

# A Reformer Performance Model for Fuel Cell Applications

S.S. Sandhu<sup>+,a</sup>, Y.A. Saif<sup>a</sup>, J.P. Fellner<sup>b</sup>

<sup>a</sup>Department of Chemical and Materials Engineering, University of Dayton  
300 College Park, Dayton, OH 45469-0246

<sup>b</sup>Air Force Research Laboratory, Propulsion Directorate, Plans and Analysis Branch, 1950 Fifth Street, Wright-Patterson AFB, OH 45433-7251

## Abstract

A performance model for a reformer, consisting of the catalytic partial oxidation (CPO), high and low temperature water-gas shift (HTWGS and LTWGS), and preferential oxidation (PROX) reactors, has been formulated. The model predicts the composition and temperature of the hydrogen-rich reformed fuel-gas mixture needed for the fuel cell applications. The mathematical model equations, based on the principles of classical thermodynamics and chemical kinetics, were implemented into a computer program. The resulting software was employed to calculate the chemical species molar flow rates and the gas mixture stream temperature for the steady-state operation of the reformer. Typical computed results, such as the gas mixture temperature at the CPO reactor exit and the profiles of the fractional conversion of carbon monoxide, temperature, and mole fractions of the chemical species as a function of the catalyst weight in the HTWGS, LTWGS, and PROX reactors, are here presented at the carbon-to-oxygen atom ratio, (C/O), of 1 for the feed mixture of n-decane and dry air.

Keywords: Reformer model; Preferential oxidation; Water-gas shift reaction

<sup>+</sup>Corresponding author: e-mail address: [Sarwan.Sandhu@notes.udayton.edu](mailto:Sarwan.Sandhu@notes.udayton.edu)

## 1. Introduction

Due to the global enhanced concern about conserving the earth energy resources and reducing pollution, the fuel cell is a promising technology to replace the conventional internal combustion engine for power production. The ideal fuel for efficient performance is pure hydrogen in low temperature fuel cells since it simplifies system integration, maximizes system efficiency, and produces zero harmful emissions (Song, 2002). However, hydrogen is not naturally available as a fuel, but it is stored in high density in hydrocarbon fuels. Processing of hydrocarbon fuels is, therefore, necessary to extract hydrogen for stationary and mobile fuel cell applications.

## 2. Preliminary reformer performance mathematical model

The fuel reformer performance model reported here quantitatively simulates a fuel processor to supply hydrogen-rich fuel gas mixture to a fuel cell stack operating at a relatively low temperature (e.g. proton exchange membrane fuel cell stack). Figure 1 shows the flow diagram of the process units of the fuel reformer. A liquid fuel (for example, n-decane) is vaporized and heated/mixed with air in a heater-vaporizer unit. The gas mixture leaving the heater-vaporizer unit is fed to the monolith, Rh-on-  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, catalytic partial oxidation

microreactor. Partial oxidation of the fuel, n-decane, on the Rh-on- $\alpha$ - $\text{Al}_2\text{O}_3$  catalyst is so fast that the conversion of n-decane is 100% (Schmidt et al., 2003) at the carbon-to-oxygen atom ratio of 1. To avoid sintering of the HTWGSR catalyst,  $\text{Fe}_3\text{O}_4$ -on- $\text{Cr}_2\text{O}_3$ , temperature of gas exiting from the CPO reactor is decreased to an acceptable level (suitable HTWGSR operational temperature range: 320-400 °C (Keiski et al., 1996)). This requirement is achieved by water injection, directly, into the hot gas stream exiting from the CPO reactor. Water is also needed for the CO conversion via water-gas shift reaction. The needed water may be supplied from the cathode-side of a fuel cell stack being fueled by the reformer. An external intercooler (EXT-I) is necessary between the HTWGSR and LTWGSR reactors to prevent sintering of the LTWGSR catalyst, Cu-on- $\text{ZnO}/\text{Al}_2\text{O}_3$  (the operational temperature range: 120-250 °C) (Choi and Stenger, 2003). The gas mixture stream leaving the LTWGSR is cooled in the second external intercooler (EXT-II) before it enters the preferential oxidation (PROX) reactor. A small amount of air (about 2 mol %) is also added to the gas mixture stream, being cooled in the intercooler (EXT-II), for the preferential oxidation of CO on the Pt-on- $\text{Al}_2\text{O}_3$  catalyst; with the operational temperature range: 150-350 °C (Kim and Lim, 2002). The product gas mixture from the preferential oxidation reactor may be fed directly to a fuel cell stack, further treated for obtaining pure hydrogen (if needed) or stored in cylinders after cooling for its later use.

