

Reforming system for co-generation of hydrogen and mechanical work

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Abstract

The paper describes a new design for a reforming system for converting hydrocarbon fuels into pure hydrogen. The system is based on an autothermal reforming (ATR) reactor operating at elevated pressures followed by membrane-based hydrogen separation. The high-pressure membrane discharge stream is combusted and expanded through a turbine generating additional power. Process simulation modeling illustrates the effect of pressure and other operating parameters on system performance and demonstrates a system reforming efficiency approaching 80%. When coupled with a PEM fuel cell and an electrical generator, fuel to electricity efficiency is above 40%. Other anticipated benefits of the system include compact size, simplicity in control and fast start up.

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1. Introduction

Transitioning to a “hydrogen economy” is broadly considered as a route to establishing a long-term sustainable energy future. It should be realized, though, that unlike coal, oil, or natural gas, hydrogen in the free H₂ form is not present in nature. To establish the “hydrogen economy”, hydrogen will have to be produced from other chemical feedstocks and, therefore, it should be considered as an energy carrier rather than an energy source. In this sense, hydrogen should be viewed as competing with another common energy carrier—electricity. Comparison between these two media should include considerations of efficiency, cost and safety issues and should account for complete energy cycles including power generation, transmission, storage, and consumption stages [1,2]. When hydrogen is produced from hydrocarbons such as natural gas or oil and then is used as fuel in a fuel cell system, such power system should be compared with the alternative use of the same hydrocarbon fuel in internal combustion or turbine engines in terms of cost, size, safety and efficiency (i.e. the total amount of useful mechanical work and/or electrical power produced per a unit of the hydrocarbon fuel).

The feasibility of both centralized and small-scale distributed hydrogen production requires consideration. If an inexpensive and efficient small-scale fuel reforming system is available, then distributed generation of hydrogen and electrical power in fuel cell units becomes feasible. This would avoid energy losses associated with transporting hydrogen or electricity over long distances and increase the efficiency of the overall power cycle [1,2].

Currently hydrogen is produced industrially via large scale, high-pressure, steam reforming (SR) or autothermal reforming (ATR) of natural gas, at capacities of thousands of tons of hydrogen per day [3]. Due to the critical role of heat transfer in SR process, scaling it down to the sizes required for distributed hydrogen production applications faces significant challenges. In industrial ATR systems, oxygen is used instead of air in order to avoid stream dilution by nitrogen. Cost analysis, however, suggests that, for hydrogen production on a small-scale, an oxygen plant must be excluded [4], i.e. only air blown systems would be economically feasible.

In recently proposed small-scale reforming systems, this limits the application of ATR reactors to the systems operating at low pressures, such that power losses associated with compression of process air could be avoided [5]. Low-pressure approaches to small-scale H₂ production involve a primary reformer (either an ATR or an SR) followed by multiple water-gas-shift (WGS) and preferential CO oxidation (PROX) reactors that reduce CO in the reformat stream to a level acceptable for a PEM fuel cell

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(<10 ppm) [6–8]. This method yields hydrogen diluted with CO₂ and water (as well as N₂ if an ATR is used). The train of catalytic reactors, heat exchangers, and stream conditioning units between the reactors make such systems large, heavy, slow to start and challenging to control.

Unlike ATR, steam reforming allows operation at high-pressure without expending work on air compression. Furthermore, the SR reactor produces a stream not diluted by nitrogen and can utilize waste heat on the combustion side of the reactor. One approach to adapting high-pressure SR to the small-scale hydrogen production applications involves following the high-pressure steam reformer with a hydrogen separation unit (e.g. a Pd alloy membrane) to yield essentially pure hydrogen. Residual CO and H₂ in the membrane retentate are combusted at ambient pressure to provide process heat required for the SR reactor [9]. In addition to pure hydrogen product, this type of system has fewer components and simplified design. Still, steam reformers, which are essentially large heat exchangers, are much larger than ATR or catalytic partial oxidation (CPOX) reactors, have longer start up times, slower transient responses and are difficult to control. They also require large amounts of water to operate (typically S:C ~3). Water vaporization consumes unrecoverable heat, thus, impacting the system efficiency.

In this paper, we describe a new high-pressure approach to small-scale fuel reforming, which combines size and operational advantages of using an autothermal reforming reactor with the relative simplicity of membrane-based hydrogen separation. The system co-generates pure hydrogen and mechanical power. System modeling is used to demonstrate high efficiency and other performance advantages of the proposed approach.

