FINITE DIFFERENCE SIMULATION OF A WATER-EXHAUST GASES EVAPORATOR IN SOLID OXIDE FUEL CELL SYSTEMS

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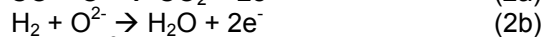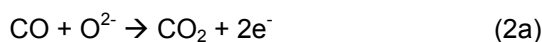turhan@mam.gov.tr

ABSRACT

Fuel cells are isothermal devices. Solid oxide fuel cells operate at temperatures up to 1000^oC. Fuel cell exhaust gases may include a certain amount of unburned gases. These gases can be burned in catalytic converters to supply additional heat energy. Exhaust gases in the temperature range of 300^oC to 800^oC can be obtained from fuel cell stack. On the other hand, original fuels, for example natural gas, should be converted to carbon monoxide and hydrogen in order to utilize in fuel cell. This fuel reforming process occurs by reacting of fuel and steam in high temperatures. Required high temperature steam can be obtained by using exhaust gas stream in an evaporator. In order to develop design parameters of a 2 kW solid oxide fuel cell exhaust gas-water evaporator, a finite difference model is developed and temperature and pressure drop profilers are calculated. This paper will explain details and the formulations of such a simulation model.

INTRODUCTION

Solid oxide fuel cells are devices to convert chemical energy directly to electrical energy. The basic building blocks of the fuel cells are electrodes and electrolyte. The electrolyte layer of the solid oxide fuel cells are made of yttrium stabilized zirconia (For example 0.08 Y_2O_3 0.92 ZrO_2), Strontium doped lanthanum manganite ($LaSrMnO_3$; $LaCo0_.8Mn_{0.2}O_3$ …) and nickel zirconia cermets ($Ni-ZrO_3$) are used as cathode and anode materials. Air is ionized in cathode by using electrons coming through the electrical connections from anode site.

$$O_2 + 4e^- \rightarrow 2O^{2-} \quad (1)$$

Where O^{2-} ions pass through the electrolyte to the anode site. In the anode site fuel is reacted with ionized air, combustion products and electrons are resulted.

$$CO + O^{2-} \rightarrow CO_2 + 2e^- \quad (2a)$$
$$H_2 + O^{2-} \rightarrow H_2O + 2e^- \quad (2b)$$
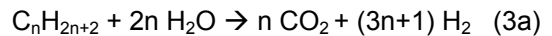$$CH_4 + O^{2-} \rightarrow 2H_2O + CO_2 + 8e^- \quad (2c)$$

Electrons are sent through the external wires to cathode and used as electrical energy.
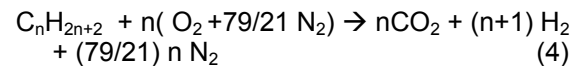
The optimum operation conditions of this device are approximately 900 °C and atmospheric pressure. Enthalpy of the exhaust gases is very high due to high temperatures. Some of this available energy is utilized to heat up incoming air and fuel streams. Fuel is not utilized fully in fuel cells. About 85 % can be converted through above reactions. The rest is exhausted from the fuel cells together with the exhaust gases. These mixtures can be combusted by using exhaust air stream and additional air if required. If the mixture is combustible, combustion process is used. For the poor mixtures catalytic reactors similar to car exhaust systems can be used to make the combustion process.