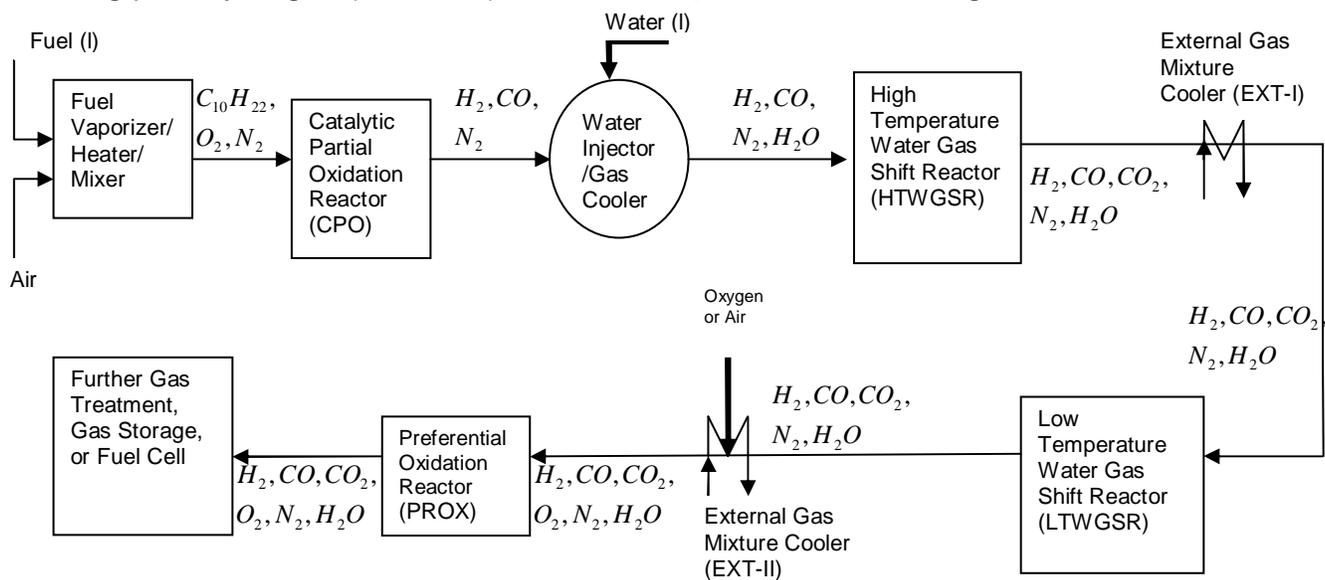


Figure 1. Schematic diagram of a reformer to produce fuel for a fuel cell.

### 3. Numerical simulation

A computer program was developed in Microsoft Visual Basic 6.0 to generate numerical data from the model performance equations (Saif, 2004). The input parameters to the computer program are the inlet molar flow rates of the fuel, n-decane, and air; the system pressure, inlet temperature of the fuel and air to the heater/vaporizer unit, inlet temperature of the gas mixture to the catalytic partial oxidation (CPO) reactor, temperatures at the inlets of the HTWGS, LTWGS and PROX reactors, and molar flow rate ratio,  $\text{O}_2/\text{CO}$ , at the inlet of the PROX reactor.

#### 4. Results and discussion

Figure 3 shows the effect of the CPO reactor inlet temperature on the gas mixture temperature leaving the CPO reactor at the carbon to oxygen atom ratio of 1. It is a straight line over the inlet temperature range of 480-520 K. Results presented in Figures 4 and 5 correspond to the parametric conditions given in Table 1 below.

Table 1: Parametric data at carbon-to-oxygen atom ratio of 1.

