

Short communication

Analysis of an energy recovery system for reformat-based PEM fuel cells involving a binary two-phase mixture

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Abstract

A comprehensive analysis on a novel energy recovery system for reformat-based proton exchange membrane (PEM) fuel cell systems is presented. The energy recovery system includes a throttling valve, a heat exchanger, a compressor, and is coupled with a coolant loop for the fuel cell stack. The feed stock of the fuel reformer, which is primarily a mixture of water and fuel, is vaporized in the heat exchanger and is then compressed to a sufficiently high pressure before it is ducted into the fuel reformer. The analysis includes the throttling of two-phase fuel/water mixture and vaporization in the heat exchanger to obtain the temperature and pressure of the mixture at the inlet of the compressor. The results indicate that the power plant efficiency with the energy recovery system can be increased by more than 20% compared to that of a fuel cell power plant without the energy recovery system. Additionally, more than 25% of the waste heat generated by the fuel cell stack can be removed due to the energy recovery system, and the fuel burned for the fuel reforming purpose is reduced by more than 70%.

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1. Introduction

The polymer electrolyte membrane or proton exchange membrane (PEM) fuel cell is the most popular fuel cell for transportation and portable applications (Barbir et al. [1] and Guo and Cao [2]). The PEM fuel cell could employ compressed hydrogen gas or methanol reformat as fuel. Other hydrocarbons, such as gasoline or diesel fuel, could also be reformed to produce suitable reformat for the fuel cell. Although a fuel cell operating on pure hydrogen gas is considered to be the ultimate clean energy system, the difficulties associated with handling high pressure compressed hydrogen gas and the lack of a hydrogen infrastructure may prevent the mass use of this kind of fuel cell power plant in the foreseeable future. As a result, a fuel cell power plant using reformat from methanol or other hydrocarbons such as gasoline would represent an alternative to the pure hydrogen based fuel cell

power plant. One of the drawbacks of a reformat-based fuel cell power plant is that a large amount of energy is needed for the fuel processing purpose. It was estimated that heating value equivalent to that of about 20–30% of the hydrogen produced in the reformer is needed to provide a fuel stream with sufficient heating value to meet the heating requirement of the reformer (Edlund and Pledger [3]). This amount of heating value is usually provided through the combustion of remaining hydrogen/hydrocarbons in the exhaust gases from the fuel cell anode, burning the hydrogen/hydrocarbons in the byproduct stream of the reformer, or consumption of additional hydrocarbon fuel other than that being reformed in the reformer. It is evident that the energy input to the reformer must be reduced if the efficiency of a fuel cell power plant is to be increased.

Recently, Cao and Guo [4] proposed a novel energy recover system, which could recover a substantially large portion of the waste heat generated by the fuel cell stack and utilize it for fuel reforming purposes. Fig. 1 shows the diagram of a reformat/air PEM fuel cell power plant incorporating

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Nomenclature

List of symbols

\bar{c}_p	specific heat (kJ/kmol K)
\bar{h}	enthalpy (kJ/kmol)
\bar{h}_f^0	enthalpy of formation (kJ/kmol)
h_{fg}	latent heat of vaporization (kJ/kg)
HHV	higher heating value (kJ/kmol)
M	molecular weight (kg/kmol)
n	number of mole
p	mixture pressure (Pa)
Q	thermal energy (kJ)
\bar{R}	universal gas constant (8.314 kJ/kmol K)
s	entropy (kJ/kg K)
T	temperature (K)
W	compressor work (kJ)
x	mole fraction, or excess water in Eq. (15)
y	vapor mole fraction in Eq. (20)
η	efficiency

Subscripts

c	compressor
e	exit
i	inlet
l	liquid
L	latent heat
Me	methanol
rf	reforming
s	isentropic process
v	vapor
W, w	water

