ME 140
Advanced Thermal Systems

Reginald Mitchell
Spring 2018

Project #5/#6: PEM Fuel Cell System Evaluation and Hydrogen Production Analysis
(Due Friday, May 11th)

Background

PEM fuel cells are being developed and evaluated as power systems for the transportation sector and for use in small-scale combined heat and power (CHP) systems. One characteristic of PEM fuel cells is that they require relatively pure H_2 as an energy carrier to avoid poisoning the platinum catalyst. Hence, there is an energy penalty associated with the production of hydrogen from other sources, such as natural gas. Last week we explored the effects of operating conditions on fuel cell performance. This week in Part A, we will explore the challenges associated with putting hydrogen into a fuel cell system and running the system at a specific operating point. In Part B, we will consider hydrogen production. Remember, hydrogen is not a resource. It has to be produced from hydrogen-containing compounds.

Part A

As you are now aware, the PEM fuel cell is an attractive energy system. But it does have its drawbacks, one being the fact that the membrane that makes these cells function must be kept hydrated to function correctly. It is no coincidence that PEM fuel cells operate at temperatures above ambient (to avoid flooding) but below 100°C (to avoid drying). To maintain this temperature and humidity, there were a host of accessories required, from pumps to controllers. The power needed to run these accessory systems can use up a significant portion of the power produced by a fuel cell. There are several issues to consider when running a fuel cell system at a specified operating point. The flows of reactants, products and coolant must be tightly controlled to run a cell stack at reasonable efficiencies and loads.

The Objectives of Part A of this Project

(1) to obtain direct experience with PEM fuel cell systems,
(2) to measure the first- and second-law efficiency capabilities of PEM cells,
(3) to extend your engineering knowledge to inform "big picture" topics, and
(4) to present your ideas in a concise, informative, and persuasive manner.

The Assignment for Part A

Requirements:

(1) <u>5 points</u> Construct a series of raw-data plots (see Appendix for data set details) showing how the following quantities vary with load (power delivered only to the resistor bank): load and stack currents, load and stack potentials, stack power and accessory power, and mass flow rates of hydrogen and air.

(2) <u>15 points</u> Use your measurements to construct a series of reduced-data plots showing how the following quantities vary with load for the Ballard fuel cell power system: excess-air coefficient (λ), first-law efficiency (LHV°-based), second law efficiency and lost power (rate of irreversibility). Perform the efficiency and lost-power calculations using both stack and load data so that the effect of system losses may be separated from those of the stack itself. Assume the air coming into the stack is at 100% relative humidity.

(3) <u>10 points</u> Evaluate the performance of the Ballard PEM fuel cell system concept with respect to its potential use as a power source for use in automobiles. To address this, compare the overall first law efficiency of the PEM fuel cell with typical values for modern Diesel and gasoline hybrid engines. You'll need to do a little web-based research for input to this comparison (be sure to cite sources). What sort of scale-up would be required for use in a vehicle such as the Toyota Hybrid? Also comment on the accessory and fuel systems that would be required for this scale-up. Assume that the cooling water flows at a constant rate of 40 g/s when calculating heat rejection rates.

<u>The Write-Up for Part A</u>

Please provide the plots requested. For the numerical answers, please organize your responses into a neat, professionally formatted table.

As always, please include the following items not normally included in a professional write-up:

(1) a brief statement of how much time was spent on each part of the analysis and write-up,
(2) a brief statement giving your opinions of the most and least useful aspects of the assignment,
(3) a brief comment about anything that is still unclear to you.

<u>Part A Deliverables</u>

➢ Raw data plots showing variations in load (power delivered to the resistor bank)
  Load and stack current
  Load and stack voltage
  Stack and accessory power
  Hydrogen and air mass flow rates
➢ Reduced-data plots showing variations in load (power delivered to the resistor bank)
  Excess-air coefficient (λ)
  1st-law and 2nd-law efficiencies (stack-only and full system)
  Lost power (stack-only and full system)
➢ Comparison of fuel cell, diesel engine, and gasoline-hybrid engine performance
  Table of typical maximum first-law efficiencies
  Discussion of challenges with scaling up H-Power system for powering an automobile

  Code uploaded to the Canvas assignment.

