Simulation of a 250 kW diesel fuel processor/PEM fuel cell system

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Abstract

Polymer-electrolyte membrane (PEM) fuel cell systems offer a potential power source for utility and mobile applications. Practical fuel cell systems use fuel processors for the production of hydrogen-rich gas. Liquid fuels, such as diesel or other related fuels, are attractive options as feeds to a fuel processor. The generation of hydrogen gas for fuel cells, in most cases, becomes the crucial design issue with respect to weight and volume in these applications. Furthermore, these systems will require a gas clean-up system to insure that the fuel quality meets the demands of the cell anode. The endothermic nature of the reformer will have a significant affect on the overall system efficiency. The gas clean-up system may also significantly effect the overall heat balance. To optimize the performance of this integrated system, therefore, waste heat must be used effectively. Previously, we have concentrated on catalytic methanol-steam reforming. A model of a methanol steam reformer has been previously developed and has been used as the basis for a new, higher temperature model for liquid hydrocarbon fuels. Similarly, our fuel cell evaluation program previously led to the development of a steady-state electrochemical fuel cell model (SSEM). The hydrocarbon fuel processor model and the SSEM have now been incorporated in the development of a process simulation of a 250 kW diesel-fueled reformer/fuel cell system using a process simulator. The performance of this system has been investigated for a variety of operating conditions and a preliminary assessment of thermal integration issues has been carried out. This study demonstrates the application of a process simulation model as a design analysis tool for the development of a 250 kW fuel cell system. © 1998 Elsevier Science S.A.

Keywords: Fuel cells; Diesel reforming; Computer simulation

1. Introduction

Polymer-electrolyte membrane (PEM) fuel cell systems are currently enjoying widespread interest for utility and mobile applications. As they have relatively few waste products, fuel cells are a promising alternative energy source for automobiles. Also, since the reaction is electrochemical rather than combustion-based, their Second Law efficiency losses are smaller. Fuel cell stack performance has been demonstrated as safe and reliable over thousands of hours in a variety of stationary and transport applications. However, the development of a satisfactory hydrogen supply system is the principal deterrent to commercial production.

Gaseous hydrogen storage is relatively simple; unfortunately, the hydrogen energy density is not great. One of the most promising alternatives for large power requirements is to obtain the hydrogen from a liquid hydrocarbon fuel. A reformer is then used to obtain the hydrogen. With an effi-

cient overall system design, waste gases can be limited to carbon dioxide, water and very small amounts of NO_x.

We have previously produced a detailed process simulation of a fuel cell system using reformed methanol to obtain hydrogen [1]. This was followed with extensive plug flow modelling work on the methanol reformer itself [2]. However, there is growing interest in reforming existing logistic fuels for use in fuel cell systems. A diesel fuel infrastructure is already in place, therefore the associated start-up cost of fueling vehicles with diesel would be significantly less than for a methanol-fueled system. Diesel also has a much higher potential energy density than methanol (Table 1). Unfortunately, diesel fuel reforming is more complicated and requires much higher temperatures.

It was desired to construct a simulation of a diesel reformer system to identify potential design issues and obtain a preliminary estimate of the expected system efficiency. Significant operating conditions could then be identified, and their effect on the overall system performance or efficiency could be evaluated. To this end, a 250 kW fuel cell system that used reformed diesel as the hydrogen source has been

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Table 1

Energy storage density of hydrocarbon fuels [3]

Fuel	Energy density (MJ/kg, LHV)	(Wh/kg, 25% assumed energy efficiency)
Diesel	42.5	2900
Propane	46.4	3200
Liquid natural gas	49.0	3375
Methanol	20.0	1375

modelled in HYSYS, a process simulation package marketed by Hyprotech of Calgary, Alberta, Canada.

2. System design

Diesel fuel is a complex mixture of many different hydrocarbons. It is usually characterized by a number of ASTM standards. For the simulation, a mixture of normal paraffins, alkylated benzenes and alkylated naphthalenes was used that had a similar heat of formation, Gibbs free energy, and distillation curve to type D2 diesel (Table 2). It was assumed that there was no sulphur present in the diesel fuel, as sulphur will take part in a number of significant secondary reactions and the behaviour would be difficult to simulate. The Peng–Robinson equations of state were used to calculate the stream physical and transport properties. They are well suited to polar components for pressures above 10 bar [4]; furthermore, Hyprotech has devoted significant resources to obtaining interaction data for the Peng–Robinson equations.