such an energy recovery system. A water recovery unit recovers water from the cathode exhaust air stream and discharges it to a water tank. The water is then pumped into a mixing chamber and is mixed with the liquid methanol pumped from a methanol tank with an appropriate ratio. After flowing through an expansion valve, the pressure of the water and methanol mixture is substantially reduced. The mixture with a reduced pressure enters a heat exchanger or evaporator and absorbs heat from the coolant of the fuel cell stack cooler. The pressure of the mixture is sufficiently low so that the liquid mixture is substantially vaporized while absorbing heat from the coolant in the heat exchanger. The vapor mixture of water and methanol emerges from the heat exchanger and enters a compressor where its pressure is raised to a sufficiently high level. Then the water/methanol vapor mixture leaves the compressor and enters a fuel reformer as the vapor feedstock of the reformer. Additional thermal energy may be needed for the reforming reaction. This is usually provided through a burner in the reformer that burns the hydrogen/hydrocarbons remaining in the anode exhaust stream as shown in the figure. The water/methanol vapor feed stock is converted in the

reformer into a mixture of H_2 and CO_2 . The advantage of the proposed energy recovery system is significant. The latent heat that is needed to vaporize the liquid water/methanol feedstock would come from the waste heat from the fuel cell stack that could otherwise be dumped into the surroundings. Since the latent heat normally constitutes a large portion of the total reforming heat (sometimes higher than 50%), the fuel burned in the reformer burner would be reduced and the energy utilization efficiency of the fuel cell power plant could be significantly increased. Since the fuel burned in the reformer is substantially decreased, the potential emission associated with the combustion is significantly reduced; therefore, a vehicle utilizing the proposed energy recovery system could approach a zero-emission vehicle. Additionally, since a large amount of the waste heat from the stack is absorbed by the feedstock of the reformer, the heat dissipation load of the radiator following the heat exchanger can be reduced, which substantially reduces the size of the radiator and power consumption of the cooling fan.

A preliminary thermodynamic analysis was conducted (Cao and Guo [4]) and the results indicated that the energy efficiency of a fuel cell power plant utilizing the proposed energy recovery system was improved significantly. However, the analysis was made assuming the vapor pressure and temperature at the inlet of the compressor without analyzing the methanol/water throttling and two-phase heat absorption in the heat exchanger. Without including the mixture throttling and heat absorption processes, the accuracy of the analytical results could suffer. In this paper, a more comprehensive analysis is provided, which would cover the entire energy recovery system including the methanol/water two-phase binary mixture. Through this comprehensive analysis, more realistic results related to energy efficiency and required compressor ratio could be obtained.

2. Analysis of the methanol/water mixture flowing through the throttling valve and heat exchanger

Consider the throttling valve/heat exchanger assembly in Fig. 1. At the inlet of the throttling valve, the feed stock of methanol/water mixture is in a liquid state. The mole fractions of methanol and water are denoted by $x_{Me,i}$ and $x_{W,i}$, respectively, and the corresponding enthalpies per mole for methanol and water are denoted by $\bar{h}_{Me,i}$ and $\bar{h}_{W,i}$. Upon passing through the expansion valve, the pressure of the methanol/water mixture is reduced. Some liquid methanol and water flashes into vapor and the methanol/water mixture is in a two-phase condition at the outlet of the valve. Neglecting any heat transfer into the throttling valve, the energy equation for the throttling process can be written as follows:

$$\begin{aligned}
 & x_{Me,i}\bar{h}_{Me,i} + x_{W,i}\bar{h}_{W,i} \\
 & = x_l(x_{Me,l}\bar{h}_{Me,l} + x_{W,l}\bar{h}_{W,l}) \\
 & \quad + x_v(x_{Me,v}\bar{h}_{Me,v} + x_{W,v}\bar{h}_{W,v})
 \end{aligned} \tag{1}$$

