

The object of this column is to enhance our readers' collections of stimulating problems in chemical engineering education. Ideal problems, which may be "open-ended," are those that motivate the student either by the novel illustration of a particular principle, or by the elucidation of a difficult concept in a more traditional setting. Practical relevance is encouraged. The text portion of a manuscript (excluding figures) should not normally exceed 10 double-spaced pages (about 2,500 words). Please send manuscripts to Professor James O. Wilkes (e-mail: wilkes@umich.edu), Chemical Engineering Department, University of Michigan, Ann Arbor, MI 48109-2136. Preliminary ideas may be discussed with Prof. Wilkes before submitting a manuscript.

Design of a Fuel Processor System for GENERATING HYDROGEN FOR AUTOMOTIVE APPLICATIONS

PANINI K. KOLAVENNU, JOHN C. TELOTTE, AND SRINIVAS PALANKI

Florida State University and Florida A & M University • Tallahassee, FL 32310-6046

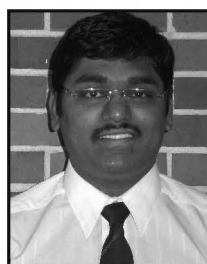
Fuel cell power systems for automotive applications have received increased attention in recent years because of their potential for high fuel efficiency and lower emissions.^[1] While there have been significant advances in fuel cell technology, this technology has not seen widespread application in the automotive industry due to the lack of an efficient hydrogen distribution system.^[2] One option is to develop a system that utilizes a commonly available carbon-based hydrogenous fuel such as gasoline or methane to generate the necessary hydrogen in situ on an "as needed" basis.

In this paper, the objective is to design a fuel processor system that utilizes methane to generate sufficient hydrogen of desired purity, generating 50 kW of power, or enough to drive a small car.^[1]

PROBLEM STATEMENT

A schematic of the fuel cell system under consideration is shown in Figure 1 (next page).^[3] Methane enters the fuel processing system and is converted to hydrogen. Hydrogen enters the fuel cell where it reacts with oxygen to generate electrical power, driving an electric motor.

The fuel processing system has a train of three packed-bed reactors: (1) the reformer, (2) the water-gas shift reactor, and (3) the preferential oxidation reactor.



Panini K. Kolavennu has a B.Tech in chemical engineering with specialization in biotechnology from Andhra University, Visakhapatnam, India. He is currently pursuing his Ph.D. in chemical engineering at FAMU-FSU College of Engineering, Tallahassee, Fla. His research interests include fuel cell and fuel processor design and analysis, model predictive control, and adaptive control.

John C. Telotte has a B.S. and M.S. in chemical engineering from Tulane University. He also received a Ph.D. in chemical engineering from the University of Florida. He was a member of the chemical engineering faculty at the University of Wisconsin and Louisiana Tech University before joining the FAMU-FSU College of Engineering in 1985. He is currently associate professor of chemical and biomedical engineering. His current research focuses on hydrogen storage problems and design of fuel cell systems.



Srinivas Palanki received his B.Tech. in chemical engineering from the Indian Institute of Technology, Delhi, and his M.S. and Ph.D. in chemical engineering from the University of Michigan, Ann Arbor. He joined the faculty of the FAMU-FSU College of Engineering in 1992. He is currently a professor of chemical and biomedical engineering. His current research interests are in real-time optimization and nonlinear robust control with applications in the fuel cell and biomedical areas.

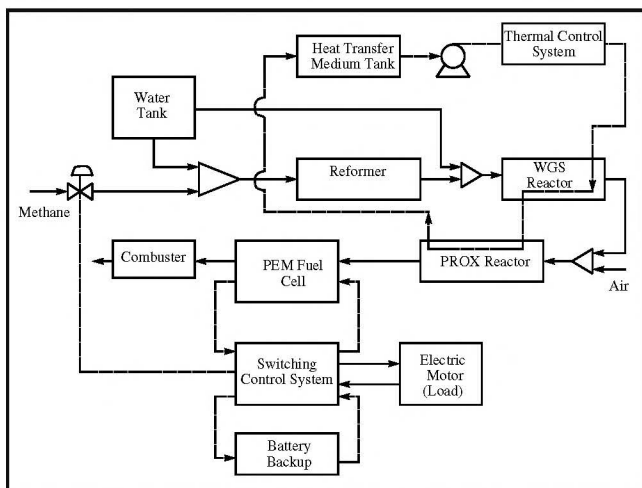


Figure 1. Schematic of fuel cell system.

