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CFD Modeling of PROX Microreactor for Fuel Processing

M. Vahabi, and M. H. Akbari

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***Abstract*—**In order to investigate a PROX microreactor performance, two-dimensional modeling of the reacting flow between two parallel plates is performed through a finite volume method using an improved SIMPLE algorithm. A three-step surface kinetics including hydrogen oxidation, carbon monoxide oxidation and water-gas shift reaction is applied for a Pt-Fe/γ-Al_2O_3 catalyst and operating temperatures of about 100ºC. Flow pattern, pressure field, temperature distribution, and mole fractions of species are found in the whole domain for all cases. Also, the required reactive length for removing carbon monoxide from about 2% to less than 10 ppm is found. Furthermore, effects of hydraulic diameter, wall temperature, and inlet mole fraction of air and water are investigated by considering carbon monoxide selectivity and conversion. It is found that air and water addition may improve the performance of the microreactor in carbon monoxide removal in such operating conditions; this is in agreement with the pervious published results.

***Keywords*—**CFD, Fuel Processing, PROX, Reacting Flow, SIMPLE algorithm.

I. INTRODUCTION

NOWADAYS exploitation of hydrogen rather than conventional sources of energy is in the spot light because of its high energy density and low environmental impact. Usually methane or methanol is used for hydrogen generation which also generates some amount of carbon monoxide. However, if the mole fraction of carbon monoxide exceeds 10 ppm in the reformate, the catalyst of some fuel cell types (such as PEMFC) will be damaged. In such cases removing carbon monoxide in a hydrogen-rich stream is a vital issue when hydrogen is used as the source of energy. One of the methods to reduce the carbon monoxide content of a hydrogen-rich stream is preferential oxidation of carbon monoxide (PROX).

Microreactors are considered for the generation of the required hydrogen to power small portable devices such as laptops and mobile phones. Application of microreactor improves mass and heat transfer characteristics of the fuel processor due to its high surface-to-volume ratio. It also improves the response time of the fuel processor. Another important advantage of a microreactor is its safety of handling smaller quantities of materials, especially in hazardous reactions [1].

Several detailed kinetic rate equations are proposed in the literature for the preferential oxidation of carbon monoxide, depending on the catalyst type and operating temperature. However, Pt-based catalysts are more attractive in preferential oxidation because of their high conversion capabilities and their stabilities. Choi and Stenger [2] studied experimentally CO preferential oxidation for the Pt-Fe/γ-Al_2O_3 catalyst with operating temperatures between 100 and 300ºC, and proposed rate expressions for a three-step kinetics. They also showed that adding water will increase the performance of a PROX reactor. Ouyang et al. [3] simulated a PROX microreactor applying plug-flow model with three global reactions and 28 detailed surface reactions for the Pt-Fe/γ-Al_2O_3 catalyst using CHEMKIN package. They showed that mass transfer does not affect the kinetics below 220ºC.

Ternan [4] reported four different processes for purification of hydrogen including preferential oxidation, and suggested three methods to decrease the size of a PROX reactor including water addition and higher working temperature, although it is mentioned that the latter has an inverse effect on CO selectivity.

Sirijarphan et al. [5] experimentally studied effects of temperature and pressure on the surface kinetics of PROX reactions for the Pt/γ-Al_2O_3 catalyst and reported that conversion of CO is increased by increasing working temperature and pressure in the range of 80 to 110ºC and 1.2 to 3 atm.

In most numerical studies reported in the literature (i.e. [6]) simulation of a PROX reactor has been done by neglecting flow pattern and pressure gradients along the reactor, which is not always a realistic approximation. In this work numerical simulation of a reacting flow containing carbon monoxide and hydrogen is performed in a two dimensional channel. The aim is to prepare a stream with less than 10 ppm carbon monoxide content that is suitable for proton exchange membrane fuel cells (PEMFC). This is done by solving conservation equations of mass, momentum, energy, and species for an ideal mixture with three surface reactions. The required reactor length for the removal of CO to less than 10 ppm, and the effects of various parameters on the microreactor performance are investigated.

II. PROBLEM FORMULATION

In order to simulate the reacting flow in the catalytic microreactor, it is necessary to solve simultaneously the conservation equations of mass, momentum, energy, and species as well as the state equation of an ideal mixture.

