the same reason given above, the source term in this equation is non-zero only on the internal walls of the reactor.

Gas mixture density is computed using the ideal gas relationship for a multi-component mixture which is given in Eq. 7. However, since the temperature and pressure have negligible variations along the simulated ATR microreactor, the temperature and pressure are taken at their inlet values in the following equation.

$$\rho = \frac{P M W_{mix}}{R_u T} \tag{7}$$

The mixture molecular weight in the above equation is computed from the following.

$$MW_{mix} = \sum_{i} \chi_{i} MW_{i} = \frac{1}{\sum_{i} \frac{Y_{i}}{MW_{i}}}$$
(8)

The effective mass diffusion coefficient,  $D_{eff}$ , in Eq. 3 is computed using Eq. 9.

$$D_{eff,i} = \frac{1 - \chi_i}{\sum_{j \neq i}^{\forall j} \frac{\chi_j}{D_{ij}}}$$
(9)

In this equation  $D_{ij}$  is the binary diffusion coefficient. The binary mass diffusivity is calculated by the relationships given by Reid et al. [10]. The methodology is based on the Chapman-Enskog theoretical description of a binary mixture of gases at low to moderate pressures. In this theory, the binary diffusion coefficient for the species pair *i* and *j* is given by Eqs. 10-14.

$$D_{ij} = \frac{0.0266 T^{3/2}}{P M W_{ij}^{1/2} \sigma_{ij}^2 \Omega_D}$$
(10)

$$MW_{ij} = 2[(1/MW_i) + (1/MW_j)]^{-1}$$
(11)

$$\sigma_{ij} = (\sigma_i + \sigma_j)/2 \tag{12}$$

$$T^* = k_B T / (\varepsilon_i \, \varepsilon_j)^{1/2} \tag{14}$$

Table 1 gives the values of hard-sphere collision diameter,  $\sigma$ , as well as Lennard-Jones energy,  $\varepsilon$ , for various species involved in our calculations.

Table 1. Hard-sphere collision diameter and Lennard-Jones energy parameter for each species.

Species	$\sigma\left(\stackrel{\circ}{ m A} ight)$	$\varepsilon/k_B(K)$
$CH_4$	3.758	148.6
$O_2$	3.467	106.7
$CO_2$	3.941	195.2
$H_2O$	2.641	809.1
CO	3.690	91.7
$H_2$	2.827	59.7
Na	3 798	714

The constant pressure specific heat, dynamic viscosity, and thermal conductivity of the gas mixture are computed using Eqs. 15-17.

$$c_{p,eff} = \sum_{i} c_{p,i} Y_i \tag{15}$$

$$\mu_{eff} = \sum_{i} \mu_i Y_i \tag{16}$$

$$k_{eff} = \sum_{i} k_i \chi_i \tag{17}$$

Methane conversion is given by the following equation.

$$CH_4 \ conversion \ (\%) = \frac{\chi_{CH_4}^{in} - \chi_{CH_4}^{out}}{\chi_{CH_4}^{in}} \times 100$$
(18)

#### 2.3. Chemical Kinetics

Most proposed mechanisms for ATR contain many reactions which make the numerical simulations complex and difficult to solve. Some of these reactions are reported by Halabi et al. [9]. Excluding the non-significant reactions that posses low rates is a usual approach that makes the calculations practicable with reasonable accuracy. Therefore, as it has been shown (Hoang [1], Halabi [9]) that four reactions can be considered as the major reactions which are listed below. 1) The exothermic total combustion of methane,

**R1**:  $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad \Delta H_{298} = -802 \text{ kJ/mol}$ 

(19)2) The endothermic steam reforming of methane to carbon monoxide,

**R2**:  $CH_4 + H_2O \leftrightarrow CO + 3H_2$  $\Delta H_{298} = 206 \text{ kJ/mol}$ (20)3) The water-gas shift reaction,

**R3**:  $CO + H_2O \leftrightarrow CO_2 + H_2$  $\Delta H_{298} = -41 \text{ kJ/mol}$ (21)4) The steam reforming of methane directly to carbon dioxide.