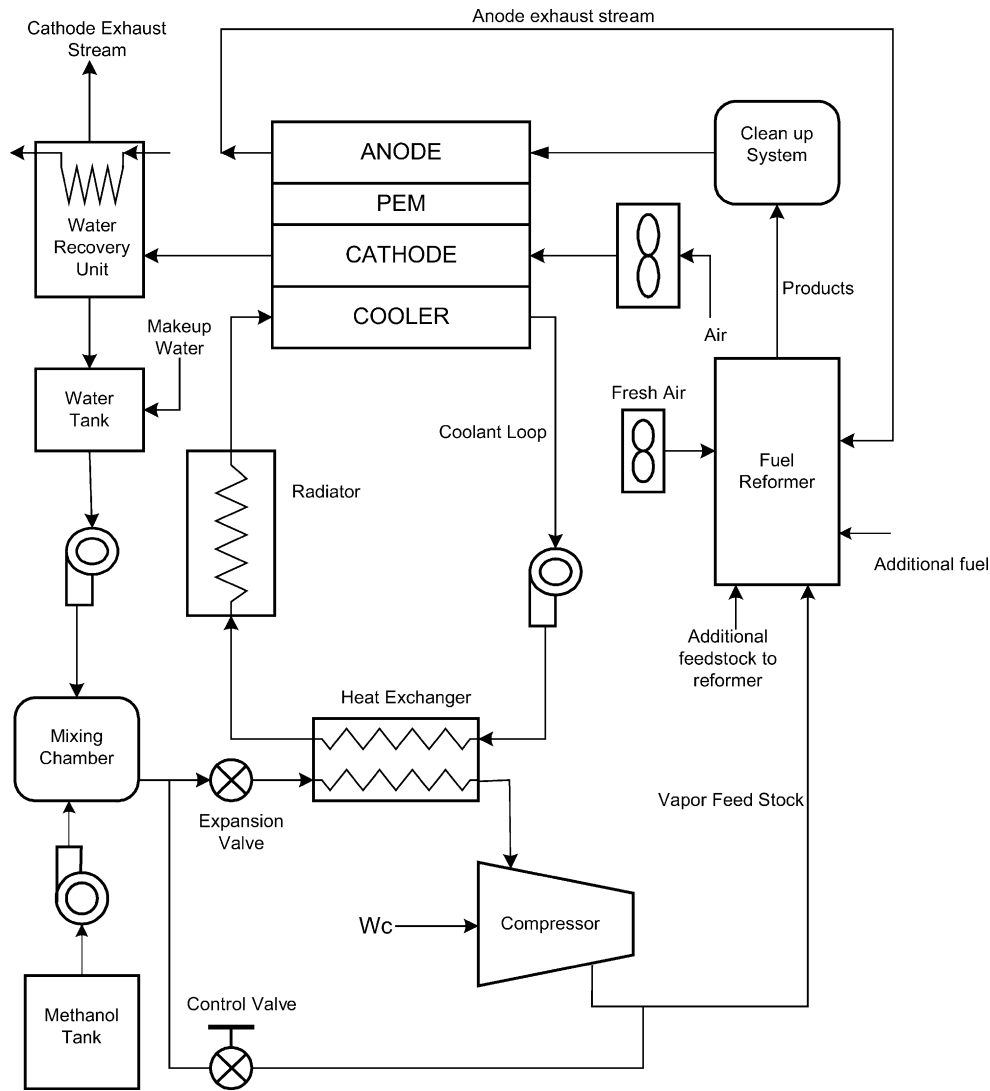


Fig. 1. Schematic of a fuel cell power plant incorporating the energy recovery system.

where x_l is the number of mole in liquid state for 1 mol of combined methanol/water mixture, x_v is the number of moles in vapor state for 1 mol of combined methanol/water mixture, $x_{Me,l}$ and $x_{W,l}$ are the respective mole fractions of methanol and water in liquid, $\bar{h}_{Me,l}$ and $\bar{h}_{W,l}$ are the corresponding enthalpies in liquid for methanol and water, $x_{Me,v}$ and $x_{W,v}$ are the respective mole fractions of methanol and water in vapor, $\bar{h}_{Me,v}$ and $\bar{h}_{W,v}$ are the corresponding enthalpies in vapor for methanol and water. The inlet condition of the throttling valve is primarily determined by the parameter called percent theoretical water, which is defined as the actual molar water–methanol ratio divided by the stoichiometric water–methanol ratio for the methanol reforming process, and is often used to measure the amount of excess water for the reforming process (please see Eq. (16) in the following section). The primary unknowns in Eq. (1) are the temperature, T , and pressure, p , of the mixture at the outlet of the expansion valve. It should be pointed out that unlike a pure substance, the temperature and pressure of a binary mix-

ture are independent to each other even under a two-phase condition. To calculate the mole fractions appearing in the equation, Raoult's and Dalton's laws are used. Applying the Raoult's law to both methanol and water (Stoecker [7]), the following two relations are obtained:

$$p_{Me} = x_{Me,l} P_{Me}(T) \quad (2)$$

$$p_W = x_{W,l} P_W(T) \quad (3)$$

where p_{Me} and p_W are partial vapor pressures of methanol and water, respectively, and $P_{Me}(T)$ and $P_W(T)$ are the saturation pressures for pure methanol and pure water, respectively. The saturation pressures for pure methanol and water are a function of mixture temperature only, and can be found through saturated methanol and water tables (Moran and Howard [5], Faghri [6]). Additionally, the following relations are available according to the Dalton's law:

$$p = p_{Me} + p_W \quad (4)$$

$$p_{\text{Me}} = x_{\text{Me},v} p \quad (5)$$

$$p_{\text{W}} = x_{\text{W},v} p \quad (6)$$

Based on the definition of mole fraction, the following two relations are also available:

$$x_{\text{Me},l} + x_{\text{W},l} = 1 \quad (7)$$

$$x_{\text{Me},v} + x_{\text{W},v} = 1 \quad (8)$$

Combing Eq. (2) through Eq. (8) yields the following four relations for the calculation of $x_{\text{Me},l}$, $x_{\text{W},l}$, $x_{\text{Me},v}$, $x_{\text{W},v}$ under given p and T :

$$p = x_{\text{W},l} P_{\text{W}}(T) + (1 - x_{\text{W},l}) P_{\text{Me}}(T) \quad (9)$$

$$x_{\text{Me},l} = 1 - x_{\text{W},l} \quad (10)$$

$$p x_{\text{W},v} = x_{\text{W},l} P_{\text{W}}(T) \quad (11)$$

$$x_{\text{Me},v} = 1 - x_{\text{W},v} \quad (12)$$

Finally, to calculate the mass of liquid and vapor in the mixture, a mass balance on methanol between the inlet and outlet of the throttling valve gives:

$$x_{\text{Me},i} = x_{\text{Me},l} x_1 + x_{\text{Me},v} x_v \quad (13)$$

The above equation can be used to calculate x_1 and x_v in conjunction with the mass conservation relation:

$$x_1 + x_v = 1 \quad (14)$$

With Eqs. (9)–(14), Eq. (1) can be used to calculate the mixture temperature T at the outlet of the throttling valve for a specified throttling pressure p . The temperature and pressure thus obtained also represent the temperature and pressure of the mixture at the inlet of the heat exchanger. To satisfy heat transfer requirement from the fuel cell stack coolant to the feed stock mixture, a sufficient temperature difference between the fuel cell stack and the mixture should be maintained. Alternatively, a mixture temperature at the inlet of the heat exchanger can be specified and Eq. (1) can be used to find the throttling pressure p . The minimum requirement for the heat transfer in the heat exchanger is to completely vaporize the methanol/water mixture into vapor before it is ducted into the compressor as shown in Fig. 1. It is well known that for a binary mixture, the temperature of the mixture will continue to rise during the vaporization process in the heat exchanger (Stoecker [7]). The temperature at which the mixture is completely vaporized into vapor ($x_l = 0$) can also be found through Eqs. (9)–(14) by assuming that the pressure remains constant through out the heat exchanger. The temperature thus found is considered to be the temperature of the mixture at the inlet of the compressor for the present analysis.

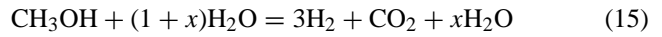
Extensive calculations have been undertaken using Eq. (1) in conjunction with Eqs. (9)–(14). Some of the results that will be used for the current performance evaluation are presented in Table 1 as a function of the percent theoretical water. The results were obtained based on the condition that an average temperature drop of 13–15 °C between the stack coolant

and the water/methanol mixture is maintained in the heat exchanger when the fuel cell stack is working at a temperature of 80 °C.

Once the condition at the inlet of the compressor is identified, the calculation can proceed to evaluate the performance of a PEM fuel cell system with and without the energy recovery system. The following formulations are similar to those presented by Cao and Guo [4] and are briefly summarized for completeness.