Fuel ( $n\text{-C}_{10}\text{H}_{22}$ ) feed rate	$1.087 \times 10^{-3}$ g-mol/s
Air feed rate	$2.5879 \times 10^{-2}$ g-mol/s
System pressure	1.2 bar
Fuel and air inlet temperature	25°C
Temperatures at the inlets of CPO, HTWGS, LTWGS, and PROX reactors	250, 200, 177, 147°C, respectively

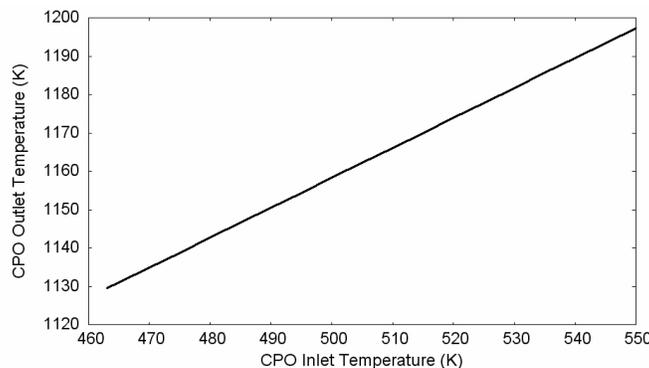


Figure 3. The effect of the inlet temperature of the gas mixture on the exit temperature of the CPO reactor.

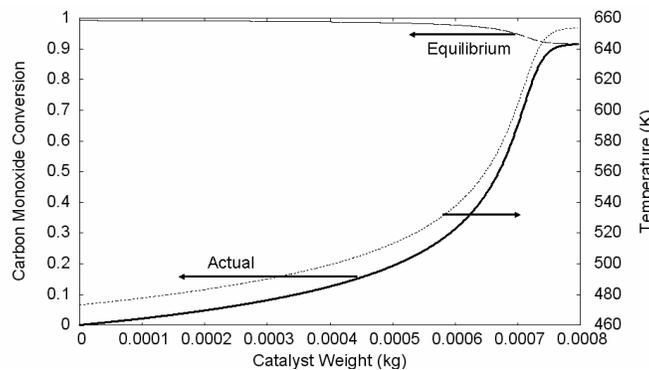


Figure 4. Temperature, actual and equilibrium CO conversion vs. catalyst weight in the HTWGSR.

Figure 4 shows the change of actual CO conversion, equilibrium CO conversion, and gas mixture temperature as a function of the catalyst weight in the HTWGSR. The gas mixture temperature increases with an increase in the catalyst weight due to the exothermic nature of the water-gas shift reaction; whereas the equilibrium CO conversion decreases and the actual CO conversion increases with the catalyst weight increase. Since the water-gas shift reaction is reversible and the actual CO conversion is limited by the principles of equilibrium

thermodynamics; the point, where the actual and equilibrium CO conversion curves meet, is the point of maximum actual CO conversion.

Figure 5 shows the species mole fraction profiles as a function of the catalyst weight in the HTWGSR. Nitrogen and oxygen (oxygen in trace amount) mole fractions are constant with respect to the catalyst weight along the reactor length; because, they are not involved in the water-gas shift reaction and the total gas mixture molar flow rate does not change due to the nature of the reaction stoichiometric equation. Mole fractions of the product species, hydrogen and carbon dioxide, increase; whereas those of the reactant species, carbon monoxide and water, decrease. Figure 6 shows the effect of the total fuel and air molar feed rate on the actual CO conversion vs. the catalyst weight profile in the HTWGSR at the carbon-to-oxygen atom ratio of 1. The total molar feed rate setting numbers I, II, III and IV correspond to the molar flow rates given in Table 2 and the other parametric data are the same as shown in Table 1.

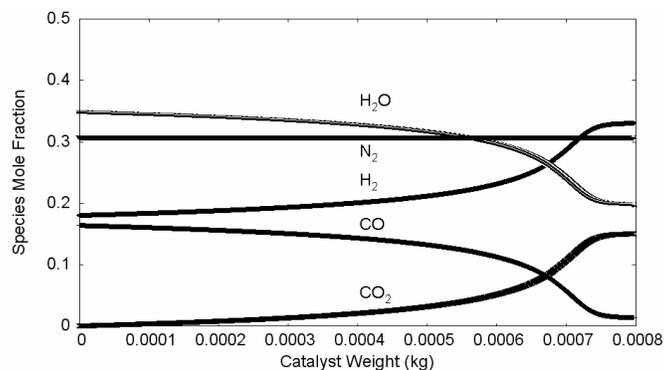


Figure 5. Mole fraction profiles of chemical species in the gas mixture in the HTWGSR vs. the catalyst weight.

