

Analysis Of Heat Transfer And Fluid Flow Characteristics Of A Hydrogen Reformer For Fuel Cell Applications

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ABSTRACT

Fuel cells that utilize hydrogen are promising energy conversion units that have a high intrinsic efficiency. However there are operational difficulties in storing hydrogen. One way to alleviate this problem is to generate hydrogen *in situ* from a liquid fuel such as ethanol in a reformer. In this paper, an ethanol reformer was modeled as a tubular non-isothermal, non-isobaric packed-bed reactor with an annular heat transfer jacket, operating at unsteady state. Since the reforming reaction is endothermic, it is necessary to design a suitable heat transfer jacket to provide heat to the reformer. The partial differential equations of the reformer model were solved numerically after estimating the model parameters from the literature. The effect of inlet conditions on the heat transfer characteristics were studied. Model predictions of hydrogen generation were compared to experimental data available in the literature for a laboratory-scale reformer and were shown to be in excellent agreement. A commercial-scale reformer was designed using this high-fidelity model that can produce sufficient hydrogen to generate up to 5 kW of power when used in conjunction with a Ballard Mark V fuel-cell stack. Experimental data from the dynamic power consumption in a 3-bedroom house were used to determine the size of the reformer as well as a back-up battery that supplies power when the reformer is unable to meet the power demand.

INTRODUCTION

Fuel cells that utilize hydrogen are promising energy conversion units that have a high intrinsic efficiency [1]. Hydrogen gas produces almost no pollution when used in an energy system. In addition, hydrogen is high on energy content and it is a poison-free element. However there are operational difficulties in storing hydrogen. One way to alleviate this problem is to generate hydrogen *in situ* from a liquid fuel such as ethanol. Steam reforming of ethanol has the advantages of being a sulfur-free compound, process requires no pre-reforming, high hydrogen-to-carbon ratio, high energy density, is easy to store, safe to handle and transport, has low toxicity and volatility, and is commercially available [2]. For this reason, there is current interest in design and operation of ethanol reformers for producing hydrogen for fuel cell

applications. However, a review of the literature indicates that there are no dynamic models available that predict the performance of ethanol reformers in conjunction with a fuel cell stack and these are currently being design using *ad hoc* methods based on rules of thumb or based on steady state mathematical models. This provides the motivation for the present study.

O'Keefe and Palanki [3] used the kinetic model of Soyol-Baltacioglu *et al.* [4] to develop a mathematical description for a steady-state reformer that can supply 5 kW of energy. While this model is useful for designing an energy system that supplies a steady rate of power, this model cannot predict the dynamic behavior of the reformer, which is essential for design and operation of energy system where the power demand fluctuates with time. There have been recent attempts to develop dynamic models to describe the behavior of packed-bed reformers that produce hydrogen from hydrocarbon sources. Hoang and Chan [5] developed a two-dimensional dynamic model for a methane autothermal reformer and conducted simulation studies to determine the optimal operating conditions to maximize hydrogen yield. Sabeeh [6] developed a mathematical model for an ethanol reformer that captures the temporal and spatial variation of the species involved in the reforming reactions. In this paper, this model is utilized to study the heat transfer and fluid flow characteristics of the reformer and use these results to design a reformer that produces sufficient hydrogen for a 5 kW fuel-cell stack for residential power applications.

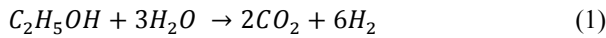
NOMENCLATURE

r_e	[$mol.m^{-1}.s^{-1}$]	Reaction rate
ρ_{cat}	[$kg.m^{-3}$]	Catalyst density
k_0	[$mol.kg^{-1}.s^{-1}.atm^{0.92}$]	Reaction rate constant
T	[K]	Reformer temperature
T_j	[K]	Jacket temperature
T_{ref}	[K]	Reference temperature
C_i	[$mol.m^{-3}$]	Molar concentration
D_{ms}	[$m.s^{-2}$]	Mass dispersion coefficient
D_{hs}	[$W.m^{-1}.K^{-1}$]	Heat dispersion coefficient
r	[m]	Radial component
z	[m]	Axial component
v_z	[$m.s^{-2}$]	Axial velocity
C_{pi}	[$J.kg^{-1}.K^{-1}$]	Specific heat of species i