Formulation for a base fuel cell system without the present energy recovery system:

Chemical reaction equation:



Percent theoretical water

$$= [(1.0 + x)/1]/(1.0/1.0) = 1.0 + x \quad (16)$$

Combustion heat required:

$$Q_{\text{rf}}^0 = \sum_P n_e (\bar{h}_f^0 + \Delta \bar{h}) - \sum_R n_i (\bar{h}_f^0 + \Delta \bar{h}) \quad (\text{kJ}/3 \text{ kmol of H}_2) \quad (17)$$

Hydrogen burnt:

$$(\text{H}_2)_{\text{burner}} = \frac{Q_{\text{rf}}^0}{(\text{HHV})_{\eta_{\text{burner}}}} \quad (18)$$

Energy efficiency:

$$\eta_0 = \frac{1}{3} [(3 - Q_{\text{rf}}^0 / (\text{HHV})_{\eta_{\text{burner}}})] \eta_{\text{stack}} \quad (19)$$

Formulation for a fuel cell system with the present energy recovery system:

Compressor work input:

$$\begin{aligned} \Delta \bar{s} &= y_{\text{w}} \Delta \bar{s}_{\text{w}} + y_{\text{Me}} \Delta \bar{s}_{\text{Me}} \\ &= y_{\text{w}} \left[\bar{c}_{p,\text{w}} \ln \left(\frac{T_{\text{out},s}}{T_{\text{in}}} \right) - \bar{R} \ln \left(\frac{P_{\text{out}}}{P_{\text{in}}} \right) \right] \\ &\quad + y_{\text{Me}} \left[\bar{c}_{p,\text{Me}} \ln \left(\frac{T_{\text{out},s}}{T_{\text{in}}} \right) - \bar{R} \ln \left(\frac{P_{\text{out}}}{P_{\text{in}}} \right) \right] \\ &= (y_{\text{w}} \bar{c}_{p,\text{w}} + y_{\text{Me}} \bar{c}_{p,\text{Me}}) \ln \left(\frac{T_{\text{out},s}}{T_{\text{in}}} \right) \\ &\quad - (y_{\text{w}} + y_{\text{Me}}) \bar{R} \ln \left(\frac{P_{\text{out}}}{P_{\text{in}}} \right) = 0 \end{aligned} \quad (20)$$

$$T_{\text{out},s} = T_{\text{in}} \exp \left[\frac{y_{\text{w}} + y_{\text{Me}}}{y_{\text{w}} \bar{c}_{p,\text{w}} + y_{\text{Me}} \bar{c}_{p,\text{Me}}} \bar{R} \ln \frac{P_{\text{out}}}{P_{\text{in}}} \right] \quad (21)$$

$$W_{\text{c},s} = (n_{\text{w}} \bar{c}_{p,\text{w}} + n_{\text{Me}} \bar{c}_{p,\text{Me}}) (T_{\text{out},s} - T_{\text{in}}) \quad (\text{kJ}/3 \text{ kmol of H}_2) \quad (22)$$

Table 1
Heat exchanger inlet and outlet temperatures as well as the compressor inlet pressure at different values of the percent theoretical water

Percent theoretical water	Compressor inlet pressure, P_{in} (bar)	Heat exchanger inlet temperature, $T_{HE,in}$ ($^{\circ}C$)	Heat exchanger outlet temperature, $T_{HE,out}$ or compressor inlet temperature, T_{in} ($^{\circ}C$)
1.1	0.43	55.76	67.0
1.2	0.42	55.87	67.0
1.3	0.40	55.39	66.47
1.4	0.38	54.83	65.82
1.5	0.40	56.49	67.31
1.6	0.40	57.0	67.68
1.7	0.40	57.5	68.02
1.8	0.40	57.97	68.34

$$W_c = W_{c,s}/\eta_{comp} \text{ (kJ/3 kmol of H}_2\text{)} \quad (23)$$

Combustion heat required:

$$Q_{rf} = \left[\sum_P n_e(\bar{h}_f^0 + \Delta\bar{h}) - \sum_R n_i(\bar{h}_f^0 + \Delta\bar{h}) \right] - (Q_L + W_c) = Q_{rf}^0 - (Q_L + W_c) \quad (24)$$

$$Q_L = n_w M_w h_{fg,w} + n_{Me} M_{Me} h_{fg,Me} \text{ (kJ/3 kmol of H}_2\text{)} \quad (25)$$

$$(H_2)_{burner} = Q_{rf}/HHV/\eta_{burner} \quad (26)$$

Energy efficiency:

$$\eta = \frac{1}{3} [(3 - Q_{rf}/HHV/\eta_{burner})\eta_{stack} - W_c/HHV] \quad (27)$$

