[AMN04] Dynamic modelling of fuel cell system for mobile application using Simulink environment

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Introduction

Nowadays, the increment of the petrol price has been a major problem for the consumers and it will increase more than 4 cent per litter in period of 6 to 12 month. Thus, there are many new energy developments that friendly to the environment have been commercialized to overcome this phenomenon such as solar energy and fuel cells technology. Among these, fuel cell power systems for transportation applications have received increased attention in recent years because of the potential for high fuel efficiency and lower emissions. A fuel cell converts hydrogen and oxygen into water, directly generating electrical energy from chemical energy without being restricted by efficiency limits of the Carnot thermal cycle (Larminie et al., 2000).

Proton exchange membrane (PEM) fuel cells are preferred for mobile application, because their low operating temperatures (around 80°C) and have provided more work from a given quantity of fuel and less polluting than internal combustion and gas turbine engines. Although, the limitation of hydrogen produce may become a minor problem, a fuel processor may be required to generate a hydrogen-rich stream using natural gas such as methane and methanol. So, the complete fuel cell system consists of a fuel processor unit and a PEM fuel cell stack unit as shown in Figure 1 and the aim of this study was to develop the plant simulation as a read for plantwide control configuration.

Material and Methods

The model development is divided into two main categories which are the development of the fuel processor and PEM fuel cell stack. The system generated a power of 5 kW and has been developed using Simulink environment (Matlab 6.5.1).

Fuel processor unit development

A fuel processor unit consists of an autothermal reactor (ATR), a water gas shift reactor (WGSR), a preferential oxidation reactor and two units of heat exchanger. The combinations of all these units produce a rich hydrogen stream and below 10 ppm CO concentration feed to PEM fuel cell stack.

Autothermal reactor mathematical model

A one-dimensional heterogeneous model is chosen in this work to simulate a tubular fixed-bed reactor. The mass and energy equations for the bulk and gas phase as well as the corresponding initial and boundary conditions are described below (De Smet et al., 2001):

Gas phase

\[ \frac{d}{dz} \left( \frac{C_i}{\rho_f} \right) + k_x a_f (C_i - C_{i,s}) = 0 \]  

\[ \frac{d}{dz} \left( \frac{T_g}{\rho_f} \right) + h_f a_f (T_g - T_s) = 0 \]  

Solid phase

\[ \rho_f \frac{1}{r_p} \frac{D_{i,s}}{\rho_f} \frac{d}{dz} \left( \varepsilon^2 \frac{d}{dz} \left( \frac{C_{i,s}}{\rho_f} \right) \right) + R_{w,s} \rho_s = 0 \]  

\[ h_f a_f (T_g - T_s) + \left( 1 - \varepsilon \right) \sum \Delta H_i \rho_s R_{w,i} = 0 \]  

Gas-phase boundary conditions

\[ z = 0 \quad C_i = C_i^o \quad T_g = T_g^o \]  

Solid-phase boundary conditions

\[ \varepsilon = 0 \quad \frac{d}{d\varepsilon} \left( \frac{C_{i,s}}{\rho_f} \right) = 0 \]  

\[ \varepsilon = 1 \quad \rho_f \frac{D_{i,s}}{r_p} \frac{d}{d\varepsilon} \left( \frac{C_{i,s}}{\rho_f} \right) = 0 \]

FIGURE 1 Flow diagram of PEM fuel cell plant
The simulation of the autothermal reaction is based on the following set of differential equations (Ann De Groote et al., 1996).

Continuity Equations
\[
\begin{align*}
\frac{dC_{\text{CO}}}{dz} &= \frac{\rho_z}{u} \left( \eta_{1\text{r}_1} + \eta_{2\text{r}_2} - \eta_{3\text{r}_3} \right) \\
\frac{dC_{\text{H}_2}}{dz} &= \frac{\rho_z}{u} \left( 2\eta_{1\text{r}_1} \right) \\
\frac{dC_{\text{CO}_2}}{dz} &= \frac{\rho_z}{u} \left( \eta_{2\text{r}_2} \right) \\
\frac{dC_{\text{H}_2}\text{O}}{dz} &= \frac{\rho_z}{u} \left( \eta_{1\text{r}_1} \right)
\end{align*}
\]

Energy equation
\[
\frac{dT}{dz} = \frac{\rho_z}{u \rho_z C_p} \sum \eta \beta_i \left(-\Delta H_i\right)
\]

The effectiveness factors, \( \eta \) are taken from an average value based upon a number of off-line pellet simulations for the various effectiveness factors (Ann De Groote et al., 1996).