ΔH_{rx} [J.mol ⁻¹]	Heat of reaction
U [W.m ⁻² .K ⁻¹]	Overall heat transfer coeff.
h_o [W.m ⁻² .K ⁻¹]	Outer heat transfer coeff.
h_i [W.m ⁻² .K ⁻¹]	Inner heat transfer coeff.
Re [-]	Reynolds number
Pr [-]	Prandtl number
I [A]	Current
F [C.mol ⁻¹]	Faraday Constant
ϵ [-]	Fuel cell efficiency factor
F_{H_2} [mol.s ⁻¹]	Hydrogen flow rate
n_{cell} [-]	Number of cells
V_{stack} [v]	Stack voltage

MODEL DEVELOPMENT

Ethanol steam reforming can be described by the following overall reaction



The following overall rate of reaction for ethanol steam reforming has been reported [4]

$$r_e = -(\rho_{cat} k_0 e^{\frac{E_a}{RT}}) (RT)^{\alpha+\beta} C_e^\alpha C_w^\beta \quad (2)$$

Figure 1 shows a schematic of a 2-dimensional axisymmetric reformer model.

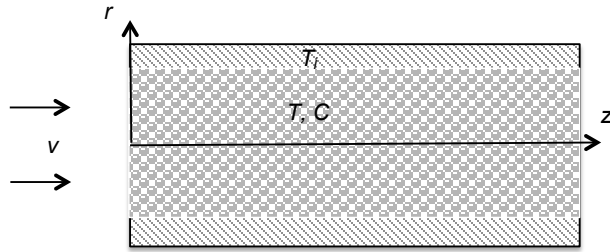


Figure 1: Schematic of 2-D axisymmetric reformer model

Assuming that the reformer is a packed bed reactor in a tubular geometry with constant cross-section, the reformer is initially empty and at room temperature, and the catalyst particles are spherical in shape, a species balance for ethanol, steam, carbon dioxide and hydrogen results in the following:

$$\frac{\partial C_i}{\partial t} = D_{ms} \left(\frac{\partial^2 C_i}{\partial r^2} + \frac{1}{r} \frac{\partial C_i}{\partial r} + \frac{\partial^2 C_i}{\partial z^2} \right) - v_z \frac{\partial C_i}{\partial z} + r_i \quad (3)$$

An unsteady state energy balance on the packed bed reactor results in the following:

$$\begin{aligned} \sum C_i C_{pi} \frac{\partial T}{\partial t} &= Ua(T_j - T) - v_z(T - T_{ref}) \left(\sum C_{pi} \frac{\partial C_i}{\partial z} \right) \\ &- (T - T_{ref}) \left(\sum C_{pi} \frac{\partial C_i}{\partial t} \right) - \left(\sum C_i C_{pi} \right) v_z \frac{\partial T}{\partial z} \\ &- \Delta H_{rx} r_e + \sum C_i C_{pi} D_{hs} \left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} + \frac{\partial^2 T}{\partial z^2} \right) \end{aligned} \quad (4)$$

where i refers to the species ethanol, water, carbon dioxide and hydrogen. The initial and boundary conditions can be written as

$$C_i(z, 0) = 0 \quad (5)$$

$$T(z, 0) = 298.15 \text{ K} \quad (6)$$

$$C_i(0, t) = C_{i,in} \quad (7)$$

$$T(0, t) = T_{in} \quad (8)$$

Assuming that the feed to the reactor has no radial variation in concentration in temperature and the concentration and temperature at the outlet of the reformer do not change as a function of length, the following additional conditions can be written:

$$\frac{\partial C_i}{\partial r}(0, t) = 0 \quad (9)$$

$$\frac{\partial T}{\partial r}(0, t) = 0 \quad (10)$$

Assuming that the tube length is sufficient for fully developed flow at the outlet, there is no change in concentration and temperature as a function of length at the outlet of the reformer, which results in:

$$\frac{\partial C_i}{\partial z}(L, t) = 0 \quad (9)$$

$$\frac{\partial T}{\partial z}(L, t) = 0 \quad (10)$$

Since the reforming reaction is endothermic, it is necessary to provide heat via a jacket for the reaction to proceed. It was assumed that ethanol was available at its flame temperature in the jacket and heat was transferred from the jacket to the packed bed reactor. The overall heat transfer coefficient was constructed from the inner and outer heat transfer coefficients and the resistance of the tube wall as shown below:

$$U = \frac{1}{\frac{1}{h_i D_i} + \frac{x_w}{k_t} \left(\frac{D_o - D_i}{\ln \left(\frac{D_o}{D_i} \right)} \right) \frac{1}{h_o} + \frac{1}{h_o}} \quad (11)$$