Based on the Figure 1 schematic diagram, students are required to complete the following tasks:

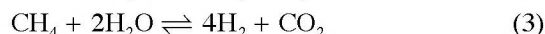
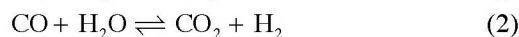
1. Write the mole balance equations for the reformer, water-gas shift reactor, and preferential oxidation reactor.
2. Calculate the volume necessary for 75% conversion in the steam reformer. Assume isothermal operation at 1000 K, with the reactor operating at 5 atm pressure. The flow rate of methane into the reactor is 9 mol/min at room temperature, and the ratio of steam to methane is 3:1.
3. Calculate the maximum conversion in the water-gas shift reactor that can be obtained at 450 K and 600 K, respectively, and the minimum volume required.
4. Calculate the volume of the water-gas shift reactor to obtain 90% conversion if:
 - (a) 20% of the total volume of the reactor is at 600 K and the rest of the reactor is at 450 K.
 - (b) 60% of the total volume of the reactor is at 600 K and the rest of the reactor is at 450 K.
5. The input to the preferential oxidation reactor consists of exhaust from the water-gas shift reactor and air. The amount of air fed should be adjusted such that the amount of oxygen in the air is 2.1 times the amount of CO in the exhaust of the water-gas shift reactor. If the preferential oxidation reactor is operating at a temperature of 473 K and a pressure of 2 atm, calculate the volume required to bring the concentration of CO to below 100 ppm. Assume 90% conversion in the steam reformer operating at 1000 K and 5 atm and a conversion of 90% in the water-gas shift reactor operating at 500 K and 2 atm.
6. Calculate the flow rate of hydrogen exiting the preferential oxidation reactor. How does this flow rate change when the flow rate of methane entering the reformer is changed?
7. Energy Balance:
 - Calculate the heat of reaction from the heat of formation for all the reactions, and list out the

exothermic and endothermic reactions.

- Calculate the enthalpies of all the feed and product streams and use this information to complete an overall energy balance for the reactor system.

DATA

Steam reformer • In this reactor, methane is converted to hydrogen and carbon monoxide. Part of the carbon monoxide reacts with water to produce carbon dioxide and hydrogen, and some methane is totally oxidized to carbon dioxide.



Xu and Froment^[4] developed intrinsic rate expressions for steam reforming of methane, accompanied by the water gas shift reaction on a Ni/MgAl₂O₃ catalyst. The following reaction rate laws were derived:

$$r_1 = \frac{k_1 \left(P_{\text{CH}_4} P_{\text{H}_2\text{O}} - \frac{P_{\text{H}_2}^3 P_{\text{CO}}}{K_1} \right)}{P_{\text{H}_2}^{2.5} \left(1 + K_{\text{CO}} P_{\text{CO}} + K_{\text{H}_2} P_{\text{H}_2} + K_{\text{CH}_4} P_{\text{CH}_4} + K_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}} / P_{\text{H}_2} \right)^2} \quad (4)$$

$$r_2 = \frac{k_2 \left(P_{\text{CO}} P_{\text{H}_2\text{O}} - \frac{P_{\text{H}_2} P_{\text{CO}_2}}{K_2} \right)}{P_{\text{H}_2} \left(1 + K_{\text{CO}} P_{\text{CO}} + K_{\text{H}_2} P_{\text{H}_2} + K_{\text{CH}_4} P_{\text{CH}_4} + K_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}} / P_{\text{H}_2} \right)^2} \quad (5)$$

$$r_3 = \frac{k_3 \left(P_{\text{CH}_4} P_{\text{H}_2\text{O}}^2 - \frac{P_{\text{H}_2}^4 P_{\text{CO}_2}}{K_3} \right)}{P_{\text{H}_2}^{3.5} \left(1 + K_{\text{CO}} P_{\text{CO}} + K_{\text{H}_2} P_{\text{H}_2} + K_{\text{CH}_4} P_{\text{CH}_4} + K_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}} / P_{\text{H}_2} \right)^2} \quad (6)$$

where r_1 , r_2 , and r_3 are the rates of formation of CO, CO₂, and CO₂ in the reactions represented by Eqs. (1), (2), and (3) respectively. The P_i are the partial pressures of the reactants. The values of the constants are given in Table 1.