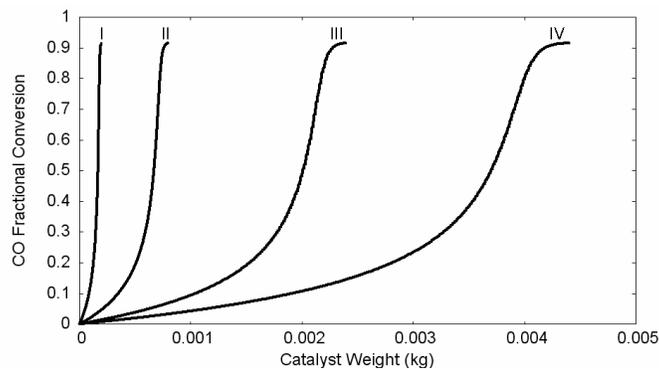


Figure 6. The effect of total inlet molar flow rate on CO conversion in the HTWGSR.

From Figure 6, it is apparent that a higher amount of the catalyst is needed for a higher total molar feed rate compared to that for a lower total molar feed rate to achieve the same fractional conversion of CO.

The results for the LTWGSR are similar to the HTWGSR, however, the catalyst weight in the LTWGSR is on the order of kilograms versus milligrams for the HTWGSR.

Table 2. Reactant feed data at the carbon-to-oxygen atom, (C/O), ratio =1.

Reactant feed rate setting number	Fuel ( $n - C_{10}H_{22}$ ) molar flow rate, (g-mol/s) (A)	Air feed flow rate, (g-mol/s) (B)	Total molar feed rate = A+B, g-mol/s
I	2.717E-04	6.4696E-03	6.7413E-03
II	1.087E-03	2.5879E-02	2.6966E-02
III	3.261E-03	7.7636E-02	8.0897E-02
IV	6.000E-03	14.2857E-02	14.8857E-02

The preferential oxidation (PROX) reactor results shown in Figures 7 through 10 correspond to the reformer parametric feed rate data given in the Table 1. Figure 7 shows the actual CO conversion and temperature profiles as a function of the catalyst weight in the PROX reactor for the inlet oxygen to carbon monoxide molar ratio of 2. Close to the reactor inlet, the CO conversion and the gas mixture temperature increase almost linearly as a function of the Pt-on- $Al_2O_3$  catalyst weight. As the CO concentration decreases with an increase in the catalyst weight, the rise in the actual CO conversion becomes relatively steep. The gas mixture temperature follows a similar trend. This observed behavior is in agreement with (Froment and Bischoff, 1990). The CO oxidation rate has a negative order with respect to CO concentration. An increase in the bed temperature and a decrease in the CO concentration in the ppm range result in a relatively high value of the CO oxidation rate, and hence, in a relatively high value of the actual CO conversion.

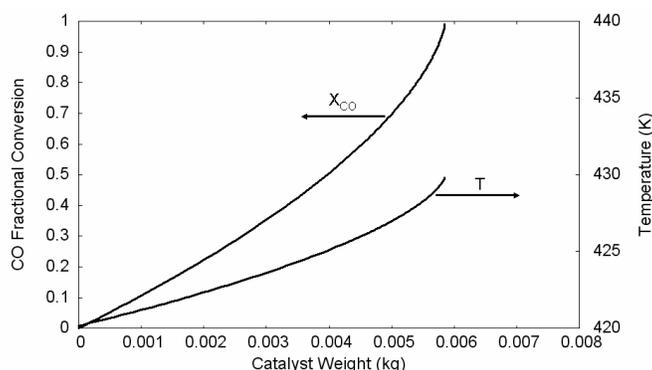


Figure 7. CO conversion and temperature profiles vs. catalyst weight in the PROX reactor.