Authors are with Department of Mechanical Engineering., Shiraz University, Shiraz, 71348-51154, Iran (e-mail: mo_vahabi@yahoo.com, corresponding author; phone: +98 (711) 613-3444; e-mail: akbari@eng.shirazu.ac.ir).

Furthermore, considering the Knudsen number of this flow which is about 0.0005, application of the Navier-Stokes equations is admissible [7]. These equations for a steady laminar flow are as follows:

$$\vec{\nabla}\cdot(\rho\vec{u})=0 \tag{1}$$

$$(\vec{u}\cdot\vec{\nabla})(\rho\vec{u})+\vec{\nabla}p=\vec{\nabla}\cdot(\mu\vec{\nabla}\vec{u}) \tag{2}$$

$$\vec{\nabla}\cdot(\rho c_p\vec{u}T)=\vec{\nabla}\cdot(k\vec{\nabla}T)+\dot{Q} \tag{3}$$

$$\vec{\nabla}\cdot(\rho\vec{u}Y_i)-\vec{\nabla}\cdot(\rho D_{eff,i}\vec{\nabla}Y_i)=\dot{\omega}_i MW_i \tag{4}$$

In these equations ρ, $\vec{u}$, μ, c_p, T, $\dot{Q}$, Y, D_{eff}, $\dot{\omega}$ and MW are density, velocity vector, dynamic viscosity, constant pressure specific heat, temperature, heat source, mass fraction, effective diffusivity, production rate of species and molecular weight, respectively.

Based on a finite volume method, the two-dimensional steady laminar flow with surface reactions is simulated using SIMPLE algorithm with power-law scheme. In order to reach a stable converged solution, nonlinear coupled equations are solved in a two-step procedure called cold and hot steps. In the cold step, flow is considered to be non-reactive, and in the hot step the reactions are allowed to occur. Furthermore, all flow parameters are underrelaxed.

Because of the slight temperature difference between the inlet and outlet of the PROX microreactor, it is assumed that the fluid properties are only dependent on the mass fraction of the species, and are calculated at the operating temperature. Multicomponent mass diffusivity coefficients are calculated based on binary assumption [8]. Therefore, mixture properties including viscosity, conductivity, and specific heat are calculated based on species mass fractions and at the local temperature. Because temperature and pressure variations are negligible, mixture density is calculated in each cell assuming an ideal mixture at the operating temperature and pressure, as follows (R_u is the universal gas constant):

$$\rho_{mix}=\frac{P_{op}MW_{mix}}{R_u T_{op}} \tag{5}$$

In this study a three-step kinetics is applied for the Pt-Fe/γ-Al_2O_3 catalyst at operating temperatures of about 100ºC. This includes hydrogen oxidation, carbon monoxide oxidation and water-gas shift reaction. These reactions are as follows:

$$CO+\frac{1}{2}O_2\rightarrow CO_2, \qquad \Delta H_1=-283\,kJ/mol \tag{6}$$

$$H_2+\frac{1}{2}O_2\rightarrow H_2O, \qquad \Delta H_2=-242\,kJ/mol \tag{7}$$

$$H_2O+CO\leftrightarrow CO_2+H_2, \qquad \Delta H_3=-41.1\,kJ/mol \tag{8}$$

Rate expressions of these equations are evaluated experimentally in [2], and are as follows (in equations 9 to 11, partial pressures are in atmospheric units):

$$r_1=3.528\times10^2\exp\left(\frac{-33092}{R_uT}\right)P_{O_2}^{0.5}P_{CO}^{-0.1} \tag{9}$$

$$r_2=2.053\times10\exp\left(\frac{-18742}{R_uT}\right)P_{O_2}^{0.5} \tag{10}$$

$$r_3=4.402\times10^3\exp\left(\frac{-34104}{R_uT}\right)\left(P_{CO}P_{H_2O}-\frac{P_{CO_2}P_{H_2}}{K_p}\right) \tag{11}$$

$$\text{where } K_P=\exp\left(\frac{4577.8}{T}-4.33\right) \tag{12}$$

III. BOUNDARY CONDITIONS

Inlet mole fractions of species (H_2, CO_2, H_2O, CO, O_2 and N_2) are predefined. Furthermore, inlet temperature is set to 90ºC and the outlet pressure is fixed at the atmosphere pressure. The microreactor walls are assumed to be at a constant temperature; isothermal condition is an advantage of microreactors over conventional reactors. The reactions occur only on the walls.