 $\Delta H_{298} = 165 \text{ kJ/mol}$ **R4**:  $CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2$ (22)An acceptable kinetic rate model for methane steam reforming over Ni-based catalyst was reported by Xu and Froment [6]. Their suggested kinetic rate equation has been used extensively in different investigations. Two different kinetic rate equations are reported for the total methane combustion. One is reported by Trimm and Lam [5] and the other is provided by Ma et al. [7]. The former is for methane combustion over Pt-based catalyst at a fixed temperature, while the latter is based on the Langmuir-Hinshelwood model adjusted for Ni-based catalyst.

In the present study, SR and WGS reaction rates are computed using the model suggested in Xu and Froment [6], and the reaction rate of methane combustion is obtained from Ma et al. [7].

The corresponding kinetic rate equations for the above reactions are given in Eqs. 23-27.

$$R_{1} = \frac{k_{1} p_{CH_{4}} p_{O_{2}}^{1/2}}{\left(1 + K_{CH_{4}}^{C} p_{CH_{4}} + K_{O_{2}}^{C} p_{O_{2}}^{1/2}\right)^{2}}$$
(23)

$$R_{2} = \frac{k_{2}}{p_{H_{2}}^{2.5}} \left( p_{CH_{4}} p_{H_{2}O} - \frac{p_{H_{2}}^{3} p_{CO}}{K_{e^{2}}} \right) \times \frac{1}{Q_{r}^{2}}$$
(24)

$$R_{3} = \frac{k_{3}}{p_{H_{2}}} \left( p_{CO} p_{H_{2}O} - \frac{p_{H_{2}} p_{CO_{2}}}{K_{e^{3}}} \right) \times \frac{1}{Q_{r}^{2}}$$
(25)

$$R_{4} = \frac{k_{4}}{p_{H_{2}}^{3.5}} \left( p_{CH_{4}} p_{H_{2}O}^{2} - \frac{p_{H_{2}}^{4} p_{CO_{2}}}{K_{e^{4}}} \right) \times \frac{1}{Q_{r}^{2}}$$
(26)

$$Q_r = 1 + K_{CO} p_{CO} + K_{H_2} p_{H_2} + K_{CH_4} p_{CH_4} + K_{H_2O} \frac{p_{H_2O}}{p_{H_2}}$$
(27)

In the above relations,  $k_j = k_{oj} \times e^{(-E_j)/R_uT}$  is the kinetic rate constant of reaction j (j = reactions R1-R4), in which  $k_1$  is determined from the data of Ma et al. [7], while  $k_2$  to  $k_4$  are from Xu and Froment [6].  $k_{oj}$  and  $E_j$  are given in Table 2.  $K_{e^j}$  in Eqs. 24-26 is the equilibrium constant of reaction j (j = reactions R2-R4) which can be found in Table 3.  $K_i^C = K_{oi}^C \times e^{(-\Delta H_c^C)/R_uT}$  in Eq. 23 is the adsorption constant of species i (i = CH<sub>4</sub>, O<sub>2</sub>) in the combustion reaction R1 and can be found in Table 4. Furthermore,  $K_i = K_{oi} \times e^{(-\Delta H^i)/R_uT}$  in Eq. 27 is the adsorption constant of species i (i = CO, H<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>O) in the reforming reactions R2-R4. The values of  $K_{oi}$  and  $\Delta H^i$  can be found in Table 4.

Table 2. Kinetic parameters.