The outer heat transfer coefficient was estimated using the Dittus-Boelter equation [7] as shown below:

$$h_o = \frac{k_j}{D_h} (0.0265 Re^{0.8} Pr^{0.3}) \quad (12)$$

The inner heat transfer coefficient was evaluated as a sum of the wall resistance and the bed resistance as shown below [7]:

$$\frac{1}{h_i} = \frac{1}{h_{wall}} + \frac{1}{h_{bed}} \quad (13)$$

where

$$h_{bed} = \frac{8k_m}{D_i} (5 + 0.1 Re_p Pr) \quad (14)$$

and

$$h_{wall} = 1.94 Re_p^{0.5} Pr^{0.33} \quad (15)$$

The correlations used in the above equation are standard for fluid flow in packed beds. The parameters of the two-dimensional axisymmetric dynamic model of the reformer were estimated or obtained from the literature as shown in Sabeeh [6].

SIMULATION RESULTS OF REFORMER

A MATLAB code for solving a generalized system of parabolic differential equations was modified to solve the dynamic 2-dimensional axisymmetric model representing the reformer. This code utilizes a combination of a finite difference method and a second-order Runge-Kutta technique [8]. First, the model was tested with experimental data collected by Soyal-Baltcaoglu *et al.* [4]. These experimental results were obtained on a laboratory-scale reactor at steady-state and so the dynamic model was run for a sufficiently long time until there was no change in concentration and temperature as a function of time. The model predictions and the experimental data are shown in Figure 2 and it is observed that with no adjustable parameters, the model is able to predict the experimental

behavior quite well despite the significant uncertainty (over 100%) in computing the heat transfer coefficient using expressions represented by Equations 12-14. No experimental data on dynamic behavior of this system is available in the literature. While the prediction of steady-state behavior by running the dynamic model for sufficient time does not conclusively prove the accuracy of the dynamic model, it provides some confidence that the formulation is correct.

After testing the fidelity of the model on laboratory-scale data, several simulation studies were conducted on a reformer of a larger size that could generate sufficient hydrogen for a 5 kW fuel cell stack that is used in residential power applications. In residential applications, the power demand fluctuates throughout the day. For example, the power demand could be high when devices such as electric dryers and microwaves are being used and can be very low at night when most devices are shut down. When the power demand increases suddenly, the flow rate of hydrogen needs to be increased quickly, which implies a corresponding increase in ethanol going into the reformer. The dynamic reformer model can be used to determine how long it takes for the necessary hydrogen to be produced to provide sufficient power when the demand goes up.

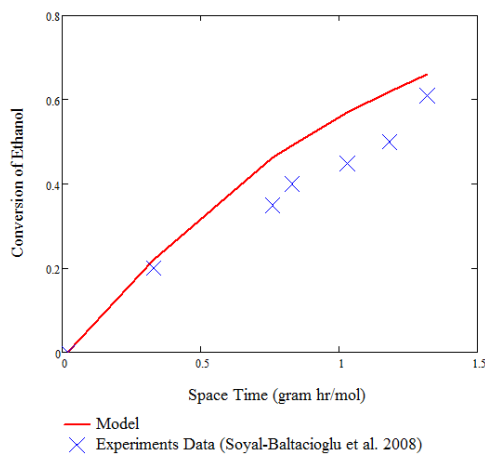


Figure 2: Comparison of model predictions with experimental data.

The dimensions of the reformer used are shown in Table 1.

Parameter	Value
Reformer Length	3 m
Inner Diameter of Reformer	20 cm
Outer Diameter of Reformer	20.5 cm
Jacket Outer Diameter	24.5 cm
Particle Diameter	0.3 mm
Inlet Temperature	900 K
Inlet Pressure	1 atm
Void Fraction	0.3
Steam to Ethanol Ratio	3

Table 1: Parameters of Reformer Used for Residential Power Application

Figure 3 shows the temperature profile that is generated after 62.4 s and it is observed that there is a sharp drop in

temperature at the reactor inlet. This is due to the fact that the reforming reaction is highly endothermic, coupled with the fact that the reaction rate at the reactor inlet is high due to high reactant concentration.