The Knudsen number for the reactor is calculated at around 0.0005, hence all cases are in the continuum regime [5]. Thus, the use of the Navier-Stokes equations with no-slip condition on the walls is permutable.

The gradient of all mixture properties at the outlet are set equal to zero. Since the geometry and inlet conditions of this problem are axisymmetric, it is sufficient to simulate only bottom half of the domain.

IV. SIMULATION RESULTS

Several simulations for different hydraulic diameters and inlet conditions with isothermal walls are performed using a uniform 187×24 grid. The required reactor length for reducing carbon monoxide to less than 10 ppm is found in each case. Convergence history is plotted in Fig. 1 for a case in which the convergence criterion is set to 10^{-7} for all variables.

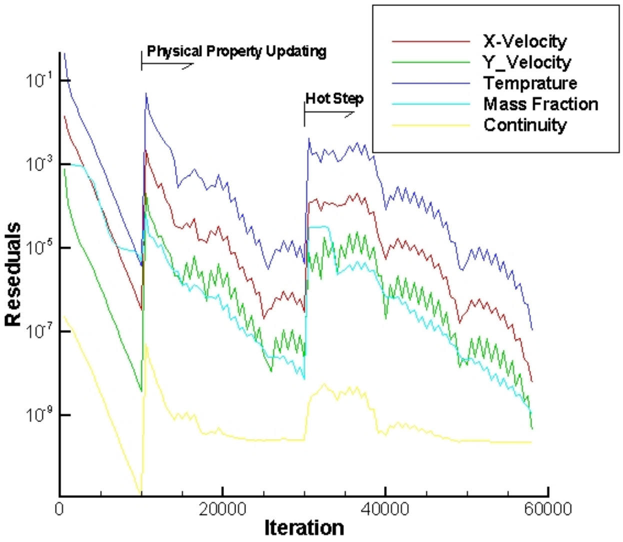

Fig. 1 Sample convergence history

Contours of mixture density, mass flux, velocity components, pressure, temperature, CO and H_2 mole fractions are presented in Figures 2 to 9 for an inlet mixture containing H_2 (9.5×10^{-8} m^3/s), CO_2 (3.22×10^{-8} m^3/s), H_2O (0.48×10^{-8} m^3/s), CO (0.48×10^{-8} m^3/s), and air (6.85×10^{-8} m^3/s). Hydraulic diameter, wall temperature, and inlet temperature for this case are set to 300 micron, 100ºC, and 90ºC, respectively. Note that the hydraulic diameter of the present geometry (two parallel infinite plates) is calculated as below:

$$D_h = \frac{4A}{P} = \lim_{w\to\infty}\frac{4\times h\times w}{2\times(h+w)} = 2h \qquad (13)$$

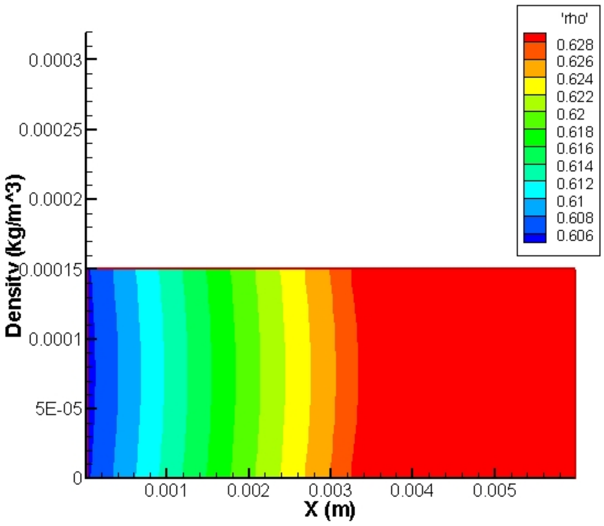

Fig. 2 Contours of mixture density

In the reactions given by equations (6) and (7) the number of moles is decreased, and the third reaction (equation (8)) is mole balanced. Therefore, the mixture molecular weight is increased along the reactor which leads to an increase of the density according to equation (5). However, the total mass flux (product of density and horizontal velocity) in each section of the channel is fixed, as indicated in Fig. 3. Therefore, the axial velocity component is to be decreased along the reactor, as its contours are shrunk in Fig. 4.