2.1. Simulation of the catalytic steam reformer

The diesel fuel was vaporised in the presence of excess steam before entering the reformer. The molar ratio of steam to the carbon in the diesel was set at 4 to 1, since a lower steam-to-diesel ratio has been found to result in carbon in the reformer exit [5]. Since the reaction kinetics of diesel reforming were unknown, the reformer was set up as a Gibbs reactor followed by a conversion reactor. A Gibbs reactor calculates the equilibrium composition of the outlet streams that minimizes the Gibbs free energy of the reacting system. This provided an estimate of the amount of heat required to complete the reaction.

With excess steam nearly 100% conversion of the diesel fuel can be assumed [6] and the reaction products will be hydrogen, water, carbon dioxide, carbon monoxide, and methane. Methane production is highly undesirable, as it represents trapped hydrogen that is not available for the fuel cell stack. Methane is thermodynamically favoured at low temperatures and high pressures; however, reformates with low methane compositions have been demonstrated [7] through the use of certain reformer catalysts that are selective for hydrogen production. To include this behaviour in the simulation, the conversion reactor converted excess

methane to hydrogen and carbon dioxide, such that the methane composition of the dry outlet stream was fixed at 0.01 mole fraction.

2.2. Simulation of the hydrogen purifier

Carbon monoxide will act as a catalyst poison for the fuel cell anode at concentrations as low as 10 ppm, therefore the reformate stream must be purified. Since there will also be methane and other trace hydrocarbons present, one effective solution is to filter the reformate stream with a metal membrane separator unit. These units, which use a Pd or Pd-alloy membrane, are nearly completely selective for hydrogen. The low pressure output stream will be essentially pure hydrogen, while everything else will exit in the retentate stream. Their principal drawback, however, is the large (10–15 bar) driving force required to obtain sufficient recovery of hydrogen. If the pressure differential between the reformate feed and the hydrogen product is too small, most of the hydrogen will not be recovered.

A model of a Pd membrane separation unit was recently developed and presented by our group [8]. It was assumed the unit operated isothermally, and that the majority of the resistance to mass transfer occurred in the metal lattice. The molar flow rate of hydrogen permeate exiting the membrane unit was given by

$$\dot{N}_{H_2} = \frac{P \, A \, LMDF}{l} \tag{1}$$

where A is the membrane surface area (m^2), l is the membrane thickness (m), $LMDF$ is the log mean driving force based on the hydrogen partial pressure, and P is the membrane permeability (mol H_2/m s $Pa^{0.5}$). An empirical correlation for the permeability was developed from data in the literature:

$$P = 2.2 \times 10^{-7} \exp(-1600/T), \quad \text{with } T \text{ in } K \tag{2}$$

Based on Eqs. (1) and (2), increasing the fuel processor

Table 2

Fuel mixture exhibiting similar characteristics to #2 diesel fuel (DF-2), LHV~41 470 kJ/kg

Component	Mass fraction	Component	Mass fraction
n-Nonane	0.0122	n-Hexylbenzene	0.0041
n-Decane	0.0243	n-Heptylbenzene	0.0055
n-C_{11}	0.0517	n-Octylbenzene	0.0058
n-C_{12}	0.0912	n-Nonylbenzene	0.0059
n-C_{13}	0.2007	n-Decylbenzene	0.0065
n-C_{14}	0.1959	n-C_{11}benzene	0.0030
n-C_{15}	0.0980	n-C_{12}benzene	0.0020
n-C_{16}	0.0490	Naphthalene	0.0302
n-C_{17}	0.0245	1-Methylnaphthalene	0.0654
n-C_{18}	0.0122	1-Ethylnaphthalene	0.0453
n-C_{19}	0.0061	1-Propylnaphthalene	0.0322
n-C_{20}	0.0031	1-Butylnaphthalene	0.0215
n-Pentyl-benzene	0.0027		

operating pressure and temperature will result in a higher hydrogen recovery.

A Fortran program was written to model the Pd separation unit performance and determine the hydrogen recovery. This program was linked to the HYSYS simulation so that a fuel processor consisting of a diesel reformer plus a Pd membrane separation unit was simulated.