2. General description of the reforming system

A schematic diagram of a general design of an ATR-based reforming system for converting hydrocarbons into pure hydro-

gen is shown in Fig. 1. Operating parameters for the ATR, such as oxygen to carbon (O:C) and steam to carbon (S:C) ratio, space velocity, inlet stream temperature etc., may vary in a wide range depending on the type of fuel. Dry operation (catalytic partial oxidation mode) may be employed for short chain hydrocarbons such as methane or propane [10]. Steam can be added to the fuel/air mixture for higher molecular weight hydrocarbons such as gasoline or diesel [11]. A water-gas-shift reactor is placed downstream of the ATR to lower CO concentration and to produce additional hydrogen. Note that application of a membrane separator downstream of the WGS allows higher CO concentrations at the WGS exit than that permitted for PROX reactors. Therefore, a single WGS reactor operating at relatively high temperature, and thus having smaller size, can be employed. Additional water in liquid form is sprayed into the hot ATR exit stream before the WGS reactor. This cools the stream to the required WGS inlet temperature, thereby eliminating the need for a heat exchanger, while increasing the WGS feed water concentration, thus, shifting the equilibrium towards hydrogen.

The hydrogen rich reformat exiting the WGS reactor enters a membrane separation unit from which an essentially pure low-pressure hydrogen stream is recovered. A high-pressure retentate stream exits the separator and contains unconverted hydrocarbon from the ATR, unconverted CO from the WGS, and residual H₂. The retentate stream is mixed with excess air and combusted. Depending on the operating conditions and adiabatic temperature of the mixture, homogeneous or catalytic combustion may be employed. Hot burner exhaust is expanded through a gas turbine producing mechanical work, which powers compressors supplying air to the ATR and the burner. This may be accomplished by directly coupling the turbine and the compressors through a single shaft. Alternatively, the turbine work may be used to generate electricity, part of which can be used to run the compressors.

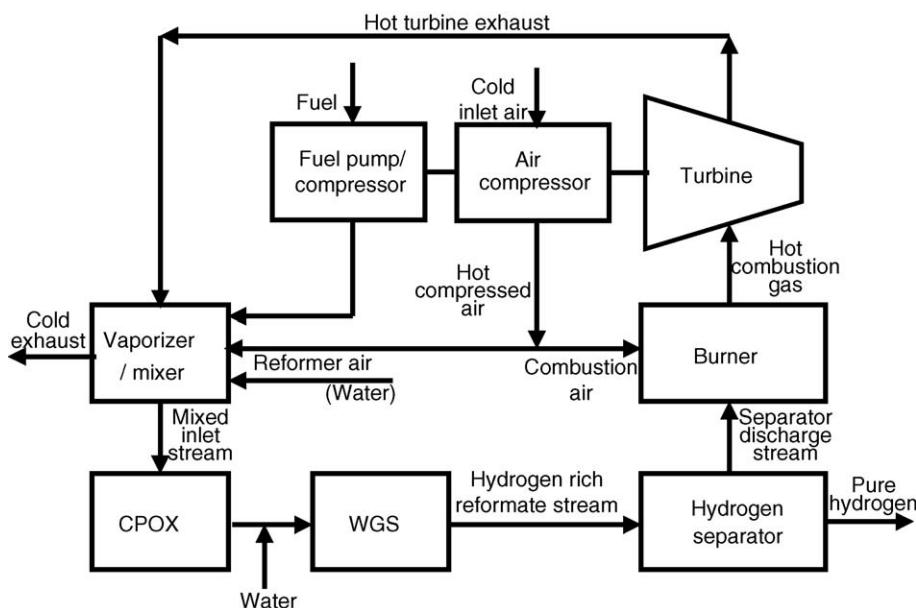


Fig. 1. Schematic diagram of the reforming system.

Note that while pressure-swing adsorption (PSA) is commonly used industrially for hydrogen purification, PSA yields high-pressure hydrogen and low-pressure contaminant streams. Since one aspect of the proposed approach is to produce work by burning the retentate stream at high-pressure and expanding the hot product gases through a turbine, employing PSA for hydrogen separation is not appropriate in this instance.