In the modelling of autothermal reforming of methane, it is necessary to combine all the rate equations for the total combustion, steam reforming for CO production and \( \text{CO}_2 \) production in the calculations. In this paper, the intrinsic reforming models (Xu et al., 1989) are adopted as presented below. These authors derived the intrinsic rate equations for the steam reforming of methane on Ni/MgAl\(_2\)O\(_4\) catalyst.

Total oxidation
\[
\text{CH}_4 + 2\text{O}_2 \iff 2\text{H}_2\text{O} + \text{CO} + 4\text{H}_2
\]

Steam reforming (CO production)
\[
\text{CH}_4 + \text{H}_2\text{O} \iff \text{CO} + 3\text{H}_2
\]

Steam reforming (CO\(_2\) production)
\[
\text{CH}_4 + 2\text{H}_2\text{O} \iff \text{CO}_2 + 4\text{H}_2
\]

Water gas shift reactor mathematical model

The water gas shift reactor (WGSR) provides primary CO cleanup, as well a secondary \( \text{H}_2 \) production. In most hydrocarbon processor, the water gas shift reactor is the biggest and heaviest component because the reaction is relatively slow compared to the other reactions and is inhibited at higher temperatures by thermodynamic (Tongtaek et al., 2003). Therefore, the simulation of the WGSR reaction is based on the following set of differential equations.

Mass balance equations
\[
\begin{align*}
\frac{dC_{\text{CO}}}{dt} &= \left( \frac{F_{\text{in}}}{V} C_{\text{CO,in}} - \frac{F_{\text{out}}}{V} C_{\text{CO,out}} \right) - r \\
\frac{dC_{\text{H}_2}}{dt} &= \left( \frac{F_{\text{in}}}{V} C_{\text{H}_2,in} - \frac{F_{\text{out}}}{V} C_{\text{H}_2,out} \right) + r \\
\frac{dC_{\text{CO}_2}}{dt} &= \left( \frac{F_{\text{in}}}{V} C_{\text{CO}_2,in} - \frac{F_{\text{out}}}{V} C_{\text{CO}_2,out} \right) + r \\
\frac{dC_{\text{H}_2\text{O}}}{dt} &= \left( \frac{F_{\text{in}}}{V} C_{\text{H}_2\text{O,in}} - \frac{F_{\text{out}}}{V} C_{\text{H}_2\text{O,out}} \right) - r
\end{align*}
\]

Energy equation
\[
\frac{dT}{dt} = \frac{\rho_z}{u \rho_z C_p} \sum \eta \beta_i \left(-\Delta H_i\right)
\]

The kinetic for WGSR is known critical when designing an efficient fuel reformer and optimizing its operating conditions. So, in this paper, the reaction kinetic proposed by Yongtaek and Stenger (2003) is used as presented below. The authors derived the reaction kinetic on Cu/ZnO/\( \text{Al}_2\text{O}_3 \) catalyst under operating temperature between 200°C to 250°C.

\[
\text{CO} + \text{H}_2\text{O} \iff \text{CO}_2 + \text{H}_2
\]

\[
r = k_e \exp \left( -\frac{E}{RT} \right) p_{\text{CO}}^{m_p} p_{\text{H}_2\text{O}}^{n_p} (1 - \beta)
\]

where
\[
\beta = \frac{p_{\text{CO}}}{p_{\text{CO}} + p_{\text{H}_2}} \frac{p_{\text{H}_2\text{O}}}{K_{\text{eq}}}
\]