Reaction	<i>k<sub>oj</sub></i> (kmol/kg cat h)	<i>E<sub>i</sub></i> (kJ/kmol)	
R1	$5.852 \times 10^{17}  (bar^{-1.5})$	204,000	
R2	$4.225 \times 10^{15} (bar^{0.5})$	240,100	
R3	$1.955 \times 10^{6} (bar^{-1.0})$	67,130	
R4	$1.020 \times 10^{15} (bar^{0.5})$	243,900	
	Table 3. Equilibrium cor	nstants.	
Reaction	Equilibrium constant $K_{e^j}$		
R2	$5.75 \times 10^{12} \exp(-11476/T) (bar^2)$		
R3	$1.26 \times 10^{-2} \exp(4639/T)$		
R4	$7.24 \times 10^{10} \exp(-21646/T)$ (bar <sup>2</sup> )		

Species	Eq. no.	K <sub>oi</sub> (/bar)	<i>∆H<sup>i</sup></i> (kJ/kmol)
O <sub>2</sub>	23	$5.08 \times 10^4 (\text{bar}^{0.5})$	66,200
$CH_4$	23	$4.02 \times 10^{5}$	103,500
$H_2$	27	$6.12 \times 10^{-9}$	-82,900
$CH_4$	27	$6.65 \times 10^{-4}$	-38,280
$H_2O$	27	$1.77 \times 10^{5}$ bar	88,680
CO	27	$8.23 \times 10^{-5}$	-70,650

The final equations for the calculation of the reaction rate for each species are summarized as follows:

 $r_{CH4} = -\eta_1 R_1 - \eta_2 R_2 - \eta_4 R_4$   $r_{O2} = -2\eta_1 R_1$   $r_{CO2} = \eta_1 R_1 + \eta_3 R_3 + \eta_4 R_4$   $r_{H2O} = 2\eta_1 R_1 - \eta_2 R_2 - \eta_3 R_3 - 2\eta_4 R_4$   $r_{CO} = \eta_2 R_2 - \eta_3 R_3$   $r_{H2} = 3\eta_2 R_2 + \eta_3 R_3 + 4\eta_4 R_4$ (28)

As can be seen, the kinetics given by [6] implies that the rate coefficients (R1-R4) depend on the activation energies,  $E_a$ , as well as the adsorption enthalpies  $\Delta H^i$ .

#### 2.4. Boundary conditions

Velocity, pressure, temperature and composition of the inlet gas mixture are specified at the microchannel inlet. The channel walls are resistant to thermal energy (adiabatic), and are permeable to species mass transfer due to surface reactions. The no-slip condition is used at the microreactor walls. The outflow mixture is discharged to atmospheric pressure, and the gradients of all other dependent variables are set to zero at the microreactor outlet.

#### 2.5. Solution method

In order to solve the non-linear, coupled governing equations, a computational fluid dynamics (CFD) code was developed based on the finite volume method using the SIMPLE algorithm for the coupling of pressure and velocity domains [11]. To linearize the convective and diffusive terms the power-law scheme and the central difference scheme is applied, respectively [12, 13].

# 3. RESULTS AND DISCUSSION

#### 3.1. Validation

In order to qualitatively validate the present work, the experimental results reported by Dias and Assaf [14] are considered here. They performed experiments for methane ATR at different temperatures on a Ni/Al<sub>2</sub>O<sub>3</sub> catalyst in a packed-bed reactor with 9 mm diameter and 10 mm length. Numerical simulations are also performed for identical dimensions and conditions using the present CFD code, with the difference that in our simulations the catalytic reactions occur only on the reactor wall surfaces. The simulation results for the variation of H<sub>2</sub> and CO versus inlet temperature are compared with the corresponding experimental data in Fig. 2.



Fig. 2. Comparison of the outlet mole fractions of H<sub>2</sub> from present simulation results with experimental data.

The general trends are very similar, but the simulated surface reactor shows lower conversion compared with the actual packed-bed reactor. This was obviously expected, since the two reactors have the same dimensions and operating conditions but the packed-bed reactor has more reaction sites available. Nonetheless, it is observed in both sets of results that increasing temperature leads to an increase in both the  $H_2$  and CO production.

# 3.2. Baseline simulation

The operating conditions for the baseline case are specified in Table 5.