The low-pressure turbine exhaust stream may be further heat exchanged with the inlet air, water and/or fuel increasing the overall system efficiency. This heat exchange step also offers the potential for recovering at least a portion of the water in the turbine exhaust, which can then be recycled. Note that this optional heat exchanger is the only one in the system. Thus, the present system differs from the ATR-based reforming systems described above, for which several heat exchangers are required between the various process units.

3. Model study of the reforming system

System modeling was performed using ASPEN™ simulation software to develop the representation of the proposed reforming system as shown in Fig. 2 and described below.

3.1. Inlet flows

System performance was studied employing methane as the fuel. Though the general model provides for water addition to the ATR, none is fed in these simulations. This “dry ATR” operating mode corresponds, therefore, to catalytic partial oxidation of methane into syngas. Methane CPOX is well established, and steady operation at elevated pressure has been demonstrated in previous work in the authors’ laboratories [10]. (Note that most higher hydrocarbon fuels would likely require introduction of steam and adjustment of the feed fuel-to-air ratio.)

Air is represented as a mixture of 21% O₂ and 79% N₂. The model assumes all feed components at ambient conditions, i.e. without heat exchange with the hot turbine exit flow. Methane and air are compressed from ambient conditions to the operating

pressure of the system. As a convenience in the model, separate compressors are provided for the reformer and the combustor air streams. All compressors are assumed to have efficiencies of 87% relative to isentropic. Air and methane are perfectly mixed before entering the CPOX reactor.

3.2. CPOX reactor

The air-to-methane ratio in the inlet flow was chosen to provide an O:C of 1.2, which corresponds to operating conditions reported earlier [10]. Adiabatic operation at constant pressure and the achievement of a product mixture corresponding to thermodynamic equilibrium are assumed.

3.3. WGS reactor

Water at ambient temperature is added to the stream exiting the CPOX reactor prior to entering the WGS reactor. Perfect mixing is assumed. (The power required to pump this amount of water into the high-pressure stream is much lower than the power required to compress gases and is neglected in the total power balance.) The amount of water is controlled to provide a WGS inlet temperature of 300 °C. At this temperature the WGS reaction is fast and thermodynamic equilibrium can be reached at space velocities on the order of 100,000 h⁻¹. Thus, the water-gas-shift reactor is assumed to achieve an equilibrium product distribution and to operate adiabatically.

3.4. Hydrogen separation

The membrane unit is assumed to segregate pure hydrogen at ambient pressure from the high-pressure reformat mixture provided by the WGS reactor. In the ASPEN™ model shown in Fig. 2, the membrane separation is modeled as a two step process involving a flow split at constant system pressure in which a specified amount of hydrogen is segregated from the reformat stream followed by a pressure let-down, which reduces the pressure of the high purity hydrogen stream to atmospheric. (No

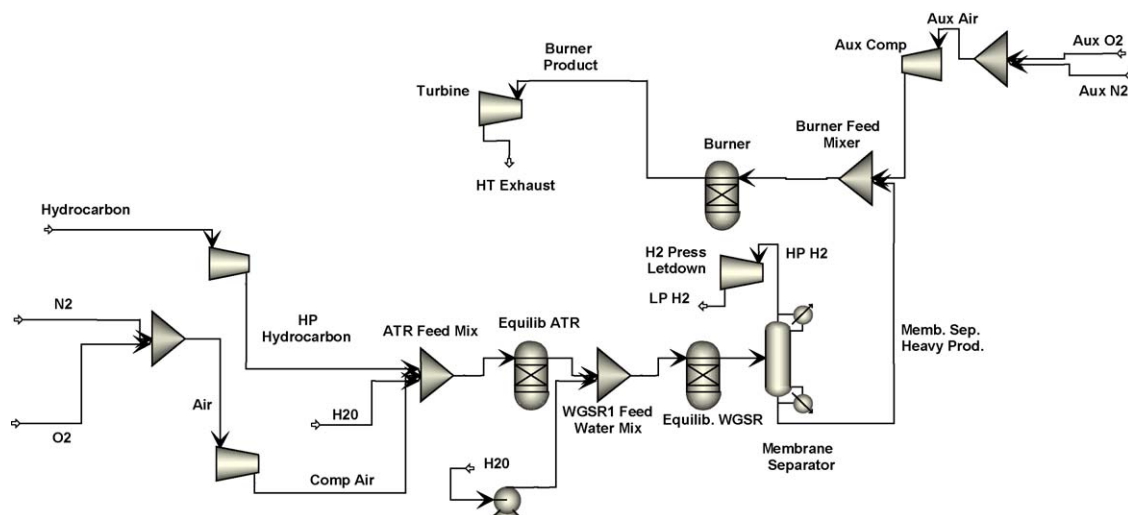


Fig. 2. Reformer system model used for performance estimates.