Preferential oxidation reactor

The preferential oxidation reactor (PROX) is used to eliminate the CO that has not been converted in the WGSR. This reactor required to reach very low level of CO content in the fuel stream at the fuel cell inlet in order to avoid poisoning of the membrane (Zalc et al., 2002). It is assumed that the PROX is operating under an isothermal condition at a temperature of 250°C. The representative model can be described in the differential equations of mass and energy balance. Mass balance equations
\[
\frac{dC_{\text{CO}}}{dt} = \left( \frac{F_{\text{PROX,in}}}{V} C_{\text{CO,in}} - \frac{F_{\text{PROX,out}}}{V} C_{\text{CO,out}} \right) - r
\]
\[
\frac{dC_{CO,\text{in}}}{dt} = \left( \frac{F_{\text{PROX}}}{V} C_{CO,\text{in}} \right) - \left( \frac{F_{\text{PROX}}}{V} C_{CO,\text{out}} \right) + r \quad (27)
\]
\[
\frac{dC_{CO,\text{out}}}{dt} = \left( \frac{F_{\text{PROX}}}{V} C_{CO,\text{out}} \right) - \left( \frac{F_{\text{PROX}}}{V} C_{CO,\text{in}} \right) - 0.5r \quad (28)
\]

Energy balance equation
\[
\frac{dT_{\text{PROX}}}{dt} = (Q_{\text{in}} + E_{\text{run}} - Q_{\text{out}}) / Ch_{\text{PROX}} \quad (29)
\]

In this paper the kinetic of selective CO oxidation over the Cu$_{0.1}$Ce$_{0.9}$O$_{2-y}$ nanostructured catalyst can be well by employing the Liu and Flytzani-Stephanopoulos model equations (Sedmark et al., 2003).

\[
\text{CO} + \frac{1}{2} \text{O}_2 \rightleftharpoons \text{CO}_2 \quad (30)
\]

\[
r = \frac{k_1 K_1 P_{\text{CO}_2}}{1 + K_1 P_{\text{CO}}} \quad (31)
\]

where

\[
k_1 = A_1 \exp \left( - \frac{E_{1/2}}{RT} \right)
\]

\[
K_1 = B_1 \exp \left( \frac{Q}{RT} \right)
\]

Cooler Units

Two cooler units are needed in order to reduce the temperatures of the outlet gas streams from the ATR and the PROX respectively. In these equipments, the cooling water charged into the shell is from the PEM fuel cell water produce and the products of the ATR and PROX enter at the tube side. Each cooler unit have different configurations and specifications. It is assumed that the cooler unit is perfectly insulated, so that no energy lose to surrounding. Furthermore, no reaction occurs during the cooling. The models were represented by the energy balances of gases and cooling water.

First cooler unit energy balance equations

Gases
\[
\frac{dT_{\text{WEAR, in}}}{dt} = (Q_{\text{in}} - Q_{\text{out}} - Q_{\text{CL1}}) / Ch_{\text{CL}} \quad (32)
\]

Cooling water
\[
\frac{dT_{\text{WEAR, out}}}{dt} = (Q_{\text{WEAR, in}} - Q_{\text{WEAR, out}} + Q_{\text{CL1}}) / Ch_{\text{WEAR}} \quad (33)
\]

Second cooler unit energy balance equations

Gases
\[
\frac{dT_{\text{PEMFC, in}}}{dt} = (Q_{\text{in}} - Q_{\text{out}} - Q_{\text{CL2}}) / Ch_{\text{CL1}} \quad (34)
\]

Cooling water
\[
\frac{dT_{\text{WEAR, out}}}{dt} = (Q_{\text{WEAR, in}} - Q_{\text{WEAR, out}} + Q_{\text{CL1}}) / Ch_{\text{WEAR}} \quad (35)
\]

PEM fuel cell stack unit development

The dynamic model developed is based on appropriated energy, mass and electrochemical equations as applied to PEM fuel cell (Yerramalla et al., 2003). The whole modelling process can be divided into two parts.

Individual cell modelling

The chemical reactions occurring at the oxidation and reduction electrode of a PEM fuel cell are as follows:

\[
2H_2 + \text{oxidation} \rightarrow 4H^+ + 4e^- \quad (36)
\]

\[
O_2 + 4H^+ + 4e^- \rightarrow \text{reduction} \rightarrow 2H_2O \quad (37)
\]

Total cell reaction: \[ 2H_2 + O_2 \rightarrow 2H_2O \quad (38) \]

The various equations necessary for the modelling of an individual cell are presented below.