The adsorption coefficients can be found using the following relations for the respective species

$$K_i = A(K_i) \exp\left(\frac{-\Delta H_i^0}{RT}\right), \text{ where } i = \text{H}_2, \text{CO}, \text{CH}_4, \text{H}_2\text{O} \quad (7)$$

The rate constants are given by a similar Arrhenius-type equation.

$$k_j = A'(k_j) \exp\left(\frac{-E_{a,j}}{RT}\right), \text{ where } j=1,2,3 \quad (8)$$

The equilibrium constants for the three reactions are given by the following expression,

$$K_j = \exp\left(A_j + \frac{B_j}{T}\right), \text{ where } j=1,2,3 \quad (9)$$

Water-gas shift reactor • In this reactor, most of the remaining carbon monoxide is converted to hydrogen. The following exothermic reaction occurs:



Choi and Stenger^[5] proposed a kinetic model for the water-gas shift reaction on a Cu/ZnO/Al₂O₃ catalyst operating between 400 K to 700 K. The following rate law was developed.

$$r_4 = k_4 P_{\text{CO}} P_{\text{H}_2\text{O}} \left(1 - \frac{P_{\text{CO}_2} P_{\text{H}_2}}{P_{\text{CO}} P_{\text{H}_2\text{O}} K_{\text{eq}}} \right) \quad (11)$$

where r_4 is the rate of formation of CO₂ in the reaction represented by Eq. (10). The equilibrium constant K_{eq} varies with temperature as follows:

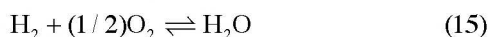
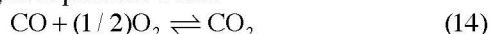
$$K_{\text{eq}} = \exp \left[\frac{4577.8}{T} - 4.33 \right] \quad (12)$$

The rate constant k_4 follows an Arrhenius type equation as given below:

$$k_4 = A'(k_4) \exp \left(\frac{-E_{a,4}}{RT} \right) \quad (13)$$

Other constant values used are given in Table 1.

Preferential oxidation reactor • The stream exiting the water-gas shift reactor may still have significant amounts of carbon monoxide that can poison the Polymer Electrolyte Membrane (PEM) fuel cell electrocatalyst. For this reason, it is necessary to have a preferential oxidation reactor where the carbon monoxide from the water-gas shift reactor is reacted with air to form carbon dioxide. Some of the hydrogen reacts with the oxygen to produce water.



The following kinetic model was taken from Kahlich, *et al.*^[6]

$$r_5 = k_5 P_{\text{O}_2}^{0.42} \left[\frac{2P_{\text{O}_2}}{P_{\text{CO}}} \right] \quad (16)$$

$$r_6 = 1.5k_5 P_{\text{O}_2}^{0.42} \left[\frac{2P_{\text{O}_2}}{P_{\text{CO}}} \right] \quad (17)$$

where r_5 represents the rate of formation of CO₂ in the reaction represented by Eq. (16), and r_6 represents the rate of formation of H₂O in the reaction represented by Eq. (17). The rate constant k_5 follows an Arrhenius-type equation:

$$k_5 = A'(k_5) \exp \left(\frac{-E_{a,5}}{RT} \right) \quad (18)$$

SOLUTION

Each reactor is modeled as an isothermal plug-flow reactor. It is assumed that no axial mixing or axial heat transfer occurs. This implies that the reactors are operating at high

Parameter	Value
A ₁	29.3014
A ₂	-4.35369
A ₃	25.225
A' (k ₁)	9.886 × 10 ¹⁶ [mol atm ^{0.5} /(m ³ min)]
A' (k ₂)	4.665 × 10 ⁷ [mol atm ⁻¹ /(m ³ min)]
A' (k ₃)	2.386 × 10 ¹⁶ [mol atm ^{0.5} /(ltr min)]
A (K _{H₂})	6.209 × 10 ⁻⁹ [atm ⁻¹]
A(K _{CO})	8.339 × 10 ⁻⁵ [atm ⁻¹]
A (K _{H₂O})	1.77 × 10 ⁵
A (K _{CH₄})	6.738 × 10 ⁻⁴ [atm ⁻¹]
B ₁	-26248.4 [K ⁻¹]
B ₂	4593.17 [K ⁻¹]
B ₃	-21825.28 [K ⁻¹]
E _{a1}	240.1 [kJ/(mol K)]
E _{a2}	67.13 [kJ/(mol K)]
E _{a3}	243.9 [kJ/(mol K)]
ΔH _{H₂} ^o	-82.90 [kJ/(mol K)]
ΔH _{CO} ^o	-70.65 [kJ/(mol K)]
ΔH _{H₂O} ^o	+88.68 [kJ/(mol K)]
ΔH _{CH₄} ^o	-38.28 [kJ/(mol K)]
A' (k ₄)	6.195 × 10 ⁸ [mol atm ⁻² /(m ³ min)]
A' (k ₅)	2.333 × 10 ¹¹ [mol atm ^{-0.4} /(ltr min)]
E _{a4}	47.53 [kJ/(mol K)]
E _{a5}	71 [kJ/(mol K)]