Table 1
Flow components and power loads along the reforming system

	CPOX air compressor	CH ₄ compressor	CPOX inlet	CPOX exit	WGS inlet	WGS exit	H ₂ output	Burner air compressor	Burner inlet	Burner exit	Turbine exit
CH ₄ (mole h ⁻¹)	0	1000	1000	73	73	73	0	0	73	0	0
O ₂ (mole h ⁻¹)	600	0	600	0	0	0	0	507	507	85	85
N ₂ (mole h ⁻¹)	2257	0	2257	2257	2257	2257	0	1908	4165	4165	4165
H ₂ O (mole h ⁻¹)	0	0	0	198	2165	1440	0	0	1440	2012	2012
CO (mole h ⁻¹)	0	0	0	852	852	127	0	0	127	0	0
CO ₂ (mole h ⁻¹)	0	0	0	75	75	800	0	0	800	1000	1000
H ₂ (mole h ⁻¹)	0	0	0	1657	1657	2382	1955	0	427	0	0
Total flow (mole h ⁻¹)	2857	1000	3857	5112	7079	7079	1955	2415	7539	7262	7262
Temperature (°C)	412	274	361	925	301	416		412	415	1129	580
Pressure (atm)	15	15	15	15	15	15	1	15	15	15	1
Heating value (kW)	0	247.1	247.1	216.4	216.4	217.0	155.1	0	61.9	0	0
Mechanical work (kW)	-9.22	-2.90							-7.79		43.21

$P = 15$ atm, O:C (CPOX) = 1.2, $T_{\text{WGS}} = 300$ °C, membrane separation—80% partial pressure equilibrium.

credit is taken for the work performed by the H₂ expander since it is only a modeling convenience—not an actual process unit.) The amount of hydrogen removed by the separator is calculated assuming an 80% approach to the partial pressure equilibrium between the pure hydrogen stream and the separator exhaust stream using the equation:

$$\eta * P_{\text{sys}} * \left(\frac{n - x}{f - x} \right) = 1 \quad [\text{atm}] \quad (1)$$

where $\eta = 0.8$ is the approach to thermodynamic equilibrium; P_{sys} , the system pressure; f , the total molar flow; n , the molar flow of H₂ at the separator inlet; and x is the molar flow of H₂ at the pure hydrogen stream exiting separator unit at 1 atm pressure.

3.5. Separator discharge burner

The separator discharge stream is mixed with excess air, which is controlled at 1.2 times the stoichiometric amount required to oxidize all burnable components in the discharge stream to CO₂ and H₂O. The burner is represented as an adiabatic, equilibrium reactor.

3.6. Gas turbine

The burner discharge stream is expanded from the system operating pressure to atmospheric pressure through a gas turbine to produce mechanical work. A turbine efficiency of 89% is assumed relative to isentropic.

4. Modeling results

Results of system simulation at 15 atm operating pressure are shown in Table 1. Methane feed to the system is chosen arbitrarily at 1 kmole h⁻¹. This corresponds to 247 kW_t thermal input taking higher heating value (HHV) of methane supplied to the system. Flows for all other streams and operating conditions for system components are based on the methane input and are calculated using the relations described above. The table shows

gas composition and temperature at different points along the system, as well as the power loads for system components.

Calculations were performed also for the system operating at pressures of 5, 10, 25 and 40 atm. Results of these calculations are summarized in Fig. 3. Hydrogen yield efficiency is calculated as ratio of HHV of the H₂ recovered from the membrane separator unit to the HHV of methane supplied to the system. Reforming efficiency is calculated as ratio of HHV of hydrogen plus the *net* mechanical work produced by the system (work produced by the turbine less the load required by all compressors) to the HHV of methane. Assuming 50% efficiency for a PEM fuel cell and 90% efficiency of a mechanical to electrical generator, electrical efficiency is estimated as total electrical power that can be produced by the system if coupled with a PEM fuel cell and a generator divided by the HHV of methane consumed by the system.