Butler-Volmer equation

The equation shows the net current density for one-step electrochemical reaction flowing through a metallic electrode is expressed using the following equation:

\[
i = i_0 \left[ e^{-\frac{nF\eta}{RT}} - e^{-\frac{nF(1-\eta)\eta}{RT}} \right] \quad (39)
\]

Normally the variables associated with this equation (the exchange current density $i_0$ and the charge transfer coefficient $\alpha$) are obtained from empirical procedures.

The anode overvoltage

The anode overvoltage can be represent by (Mann et al., 1996):

\[
\eta_{\text{an,at}} = -\frac{G_{\text{an}}}{2F} + \frac{RT}{2F} \ln \left( 4F AK_{\text{an},\eta} \right) - \frac{RT}{2F} \ln \frac{i}{i_0} \quad (40)
\]

Equation (36) after the insertion of the known parameter values and rearrangement, gives:

\[
\eta_{\text{an,at}} = -\left( 5.18 \times 10^{-6} \Delta G_{\text{an}} + 4.309 \times 10^{-5} \right) \times 7 \left[ 12.863 + \ln \left( \frac{4F K_{\text{an},\eta}}{i_0} \right) \right] \quad (41)
\]

The cathode overvoltage

Again, as previously proposed (Mann et al., 1996), the cathode overvoltage can be given by
\[ \eta_{ae, c} = \frac{RT}{\alpha_c \zeta_n \alpha_c F} \left( \ln \left[ nF4k \frac{\exp\left(-\frac{\Delta G_c}{RT}\right)}{\alpha_i} \right] + \frac{1}{\alpha_i} \ln \frac{c_{H_2}}{c_{H_2O}} \right) \]

As previously, after the insertion of the known parameter values and rearrangement, equation (38) becomes:

\[ \eta_{ae, c} = \frac{1}{\alpha_i} \left( -10.36 \times 10^{-4} \Delta G_c + 8.62 \times 10^{-3} \right) \times T \left( 12.863 \ln A + k_i + (1 - \alpha_i) \ln c_{O_2} - \ln i \right) \]  

(43)

The ohmic overvoltage

The resistance to electron transfer in the graphite collector plates and graphite electrodes plus resistance to proton transfer in the solid polymer membrane produce ohmic polarization. This could be expressed using ohm’s law equations such as:

\[ \eta_{ohmic} = -iR^{int}_{\text{internal}} \]  

(44)

The \( R^{\text{internal}} \) can be obtained from experimental results (Xue et al., 2003).

**Fuel cell stack modelling**

In this section, the various equations necessary for the modelling of the overall fuel cell system are presented. For \( N \) single cells connected in a fuel cell stack system, the total stack voltage (\( \Delta V_T \)) is calculated by:

\[ \Delta V_T = NV_{\text{cell}} \]  

(45)

Thus, for the current of a fuel cell stack is calculated by:

\[ I_{\text{stack}} = NI_{\text{cell}} \]  

(46)

Finally the total power produced by the entire stack is calculated by multiply the total stack voltage and the current of the stack.

\[ P_{\text{stack}} = \Delta V_T I_{\text{stack}} \]  

(47)