Peclet numbers for both heat and mass transfer. A more detailed analysis incorporating these diffusive effects has been conducted by Bell and Edgar.^[7] The automotive application puts a constraint on the total volume of the reactor train, since the entire system has to fit under the hood. The design equations are solved numerically in MATLAB. The process is also simulated in the process simulator CHEMCAD. The results are given below.

Mole Balance Equations

The general mole balance equation for a PFR is given by:

$$\frac{dF_j}{dV} = r_j \quad (19)$$

where j represents the species present in the reactor. It is necessary to determine the reaction rate for each species in the three reactors.

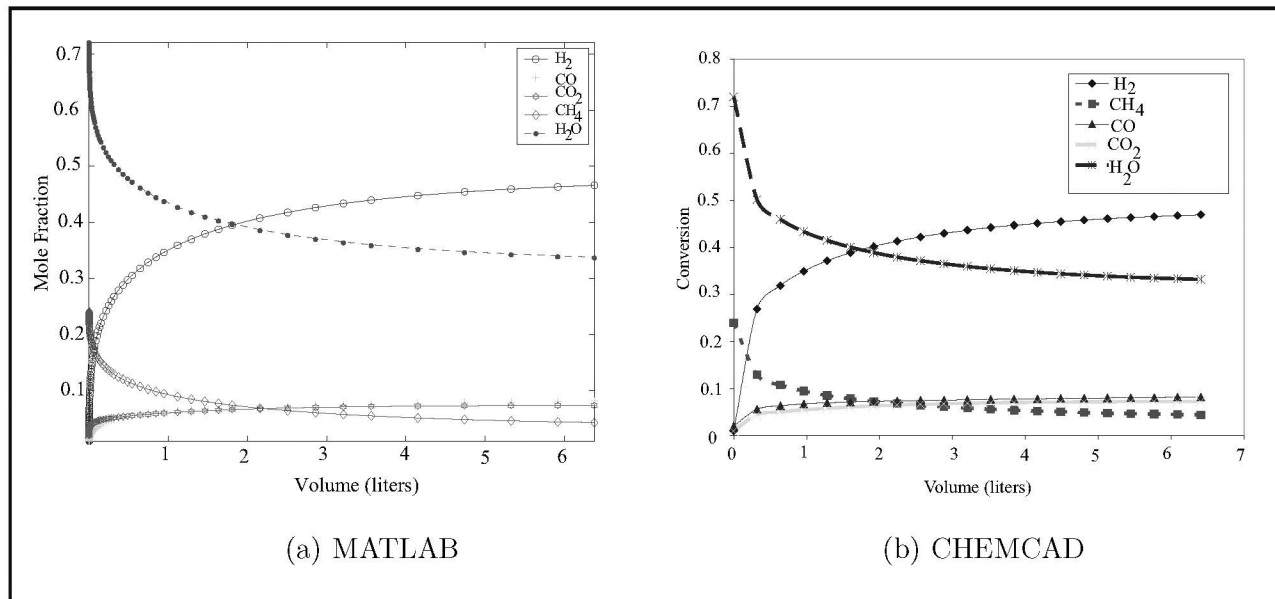


Figure 2. Concentration profiles in reformer.