The waste retentate stream from the membrane separation unit was consumed in a burner to heat the reformer. In the existing simulation, the heat from the burner was transferred directly to the fuel processor through the use of a hypothetical energy stream. Due to the direct energy transfer, this heat did not appear as a temperature rise. The remaining heat of combustion left the burner in the exhaust gas, and was used to heat the incoming reformer feed. For scenarios in which the waste retentate stream did not provide sufficient methane and hydrogen to heat the reformer, a small diesel stream was also fed to the burner. However, in future designs, extra fuel requirements would be met by producing and burning excess reformate.

2.3. Simulation of the fuel cell stack

A PEM fuel cell stack selected with performance similar to Ballard Power Systems Mark V technology was simulated. The PEM fuel cell stacks were maintained at typical operating output conditions of 80°C and 30 psig pressure, and were required to supply a nominal 400 mA/cm^2 current density (approximately 100 A). The stacks could be connected in any desired series/parallel combination to obtain a desired operating voltage. It was assumed that all waste heat

was removed using a cooling water stream. Inlet gases had to be fully saturated with water before entering the stack, and exhaust gases had to have liquid water removed from the streams before they could be further handled.

Like most chemical simulation programs, electrochemical reaction units are not available in HYSYS. Instead, the overall reaction and heat balance were performed on a spreadsheet contained in a HYSYS sub-unit. The fuel cell stack voltage was obtained using the RMC steady state electrochemical fuel cell model [9], listed as Eq. (3):

$$V = E + (\xi_1 + \xi_2 T + \xi_3 T \ln(c = O_2)$$

$$+ \xi_4 T \ln(i)) - i(\xi_5 + \xi_6 T + \xi_7 i) \tag{3}$$

The fraction of product water leaving the stack in the cathode stream was chosen to be 0.667, which is typical of many PEM fuel cell designs. For the energy balance, it was assumed that the anode and cathode gas would enter and leave at the stack temperature (80°C). The stack was thermally insulated, therefore heat loss to the surroundings was assumed to be negligible. The energy balance for the system was:

$$Q_{\text{cooling-water}} = Q_{\text{theoretical}} - (Q_{\text{electrical}}$$

$$+ Q_{\text{sensible-cathode}} + Q_{\text{sensible-anode}}) \tag{4}$$

where $Q_{\text{theoretical}}$ is the theoretical energy released by the reaction, $Q_{\text{sensible-cathode}}$ and $Q_{\text{sensible-anode}}$ are the change in sensible heat for the anode and cathode streams, and $Q_{\text{cooling-water}}$ is the remaining reaction heat that is removed from the stack in the cooling water stream. The stream
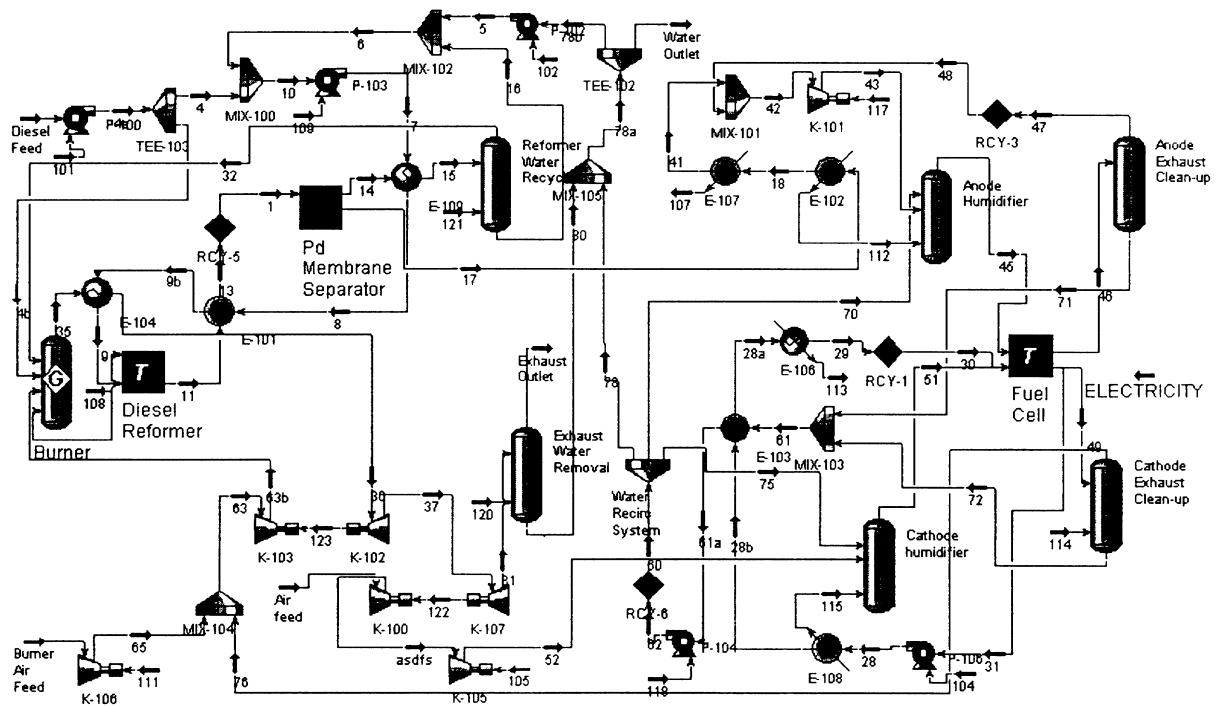