Hydrogen is an ideal fuel for fuel cell, unfortunately it is not a natural fuel existed and its storage is extremely difficult. In general other fuels are converted to hydrogen carbon monoxide and methane to be utilized as fuel in solid oxide fuel cells. Several methods are used for this conversion (fuel reforming) process. The most common reactions are

- Water shift reaction:

$$C_nH_{2n+2} + 2n\ H_2O \rightarrow n\ CO_2 + (3n+1)\ H_2 \quad (3a)$$
$$C_nH_{2n+2} + n\ H_2O \rightarrow n\ CO + (2n+1)\ H_2 \quad (3b)$$

- Partial oxidation reaction:

$$C_nH_{2n+2} + n(\ O_2 + 79/21\ N_2) \rightarrow nCO_2 + (n+1)\ H_2 + (79/21)\ n\ N_2 \quad (4)$$

From these reactions water shift reaction is endothermic, which requires an important amount of heat input. Ideal reaction temperatures could be in the range of 400 °C to 700 °C. This heat can be supplied by using additional combustion chamber or the heat of the fuel cell exhaust. The water in the reaction also should be heated to the same temperature ranges. Therefore, water first be evaporated and then superheated before it is combined with the fuel. In this study a model of water evaporator catalytic reactor exhaust gases are prepared. This model is applied to 2KW electrical output solid oxide fuel cell system. It is assumed that water is flowing inside of the tubes in a tube and shell heat exchanger, while exhaust gas mixture is flowing in shell site. The model developed is general and can be applied to any size shell and

tube exhaust gas-water evaporator. Caution should be applied to some of the formulation parameters. For example annular flow assumptions are taken in evaporation process due to small pipe diameters. This should be justified or changed for the relatively big tube diameters.

THEORETICAL FORMULATION

Calculations of thermophysical properties
Enthalpies of the gases are evaluated by using perfect gas equations and partial continuous specific heat equations.

$$Cp_i(T) = A_i + B_i*10^{-3}*T + C_i*10^5/T^2 + D_i*10^{-6}*T^2$$
$$T_{Hi} < T <= T_{Li} \tag{5}$$

Where A_i, B_i, C_i, and D_i, are equation coefficients for the temperature range T_{Li} and T_{Hi}. Nonlinear curve fitting is applied to table datas to find the coefficients [Ref 6] Enthalpy, entropy and Gibbs free energy are determined by using standard thermodynamic equations from the given specific heat equation. Enthalpy can be calculated from partial continuous Cp equations as:

$$h(T) = (\sum_{i=1}^{N-1} \int_{TLi}^{THi} Cpi(T).dT) + \int_{TLi}^{T} Cpi(T)dT \tag{6}$$

The data of kinematic viscosity and thermal conductivity are calculated from the following polynomial equations.

$$k(T) = \sum_{i=0}^{N} ka_i \cdot T^i \tag{7}$$

$$\mu(T) = \sum_{i=0}^{N} ma_i \cdot T^i \tag{8}$$

The polynomial coeeficients k_{ai} and ma_i are calculated by using table values [ref 7] and polynomial curve fitting methods. The Prandtl number is also calculated in this class from these properties through the equation 9

$$Pr(T) = Cp(T). \mu(T)/k(T) \tag{9}$$

Thermophysical properties of ideal gas mixtures such as enthalpy, entropy, gibbs free energy, viscosity, Prandtl number and Thermal conductivity are calculated. The mixture properties are basically calculated using linear volumetric mixing rules. In calculation of viscosity and thermal conductivity, Wilke [ref 1] equations are used.

$$\mu_{mix} = \sum_{i=1}^{n} ((x_i\mu_i) / \sum_{j=1}^{n} (x_j\phi_{ij})) \tag{10}$$

$$\phi_{ij} = (1+(\mu_i/\mu_j)^{1/2}(M_j/M_i)^{1/4}))^2/(8+8M_i/M_j)^{1/2}) \tag{10a}$$

where M_i is the molecular weight, x_i is the mole fraction.