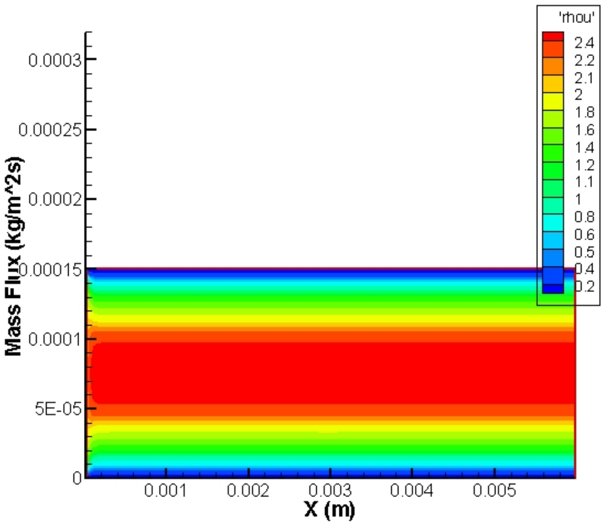

Fig. 3 Contours of mass flux

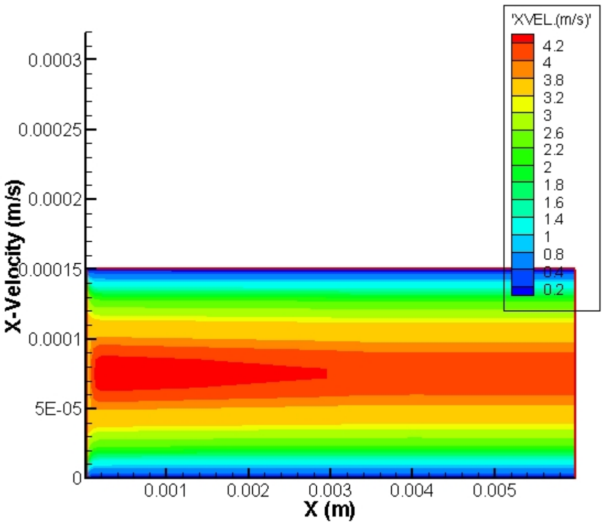

Fig. 4 Contours of the axial velocity component

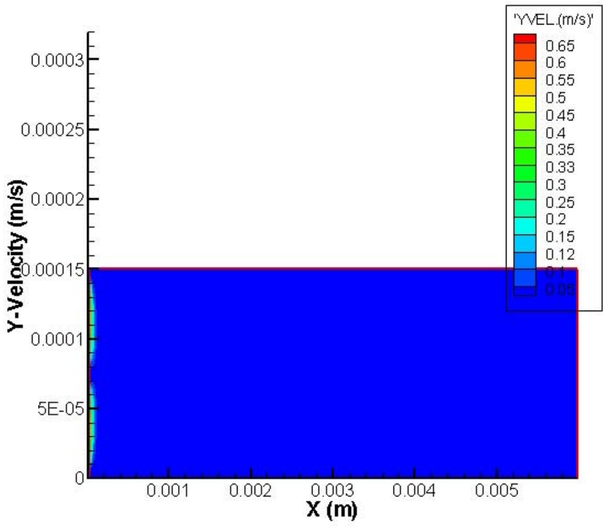

Fig. 5 Contours of the transverse velocity component

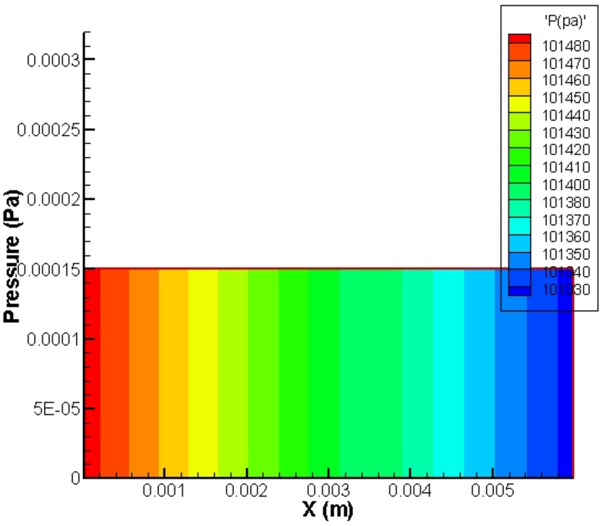

Fig. 6 Contours of static pressure

As shown in Fig. 6, the pressure gradient along the microreactor is below 200 pa. Therefore, compared to the atmospheric working pressure of the reactor, this pressure loss will not have any noticeable effect on the PROX performance.