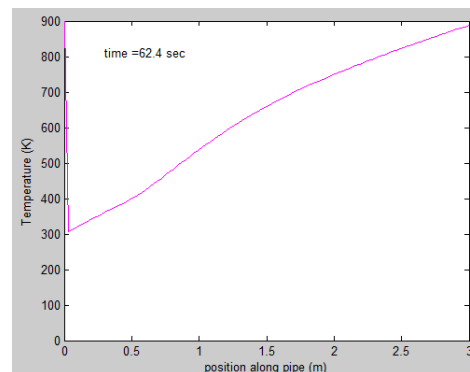


Figure 3: Temperature profile in reformer

Figures 4, 5 and 6 show the concentration profiles of ethanol, steam, carbon dioxide and hydrogen at three different time points: 51 s, 77.4 s and 169.8 s. It is observed that initially, there is no hydrogen coming out of the reformer as it takes some time for the gaseous reactants and products to go through the reactor. It is clear from Figure 6 that there is a significant time lag between changing ethanol flow rate and the corresponding change in hydrogen flow rate. If the power demand goes through a step increase, the hydrogen flow rate cannot be changed instantaneously. In this scenario, it is necessary to draw the required power from a back-up battery until the reformer outlet has sufficient hydrogen.

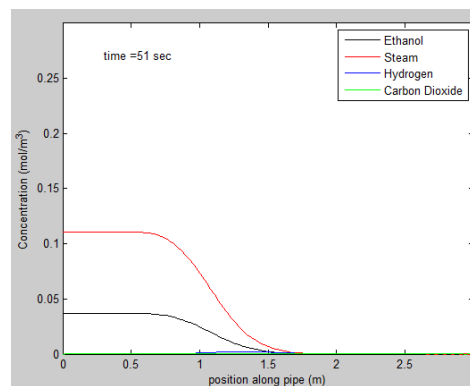


Figure 4: Species profile along the reformer length at 51 s

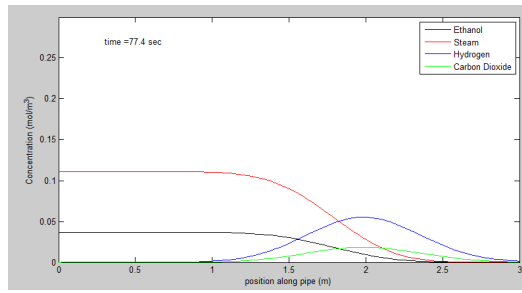


Figure 5: Species profile along the reformer length at 77.4 s

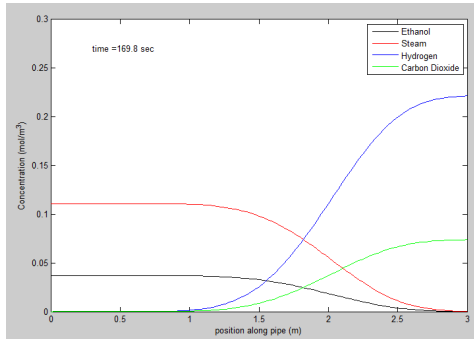


Figure 6: Species profile along the reformer length at 169.8 s

Furthermore, it is observed from Figure 6 that when the reactor reaches steady-state, the hydrogen yield is 0.021 mol/s and the conversion is 99.8%.

Next, the effect of changing inlet temperature on conversion was studied. The inlet temperature was varied from 650 K to 900 K and the resulting steady-state conversion was noted. Figure 7 shows the plot of ethanol conversion as a function of inlet temperature and it is observed that inlet temperature has a significant effect on steady-state conversion.

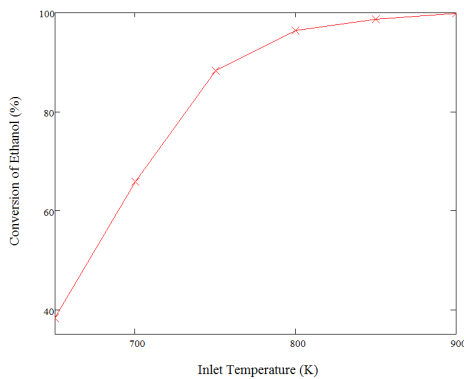


Figure 7: Plot of ethanol conversion as a function of inlet temperature

The effect of ethanol feed rate on the conversion of ethanol and hydrogen yield was studied and the results are shown in Figure 8. It is observed that as the molar flow rate increases from 0.003 mol/s to 0.008 mol/s, the conversion decreases from 99.8% to 3%. This is because the increased flow rate results in reduced residence time, and thus lower conversion.