The thermodynamic properties of water and steam is calculated by using J.H. Keenan, F.G. Keyes , P.G. Hill and J.G. Moore equation of state [ref 3] . In this equation of state Helmholtz free energy is given as basic form

$$\Psi(T) = \Psi_0(T) + RT(\ln(\rho) + \rho Q(\rho,\tau)) \tag{11}$$

$$\Psi_0(T) = \sum_{i=1}^{6} C_i/\tau^{I-1} + C_7\ln T + C_8\ln T/\tau \tag{11a}$$

$$Q(\rho,\tau) = (\tau-\tau_c)\sum_{j=1}^{7}(\tau-\tau_{aj})^{j-2}[\sum_{i=1}^{8}A_{ij}(\rho-\rho_{aj})^{i-1}$$

$$+ e^{-E\rho}\sum_{i=1}^{8}A_{ij}\rho^{i-9}] \tag{11b}$$

where $\tau = 1000/T$, T is temperature, K, and R is the gas constant. A_{ij} and C_i and E_i are constants.

The derivatives of this function define the water thermodynamic properties. Like
$$P = \rho^2(\delta\psi/\delta\rho)_\tau \tag{12a}$$
$$U = [\delta(\psi\tau)/\delta\tau]_\rho \tag{12b}$$
$$s = -(\delta\psi/\delta T)_\rho \tag{12c}$$
$$h = u + Pv \tag{12d}$$
Saturation curve of the steam is defined in the same source as:

$$P_s = P_c*\exp[\tau 10^{-5}(T_c-T)] \sum_{i=1}^{8}F_i(0.65-0.01T)^{i-1}] \tag{13}$$

where F_i coefficients are constants, T_c and P_c are critical temperature and pressure, respectively. For water and steam viscosity, thermal conductivity and surface tension between water and liquid phases are also calculated in the model by using curve-fitting equations of two dimensions (pressure and temperatures)

The friction coefficients inside the tubes are calculated using the critical Reynolds number concept:

$$Re = \rho(T,P) V_m D_H / \mu(T,P) \tag{14}$$

Note that properties to be calculated could be multiphase. Critical Reynolds number is assumed to be equal to 2300. The pipe class assumed as laminar flow below this value. For laminar flow circular tubes

$$f = 64/Re(T,P) \tag{15}$$

For the flow above the critical Reynolds number model assumes turbulent flow and friction coefficient is calculated by using turbulent model. Therefore friction factor is determined by solving Colebrook's equation

$$g(T,P)=1/\sqrt{f} +2.0\log_{10}(((\epsilon/D_H)/3.7+$$

$$2.51/(Re(T,P)\sqrt{f})) = 0 \qquad (16)$$

where ϵ is the surface roughness, D_H is the hydraulic diameter. This is a nonlinear equation and it should be solved to obtain a value for friction factor. Newton-Raphson method is used to solve this equation. Newton Raphson is an iterative method, defined by equation 17.

$$f_i(T,P) = f_{i-1}(T,P) - g(T,P) / (dg(T,P)/df(T,P)) \quad (17)$$

In order to determine the initial conditions equation 18 is used.

$$f(T,P)=1.325/(\log_e((\epsilon/D_H)/3.7+5.74/Re(T,P)^{0.9}))^2 \qquad (18)$$

In order to calculate convective heat transfer coefficients for the boiling, it is assumed that flow is annular due to very small tube diameter (internal diameter is less than 3.75 mm). For this assumption the following heat transfer equation [Ref 4,5] is used:

$$Nu=hD/k=0.029*Re_{TP}^{0.87}*Pr_{sivi}^{0.33}(\mu_{liquid-boiling}/\mu_{liquid-wall})^{0.14} (3.5*1/X_{tt}^{0.5}) \qquad (19)$$

$$Re_{TP}=(1x)\rho_{liquid}V_{liquid}D/\mu_L+ x\rho_{vapour}V_{vapour}D/\mu_{vapour} \qquad (19a)$$

$$X_{tt}=((1-x)/x)^{0.9}(\rho_{liquid}/\rho_{vapour})^{0.5}(\mu_{liquid}/\mu_{vapour})^{0.14} \qquad (19b)$$

Where U is velocity, x is quality, percent of vapor in the mixture kg kg/kg mixture, X_{tt} is Lockhart and Martinelli parameter and Re_{TP} is the two phase Reynolds's number.

