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Exergy Analysis of Hydrogen Production via Steam Methane Reforming

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Abstract

The performance of hydrogen production via steam methane reforming is evaluated using exergy analysis, with emphasis on exergy flows, destruction, waste, and efficiencies. A steam methane reformer model was developed using a chemical equilibrium model with detailed heat-integration. A base-case system was evaluated using operating parameters from literature. Reformer operating parameters were varied to illustrate their influence on system performance. The calculated thermal and exergy efficiencies of the base-case system are lower than those reported in literature. The majority of the exergy destruction occurs due to the high irreversibility of combustion and heat-transfer. A significant amount of exergy is wasted in the exhaust stream. The variation of reformer operating parameters illustrated an inverse relationship between hydrogen yield and the amount of methane required by the system. The results of this investigation demonstrate the utility of exergy analysis and provide guidance for where research and development in hydrogen production via steam methane reforming should be focused.

Keywords: Exergy Analysis; Hydrogen Production; Steam Methane Reforming

Introduction

Hydrogen has been proposed and aggressively pursued over the past decade as a possible alternative fuel. Hydrogen is an attractive energy carrier because it can be combusted, similar to gasoline and natural gas, or converted to electricity in a fuel cell without any carbon emissions. The major disadvantage is that hydrogen must be produced from other naturally occurring species – typically from other hydrocarbons or water.

Currently, 80-85% of the world's total hydrogen production is derived via Steam Methane Reforming (SMR) of natural gas [1]. Most of the remaining hydrogen production is accomplished via coal gasification and water electrolysis (at a smaller

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scale). Hydrogen production requires the investment of energy and capital. Over the past years hydrogen production has become more efficient and less expensive, however it remains very energy intensive and costly when compared to gasoline production.

The objective of this paper is to apply exergy analysis to the production of hydrogen via natural gas SMR with emphasis on exergy flows, destruction, waste, and efficiency. Exergy analysis is a critical evaluation tool that provides insight into a system that eludes purely first-law, or energy analysis. Specifically, exergy analysis allows for the location, cause, and true magnitude of waste and losses in a system to be determined [2]. Such information can then be used to make design improvements that optimize resource use.

The analysis presented in this paper uses system component models, a chemical equilibrium reformer model, and detailed heat-integration to perform exergy analysis. Exergy analysis of a base-case SMR system quantifies the performance of the system and demonstrates the utility of exergy analysis. Comparisons between the base-case performance results and literature are made to illustrate the importance of using a chemical equilibrium model with detailed heat-integration. Variations in the operating parameters illustrate the system's performance sensitivity and provide guidance for where research and development efforts should be concentrated.

Steam Methane Reforming Description

Fig. 1 shows a simplified diagram of a SMR system.

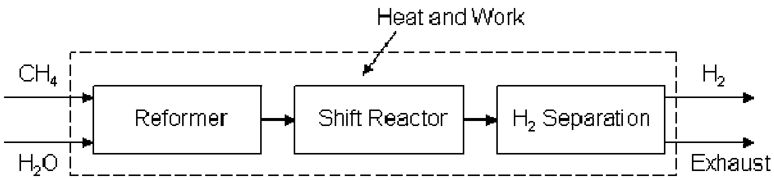

Fig. 1. Simplified schematic of SMR system.

SMR is accomplished by first reacting methane and steam over a high temperature catalyst. The reaction is endothermic and typically achieved over a nickel-based catalyst operating at elevated temperatures and pressures between 900-1200 K and

5-25 atm, respectively. Due to the endothermic reaction, heat must be provided to the reformer. Fig. 1 shows the heat coming from an external source. In practice, the required heat is typically provided through combustion of extra methane and/or from using the available energy in the separation exhaust stream through combustion or simple heat exchange. The ideal global reformation reaction is given in Eq. (1). The actual chemical composition of the syngas is determined by the kinetics within the reformer and modeled by chemical equilibrium. Depending on the steam-to-carbon ratio (S/C ratio) and the reformer operating temperature and pressure, there may also be significant amounts of CH_4, H_2O, and CO_2 in the product gas (syngas).

$$\mathrm{CH_4 + H_2O(g) \longrightarrow CO{+}3H_2} \qquad \Delta H_R = +\,251\ \mathrm{MJ/kmole_{CH_4}} \quad (1)$$