Table 5. Operating conditions for the baseline case.

Parameter	Value
Space velocity $(h^{-1})$	20,000
Molar A/F ratio	3.5
Molar W/F ratio	1.0
Inlet temperature (K)	873
Inlet pressure (Pa)	101,325

Species mole fraction and temperature variations along the microchannel are presented in Fig. 3 for the baseline conditions. It is seen in this figure that most of the methane consumption occurs in the first quarter of the microchannel length which results from high kinetic rates of total combustion of methane (R1) and then SR of methane to CO (R2).  $CO_2$  mole fraction keeps rising along the microchannel length, although it reaches 75% of its final value at the first 5% of the channel length due to high kinetic rates of reactions R1 and R2 (Eqs. (19) and (20)).



Fig. 3. Variations of the species mole fractions and temperature along the microchannel for the baseline conditions.

The variation of  $H_2$  mole fraction is also shown in Fig. 3. Hydrogen production is the main objective of the ATR reactor which appears in reactions R2-R4 (SR and WGS reactions). The hydrogen mole fraction increases to 85% of its final value in the middle of the microchannel, while it keeps an increasing trend at a lower rate in the second half of the microchannel length. The temperature variation along the microchannel indicates that the temperature varies very little (less than 2°C) along the channel, which is consistent with the nature of the overall process being autothermal.

The simulation results for the baseline conditions show that the outlet  $H_2$  mole fraction is 18.5% (dry basis), while there is also 6.5% CO at the reactor outlet. It is noted that the microreactor considered in this investigation is of a surface reaction type; hence a lower hydrogen production is expected compared with a packed-bed reactor for the same space velocity and gas feed composition.

#### 3.3. Parametric study

In this section, the influence of different parameters on hydrogen yield and carbon monoxide production of the microreactor are investigated. These parameters include space velocity, gas feed temperature, air/CH<sub>4</sub>-supplied molar ratio (A/F), and water/CH<sub>4</sub>-supplied molar ratio (W/F).

#### 3.3.1. Effects of space velocity

Presented in Fig. 4 are the variations of the outlet species mole fractions for a space velocity range among 1,000-100,000  $h^{-1}$  with other parameters at their baseline values (given in Table 5). These results indicate that the outlet mole fraction of methane increases as SV is increased. Fig. 4 also shows that the outlet carbon dioxide mole fraction decreases as SV is increased. Although the production of carbon dioxide is chiefly due to total combustion of methane, however reaction R4 also has some contribution in the CO<sub>2</sub> production.



Fig. 4. Effect of space velocity on outlet species mole fractions (other parameters at their baseline values).

#### 3.3.2. Effects of gas feed temperature

Variations of the outlet mole fractions of hydrogen and carbon monoxide with the gas feed temperature are presented in Fig. 5, with other parameters at their baseline values. These results show that the mole fractions of both hydrogen and carbon monoxide increase as the inlet temperature is increased in the range of 400-600°C. This is mainly due to an increase in the rate of SR reactions R2 and R4 with temperature, as can be inferred from their activation energy values given in Table 2. The hydrogen mole fraction is 18% at a temperature of 600°C which is about 4.5 times more than that at 400°C.



Fig. 5. Effect of inlet temperature on outlet dry mole fractions of: (a)  $H_2$  and (b) CO.

#### 3.3.3. Effects of A/F and W/F molar ratios

Presented in Fig. 6(a) is the variation of methane outlet mole fraction (dry basis) versus A/F ratio, with W/F ratio as variable; other parameters are at their baseline values. Fig. 6(b) shows methane conversion corresponding to the above conditions. It is seen that by increasing air or water content of the gas feed mixture, methane outlet fraction will decrease, i.e., its conversion will increase.