The profiles of the mole fractions of chemical species as a function of the catalyst weight in the (PROX) reactor are shown in Figure 8. Carbon monoxide and oxygen being the reactant species, their mole fractions decrease with an increase in the catalyst weight; whereas, the mole fraction of the product  $CO_2$  increases with the catalyst weight increase. Hydrogen, nitrogen, and water species were assumed not to take part in any reaction. Therefore, their molar flow rates do not change with an increase in the catalyst. However, their mole fractions increase slightly with an increase in the catalyst weight due to the decrease in the total mixture molar flow rate associated with the occurrence of the CO oxidation reaction. Figure 9 shows the effect of the PROX reactor inlet temperature on the actual CO conversion vs. catalyst weight profile. One observes that the weight of the catalyst needed is less for a higher inlet temperature for the same actual CO conversion. However, with an increase in the bed temperature, CO desorption from the catalytic surface is enhanced. This affects the

catalyst selectivity towards the CO oxidation relative to the hydrogen oxidation. At a higher temperature, the hydrogen oxidation rate increases (Kahlich et al., 1997; Kim and Lim, 2002). Therefore, optimization of the gas mixture temperature at the PROX reactor inlet is essential to realize the enhanced catalyst selectivity to CO oxidation. The inlet oxygen-to-carbon monoxide molar ratio is an important parameter in the CO oxidation process in the preferential oxidation reactor. Figure 10 shows the effect of the inlet oxygen-to-carbon monoxide molar ratio on the actual CO conversion vs. the catalyst weight profile. From the plots, it is apparent that a lesser amount of the catalyst is needed at a higher oxygen-to-carbon monoxide molar ratio than that at a lower oxygen-to-carbon monoxide molar ratio to achieve the same actual CO fractional conversion. This suggests that the PROX reactor should be operated at a value higher than the stoichiometric value of 0.5 of the oxygen to carbon monoxide molar ratio to reduce the amount of catalyst needed. However, the selected oxygen to carbon monoxide molar ratio should be such that the hydrogen (desired fuel cell fuel) oxidation is still insignificant relative to the CO oxidation process on the Pt-on- $\text{Al}_2\text{O}_3$  catalyst in the PROX reactor. Figure 11 shows the effect of the total reactant molar feed rate to the reformer on the actual CO conversion vs. catalyst weight profile for the four flow rates given in Table 2. It is quite obvious that a larger amount of catalyst is needed for a larger total reactant molar feed rate to the reformer for a fixed actual CO fractional conversion. This is so because the PROX reactor is then required to oxidize a larger amount of CO.

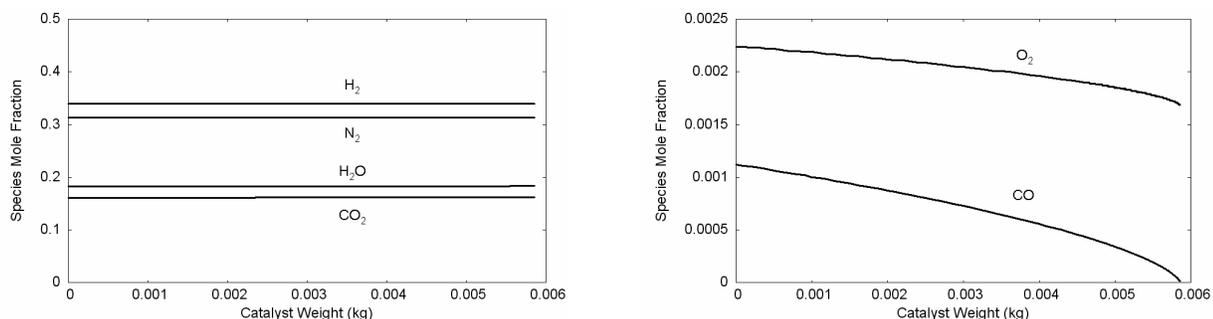


Figure 8. Mole fraction of the chemical species vs. catalyst weight in the PROX reactor.