The syngas exiting the reformer is passed through a water-gas shift reactor that converts the CO in the syngas to CO_2 and H_2 using the available H_2O in the syngas or additional H_2O to system. Although the shift reaction in Eq. (2) is exothermic, the net reaction of (1) and (2) is endothermic. In practice, the shift reaction takes place over two reactors that operate between 473-673K and 400-450K. The shift reaction converts 98-99.9% of the CO to CO_2 and H_2.

$$\mathrm{CO + H_2O(g) \longrightarrow CO_2{+}H_2} \qquad \Delta H_R = -\,41.2\ \mathrm{MJ/kmole_{CO}} \quad (2)$$

The final step in SMR is the separation of the hydrogen from the syngas exiting the water-gas shift reactor, which is mostly H_2, H_2O, and CO_2. This separation process can be accomplished through a number of techniques. The three most common methods are: 1) pressure-swing-adsorption (PSA) to separate the H_2, 2) PSA to separate the CO_2 followed by condensation of the remaining H_2O, and 3) a membrane to separate the H_2. Both PSA separation techniques are relatively mature technologies that are energy intensive and provide various degrees of end stream H_2 purity. Hydrogen membrane separation is a promising and developing technology that is capable of producing high end stream H_2 purity (>99%). Metallic membranes operate at temperatures between 573-

873 K and with a pressure gradient across the membrane between 1-40 atm. A detailed overview of hydrogen membrane separation technologies is given in Sushil et al. [3].

Model Description

The model developed for this investigation uses a library of component models developed in Simulink [4]. The key components of the developed model are the chemical equilibrium reformer, heat transfer blocks for detailed heat-integration, the expansion valve, and the hydrogen separation membrane. A diagram of the model developed for this investigation is shown in Fig. 2. The purpose of this model is to investigate the steady-state production of hydrogen via natural gas reforming; the model is not applicable to start-up operations.

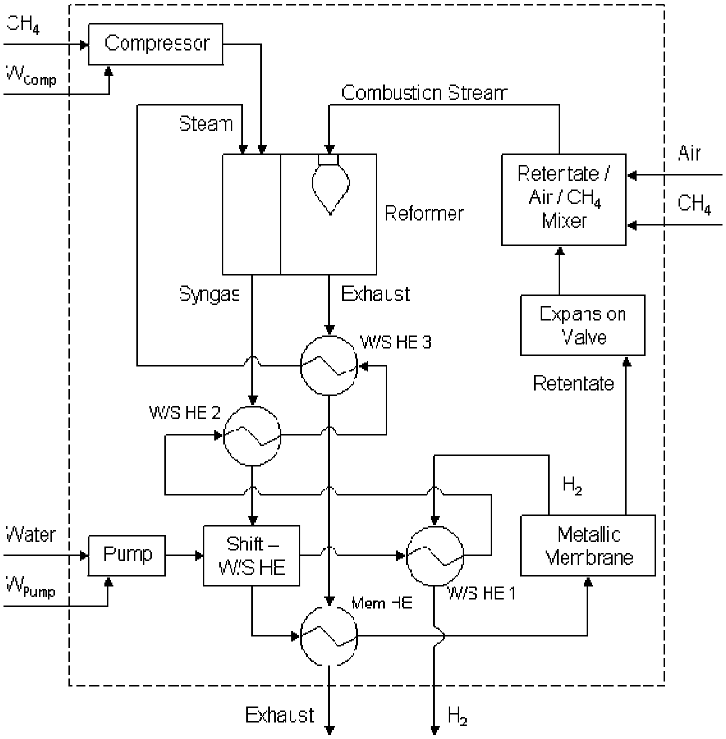

Fig. 2. Detailed schematic of SMR system. Dashed line represents system boundary.

The model begins by compressing the natural gas and pumping the inlet water to the reforming operating pressure. For simplicity the natural gas is represented by pure methane, CH_4. In practice, the natural gas must be desulphurized before entering the reformer to avoid contamination of the catalyst, which requires additional work that is not accounted for in this investigation. The pumped water is heated to steam before entering the reformer and mixing with methane. This heating is achieved through heat exchange with the shift reactor (Shift – W/S HE), H_2 cooling heat exchanger (W/S HE 1), pre-shift heat exchanger (W/S HE 2), and exhaust stream heat exchanger (W/S HE 3).