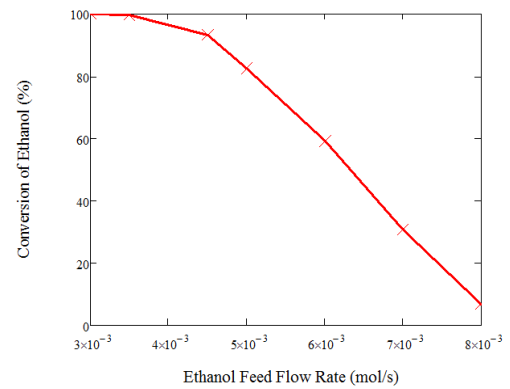


Figure 8: Plot of ethanol conversion as a function of ethanol feed rate

ANALYSIS OF REFORMER AND FUEL CELL SYSTEM

The dynamic model of the reformer was simulated in conjunction with a 5 kW Ballard Mark V fuel cell stack. The fuel cell stack current was calculated via the following equation [8]:

$$I = \frac{2F\epsilon F_{H_2}}{n_{cell}} \quad (16)$$

The voltage and current were correlated using the following expression for the polarization curve [6]:

$$V_{stack} = 6.963 \times 10^{-8} I^4 - 2.689 \times 10^{-5} I^3 + 3.611 \times 10^{-3} I^2 - 0.245 I + 35.217 \quad (17)$$

The stack power was computed from the current and the voltage as follows:

$$P_{stack} = n_{cell} I V_{stack} \quad (18)$$

Figure 9 shows a plot of power demand versus time from experimental data collected in a 3-bedroom house as well as the power supplied by reforming hydrogen and using it in the fuel cell.

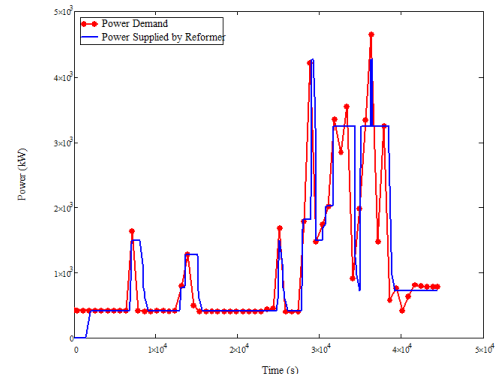


Figure 9: Plot of power demand and power supplied as a function of time in a 3-bedroom house

It is observed that when the power demand increases suddenly, there is a time lag of several minutes before the reformer is able to generate the necessary hydrogen to account for the increased demand in power. This is clearly not acceptable and it is necessary to design a backup battery that can supply the necessary power when the reformer is not able to supply sufficient hydrogen. A 12 v, 100 Ah lead-acid battery was chosen to account for the time lag in generating sufficient

hydrogen when the power demand increases suddenly. Figure 10 shows a plot of the power supplied by the battery when the reformer and fuel cell system is unable to provide sufficient power. It is observed that when the power demand increases suddenly, the extra power is drawn from the battery.

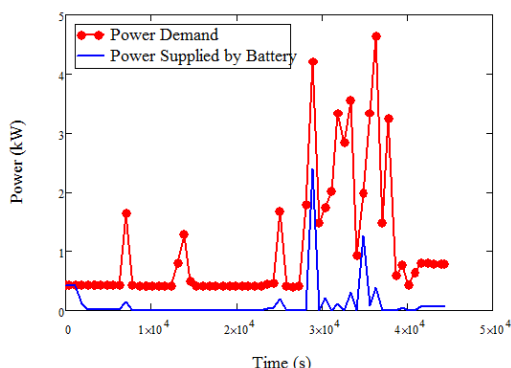


Figure 10: Plot of power provided by the backup battery as a function of time

CONCLUSIONS

A two-dimensional axisymmetric dynamic model of a reformer where ethanol is reformed to produce hydrogen was developed. Heat transfer correlations from the literature were used to compute the overall heat transfer coefficient and it was shown that the steady-state predictions were in good agreement with laboratory-scale experimental data available in the literature [4]. Dynamic simulations indicate that there is a significant decrease in temperature at the reformer inlet due to the endothermic nature of the reaction. Furthermore, there is a time lag in the order of minutes between changing ethanol flow rate and seeing the corresponding change in hydrogen flow rate. This time lag has to be accounted for when designing a reformer and fuel cell system for residential power applications where the power demand can fluctuate with time. The ethanol conversion was affected significantly by inlet temperature as well as the feed flow rate. Simulation results of a reformer with a 5 kW Ballard Mark V fuel cell stack indicated that while the hydrogen produced by the reformer changes with time to account for the fluctuating power demand, this power system is unable to meet the instantaneous power demand of a 3-bedroom house when the demand increases suddenly. A 12 v, 100 Ah backup battery was sufficient to provide the necessary power when the reformer was unable to provide sufficient hydrogen.

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