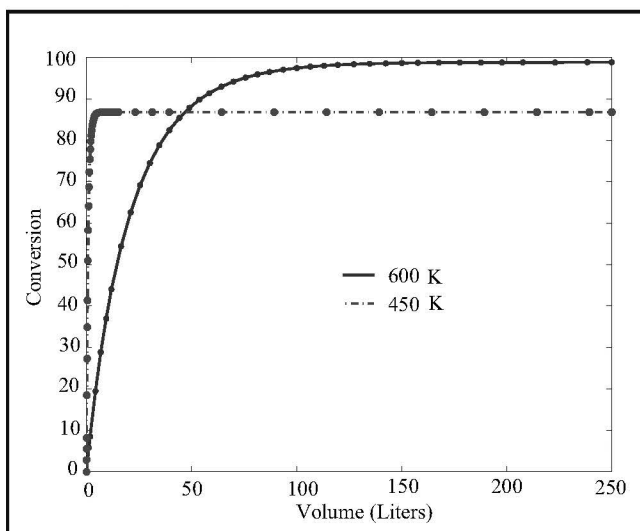


Figure 3. Conversion of carbon monoxide in water-gas shift reactor.

In the reformer, the reactions taking place are represented by Eq. (1)-(3). The reaction rates in terms of the species involved can be expressed in terms of the reaction rates represented by Eq. (4)-(6) as shown below.

$$r_{\text{CH}_4} = -r_1 - r_3 \quad (20)$$

$$r_{\text{CO}} = r_1 - r_2 \quad (21)$$

$$r_{\text{CO}_2} = r_2 + r_3 \quad (22)$$

$$r_{\text{H}_2\text{O}} = -r_1 - r_2 - 2r_3 \quad (23)$$

$$r_{\text{H}_2} = 3r_1 + r_2 + 4r_3 \quad (24)$$

There is only one reaction occurring in the water-gas shift reaction as shown by Eq. (10). We can express the reaction rate of each Eq. (10) species in terms of the reaction rate of

Eq. (11) as follows:

$$r_{\text{CO}} = -r_4 \quad (25)$$

$$r_{\text{H}_2\text{O}} = -r_4 \quad (26)$$

$$r_{\text{CO}_2} = r_4 \quad (27)$$

$$r_{\text{H}_2} = r_4 \quad (28)$$

In the preferential oxidation reactor, the reactions taking place are represented by Eq. (14)-(15). The reaction rates, in terms of the species, involved can be expressed in terms of the reaction rates represented by Eq. (16)-(17).

$$r_{\text{O}_2} = -0.5r_5 - 0.5r_6 \quad (29)$$

$$r_{\text{CO}} = -r_5 \quad (30)$$

$$r_{\text{CO}_2} = r_5 \quad (31)$$

$$r_{\text{H}_2\text{O}} = r_6 \quad (32)$$

$$r_{\text{H}_2} = -r_6 \quad (33)$$

Volume of Steam Reformer

Rate expressions for the different reactions are given in terms of partial pressures of reacting species. The given molar feed rate of the gases, F_j , should be converted to partial pressures. Using the molar feed rates, we can calculate the mole fraction of the feed used to calculate the partial pressures as follows:

$$X_j = \frac{F_j}{F_T} \quad (34)$$

$$P_j = X_j P_T \quad (35)$$

The partial pressure obtained is substituted into the rate expression to calculate the change in flow rate along the volume of the reactor.

Temperature(K)	Volume (l)	Conversion CHEMCAD	Conversion MATLAB
20 % at 600 K	15.28	90%	90.14%
60 % at 600 K	19.74	90%	90.15%

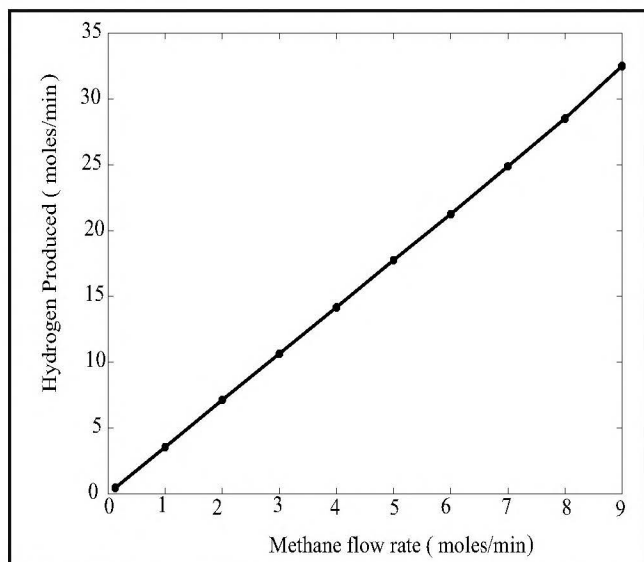


Figure 4. Hydrogen produced as a function of methane feed.