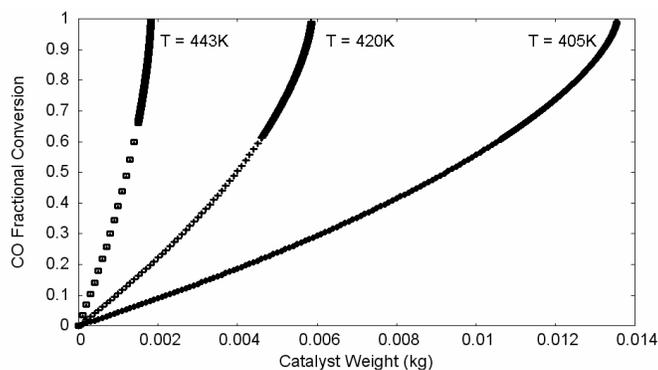


Figure 9. Inlet gas mixture temperature effect on CO conversion in the PROX reactor.

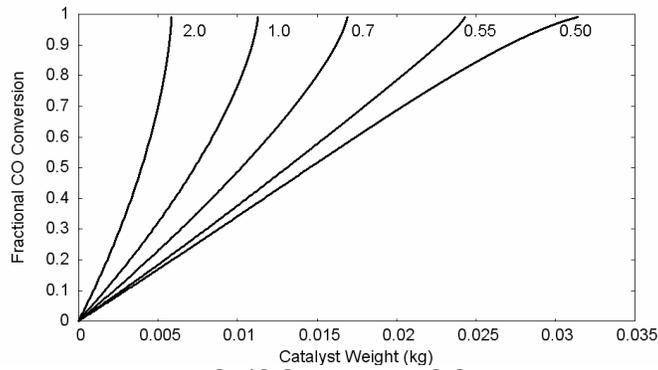


Figure 10. Effect of the inlet molar  $O_2/CO$  ratio on CO conversion in the PROX reactor.

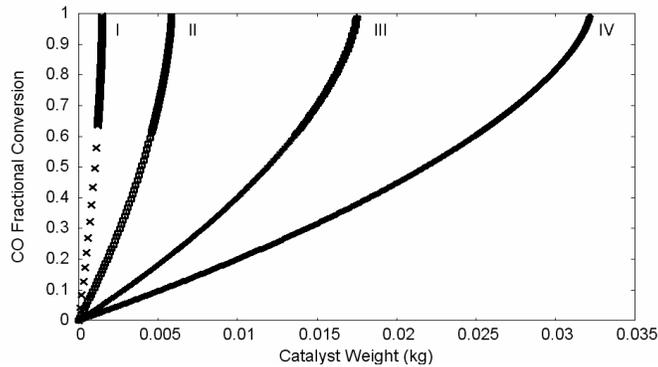


Figure 11. Effect of total inlet molar flow rate on CO conversion in the PROX reactor.

## 5. Conclusions

A mathematical model has been developed to predict the performance of a reformer for the production of hydrogen-rich gas mixture from a hydrocarbon fuel, such as n-decane, for fuel cell applications. Although the model was originally developed for the carbon-to-oxygen atom ratio of one with n-decane as the fuel and air as the oxidant, the model can be adapted to the non-stoichiometric feeds of a fuel and air for the partial oxidation of the fuel in the Rh-on- $\alpha$ - $Al_2O_3$  catalytic partial oxidation reactor to produce syngas for its further treatment in the water-gas shift and preferential oxidation reactors.

A computer program, based on the performance model equations, was developed and implemented to numerically simulate the performance of the fuel processor shown in Figure 1. The relation between the predicted exit gas mixture temperature and the inlet temperature of the gas mixture entering the CPO reactor may be approximated by a linear relation.

The computed performance data for the HTWGS and LTWGS reactors show similar trends. The gas mixture temperature and the actual CO conversion increase, with an increase in the catalyst weight, to their equilibrium state values. Optimization of the gas mixture temperature at the inlet of the HTWGSR as well as of the LTWGSR is important to avoid sintering of the catalyst and reduce its weight in each reactor for a desired overall actual CO conversion in these reactors. This also has the effect on the amount of water needed for injection into the water injector/gas cooler unit. One should make it certain that the amount of

water injected is sufficient to convert the entire amount of CO in the gas mixture entering the HTWGSR-external cooler-LTWGSR module.

Finally, the reaction rate for the CO oxidation in the PROX reactor shows an interesting behavior. It changes from a low to a relatively high value as the actual CO conversion approaches unity. One may explain this in terms of the competition between carbon monoxide, hydrogen, and oxygen for their chemisorption at the catalytic active sites for the overall CO oxidation process.

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