Note that while reforming efficiency calculations based on lower heating values (LHV) are often cited in the literature, by analogy with combustion systems, a definition based on true energy content, i.e. higher heating value, better accounts for the thermodynamics of the reforming process [12]. Application of LHV does not properly account for the heat required/released in water vaporization/condensation. Therefore, HHV basis is used in this analysis.

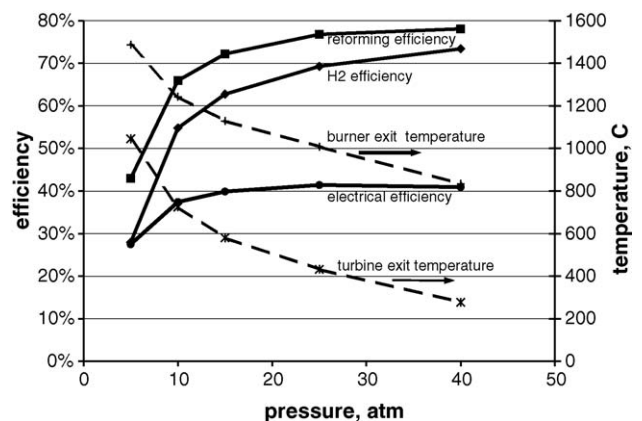


Fig. 3. Dependence of the reformer performance on the operating pressure.

Table 2
Flow components and power loads along the reforming system

	CPOX air compressor	CH ₄ compressor	CPOX inlet	CPOX exit	WGS inlet	WGS exit	H ₂ output	Burner air compressor	Burner inlet	Burner exit	Turbine exit
CH ₄ (mole h ⁻¹)	0	1000	1000	23	23	23	0	0	23	0	0
O ₂ (mole h ⁻¹)	650	0	650	0	0	0	0	328	328	55	85
N ₂ (mole h ⁻¹)	2445	0	2445	2445	2445	2445	0	1233	3678	3678	3678
H ₂ O (mole h ⁻¹)	0	0	0	242	2748	1922	0	0	1922	2352	2352
CO (mole h ⁻¹)	0	0	0	896	896	70	0	0	70	0	0
CO ₂ (mole h ⁻¹)	0	0	0	81	81	907	0	0	907	1000	1000
H ₂ (mole h ⁻¹)	0	0	0	1711	1711	2537	2154	0	383	0	0
Total flow (mole h ⁻¹)	3095	1000	4095	5399	7905	7905	2154	1561	7312	7085	7085
Temperature (°C)	412	274	363	979	250	368		412	376	870	412
Pressure (atm)	15	15	15	15	15	15	1	15	15	15	1
Heating value (kW)	0	247.1	247.1	211.8	211.8	212.4	170.9	0	41.6	0	0
Mechanical work (kW)	-9.98	-2.90						-5.03			34.08

$P = 15$ atm, O:C (CPOX) = 1.3, $T_{\text{WGS}} = 250$ °C, membrane separation—100% partial pressure equilibrium.

As expected, at higher operating pressure more hydrogen is removed from the reformat stream by the membrane thereby increasing the hydrogen efficiency. At 40 atm the hydrogen efficiency is ~73%. As the system pressure increases, so does the work required to compress air and methane feeds. However, over the range of investigated pressures, the gas turbine produces more work than is required to run the compressors, resulting in overall reforming efficiencies higher than the hydrogen efficiency (~78% total reforming efficiency at 40 atm). The electrical efficiency of the system when combined with a PEM cell and a generator is nearly constant at ~40% above 15 atm. This is due to the interplay between the lower assumed efficiency for a PEM cell versus that of an electrical generator.

To study power load variations between the fuel cell (hydrogen yield) and the turbine, two additional cases were considered at 15 atm operating pressure. For these cases, system operating parameters were modified from the previously described Case 1 (Table 1) to vary the composition and heating value of the membrane retentate stream. In a high conversion/low heat case (Case 2), the O:C ratio for the CPOX reactor was increased to 1.3, WGS inlet temperature was specified at 250 °C (achieved by increasing water injection), while the H₂ membrane separation coefficient was increased to 1.0. These conditions provide higher

conversion of CH₄ in the CPOX reactor, higher conversion of CO in the WGS reactor and a higher level of H₂ separation in the membrane. Conversely, in a low conversion/high heat case (Case 3), the O:C ratio was decreased to 1.1, the WGS inlet temperature was set at 350 °C, and the H₂ membrane separation coefficient was set at 0.6. All other system parameters for these cases were the same as in the Case 1. System gas compositions and temperatures for Cases 2 and 3 are shown in Tables 2 and 3, respectively, and the system efficiencies for all three cases are summarized in Table 4.