**Results and Discussion**

**Fuel cell system dynamic model simulation**

In this section, a detailed parametric analysis to study the dynamic effects within the system was carried out. The parameters and variables used in this part of study are listed in Table 1. The model was developed under Simulink environment (Matlab 6.5.1) and as some parameters are small such as a cell volume, stiff differential equation solver ODE23S is employed in the simulation. The time length for the simulation is 3500 s.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( D_r )</td>
<td>Diameter of ATR, m</td>
</tr>
<tr>
<td>( L_r )</td>
<td>Length of ATR, m</td>
</tr>
<tr>
<td>( T )</td>
<td>Temperature of ATR, K</td>
</tr>
<tr>
<td>( \rho_{\text{ATR}} )</td>
<td>ATR operating pressure, atm</td>
</tr>
<tr>
<td>( \rho_{\text{c}} )</td>
<td>Catalyst density, kg/m³</td>
</tr>
<tr>
<td>( \rho_i )</td>
<td>Species partial pressure</td>
</tr>
<tr>
<td>( K_{\text{eq}} )</td>
<td>Equilibrium Constant</td>
</tr>
<tr>
<td>( D_w )</td>
<td>Diameter of WGSR, m</td>
</tr>
<tr>
<td>( L_w )</td>
<td>Length of WGSR, m</td>
</tr>
<tr>
<td>( T_w )</td>
<td>Initial WGSR temperature, K</td>
</tr>
<tr>
<td>( P_{\text{WGSR}} )</td>
<td>WGSR operating pressure, atm</td>
</tr>
<tr>
<td>( D_p )</td>
<td>Diameter of PROX, m</td>
</tr>
<tr>
<td>( L_p )</td>
<td>Length of PROX, m</td>
</tr>
<tr>
<td>( T_p )</td>
<td>Initial PROX temperature, K</td>
</tr>
<tr>
<td>( P_{\text{PROX}} )</td>
<td>PROX operating pressure, atm</td>
</tr>
<tr>
<td>( L_{\text{WCL}} )</td>
<td>First cooler unit length, m</td>
</tr>
<tr>
<td>( n )</td>
<td>Number of tube</td>
</tr>
<tr>
<td>( T_o )</td>
<td>Initial cooler temperature</td>
</tr>
<tr>
<td>( L_{\text{WCL2}} )</td>
<td>Second cooler unit length, m</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>Transfer coefficient, anode</td>
</tr>
<tr>
<td>( \alpha_a )</td>
<td>Transfer coefficient, cathode</td>
</tr>
<tr>
<td>( F )</td>
<td>Faraday constant, C/mole</td>
</tr>
<tr>
<td>( R )</td>
<td>Universal constant of gases, J/mole.K</td>
</tr>
<tr>
<td>( \rho_{\text{a}} )</td>
<td>Air side pressure, atm</td>
</tr>
<tr>
<td>( \rho_{\text{f}} )</td>
<td>Fuel side pressure, atm</td>
</tr>
<tr>
<td>( T_{\text{cell}} )</td>
<td>Initial cell temperature, K</td>
</tr>
<tr>
<td>( N )</td>
<td>Number of cell</td>
</tr>
<tr>
<td>MEA active area, cm²</td>
<td>360</td>
</tr>
</tbody>
</table>

The parametric sensitivity of fuel cell system behaviour and its performance have been investigated for several parameters including operating temperatures and kinetic parameter. The influence of these operational parameters on the product composition depends strongly on the thermodynamics of the reactions. For this purpose, analysis has been studied over the ATR temperature of 800-1015 K and total feed flowrate from 2.0-3.0 m³/s to see the effect on other units compositions and power production.

The results are as follow:

1. Effect of step change in temperature
FIGURE 2   Results of step change in temperature

Figure 2 shows the CH₄ and H₂ concentrations of ATR, the ATR CH₄ and WGSR CO conversions, the power production, the temperature of WGSR and PROX units and the gas stream temperatures of first cooler and second cooler units. While the results of step change in temperature are shown in Table 2.

TABLE 2   The Effect of step change in temperature

<table>
<thead>
<tr>
<th>Parameter</th>
<th>800K</th>
<th>1015K</th>
</tr>
</thead>
<tbody>
<tr>
<td>ATR H₂ concentration, mol/m³</td>
<td>0.2469</td>
<td>0.7725</td>
</tr>
<tr>
<td>ATR CH₄ concentration, mol/m³</td>
<td>0.2428</td>
<td>0.0563</td>
</tr>
<tr>
<td>ATR CH₄ conversion, %</td>
<td>48.86</td>
<td>88.15</td>
</tr>
<tr>
<td>WGSR CO conversion, %</td>
<td>4.242</td>
<td>42.81</td>
</tr>
<tr>
<td>WGSR temperature, K</td>
<td>514.3</td>
<td>523.7</td>
</tr>
<tr>
<td>PROX temperature, K</td>
<td>509.7</td>
<td>519.1</td>
</tr>
<tr>
<td>Gas stream temperature of first cooler, K</td>
<td>515.9</td>
<td>526</td>
</tr>
<tr>
<td>Gas stream temperature of second cooler, K</td>
<td>350.4</td>
<td>352</td>
</tr>
<tr>
<td>Power production, kW</td>
<td>4.661</td>
<td>5.126</td>
</tr>
</tbody>
</table>