The mole balance equations for the species in the steam reformer are given in the mole balance equation section. A volume for the reformer was estimated, and the mole balance equations were integrated numerically in MATLAB for this guessed volume using the initial conditions given in the problem statement. The methane concentration exiting the reformer was computed, and the methane conversion was calculated. The reactor volume was iteratively adjusted using a secant method until the computed conversion was 75% as specified in the problem statement. Students found a reformer volume of 6.38 liters resulted in the specified conversion. The concentration profiles, as a function of reactor volume, are shown in Figure 2(a).

This reactor configuration was also simulated in CHEMCAD. Shown in Figure 2(b), the reformer with a volume of 6.38 liters resulted in a conversion of 75%.

Volume of Isothermal Water-Gas Shift Reactor

The mole balance equations for the species in the water-gas shift reactor are given on pp. 241-242.

This reactor was simulated in CHEMCAD and MATLAB, producing identical results. The specific reaction rate constants were computed for the temperatures given in the problem statement first. Using the exit conditions of the reformer as the initial conditions of the water-gas shift reactor,

the mole balance equations were integrated numerically for a variety of reactor volumes till the maximum conversion was attained. The conversion of carbon monoxide as a function of reactor volume at two different isothermal conditions (450 K and 600 K) is shown in Figure 3. If the reactor is operated isothermally at 450 K, the maximum conversion possible is

98.8%. The minimum volume required to obtain this conversion is about 250 liters. The maximum possible conversion at a temperature of 600 K is only 86.6%, and the minimum volume required is 9.4 liters.

Volume of Two-Temperature-Zone Water-Gas Shift Reactor

At low temperatures, the reaction is kinetically limited. At high temperatures, the reaction conversion is limited, *i.e.*, the extent of reaction is limited by the thermodynamics. To minimize the volume, the reactor is operated at a high temperature (600 K), and to increase the conversion it is operated at a lower temperature (450 K). The reactor volume for 90% conversion under two different reactor temperature regimes is calculated in CHEMCAD, and verified with MATLAB. The results are shown in Table 2. It is observed that the reactor volume can be substantially reduced as compared to the isothermal operation if 20% of the reactor is operated at 600 K.

Volume of Preferential Oxidation Reactor

The last reactor in the series is the preferential oxidation reactor. Here, the concentration of CO is brought to less than 100 ppm. Along with the combustion of CO, some hydrogen is also burned. For the gases that have a 75% conversion in the reformer and a 90% conversion in the water-gas shift reactor, the amount of conversion in the preferential oxidation reactor (PROX) is approximately 98.7%. The volume obtained for this conversion is 0.335 liters.

Hydrogen Flow Rate

From calculations performed in the section on “Volume of Preferential Oxidation Reactor,” the flow rate of hydrogen exiting the preferential oxidation reactor is 28.08 moles/min. Using the reactor volumes given above, the reactor train was simulated for varying methane flow rates. A plot of hydrogen flow rate out of the fuel processor vs. methane flow rate into the reformer is shown in Figure 4. Note that the relation between the two flows is linear, and 3.12 moles of hydrogen are formed for every mole of methane entering the reformer.

Energy Balance

The standard heat of reaction can be obtained from the standard heat of formation of individual species involved in the reaction using Hess’s Law. The standard heat of formation can be obtained from the NIST Chemistry Web book.^[8] For oxygen and hydrogen, the standard heat of formation (at 298

Species	Standard Heat of Formation (kJ/mol)
CO	-110.53
CO ₂	-393.51
H ₂ O	-242
CH ₄	-74.5

Reaction	Standard Heat of Reaction (kJ/mol)	Type
CH ₄ + H ₂ O ⇌ 3H ₂ + CO	205	endothermic
CO + H ₂ O ⇌ CO ₂ + H ₂	-41	exothermic
CH ₄ + 2H ₂ O ⇌ 4H ₂ + CO ₂	164	endothermic
CO + (1/2)O ₂ ⇌ CO ₂	-283	exothermic
H ₂ + (1/2)O ₂ ⇌ H ₂ O	-242	exothermic

K) is zero. The heat of formation for other species is given in Table 3. Using heat of formation data, the standard heats of reaction were found. These results are given in Table 4.