The process simulation results demonstrate that, as expected, increasing fuel conversion and hydrogen separation in the membrane increases H₂ yield and decreases turbine work and net mechanical work. Conversely, decreasing fuel conversion and H₂ separation leads to lower H₂ yield and higher net mechanical work. Due to increasing combustion air requirements, net mechanical work does not fully compensate for decreasing H₂ yield, such that reforming efficiency decreases with decreasing conversion and hydrogen separation. On the other hand, the large difference in assumed efficiency for electricity production between the PEM fuel cell and the mechanical generator results in a very low difference in system electrical efficiency for all three cases.

Table 3
Flow components and power loads along the reforming system

	CPOX air compressor	CH ₄ compressor	CPOX inlet	CPOX exit	WGS inlet	WGS exit	H ₂ output	Burner air compressor	Burner inlet	Burner exit	Turbine exit
CH ₄ (mole h ⁻¹)	0	1000	1000	141	141	141	0	0	141	0	0
O ₂ (mole h ⁻¹)	550	0	550	0	0	0	0	761	761	127	127
N ₂ (mole h ⁻¹)	2069	0	2069	2069	2069	2069	0	2861	4930	4930	4930
H ₂ O (mole h ⁻¹)	0	0	0	171	1737	1128	0	0	1128	1934	1934
CO (mole h ⁻¹)	0	0	0	789	789	180	0	0	180	0	0
CO ₂ (mole h ⁻¹)	0	0	0	70	70	679	0	0	679	1000	1000
H ₂ (mole h ⁻¹)	0	0	0	1548	1548	2157	1632	0	525	0	0
Total flow (mole h ⁻¹)	2619	1000	3619	4787	6354	6354	1632	3622	8343	7991	7991
Temperature (°C)	412	274	358	892	350	457		412	439	1384	745
Pressure (atm)	15	15	15	15	15	15	1	15	15	15	1
Heating value (kW)	0.0	247.1	247.1	219.6	219.6	220.1	129.5	0.0	90.6	0.0	0.0
Mechanical work (kW)	-8.45	-2.90						-11.69			56.47

$P = 15$ atm, O:C (CPOX) = 1.1, $T_{\text{WGS}} = 350$ °C, membrane separation—60% partial pressure equilibrium.

Table 4
Summary of conversion, power loads and efficiency for the reforming system operating under different sets of conditions

CPOX O:C ratio	WGS inlet temperature (°C)	H ₂ separation coefficient	CH ₄ conversion CPOX (%)	CO conversion WGS (%)	H ₂ separation (%)	H ₂ yield (kW)	Net mechanical work (kW)	H ₂ efficiency (%)	Reforming efficiency (%)	Electrical efficiency (%)	T _{burner exit} (°C)	T _{turbine exit} (°C)
Case 1 1.2	300	0.8	92.7	85.1	82.1	155.1	23.3	62.8	72.2	39.9	1129	580
Case 2 1.3	250	1.0	97.7	92.2	84.9	170.9	16.2	69.2	75.7	40.5	870	411
Case 3 1.1	350	0.6	85.9	77.2	75.7	129.5	33.4	52.4	65.9	38.4	1384	745

P = 15 atm.

Increased heating value of the membrane retentate stream results in much higher burner temperatures. This may require a different burner design and may restrict the choice of materials for the turbine. A potentially simpler solution to reducing the burner exit temperature would be to increase the amount of air added to the membrane exhaust stream, but this will increase the load on the compressor and lower the system efficiency.

5. Discussion

System modeling results demonstrate a relatively simple and efficient reforming system for production of pure hydrogen based on CPOX/autothermal reforming of hydrocarbon fuel under high-pressure conditions. Power required for compressing air for the ATR process, which is generally considered as waste [9] can be recovered by a downstream gas turbine, leading to high system efficiency. Alternatively, the system can be viewed as a turbine cycle in which part of the heating value of the fuel is removed for alternative use prior to combusting fuel in the combustion chamber of the turbine. Lowering the heating value of the fuel in the turbine cycle greatly reduces the amount of air that has to be compressed for the system and increases the cycle efficiency. In addition to high efficiency, the system has other advantages discussed below.