The reformer model can be broken into three parts: 1) methane/steam mixing, 2) reformation, and 3) combustion of the retentate/air/methane stream to provide heat for the reformation. The mixing is modeled as an adiabatic process with the mixed stream entering the reformer at the reformer operating temperature. The reforming model replaces the global reaction shown in Eq. (1) with a calculation of the chemical equilibrium composition that produces a more realistic estimate of the syngas composition. The equilibrium computation incorporates a temperature and pressure dependence, without requiring information on the specific reactions, flow characteristics within the reformer, or catalyst material. It is assumed that the syngas exits the reformer at the reformer operating temperature and pressure. The required heat is provided by combustion of the *retentate*/air/methane stream (combustion stream). The retentate stream is the gas that is not separated in the membrane. Methane addition into the combustion stream is only required when the there is not enough energy available in the retentate stream to provide the total heat for the system. The reformer exhaust stream exits at the reformer operating pressure and a temperature.

Heat-integration is an integral part of this investigation because the performance of a SMR system depends largely on the amount of methane required by the system. The heat exchangers are modeled using a prescribed effectiveness and minimum temperature difference between inlet and outlet streams. It is assumed that there are no pressure losses across the heat exchangers. If a minimum temperature difference is not achieved in any of the heat-exchangers, methane is added to the combustion stream in order to attain the prescribed temperature difference. Any excess thermal energy in the exhaust stream following all heat transfers is wasted.

The water-gas shift reactor is modeled as a single stage shift reactor that operates at constant temperature and pressure and converts 100% of the CO in the syngas stream to CO_2 and H_2 using the available H_2O in the syngas stream. Following the shift reactor, the syngas stream is heated through heat transfer with the exhaust stream to the operating temperature of the hydrogen separation membrane.

The hydrogen separation membrane is modeled as an isothermal metallic membrane that produces a pure hydrogen stream (product stream) with a prescribed *effectiveness*. The membrane effectiveness is defined as the molar percentage of the inlet hydrogen that is transferred to the product stream. Both the pure hydrogen and waste (retentate) streams exit the membrane at the membrane operating temperature. The pure hydrogen stream exits the membrane at the environmental pressure and is cooled to the environmental temperature through heat exchange with the pumped water before exiting the SMR system. The retentate stream exits the membrane at the membrane inlet stream pressure (the reformer operating pressure) and is expanded across a valve to the environmental pressure. The retentate stream is then mixed with a stoichiometric amount of air and additional methane (if needed) for combustion in the reformer.

Operating Parameters and Evaluation Methods

Table 1 provides a complete list of the base-case operating parameters. The reformer operating parameters are based on the operating parameters of a DOE demonstration SMR facility at the city of Las Vegas, NV [4, 5]. The S/C ratio was adjusted so that no additional methane was required in the combustion stream. The water-gas shift reactor operating temperature represents an average between the high- and low-temperature shift reactors reported in literature [6]. The membrane operating temperature is an averaged metallic membrane temperature taken from Sushil et al. [3]. The dead state chemical composition represents atmospheric air and gives liquid water zero chemical exergy. More information on the treatment of liquid water chemical exergy can be found in Szargut et al. [7], Moran [8], and Bejan et al. [2].

Dead State			**Reformer**		
T	298	K	T	973	K
P	1	atm	P	10	atm
O_2	20.3406	% v/v	S/C Ratio	3.2	---
N_2	76.5195	% v/v			
H_2O	3.1029	% v/v	**Shift Reactor**		
CO_2	0.0370	% v/v	T	573	K
			P	10	atm
Inlet Fuel (CH4)					
T	298	K	**Membrane**		
P	1	atm	T	723	K
			P_{H2}	1	atm
Inlet Water			$P_{Retentate}$	10	atm
T	298	K	H_2 Purity	100	%
P	1	atm	$\varepsilon_{Membrane}$	90	%
Inlet Air			**Other Parameters**		
T	298	K	$\eta_{s,\ Compressor}$	70	%
P	1	atm	$\eta_{s,\ Pump}$	85	%
O_2	21	% v/v	$\varepsilon_{Heat\ Exchange}$	90	%
N_2	79	% v/v	$\Delta T_{HE\ -\ Inlet/Outlet}$	5	K

Table 1. Base-case operating parameters.