Fraction of the heat recovered from the coolant loop:

$$Q_L/Q_{stack} = Q_L/[(3 - Q_{rf}/HHV/\eta_{burner})(1 - \eta_{stack})HHV] \quad (28)$$

3. Analytical results

Based the compressor inlet condition and formulations presented above, systematic calculations are then undertaken to evaluate the performance a fuel cell power plant incorporating the energy recovery system, as shown in Fig. 1, with different values of the percent theoretical water. The calculations were based on a burner efficiency of 70% and a fuel cell stack efficiency of 47.5%. The value of the stack efficiency was obtained using the expression $\eta_{stack} = \eta_{rev} = \eta_{voltage}$, where η_{rev} is the reversible efficiency, and $\eta_{voltage}$ is the voltage efficiency of the stack, which was taken to be 0.59 (corresponding to a voltage of 0.7 V for a single cell). A value of 0.8 was used for the compressor isentropic efficiency. In addition to the variables given in Table 1, another parameter that is varied in the present calculations is the feed stock pressure at the outlet of the compressor, p_{out} , which is directly related to the reforming pressure and the operating pressure of the fuel cell stack. In the present calculation, the values of p_{out} are varied from 1.5 to 2.5 bar.

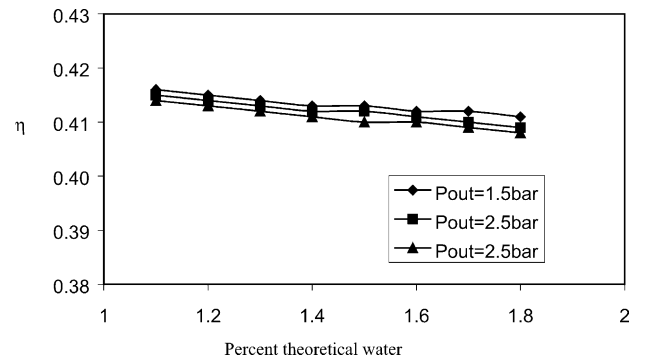


Fig. 2. Variation of the fuel cell power plant efficiency with different percent theoretical water.

Fig. 2 shows the power plant efficiency, η , with the energy recovery system, at different reforming pressures, p_{out} , as a function of the percent theoretical water. As can be seen from the figure, the power plant efficiency is maintained at above 40%, varying slightly with the variation of p_{out} and percent theoretical water. A more important gage that would be used to justify the use of the present energy recovery system is the improvement of the plant efficiency over that of a base power plant, η_0 (without the energy recovery system). Fig. 3 illustrates the variation of $(\eta - \eta_0)/\eta_0$ with different p_{out} and percent theoretical water. In most cases, the improvement of the power plant efficiency is maintained at above 20% and is also relatively insensitive to the change in p_{out} . The results

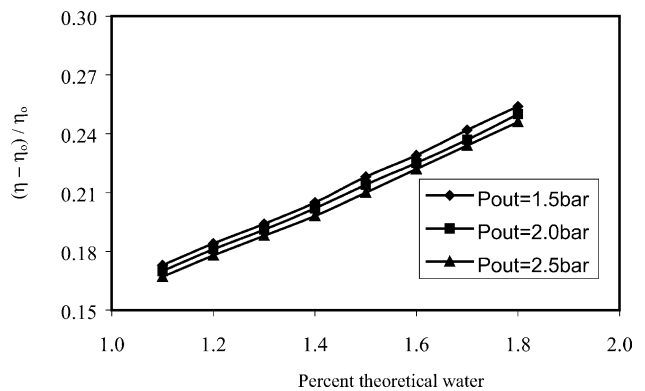


Fig. 3. Improvement of fuel cell power plant efficiency with different percent theoretical water.

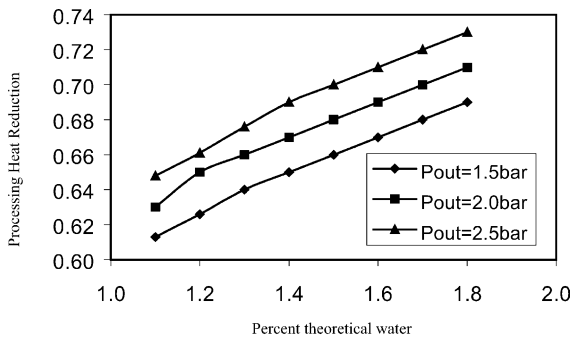


Fig. 4. Processing heat reduction at different percent theoretical water.

from Figs. 2 and 3 indicate that the energy recovery system could substantially improve the power plant efficiency and work at a relatively large range of fuel cell stack pressures. The results also indicate that with higher percent theoretical water, the efficiency improvement is more pronounced. However, even at a low percent theoretical water of 1.1, the improvement is still close to 20%.