Fig. 1. Process flow diagram of the 250 kW fuel cell system with diesel reformer.

Table 3

Fuel cell/fuel processing operating conditions for base-case scenario

Reformer temperature	600°C
Reformer pressure	300 psig
Pd membrane temperature	400°C
Pd membrane H_2 outlet pressure	30 psig
Steam/carbon ratio	4
Stack temperature	80°C
Stack pressure	30 psig
Fuel cell current density	400 mA/cm^2
Gross electrical power	250 kW DC

enters the stack at 77°C, and the flow rate was selected to be consistent with the above constraints. A process flow diagram of the entire fuel processor/fuel cell system is shown in Fig. 1.

A number of optimization techniques were incorporated into the system. The anode exhaust stream was recycled back to the fuel cell, and the cathodic exhaust stream was sent to the burner. Although relatively low in oxygen concentration, the cathodic exhaust stream was already under pressure, and therefore helped to reduce the compressor requirements. Similarly, water was collected, wherever possible, and recirculated back into the reformer inlet stream, therefore no water storage was required. High pressure exhaust gases were used to provide shaft power for compressors (via turbochargers), and streams requiring heating were coupled with high temperature exhaust lines.

3. Results

The base-case operating conditions for the system are shown in Table 3.

The fuel cell efficiency was defined as:

$$\epsilon_{\text{fuel cell}} = \text{DC Power}/\text{LHV of anode feed gas} \qquad (5)$$

Since the fuel cell operating conditions were fixed, the fuel cell efficiency using Eq. (5) was always approximately 60%. However, the fuel cell thermal efficiency was 51%. This meant that over 230 kW of excess heat had to be removed from the fuel cell stacks in the cooling water stream. The Pd membrane separation unit under the base case conditions recovered 80% of the hydrogen stream, and the mole fraction of hydrogen in the inlet stream and the inlet flow rate were found to have an impact on the recovery value.

The fuel processor efficiency was determined using:

$$\epsilon_{\text{fuel processor}} = \text{LHV of anode feed gas}/$$

$$\text{LHV of reformer fuel} \qquad (6)$$

The reformer produced 47% hydrogen on a wet basis (73% hydrogen dry basis), along with 0.9% (w.b.) carbon monoxide and 0.6% (w.b.) methane (1% dry basis).

Normally, the effect of converting power to AC is also included in gross efficiency calculations. The power conditioner efficiency for a 250 kW system was suggested to be 96% [10]. The gross efficiency, which combined the fuel cell, fuel processor, and power conditioning efficiencies in equation [7], was, therefore, 46%.

$$\epsilon_{\text{gross}} = \epsilon_{\text{fuel cell}} \, \epsilon_{\text{power conditioner}} \, \epsilon_{\text{fuel processor}}$$

$$= 60\% \times 96\% \times 80\% = 46\% \qquad (7)$$

The parasitic energy load included all of the electrical power that would be required to power any pumps and compressors in the system. In a more detailed simulation, it would have also included such items as the electrical requirements for the control system. However, the energy requirements of compressors connected to turbochargers were not included in the parasitic load, as their energy requirements were not external to the system. From the base case simulation, the parasitic energy load was over 16% of the total power produced (Table 4).