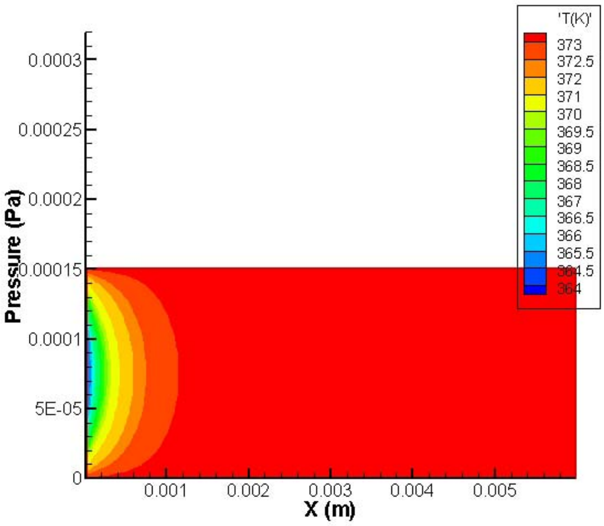

Fig. 7 Contours of static temperature

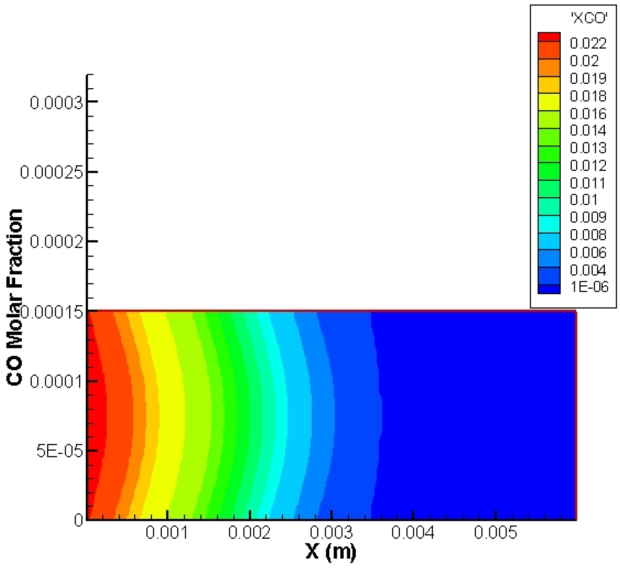

Fig. 8 Contours of CO mole fraction

According to the results shown in Fig. 8, a microreactor with 6 mm length is enough to reduce CO content from 2-3% to below 10 ppm. It is worth mentioning that by refining the grid to 300×48, virtually no change is observed in the results; it is therefore concluded that our original grid is fine enough to predict the flow domain accurately.