From the simulation results, temperature has a significant effect on kinetic productions of hydrogen and carbon monoxide due to the increment of methane converted toward high temperature. Furthermore, the temperature of other units increase since more heat energy is supplied.

2. Effect of step change in steam feed flowrate

Figure 3 shows the ATR products concentration, the WGSR products concentration, the PROX products concentration, the conversion of CH₄ for ATR and CO for WGSR and PROX. While Figure 4 indicates the power production towards step change in steam feed flowrate. The results of step change 0.5 m³/s to 1 m³/s in steam feed flowrate are shown in table 3.

FIGURE 3   Results of step change in steam feed flowrate

FIGURE 4   Power production of step change in steam feed flowrate

TABLE 3   The Effect of step change in steam feed flowrate

<table>
<thead>
<tr>
<th>Parameter</th>
<th>0.5</th>
<th>1.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>ATR concentration, mol/m³</td>
<td>0.7725</td>
<td>0.5788</td>
</tr>
<tr>
<td>H₂O</td>
<td>0.4272</td>
<td>0.4594</td>
</tr>
<tr>
<td>CO</td>
<td>0.4112</td>
<td>0.2897</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.2675</td>
<td>0.1748</td>
</tr>
<tr>
<td>O₂</td>
<td>0.0307</td>
<td>0.0148</td>
</tr>
<tr>
<td>CH₄</td>
<td>0.0563</td>
<td>0.0058</td>
</tr>
<tr>
<td>WGSR concentration, mol/m³</td>
<td>1.207</td>
<td>0.9657</td>
</tr>
<tr>
<td>H₂O</td>
<td>0.2979</td>
<td>0.2383</td>
</tr>
<tr>
<td>CO</td>
<td>0.2352</td>
<td>0.1881</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.2234</td>
<td>0.1787</td>
</tr>
<tr>
<td>PROX concentration, mol/m³</td>
<td>0.0314</td>
<td>0.0269</td>
</tr>
<tr>
<td>CO</td>
<td>0.2744</td>
<td>0.2352</td>
</tr>
<tr>
<td>O₂</td>
<td>0.0315</td>
<td>0.0230</td>
</tr>
<tr>
<td>ATR CH₄ conversion, %</td>
<td>88.15</td>
<td>98.47</td>
</tr>
<tr>
<td>WGSR CO conversion, %</td>
<td>42.81</td>
<td>35.07</td>
</tr>
<tr>
<td>PROX CO conversion, %</td>
<td>87</td>
<td>85.71</td>
</tr>
<tr>
<td>Power production, kW</td>
<td>5.126</td>
<td>3.877</td>
</tr>
</tbody>
</table>
Base on the results, the increment of steam flowrate has a significant effect on methane consumption in ATR. Since, more steam feed to the ATR, more CH₄ is reacted. But the production of CO, CO₂ and H₂ become lower since the steam to methane ratio is constant. It is also resulted in other units’ productions.

3. Effect of step change in methane feed flowrate

In this study, the increment of methane flowrate has a significant effect on methane and oxygen consumption in ATR. Since, more methane feed to the ATR, less methane and oxygen are reacted. So, the production of CO, CO₂ and H₂ become lower since the methane to oxygen ratio is constant. It is also effected other units’ productions.

From the thermodynamic analyses and kinetic simulation performed, the optimal operating conditions of the temperature is 1015 K, H₂O/CH₄ and CH₄/O₂ ratios of 2-3, feed flowrate of 2.0 m³/s (1 m³/s for CH₄, 0.5 m³/s for H₂O and O₂) for ATR and fuel processor pressure at 1 atm is favourable for PEM fuel cell stack.

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