For one phase laminar flow Nu number is constant, for one phase turbulent flow. For Turbulent flow Gnielenski [Ref 2] equation is used

$$Nu= hD/ k = f / 8* (Re – 1000)* Pr / (1+12.7*(f/8)^{0.5}*Pr^{2/3}-1)) \qquad (20)$$

Heat transfer of the external tube (for gas mixture) is calculated from:

$$Nu=hD/k=[0.3+0.62*Re**0.5*Pr**(1/3)/(1+(0.4/Pr)**(2.0/3.0))**(1.0/4.0)*(1+(Re/282000.0)**(5.0/8.0))**(4.0/5.0)] \qquad (21)$$

Total overall heat transfer coefficient is calculated from overall heat transfer coefficient. For a pipe piece of length dX, outside diameter D_0, inside diameter D_i, internal and external fouling resistance 0.0001,

overall heat transfer coefficient can be written as :

$$U_0=A_0/[1/(h_iA_i)+0.0001/A_i+\log(A_i/A_0)/(2*\pi*k*dX)+0.00001/A_0+1/(h_0A_0)] \qquad (22)$$

where

$$A_0= \pi*D_0*dX \qquad (22a)$$
$$A_i= \pi*D_i*dX \qquad (22b)$$

Pressure drop inside of the pipe can also be calculated from

$$dP= f(T,P)/D_H * dX * V(T,P)* V(T,P) / 2 \qquad (23)$$

In this equation dP indicates the pressure drop, D_H is hydraulic diameter, V(T,P) is the velocity and dX is the length of the pipe. Velocity, V, can be calculated from mass flow rate, density and pipe diameter

$$V=4*m/(\rho*\pi*D_i^2) \qquad (24)$$

Finite difference formulation
Consider a tube of finite length dX, as shown in Figure 1, sufficiently small, so that thermopyhsical properties can be assumed to be constant for this small element. If mass and heat transfer is investigated for this pipe section following heat balance equations can be written:

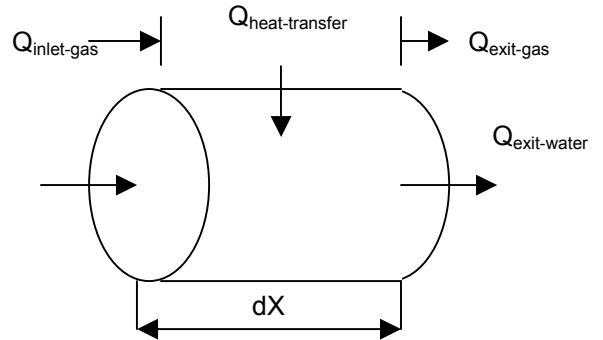$$dQ = Q_{inlet-gas}-Q_{exit-gas} = Q_{exit-water} – Q_{inlet-water} = Q_{heat-transfer} \qquad (25)$$

Figure 1: Finite difference element of the tube

From equation [25] the following equation can be written:

$$dQ = Q_{heat-transfer} = U_0* A_0*(T_{gas} – T_{water}) \qquad (26)$$

where T_{gas} is the temperature of the gas mixture, T_{water} is the temperature of the water-steam phases inside of the tube and A_0 is the outside surface area of the tube. If first law of thermodynamic (energy balance) of the entering and exiting gas and water is written, equation 27 and 28 can be written:

$$dQ = Q_{inlet-gas} - Q_{exit-gas} = m_{gas} * (h_{gas-inlet} - h_{gas-exit}) \quad (27)$$

$$dQ = Q_{exit-water} - Q_{inlet-water} =$$
$$m_{water} * (h_{water-exit} - h_{water-inlet}) \quad (28)$$