5.1. Reduced size

The reforming system is expected to have relatively small size and weight. Recently we have demonstrated a CPOX reactor operating at 8 atm and having a power density above 15 MW L⁻¹ [10]. The power density was proportional to the operating pressure, such that even higher values can be expected for a system operating at 15 atm or higher. A WGS reactor was demonstrated having power density ~25 kW L⁻¹ when operating at atmospheric pressure [11]. The reaction is approximately first order with respect to CO and H₂O, and therefore it can be expected that power density for the WGS reactor will increase proportionally with operating pressure such that power density in excess of 250 kW L⁻¹ can be expected.

A separation unit is expected to be much larger than the reforming reactors. While H₂ membranes based on thin self-supporting Pd alloy films are available commercially from several manufacturers, they are still too large and expensive to be used with power systems. Much effort is being directed into development of other types of membranes, such as multilayered membranes supported on porous ceramics that promise much higher hydrogen flux and lower cost [13]. These novel membranes are estimated to produce hydrogen flux of about 50 kW m⁻² [14], which translates into about 5 kW L⁻¹ when packaged into a separation unit. Hydrogen flux across a membrane is highest at the inlet section, where the partial pressure differential is the greatest. As hydrogen partial pressure approaches equilibrium, the flux decreases such that a significant increase in area of membrane is required to approach high separation coefficients. In the proposed process scheme, however, recovering the energy of hydrogen remaining in the membrane retentate by combustion and expansion through the turbine, relaxes the

requirement for obtaining a very high level of hydrogen separation. As a result, membrane size can be reduced significantly.

Power density for gas turbines varies in a wide range depending on the turbine size, pressure ratio, type of fuel and operating cycle. Modern utility turbines provide power densities of several kilowatts per liter, with the air compressor being the largest component. These turbines operate at an equivalence ratio $\phi \sim 0.5$, i.e. they require O_2/CH_4 ratio of ~ 4 in the combustion chamber. Additional air is supplied between the combustion chamber and the turbine to lower the turbine inlet temperature to the level tolerated by the turbine blades. Simulations of the reforming system discussed here show that the total amount of air required by the system (both CPOX and burner air) corresponds to an O_2/CH_4 ratio of ~ 1 (Tables 1–3), i.e. at least four times lower than for regular gas turbine systems. Therefore, for a system with a similar power rating, compressor size can be reduced by a factor of four. Tables 1–3 also show that, for a $\sim 100\text{ kW}_e$ system (247.1 kW_{th} fuel with 40% electrical efficiency), a turbine rated for only $\sim 35\text{--}60\text{ kW}$ is required, i.e. smaller by about a factor of two than a regular gas turbine of the comparable power rating.

Another important feature contributing to the relatively small size of the system is matching operating conditions between all consecutive components in the fuel processing train. Each component of the system operates under the inlet conditions existing at the exit from the previous element. No heat exchangers or recuperators are required anywhere in the system. This is an important advantage because multiple stream conditioning devices needed between most components in alternative reforming systems dramatically increase size, weight and complexity.

5.2. Simplified control

Another advantage of the proposed reforming system is the anticipated simplicity of control. Unlike SR, ATR reactor performance is determined only by the inlet mixture composition. Simulations shown above suggest that the performance of the whole system can be controlled by adjusting air-to-fuel ratio in the CPOX reactor inlet, the amount of water injected prior to WGS reactor, and the amount of combustion air added before the burner. Burning the membrane discharge gas and utilizing the energy in the gas turbine relaxes upstream conversion and separation requirements. As illustrated the examples shown in Tables 1–3, lowering conversion in the CPOX and WGS reactors lowers the hydrogen output, but this essentially shifts the load from the PEM cell to the turbine generator. Therefore, a wider range of operating conditions for the CPOX, WGS reactors and the membrane can be adopted, allowing for greater flexibility and variation in the operating conditions without a substantial loss in system efficiency.