A very important advantage of adopting the present energy recovery system is that the amount of the fuel burned for providing the fuel reforming heat can be drastically reduced. With this reduced burning, the potential pollution from a reformat-based fuel cell power plant could be drastically reduced. Fig. 4 shows the processing heat reduction at different percent theoretical water and compressor outlet pressures. As can be seen, the fuel burned for the processing heat can be reduced by more than 70%. It should be noted that even for a reformat-based fuel cell power plant without using the present energy recovery system, the fuel burned for the processing heat is about 25% that of an internal combustion engine having the same power output. With this further reduction in the fuel burned, a reformat-based fuel cell vehicle employing the present energy recovery system could approach a true pollution free vehicle.

As discussed in the earlier sections, additional benefit of the present energy recovery system is the reduction of the waste heat that needs to be dissipated by the radiator. Fig. 5 shows the ratio of the waste heat recovered by the energy re-

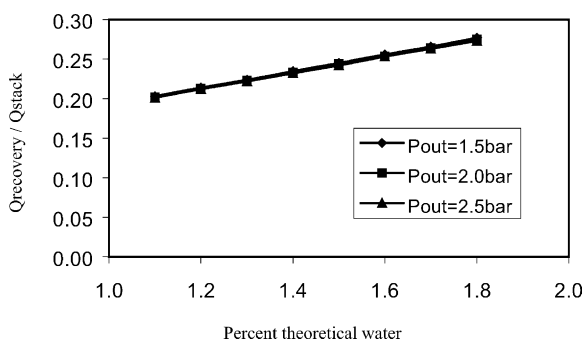


Fig. 5. The ratio of waste heat recovered from the stack at different percent theoretical water.

covery system to the total waste heat energy generated by the fuel cell stack as a function of p_{out} and the percent theoretical water. It can be seen from the figure that more than 25% of the waste heat could be recovered from the stack. As a result, the needed heat dissipation capacity of a radiator could be reduced by more than 25%, and the size of the radiator and the associated fan power consumption could be reduced accordingly.

A critical or the most expensive component of the present energy recovery system is the compressor. The compression ratios of the compressor range from 3.5 to 6.6 and the outlet temperatures of the compressor range from 200 to 270 °C in the present calculations. Since the mass flow rate of the water/methanol mixture is relatively small, a compact and inexpensive reciprocating compressor may be used. Therefore, the costs associated with the implementation of the present energy recovery system should be relatively low.

The foregoing descriptions and evaluations are all based upon a fuel cell power plant using methanol as fuel. The energy recovery system described in this paper, however, can also be employed for a fuel cell power plant using other hydrocarbon fuels such as gasoline or ethanol as the fuel. The primary objective of the present energy recovery system is to provide thermal energy for steam reforming through the waste heat recovery from the fuel cell stack. It is believed that the present energy recovery system could be found useful whenever a large amount of steam is needed for a fuel cell power plant working at a relatively low temperature. It also serves as an effective means to cool the fuel cell stack.

4. Conclusions

A comprehensive analysis on a fuel cell power plant incorporating the energy recovery system has been undertaken, including the throttling valve/heat exchanger assembly involving a methanol/water two-phase mixture. The results indicate that the power plant efficiency can be increased by more than 20% compared to that of a base power plant without the energy recovery system. In addition, more than 25% of the waste heat generated by the fuel cell stack is recovered from the stack, which would reduce the size of the radiator and the associated fan power consumption. The results also indicate that the performance of the fuel cell power plant is relatively insensitive to the operating pressure of the fuel cell stack. The excess water used for the steam reforming would have a significant effect on the performance improvement. However, even with low excess water, the improvement in the power plant efficiency is still close to 20%. Finally, because of the energy recovery system, the fuel burned for providing the reforming heat can be reduced by more than 70%. As a result, a reformat-based fuel cell vehicle employing the current energy recovery system could approach a true pollution free vehicle.

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