The net efficiency, estimated as 38.6%, included the effect of the parasitic energy load on the system required to power the pumps and compressors.

$$\epsilon_{\text{net}} = (\text{AC power} - \text{parasitic energy load})/$$

$$\text{LHV of reformer fuel} \qquad (8)$$

For comparison, simulation net efficiencies obtained for 50 kW natural gas reforming systems [11] were between 25 and 35%. However, their simulations were at higher operating temperatures, and their efficiencies were based on the higher heating value of the fuel. If the HHV was used in Eq. (6), our base-case net efficiency would be about 36%.

The base case simulation was compared to a variety of operating conditions. The reformer temperature was varied between 500 and 700°C, while the reformer steam to carbon ratio was maintained at 4:1. The system pressure was varied from 150 to 350 psig, and the Pd membrane temperature ranged between 300 and 500°C. As the objective was to identify and observe principal variables, rather than produce optimal operating conditions, the process was not highly optimized. It should be noted that, since the desired elec-

Table 4

Output conditions for base-case simulation

Reformer exit: dry mole fn H_2	0.732
Reformer exit: dry mole fn CH_4	0.01
Total diesel feed required	44.9 kg/h
Diesel flow to reformer	39 kg/h
Pd membrane unit recovery	0.80
Power conditioner efficiency	96%
Fuel cell efficiency	60%
Fuel processor efficiency	80%
Gross efficiency	46%
Parasitic load	40 kW
Net efficiency	38.6%
Electrical power produced	250.5 kW
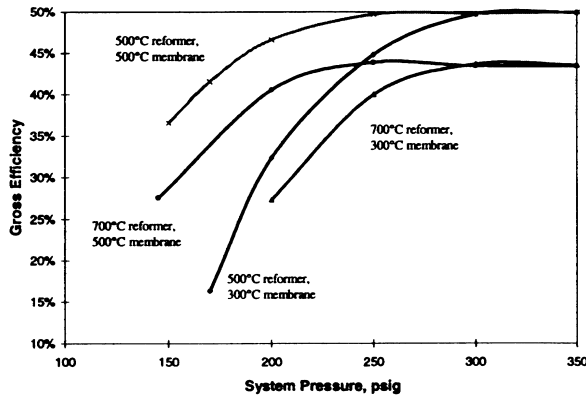
Fig. 2. Dependency of gross efficiency on operating conditions.

Fig. 4. Dependence of gross efficiency on the Pd membrane unit's hydrogen recovery.

trical power was fixed, the molar flow of hydrogen to the fuel cell was constant. Since the fraction of hydrogen the Pd membrane would pass (the recovery) would change with Pd membrane temperature and pressure, this meant that the reformate flow rate leaving the reformer would also change to compensate.

The system's gross efficiency was found to be considerably higher at lower reforming temperatures (Fig. 2). This is consistent with the assumption that operation at higher operating temperatures would require extra heat for the same rate of hydrogen production. However, two distinct operating regions became apparent when observing the effects of Pd membrane temperature and system pressure. At low operating pressures, an increase in pressure would improve efficiency, as would an increase in Pd membrane temperature. However, at high operating pressures, the efficiency reaches a plateau, and is no longer sensitive to changes in pressure or Pd membrane temperature.

This effect was due to the behaviour of the Pd membrane separation unit. At low pressures and temperatures, the recovery of hydrogen was quite low (Fig. 3), meaning that a large excess of hydrogen was required in the reformate stream to obtain sufficient quantities for the fuel cell. However, once the hydrogen recovery was above a certain value, the waste stream no longer had sufficient hydrogen for the burner. At the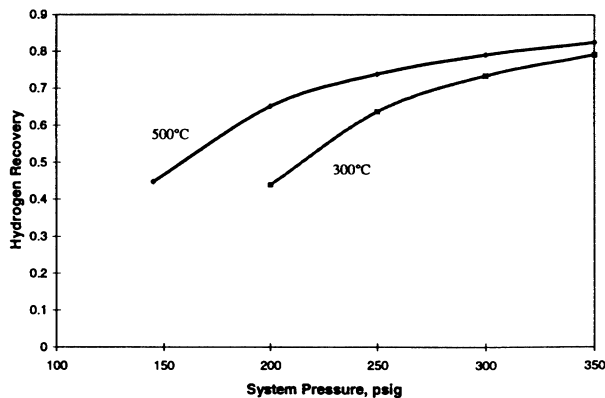se conditions, extra diesel was required to be sent to the burner. This is visible in Fig. 4, which shows that gross efficiency was solely a function of reformer temperature and Pd membrane hydrogen recovery. In a highly optimized system, it would be expected that the gross efficiency would actually fall slightly as extra fuel was added for reformer heating.