Part B (your team should be starting this part of the project no later than Sunday, May 6)

<u>The Problem</u>

Hydration is not the biggest issue with PEM fuel cells. The biggest issue is hydrogen. PEM fuel cells require hydrogen - very pure hydrogen - to operate. As little as 10 parts per million (ppm, a common unit for expressing very low mole fractions) of carbon monoxide (CO) is sufficient to "poison" the catalyst at the anode of a PEM fuel cell. This occurs because the CO has a great affinity for the catalyst; it attaches to active sites (the locations where the electrochemical reactions occur) and will not release. This problem is aggravated by the low-temperature operating requirement of the PEM cell. At higher temperatures, CO cannot remain attached to the catalyst and CO poisoning becomes a progressively less important issue. Stated another way, the higher the catalyst temperature, the more CO can be tolerated in the fuel stream.

One way to circumvent this issue is to do just what we did in the ME 140 lab, viz., buy "pure" hydrogen (dry and sub-ppm CO) in a cylinder and use it to fuel our cell. This is fine for demonstration and/or testing purposes, and it would be a practical solution in a world awash in pure hydrogen. But the fact is that we do not live in that world. Our surroundings do not contain

lots of molecular hydrogen. Instead, our surroundings contain lots of water, the stable oxide of hydrogen. But, the elemental hydrogen in water is not available for our use. This has lead to a significant problem in public perception: "The supply of hydrogen is limitless; you can just make it out of water." What is neglected in this perception is recognition of the fact that to transform the elemental hydrogen in water to molecular hydrogen (and oxygen) by electrolysis requires a rather large amount of energy of a rather high quality - electricity.

Making hydrogen by electrolysis isn't the only way. We know that if you burn hydrocarbons under rich conditions ($\phi > 1$), molecular hydrogen will be found in the products. This is possible because hydrocarbons contain hydrogen and, if there isn't enough oxygen around, it simply can't all be made into water. Having molecular hydrogen form under these conditions makes a fair bit of sense. What makes less sense is the idea of burning a lot of hydrocarbon fuel just to convert a small fraction of it into hydrogen. Maybe there is a better way.

One way that might come to mind is to sort of "cook" the fuel with some water. An example of this is the steam methane reformation (SMR) reaction

$$CH_4 + H_2O \rightarrow CO + 3\,H_2 \tag{1}$$

This process is called reforming (or more precisely, steam reforming) because it is the inverse of what you did in the enthalpy-of-formation problem. That is, instead of using hydrogen (and carbon) to form methane, here you are using methane (and water) to form hydrogen - hence the term re-forming. As you can see from the reaction, steam reforming could be an effective way to make hydrogen from a methane-rich fuel like natural gas. In fact, methane is particularly good because it has the highest hydrogen-to-carbon ratio of any hydrocarbon. If you can get this reaction to move far "to the right" then you will get a lot of moles of hydrogen for each mole of methane (and water) invested. It sounds a lot like, and is, a chemical equilibrium problem.

So we have a way to make hydrogen from natural gas (or any hydrocarbon for that matter), but we are not there yet. The problem that arises is the unwanted byproduct that goes along with the hydrogen production, carbon monoxide. If only PEM fuel cells were tolerant of CO, but they are not. They require less than 10 ppm CO, yet the right side of the steam reforming reaction gives us 25 percent. Clearly we have more work to do.

The answer to this lies in the example problem discussed in class. We found the composition of rich products from the primary zone of a gas turbine combustor by considering how chemical equilibrium is achieved between water, carbon dioxide, carbon monoxide, and hydrogen. That was expressed via the water-gas shift (WGS) reaction

$$H_2O + CO \rightarrow CO_2 + H_2 \tag{2}$$

which shows how water can be used to "shift" the composition of a gas from carbon monoxide to carbon dioxide.

Of course the whole situation would just be much better if fuel cells were not so sensitive to CO in the first place. If only we could get the advantages of the PEM fuel cell but operating at a temperature that is high enough that CO cannot adhere to the catalyst. In class we talked about types of fuel cells that can do some of these things. The phosphoric acid fuel cell operates at about 220°C and, as such, can tolerate ~1% CO in its fuel stream. This makes it an excellent match to a methane reformer. The molten-carbonate and solid-oxide fuel cells operate at sufficiently high temperatures that they can execute the steam reforming reactions internally, right next to the membrane.

The Objectives of Part B of this Project

Part B: (your team should be starting this part no later than Sunday)

(1) to gain experience working with reactive equilibrium,
(2) to gain experience working with equilibrium constants,
(3) to understand the problems of providing hydrogen fuel for fuel cells,
(4) to get some exposure to reaction engineering, and
(5) to understand the challenges of running fuel cells in a system.