Due to small size of the finite element all the properties are assumed to be constant. Properties are taken for the inlet point of the element. Exit conditions can be calculated from the inlet conditions by considering the energy balance of the element(eqns (25)-(28)). Enthalpies at the exit of the finite pipe section can be calculated as:

$$h_{gas-exit} = h_{gas-inlet} - dQ/m_{gas} = h_{gas-inlet} - Q_{heat-transfer} /m_{gas} \quad (29)$$

$$h_{water-exit} = h_{water-inlet} - dQ/m_{water} = h_{water-inlet} + Q_{heat-transfer} /m_{water} \quad (30)$$

Pressure at the exit can be calculated from inlet pressure and pressure drop:

$$dP = P_{exit-water} - P_{inlet-water} = f(T,P)/D_H * dX *$$
$$V(T,P) * V(T,P) / 2 \quad (23)$$
$$P_{exit-water} = P_{inlet-water} - dP \quad (23a)$$

When enthalpy and pressure at the exit of the finite tube section is known, temperature can be calculated, by using thermodynamic properties of water-steam system (eqns 11..13)

Due to non-linear nature of the equations, these equations are solved by using non-linear equation solving methods such as Newton-Raphson iterative methods:

$$T_{exit-water-(iteration\ i)} = T_{exit-water-(iteration\ i-1)} - h_{exit-water}$$
$$* (T_{exit-water-(iteration\ i-1)}, P_{exit-water-(iteration\ i-1)})/$$
$$[dh(T_{exit-water-(iteration\ i-1)}, P_{exit-water-(iteration\ i-1)})/dT]$$
$$(31)$$

In the steam property calculations operation region is also an important parameter. For example, in the saturation region calculated function is not temperature (as known temperature is direct function of pressure for this region), but quality, x.

For the exit of the tube (gas phase) can be calculated by using similar methods, but due to perfect gas assumption gas mixture enthalpies are only function of temperatures and calculation process is relatively easy for this gas mixture.

$$T_{exit-gas-(iteration\ i)} = T_{exit-gas-(iteration\ i-1)} - h_{exit-gas}(T_{exit-water-(iteration\ i-1)})/[dh(T_{exit-gas-(iteration\ i-1)})/dT]$$
$$(32)$$

$$T_{exit-gas-(iteration\ i)} = T_{exit-gas-(iteration\ i-1)} - h_{exit-gas}(T_{exit-water-(iteration\ i-1)})/C_p(T_{exit-gas-(iteration\ i-1)})$$
$$(32a)$$

Total heat transfer can be calculated by summation of the each finite section heat transfer. Note that heat loss is not considered in this model due to good layer of insulation used around actual systems.

CASE STUDY
Finite difference calculations in here are performed for the following case: A 2 kW solid oxide fuel cell shell and tube water evaporator. Exhaust gases used has the following mixture gases:
0.0385 CO_2
0.7008 N_2
0.149 O_2
0.1117 H_2O

The temperature of the inlet gas was 350 °C. By using two, 2 m tube coil inside of the heat exchanger, evaporator temperature profile is calculated as given in Figure 2.
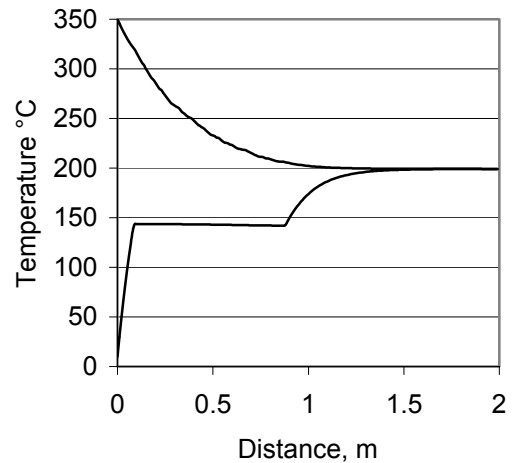

Figure 2: 2 KW SOFC tube and shell water evaporator temperature profile

The change of steam quality vs. distance is given in Figure 3. Due to high temperature difference and small pipe diameter, steam-boiling process is completed less then 1 m pipe length. In Figure 4, pressure drop of the evaporator is shown. This evaporator is a prototype therefore in order to achieve complete evaporation high pressure drop is specifically selected

Using the result of these simulations, actual evaporator is designed and operated. Results are found to be satisfactory. The total steady state error is found to be less then 30%.