A slight maximum is, in fact, visible in the net efficiency values (Fig. 5). The net efficiency rises quite rapidly with system pressure, and then, after reaching a plateau, begins to fall. However, once on the plateau, the net efficiencies only varied by approximately 2% over the entire range of conditions. These small variations were not significant and could be attributed to some artifact of the system design. For example, one apparent trend on the plateau was that the net efficiency depended on Pd membrane temperature. Operation at a Pd membrane temperature of 500°C resulted in a lower net efficiency than operating at 300°C. However, the 200°C difference in operating temperature meant that the purified hydrogen stream leaving the Pd membrane unit carried away an extra 10 kW of sensible heat.

When comparing the scenarios, the net efficiency was chiefly influenced by the size of the parasitic load. The largest component of the parasitic load was the compressor energy requirements, especially to provide pressurized air for the burner. At present, all of the fuel cell cathode exhaust, along with a small amount of external air, have to be brought up to system pressure before entering the burner. Changing the ratio of oxygen to fuel in the burner would certainly have a significant impact on the parasitic load, and therefore the net efficiency. Similarly, the efficiency of the compressors and turbochargers would also effect net efficiency.

The simulation demonstrated that there was a considerable quantity of low grade heat available for potential use. Only a small amount of the low grade heat from the fuel cell was used; possibly this could be used elsewhere in a cogeneration system. Similarly, during simulations at high reformer temperature, there was significant residual heat remaining in the burner exhaust stream, even after it had been used as a preheater and sent through a turbocharger.

In future simulations, the size and physical constraints of

Fig. 3. Percentage of hydrogen recovered from the reformate stream in the Pd membrane separation unit.

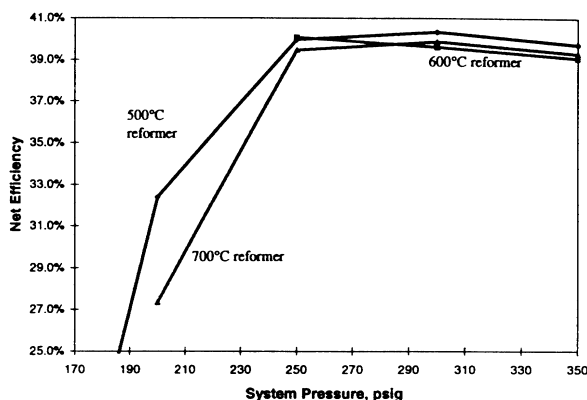Fig. 5. Dependence of net efficiency on system pressure and reformer temperature (Pd membrane unit maintained at 300°C).

units have to be factored into the analysis. For example, there was no size constraint placed on the Pd membrane separator unit in the existing design. High throughputs might possibly require an unrealistically large unit. Cost considerations would eventually also have to be included in the analysis.

For this preliminary study, the system was not optimized. In a fully optimized system, a reformer operating at low temperature would have different heat exchanger placements to preheat the reformer inlet stream than a reformer operating at high temperature. Furthermore, to do an in-depth optimization it would be necessary to include kinetic information for the reformer performance. There is very limited information currently available concerning the kinetics of hydrogen production from diesel. Ideally, once the operating characteristics of the reformer are better known, a more detailed study on the efficiency can be attempted.

4. Conclusions

A simulation of a PEM fuel cell power plant was used to investigate the integration of a diesel reforming unit with a Pd membrane hydrogen separation unit. Simulations were performed to investigate the effect of reformer temperature, system pressure, and Pd membrane temperature on the system. Assuming one has a highly selective catalyst for hydrogen production, the gross efficiency would be improved and

less diesel fuel required by reforming at lower temperatures. There were two distinct operating regions visible, dependent upon the behaviour of the Pd membrane separation unit. Increasing the system pressure and the Pd membrane unit temperature would initially improve the system efficiency; however, once the separation unit was beyond a certain hydrogen recovery rate further pressure and temperature increases would not improve the efficiency. Nevertheless, diesel reforming did result in a high parasitic load, suggesting that careful use of waste stream energy is essential. It is apparent that a process simulation of a diesel reforming/fuel cell system is extremely useful at identifying energy and water management issues.

Acknowledgements

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