The Assignment for Part B

Requirements:

(1) <u>10 Points</u> Calculate the equilibrium constants of the steam methane reforming reaction (1) and water-gas shift reaction (2) as functions of temperature from 25°C to 1200°C. Put both reactions on the same plot and make it a semi-log plot (*i.e.,* plot $\log_{10} K_P$ vs. T). Confine the plot to the limits at which the reaction is driven to the left (essentially no reaction, $K_P \sim 10^{-3}$) and to the right (essentially complete reaction, $K_P \sim 10^3$) if they are reached in this temperature range. You might also take note of the temperatures at which the reactions are balanced ($K_P \sim 1$).

(2) <u>15 Points</u> Begin exploring the question of how to produce hydrogen from methane by plotting the equilibrium composition (mole fractions) of the SMR reaction as a function of temperature from 25°C to 1200°C. Is the composition pressure dependent? If so, plot the results at pressures of 1, 10, and 100 atm in order to explore the effect of pressure. Since real reformers use a 3:1 ratio of water to methane (molar) to avoid carbon formation, use atom ratios that correspond to these conditions. (For the purposes of this analysis, you may neglect the possibility of condensation of water vapor at the lower temperatures. Also do not consider the WGS reaction at this point, only the SMR reaction.)

(3) <u>15 Points</u> Explore the question of how to reduce the carbon monoxide in the reformed gas stream by using the water-gas shift reaction. Plot the equilibrium composition (mole fractions) of the WGS reaction as a function of temperature from 25°C to 1200°C. Is the composition pressure dependent? If so, plot the results at pressures of 1, 10, and 100 atm. Use the same atom ratios as in Part 2 (corresponding to a 3:1 ratio of water to methane). Again you may neglect condensation. (Do not consider the SMR reaction here, only the WGS reaction.)

(4) <u>30 Points</u> Now, let's make some hydrogen by reforming methane. Typical practice is to use three flow reactors (constant-pressure flow tubes packed with the appropriate catalyst) in series. In the first reactor, methane and water are injected and *both* reactions (1) and (2) are driven to equilibrium at the desired temperature and pressure. After exiting this reactor, the product stream is cooled to an intermediate temperature before entering the second reactor. After exiting this stage, the products are further cooled before entering the final reactor.
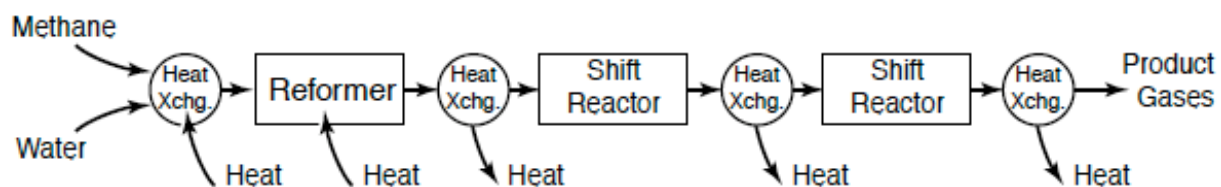
The purpose of the first reactor (the "reformer") is to get the whole process going. Although the methane reforming reaction only requires one mole of water for each mole of methane, in

practice the water-to-methane ratio used is about 3:1. This is done to avoid the possibility of forming carbon by direct pyrolysis ($CH_4 \rightarrow C + 2H_2$) of the methane. (It also makes it so that there is no need to add more water later for the subsequent "shift" reactors.) Before the reaction takes place, the methane and water are mixed together and preheated, usually using waste heat from downstream of the reformer. The reforming reaction is usually conducted over a nickel catalyst at a temperature around 800°C and it is highly endothermic. (Meaning you are going to have to transfer heat to the reactor to get it to remain at 800°C as the composition equilibrates.)

As you will soon show, the gases exiting the reformer are hydrogen rich, but they contain way too much CO to be used in a fuel cell. For this reason, the gases need to be cooled to where the equilibrium composition dictates that less CO is present. This is done using a heat exchanger to decrease the temperature to around 400°C before passing the gases over an iron-chromium catalyst. In passing through this second reactor, a small amount of chemical energy is released. If a cooled reactor design is used, this energy is removed as heat and the process remains isothermal. Alternatively, the reactor can be designed without cooling, in which case it is well modeled as being adiabatic and a temperature rise will occur.

The output of the second reactor is cooled to around 250°C before passing through the third reactor containing a copper catalyst. As with the second reactor, this one may be designed to be either adiabatic or isothermal. The output from this final reactor, if designed correctly, should be around 1% carbon monoxide. This is suitable for use in a fuel cell that operates at elevated temperatures (like a phosphoric acid fuel cell), but not for a PEM cell. To get down to 10 PPM, selective oxidation of the CO is used.