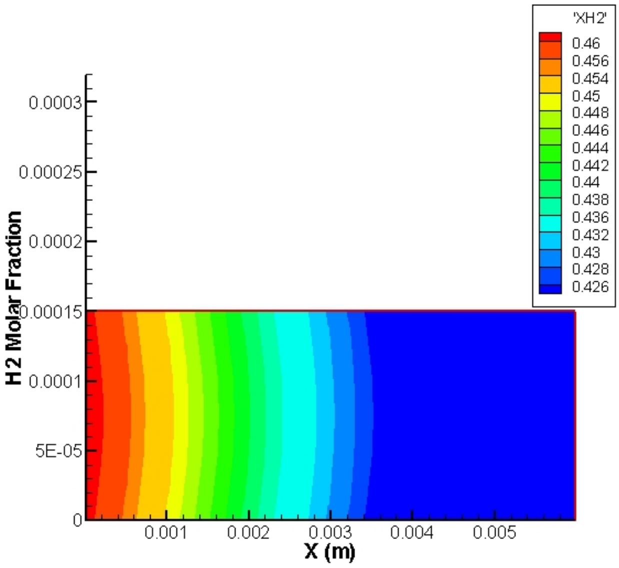

Fig. 9 Contours of H_2 mole fraction

Four case studies are performed in order to evaluate the effects of the inlet temperature, hydraulic diameter, water addition and oxygen to carbon monoxide ratio on the PROX performance.

To interpret the results, CO selectivity and conversion are calculated along the reactor by averaging CO and O_2 at different cross sections. The selectivity and conversion of CO in the PROX microreactor are defined as follows, respectively:

$$S_{CO}(\%) = \frac{0.5\left(n_{CO}^{in} - n_{CO}^{CS}\right)}{n_{O_2}^{in} - n_{O_2}^{CS}} \times 100\% \tag{14}$$

$$C_{CO}(\%) = \frac{\left(n_{CO}^{in} - n_{CO}^{CS}\right)}{n_{CO}^{in}} \times 100\% \tag{15}$$

First, the effect of inlet mixture temperature on CO removal is assessed by changing inlet temperature from 90ºC to 105ºC. The acquired results are presented in Fig. 10. As seen in this figure, the higher inlet temperature results in a higher CO conversion, although CO selectivity is greater at 100ºC. This has been found before through precise experimental studies [5]. Average mole fraction of carbon monoxide in these cases at 3.5 mm are calculated as 7000, 100, and below 1 ppm, respectively.

In order to investigate the effect of hydraulic diameter on CO removal, the above-mentioned mixture is supplied to the microreactor with different hydraulic diameters of 280, 300, and 320 µm. CO selectivity is calculated along the microreactor for each case and plotted in Fig. 11. As seen in this figure, a smaller hydraulic diameter causes a greater selectivity with a smaller CO conversion which means a longer reactor. The average mole fraction of carbon monoxide at section 3.5 mm of the microreactor for theses cases are about 2000, 100, and 1 ppm, respectively.

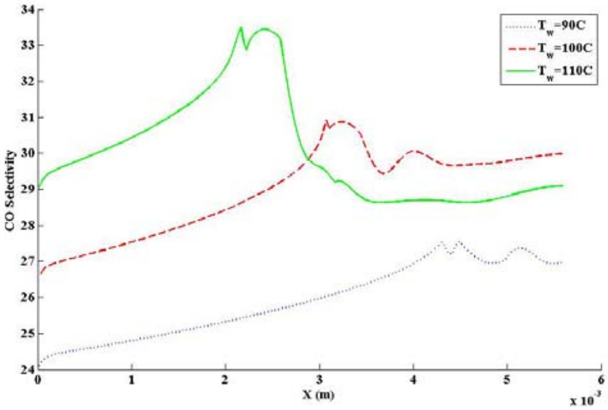

Fig. 10 CO selectivity along the microreactor for different wall temperatures

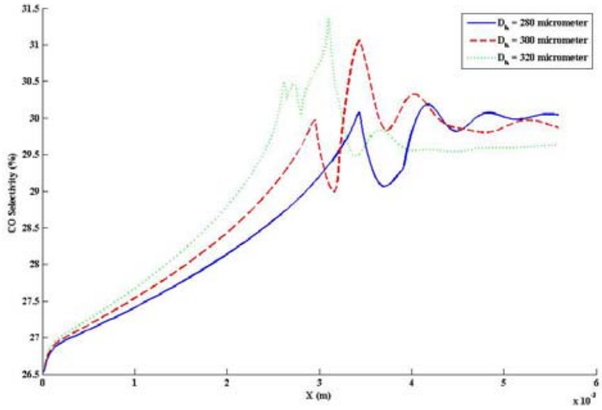

Fig. 11 CO selectivity along the microreactor for three different hydraulic diameters

The effect of water addition on the PROX reactor performance is studied in another case study by supplying two different mixtures to the microreactor where the water content in the second mixture is zero.