Due to internal evaporation nature of the evaporator, water should be very clean. In commercial processes this kind of evaporator might not be satisfactory. In the next stages of developments (bigger power output), a separate boiler and superheated might be designed for the next stages with boiling at the external tube

surfaces and gas in internal surfaces. This design will not have the same water purity requirement we faced, but the size of the total evaporator and super heater will be much bigger.
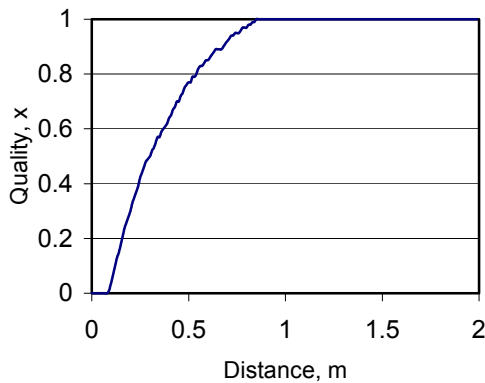

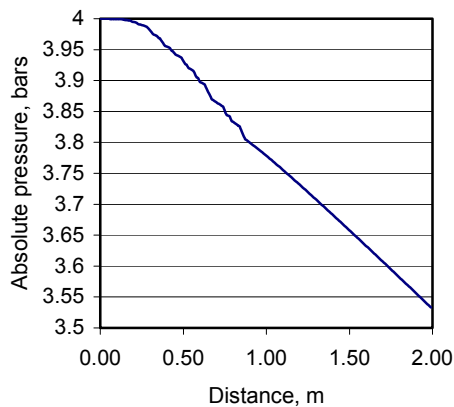Figure 3: 2 KW SOFC Tube and shell water evaporator steam quality

Figure 4: 2 KW SOFC Tube and shell water evaporator pressure drop

CONCLUSITION

A steady state tube and shell evaporator model is developed. In this eveporator fuel cell exhaust gases flow in the shell and water evaporated inside of the tubes. Model is used to obtain physical parameters for 2KW Solid Oxide fuel cell evaporator. This evaporator is designed and used in the real system and results were satisfactory, so model provide a good data for designing and manufacturing.

NOMENCLATURE

A_i, B_i, C_i, D_i : coefficients of C_{Pi}
A_{ij}, C_i, F_i : water-steam equation coefficients
C_{Pi} : specific heat between temperatures T_{Li}, T_{Hi}
dA : the heat transfer area of the small heat exchanger section

dX : the length of small heat exchanger section
f: friction factor
Ψ : Helmholts free energy function for water and
g(T,P) Colebrook's equation
dg(T,P)/df(T,P) : derivative of colebrook's equation
h: enthalpy
k:thermal conductivity
ka_i : coefficients of thermal conductivity equation
μ : viscosity
m : mass flow rate
ma_i: coefficients of viscosity equation
Nu(T,P) : Nussel's number
Pr(T) : Prantl number
Re(T,P) Reynolds's number
Re_{TP} : Two phase Reynolds number steam
$Q(\rho,\tau)$: subterm of the Ψ = Helmholts free energy function for water and steam
Q, dQ : heat and heat transfer
x_i: molar ratio of the ith gas
X_{tt} : Lockhart and Martinelli parameter
T_{Li}, T_{Hi} : temperature range for C_{pi} equation
T : temperature
τ = 1000/T, a temperature function
U : overall heat transfer coefficient
V: velocity

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