Increasing hydrogen separation from the reformat stream, due to increasing system pressure or increasing CPOX and WGS conversion, results in declining burner temperature (i.e. the turbine inlet temperature). Fig. 3 shows that at pressures above 10 atm the burner temperature is below 1200°C , i.e. within the material limits of modern gas turbines, such that no dilution of the burner exhaust is required prior to the turbine. Increasing

hydrogen separation also leads to declining turbine mass flow and turbine exhaust temperature reducing heat loss in the exit gas. Additional turbine exhaust heat exchange could be employed to provide preheating of one or more of the CPOX inlet streams with resultant incremental benefit to system efficiency. For larger systems a recuperator can be installed and the turbine exit heat can be used in a steam turbine as in combined cycle gas turbine systems.

5.3. Fast start up

The ability to shift power between the fuel cell and the turbine permits very fast start up of the system using a starter motor (which could be the turbine generator operating as a motor for the start up). The motor would spin the turbine and the compressor to the required RPM. Compression of methane and air will adiabatically heat the stream entering the CPOX reactor (to 361°C at 15 atm operating pressure). This is sufficient to achieve the reactor light off (which is nearly instantaneous) and transition to steady state operation. Within a few seconds from the ignition, the CPOX reactor starts producing a hot gas stream ($\sim 700\text{--}800^\circ\text{C}$) heating up the remainder of the system. While it can take a longer time to heat the larger WGS reactor and Pd-based membrane unit to their operating temperatures, the membrane discharge containing essentially all the CO and H_2 can be readily combusted in the burner and drive the turbine. Thus, the system can start producing power (though with lower initial efficiency) in as quickly as starting a turbine. As all the components heat up to the operating temperature, more hydrogen can be removed in the membrane unit thereby gradually shifting power from the turbine to the fuel cell and increasing system efficiency.

6. Conclusions

Process modeling demonstrates the feasibility of a compact and simple reforming system for converting hydrocarbon fuels into pure hydrogen. Total reforming system efficiencies approaching 80% are possible with electrical efficiencies about 40%.

The system is expected to have small size, simplified control requirements, and fast start up.

References

- [1] P. Mazza, R. Hammerschlag, Carrying the energy future. Comparing hydrogen and electricity for transmission, storage and transportation, Institute for Lifecycle Environmental Assessment Report, www.ilea.org, June 2004.
- [2] R. Shinnar, Technol. Soc. 25 (2003) 455–476.
- [3] J.R. Rostrup-Nielsen, et al., Appl. Catal. A: Gen. 221 (2001) 379–387.
- [4] D.J. Wilhelm, D.R. Simbeck, A.D. Karp, R.L. Dickenson, Fuel Process. Technol. 71 (2001) 139–148.
- [5] K. Aasberg-Petersen, T.S. Christensen, C. Stub Nielsen, I. Dybkjær, Fuel Process. Technol. 83 (2003) 253–261.
- [6] S. Ahmed, M. Krumpelt, Int. J. Hydrogen Energy 26 (2001) 291–301.

- [7] J.R. Lattner, M.P. Harold, *Int. J. Hydrogen Energy* 29 (2004) 393–417.
- [8] Y.S. Seo, A. Shirley, S.T. Kolaczowski, *J. Power Sources* 108 (2002) 213–225.
- [9] D.G. Löffler, K. Taylor, D. Mason, *J. Power Sources* 117 (2003) 84–91.
- [10] M. Lyubovsky, S. Roychoudhury, R. LaPierre, *Catal. Lett.* 99 (2005) 113–117.
- [11] S. Roychoudhury, M. Castaldi, M. Lyubovsky, R. LaPierre, S. Ahmed, Microlith catalytic reactors for reforming *iso*-octane-based fuels into hydrogen, *J. Power Sources* 152 (2005) 75–86.
- [12] U. Bossel, Well-to-wheel studies, heating values, and the energy conservation principle, European Fuel Cell Forum, 29 October 2003, <http://www.efcf.com/reports/E10.pdf>.
- [13] Y.H. Ma, I.P. Mardilovich, E.E. Engwall, *Ann. N.Y. Acad. Sci.* 984 (2003) 346–360.
- [14] T.G. Kreutz, R.H. Williams, R.H. Socolow, P. Chiesa, G. Lozza, Production of hydrogen and electricity from coal with CO₂ capture, in: *Proceedings of the Sixth Greenhouse Gas Control Technologies Conference*, Kyoto, Japan, 2002.