Building on the codes you have constructed for Parts 1-3, analyze the performance of a reformer system operating at atmospheric pressure. Find the composition of the gases exiting each of the reactor modules in the system. For the reformer, assume that the process is isothermal at 800°C. For the shift reactors, assume that the inlet temperatures are 400°C and 250°C for the high- and low-temperature shift reactors, respectively. For the shift reactors, calculate the outlet temperatures that would result if these reactors were adiabatic. Determine the shift reactor exit composition for both isothermal and adiabatic assumptions. Make a plot showing the exit composition for both isothermal and adiabatic assumptions at each station.

If the heat required by the reformer is supplied by burning methane, what fraction of the total methane used would be consumed to do the heating? Assuming that all other heating steps are accomplished by heat recovery, this gives one way of measuring the "cost" of making hydrogen by this process. Another measure is the ratio of the lower heating value of the hydrogen produced to the lower heating value of the methane required to produce it. For both of these calculations, use the lower heating value at standard reference conditions, and for the latter calculation, don't forget to include the methane burned to heat the reformer.

Hint: Your plots from Part 2 should show that at 1 atm and 800°C the SMR reaction has destroyed essentially all of the methane in the gas stream. This means that in calculating the compositions for Part 4 only the WGS reaction needs to be considered. (The way this works in practice is that the catalysts used in the shift reactors are chosen so that they do not promote methane formation thereby blocking the reverse SMR reaction from occurring as the temperature is reduced.)

Questions to Consider

Suppose you wanted to supply the Ballard fuel cell system directly with methane, and hydrogen was produced internally using this reformation process. Combine the reformation efficiency with the Ballard fuel cell efficiency to come up with an overall first-law system efficiency for a PEM fuel cell that could be fed methane. In other words, what percentage of the methane's free energy would be utilized by the Ballard power system? How does this compare to burning methane in a modern gas turbine with a first law efficiency of ~50%? There is no need to answer these questions for your report.

The Write-Up for Part B

Please provide the plots requested. For the numerical answers, please organize your responses into a neat, professionally formatted table (see below).

As always, please include the following items not normally included in a professional write-up:

(1) a brief statement of how much time was spent on each part of the analysis and write-up,
(2) a brief statement giving your opinions of the most and least useful aspects of the assignment,
(3) a brief comment about anything that is still unclear to you

Part B Deliverables

➢ Plot of equilibrium constants versus temperature for both the SMR and WGS reactions
➢ Plot of equilibrium mole fractions of the SMR reaction versus temperature
    One curve for each pressure if composition is pressure dependent
➢ Plot of equilibrium mole fractions of the WGS reaction versus temperature
    One curve for each pressure if composition is pressure dependent
➢ Plot of exit composition versus system station
    One curve for the adiabatic assumption and one for the isothermal
➢ Table of final metrics (complete the following table)
➢ Code uploaded to the Canvas assignment.

	Reformer	1st Shift Reactor		2nd Shift Reactor	
	Isothermal	Isothermal	Adiabatic	Isothermal	Adiabatic
Inlet Temperature °C	800 °C	400 °C	400 °C	250 °C	250 °C
Exit Temperature °C	800 °C	400 °C	?	250 °C	?
Exit Composition					
mole-% CO_2	?	?	?	?	?
mole-% H_2O	?	?	?	?	?
mole-% CO	?	?	?	?	?
mole-% H_2	?	?	?	?	?
Heat Addition for Isothermal Reaction (MJ per kg reactants)	?	?	NA	?	NA
Methane Burned to Heat Reformer (%)	?	NA	NA	NA	NA
Efficiency: LHV° H_2 per LHV° CH_4 used (%)	NA	NA	NA	?	?

Appendix

This describes what each column in the Sample Data Sets represents. **Please remember to indicate which data set you used in your project report**.

I_load = Current flowing through the load (resistor bank) in amps
I_stack = Current flowing out of the fuel cell stack in amps
V_load = Load voltage in volts
V_stack = Stack voltage in volts
H2 flow = Hydrogen flow rate in standard cubic feet per hour.
Air flow = Air flow rate in standard cubic feet per minute.
P_humid_air = Pressure of the 100% humidified inlet air in psi gage.
P_H2 = Pressure of the inlet hydrogen in psi gage.
T1 = Air temperature into stack in degrees Celsius
T2 = Air temperature out of stack in degrees Celsius
T3 = Water reservoir temperature in degrees Celsius
T4 = Water temperature into stack in degrees Celsius
T5 = Water temperature into heat exchanger in degrees Celsius
T_stack = Stack temperature in degrees Celsius