There are two feed streams going into the reactor train and one product stream coming out. The enthalpies of these streams can be computed easily in CHEMCAD. The enthalpy of the stream containing steam and methane is -8.261 MJ/min, the air stream is -0.003 MJ/min, and the product stream is -6.042 MJ/min. Air is assumed to be 79% nitrogen and 21% oxygen. Enthalpies are calculated based on the same reference states as those used for the heat of reaction. The net heat to be supplied to the fuel processor is 2.22 MJ/min.

DISCUSSION

The purpose of this work was to demonstrate that standard reaction engineering principles could be utilized to design a fuel processor that uses methane to generate hydrogen of the required purity for a PEM fuel cell used for automotive applications. The total volume required for the fuel processor to generate hydrogen of the required purity is small enough to fit under the hood of small cars. Furthermore, the energy balanced reactions involved indicate that there is a net depletion of energy, and so it is necessary to provide a small amount of heat to the reactors. This project gives the instructor the opportunity to discuss several reactor design issues such as:

- *The importance of changing the temperature in the water-gas shift reactor to minimize the volume. This is a common approach when one looks at equilibrium limitations in exothermic reactions.*
- *The necessity of having the preferential oxidation reactor. While the reactor volume is small (the size of a soft drink can), it is necessary to have this reactor so that the concentration of carbon monoxide is reduced to a level*

acceptable for the PEM fuel cell.

- *The importance of doing an overall energy balance on the process. This exercise demonstrates it is necessary to burn some of the methane feed or the hydrogen generated for the reactions to proceed at the specified conditions.*
- *For every mole of methane utilized, more than 3 moles of hydrogen are produced. This demonstrates that hydrogen is produced not only from methane, but also from water.*
- *The equivalence of results in MATLAB and CHEMCAD for reactor design calculations.*

This problem was given as a reactor design problem in our department in summer 2005. All design teams were ultimately successful in producing an acceptable design report for this problem. A discussion with the students at the end of the semester indicated a great deal of enthusiasm in tackling this problem. Students appreciated that a practical design problem had been assigned instead of a problem from a textbook.

All the reactor design calculations were done assuming steady state. In an automotive application, however, the demand for hydrogen will fluctuate, so it is necessary to compute the dynamic response of the reactor train to sudden changes in methane flow rate and utilize this information to design a suitable control system. This requires the solution of a set of partial differential equations,^[7] and is beyond the scope of an undergraduate class in reaction kinetics.

NOMENCLATURE

- A (K) pre-exponential factor
- E_a Activation Energy, kJ/mol
- k rate constant
- K equilibrium constant or adsorption coefficient
- P partial pressure, Pascals
- r reaction rates, mol/min/l
- R gas constant, kJ/mol/K
- T temperature, K

REFERENCES

1. Zalc, J.M., and D.G. Loffler, "Fuel Processing for PEM Fuel Cells: Transport and Kinetic Issues of System Design," *J. Power Sources*, **111**, 58-64 (2002)
2. Lovins, A.B., and B.D. Williams, "A Strategy for the Hydrogen Transition," 10th Annual U.S. Hydrogen Meeting, Vienna, VA (1999)
3. Kolavennu, P.K., J.C. Telotte, and S. Palanki, "Modeling and Control of a Fuel Cell Power System for Automotive Applications," European Symposium for Computer Aided Process Engineering-14, Lisbon, Portugal (2004)
4. Xu, J.G., and G.F. Froment, "Methane Steam Reforming, Methanation And Water-Gas Shift 1. Intrinsic Kinetics," *AIChE J.*, **35**(1), 88-96 (1989)
5. Choi, Y., and H.G. Stenger, "Water-Gas Shift Reaction Kinetics and Reactor Modeling for Fuel Cell Grade Hydrogen," *J. Power Sources*, **124**, 432-439 (2003)
6. Kahllich, M.J., H.A. Gasteiger, and R.J. Behm, "Kinetics of Selective CO Oxidation in H₂-Rich Gas on Pt/Al₂O₃," *J. Catalysis*, **171**, 93-105 (1997)
7. Bell, N.H., and T.F. Edgar, "Modeling of a Fixed-Bed Water-Gas Shift Reactor," *J. Proc. Cont.*, **1**, 22-31 (1991)
8. <<http://webbook.nist.gov/chemistry/>>
9. Larminie, J., and A. Dicks, *Fuel Cell Systems*, Wiley, New York (2000) □