Outlet hydrogen and CO mole fractions (dry basis) versus A/F ratio are plotted in Fig. 7, with W/F ratio as variable and other parameters at their baseline values. It is observed in Fig. 7(a) that by decreasing A/F ratio or increasing W/F ratio the outlet hydrogen mole fraction is increased, which is very desirable for fuel cell applications. In fact, the maximum outlet H<sub>2</sub> mole fraction is 38.5% (dry basis) which occurs at A/F ratio of 1.0, W/F ratio of 3.0, and other parameters at the given baseline conditions (SV of 20,000 h<sup>-1</sup> and gas feed temperature of 600°C).



Fig. 6. Effect of A/F ratio on (a) outlet methane mole fraction and (b) methane conversion, for different W/F ratios.

Once again, by decreasing the inlet air content the combustion reaction of methane (R1) is demoted and less methane is consumed by this reaction. This will promote the SR reactions directly, and the WGS reaction indirectly, which will result in more generation of hydrogen. Furthermore, increasing the inlet water content will promote the same reactions which will further increase hydrogen production.

Fig. 7(b) shows that increasing either A/F ratio or W/F ratio will decrease the outlet CO content; this is also desirable in fuel cell applications. For the given range of parameters simulated here, the lowest mole fraction of CO is 2.3% which is obtained at A/F ratio of 5.0, W/F ratio of 3.0 and other parameters at their baseline values.

Increasing the inlet air content will consume more methane by the combustion reaction, leaving less methane available to the SR reactions. This in turn will give less chance for CO generation. Also, as the inlet water content is increased, both the SR and WGS reactions (R2-R4) are promoted. However, the WGS reaction is more sensitive to this increase, which causes a reduction in the outlet CO content.



Fig. 7. Effect of A/F ratio on outlet mole fractions of (a) H<sub>2</sub> and (b) CO, for different W/F ratios.

# 4. CONCLUSIONS

In this study, catalytic autothermal reforming of methane is simulated in a rectangular surface microreactor using a threedimensional CFD model. The main global surface reactions are included that consist of methane total combustion, steam reforming of methane to CO and CO<sub>2</sub>, and the water-gas shift reaction. The governing equations include conservations of mass, momentum, energy and chemical species, as well as the ideal gas mixture equation of state. A CFD code based on the finite volume method was developed to solve the non-linear, coupled governing equations. The following conclusions are drawn from the study:

• Pressure gradient along the microchannel is negligible.

• Temperature variation along the microreactor is less than 4°C; consequently, the process is effectively isothermal.

• Hydrogen production reaches its maximum value at a space velocity of 50,000  $h^{-1}$  for the given baseline conditions.

• Both hydrogen and CO outlet mole fractions increase with the gas feed temperature in the range of 400-600°C.

• Methane conversion increases with increasing A/F ratio or W/F ratio; it reaches its peak value at A/F ratio of 5.0 almost independent of W/F ratio.

• Hydrogen production is promoted by increasing W/F ratio or decreasing A/F ratio.

• Increasing either A/F ratio or W/F ratio hinder CO generation.

Such ATR surface microreactor will be an essential component in the development of a complete micro-fuel processor for fuel cell applications in portable electronic devices.

#### 5. NOMENCLATURE

- $c_p$  constant pressure specific heat (kJ / kg.K)
- D binary diffusion coefficient  $(m^2/s)$
- *E* activation energy (kJ / kmol)
- $\Delta H$  reaction enthalpy (kJ/kmol)
- k thermal conductivity (W / m.K) or kinetic rate constant
- *K* adsorption constant in reactions R2-R4

 $k_B$  Boltzmann constant (1.38×10<sup>-23</sup> J/K)

- $k_o$  pre-exponent coefficient of kinetic rate constant
- $K^C$  adsorption constant in reaction R1
- $K_e$  equilibrium constant in reactions R2-R4
- $K_o$  pre-exponent coefficient of adsorption constant in reactions R2-R4
- $K_o^C$  pre-exponent coefficient of adsorption constant in reaction R1
- MW molecular weight (kg / kmol)
- *p* partial pressure (*bar*)
- *P* pressure (*Pa*)