1st case: H_2 (9.5×10^{-8} m^3/s), CO_2 (3.22×10^{-8} m^3/s), H_2O (0.48×10^{-8} m^3/s), CO (0.48×10^{-8} m^3/s), and air (6.85×10^{-8} m^3/s).

2nd case: H_2 (9.5×10^{-8} m^3/s), CO_2 (3.22×10^{-8} m^3/s), CO (0.48×10^{-8} m^3/s), and air (6.85×10^{-8} m^3/s).

Comparative results are presented in Fig. 12. Average mole fraction of carbon monoxide at section 4 mm for the former case is 2.0 ppm and for the latter case is 2.3 ppm. Thus, the former case has a greater CO conversion which means that a shorter reactor is needed.

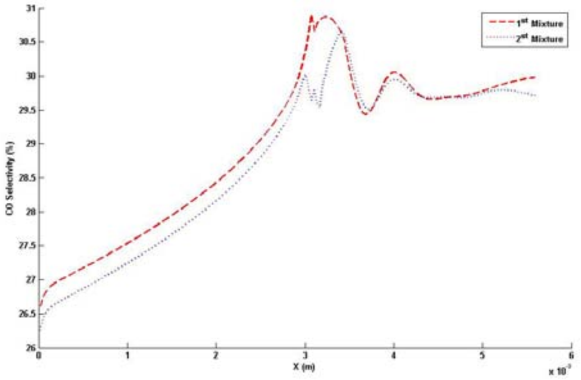

Fig. 12 CO selectivity along the microreactor for dry and wet mixtures

These results indicate that water addition increases CO selectivity and conversion which is in agreement with previous works [2,4].

Finally, the effect of excess oxygen is investigated by altering oxygen to carbon monoxide ratio from 2 to 3.5. Although mixture with the maximum oxygen content has a greater CO conversion but the mixture with oxygen to carbon monoxide ratio of 3 has a greater CO selectivity as seen in Fig. 13. CO average mole fraction at section 3.5 mm of the microreactor for these cases are about 7000, 100, and 10 ppm, respectively.

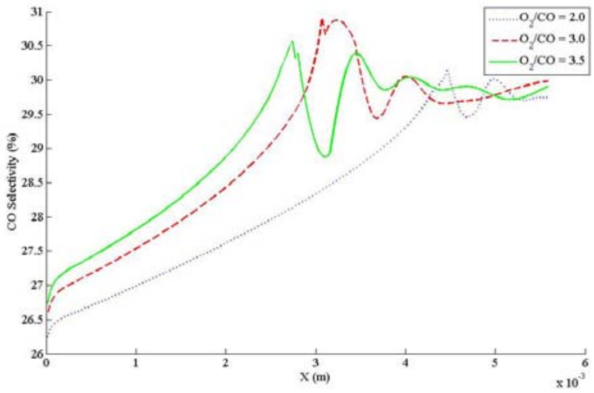

Fig. 13 CO selectivity for various oxygen to carbon monoxide ratios

V. CONCLUSION

In this study several simulations are performed and the effects of wall temperatures, hydraulic diameter, inlet water addition, and excess oxygen on CO selectivity and conversion are investigated for a PROX microreactor. In all cases mole fraction of CO is reduced to below 10 ppm, which is sufficient to feed to a PEMFC.

It is shown that with increasing wall temperature from 90 to 110ºC, CO conversion is increased, but CO selectivity is slightly greater at 100ºC; this is also reported in [5].

It is found that increasing hydraulic diameter can improve CO conversion but it decreases CO selectivity. Thus, it is possible to select more CO in a longer reactor, or to remove more CO with more hydrogen loss in a smaller reactor.

It is also shown that water addition can improve the performance of the microreactor in carbon monoxide removal, which is in agreement with pervious published results [2,4].

Another parameter that affects a PROX reactor performance is O_2/CO ratio. In the range of our operating conditions and mixtures, the best choice for this ratio is found to be 3.0.

Although acquired results are in good agreement with previous studies, for a better prediction of the reacting flow and a parametric study of the PROX microreactor, a more detailed kinetics and three-dimensional simulations are proposed. This will be the aim of our future work.

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