- r species reaction rate ( $kmol/kg_{cat}$  h)
- R total reaction rate  $(kmol/kg_{cat} h)$
- $R_{\mu}$  universal gas constant (8.315 kJ / kmol.K)
- T temperature (K)
- $T^*$  dimensionless temperature
- *u x*-velocity component (m / s)
- $\vec{V}$  velocity vector (m/s)
- *v y*-velocity component (m / s)
- w z-velocity component (m/s)
- x x-direction coordinate (m)
- *y y*-direction coordinate (m)
- *Y* species mass fraction
- z z-direction coordinate (m)

# **Greek symbols**

- $\varepsilon$  Lennard-Jones energy (J)
- $\eta$  reaction effectiveness factor
- $\xi$  stoichiometry coefficient
- $\mu$  kinematic viscosity  $(N.s/m^2)$
- $\omega$  species surface reaction rate  $(kmol / m^2.s)$
- $\Omega_D$  collision integral
- $\rho$  density  $(kg / m^3)$
- $\rho_{cat}$  catalyst surface density  $\left(kg / m^2\right)$
- $\sigma$  species molecular diameter  $\begin{pmatrix} \circ \\ A \end{pmatrix}$
- $\chi$  species mole fraction

# Sub- or superscripts

- cat catalyst
- eff effective
- *in* inlet
- i  $i^{\text{th}}$  species or reaction

- j  $j^{\text{th}}$  species or reaction
- mix gas mixture
- out outlet
- *vol* volumetric reaction

# 6. REFERENCES

[1] Hoang DL, Chan SH. Modeling of a catalytic autothermal methane reformer for fuel cell applications. Appl Catal A: General 2004;268:207-216.

[2] Armor JN. Catalysis and the hydrogen economy. Catal Letter 2005;101:131-135.

[3] Aasberg-Petersen K, Christensen TS, Nielsen CS, Dybkjaer I. Recent developments in autothermal reforming and pre-reforming for synthesis gas production in GTL applications. Fuel Processing Tech 2003;83:253-261.

[4] Heinzel A, Vogel B, Hubner P. Reforming of natural gas-hydrogen generation for small scale stationary fuel cell systems. J Power Sources 2002;105:202-207.

[5] Trimm DL, Lam C. The combustion of methane on Platinum-Alumina fibre catalysis I: kinetics and mechanism. Chem Eng Sci 1980;35:1405-1413.

[6] Xu J, Froment GF. Methane steam reforming, methanation and water-gas shift I: intrinsic kinetics. AIChE J 1989;35:88-96.

[7] Ma L, Trimm DL, Jiang C. The design and testing of an autothermal reactor for the conversion of light hydrocarbons to hydrogenI: the kinetics of the catalytic oxidation of light hydrocarbons. Appl Catal A: General 1996;138:275-283.

[8] de Groote AM, Froment GF. Simulation of the catalytic partial oxidation of methane to synthesis gas. Appl Catal A: General 1996;138:245-264.

[9] Halabi MH, de Croon MHJM, der Schaaf JV, Cobden PD, Schouten JC. Modeling and analysis of autothermal reforming of methane to hydrogen in a fixed bed reformer. Chem Eng J 2008;137:568-578.

[10] Reid RC, Prausnitz JM, Poling BE. The properties of gases and liquids. New York: McGraw-Hill, 1987.

[11] Patankar SV. Numerical heat and fluid flow. New York: Hemisphere, 1980.

[12] Hirsch C. Numerical computational of internal and external flows. Burlington: Wiley, 2007.

[13] Versteeg HK, Malalaskerea W. An introduction to computational fluid dynamics: the finite volume method. New York: Longman, 1995.

[14] Dias JAC, Assaf JM. Autothermal reforming of methane over  $Ni/\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts: the enhancement effect of small quantities of noble metals. J Power Sources 2004;130: 106-110.