The performance of a SMR system is traditionally evaluated by the thermal efficiency of the system. The thermal efficiency of the system is based on a first-law energy balance and is shown in Eq. (3).

$$\eta_{\text{Thermal}} = \frac{\dot{m}_{H_2} \cdot LHV_{H_2}}{\dot{m}_{CH_4} \cdot LHV_{CH_4} + \dot{W}_{\text{Compressor}} + \dot{W}_{\text{Pump}}} \tag{3}$$

Exergy analysis focuses on a system's exergy flows, destruction, waste, and efficiency. The steady-state exergy flows into and out of the system are defined in Eqs. (4) and (5), and the exergy destruction and un-used exergy are defined in Eqs. (6) and (7).

$$\dot{E}_{\text{In}} = \dot{E}_{CH_4} + \dot{W}_{\text{Compressor}} + \dot{W}_{\text{Pump}} \tag{4}$$

$$\dot{E}_{\text{Out}} = \dot{E}_{H_2} + \dot{E}_{\text{Exhaust}} \tag{5}$$

$$\dot{E}_{\text{Destuction}} = \dot{E}_{\text{In}} - \dot{E}_{\text{Out}} \tag{6}$$

$$\dot{E}_{\text{Un-used}} = \dot{E}_{\text{Destuction}} + \dot{E}_{\text{Exhaust}} \tag{7}$$

For a steady-state system, the exergy destruction is defined as the difference between the total amount of exergy into and out of the system. The destroyed exergy measures the lost available energy that is unrecoverable. The un-used exergy of the system is defined as the sum of the amount of exergy destroyed within the system and the amount of exergy wasted in the exhaust stream. The exergy of the exhaust stream is theoretically recoverable.

The exergy efficiency of a SMR system is defined as the ratio of exergy recovered in the hydrogen stream to the total exergy into the system. Given this definition and through manipulation of Eqs. (4) through (7), the exergy efficiency of the system can be written in terms of the amount of un-used exergy and the amount of exergy into the system. Both forms of the exergy efficiency definition are given in Eq. (8).

$$\eta_{\mathrm{Exergy}} = \frac{\dot{E}_{H_2}}{\dot{E}_{\mathrm{In}}} = \frac{\dot{m}_{H_2} \cdot E_{H_2}}{\dot{m}_{CH_4} \cdot E_{CH_4} + \dot{W}_{\mathrm{Compressor}} + \dot{W}_{\mathrm{Pump}}} = 1 - \frac{\dot{E}_{\mathrm{Un\text{-}used}}}{\dot{E}_{\mathrm{In}}} \tag{8}$$

Exergy analysis can be also applied to individual components within the system. The exergetic performance of a component is measured by the amount of exergy destroyed within the component and its exergy efficiency. Component exergy destruction and exergy efficiency definitions are given for the k-th component in Eqs. (9) and (10).

$$\dot{E}_{\mathrm{Destuction,\,k}} = \sum_{\mathrm{In}} \dot{E}_{k} - \sum_{\mathrm{Out}} \dot{E}_{k} \tag{9}$$

$$\eta_{\mathrm{Exergy,\,k}} = \frac{\sum_{\mathrm{Out}} \dot{E}_{k}}{\sum_{\mathrm{In}} \dot{E}_{k}} = 1 - \frac{\dot{E}_{\mathrm{Destruction,\,k}}}{\sum_{\mathrm{In}} \dot{E}_{k}} \tag{10}$$

Base-Case Results and Discussion

Table 2 lists the global thermal and exergy efficiencies and molar flow ratios of the SMR system operating with the base-case parameters listed in Table 1. The thermal efficiency of the system is in good agreement with the 68% thermal efficiency reported from the Las Vegas test site [5]. The exergy efficiency is 4% less than the thermal efficiency of the system. This is due to the combined influence of hydrogen having a smaller exergy content (116.69 MJ/kg) than its lower heating value (119.96 MJ/kg) and methane having a larger exergy content (51.72 MJ/kg) than its lower heating value (50.01 MJ/kg). Note that Eq. (8) takes on the same form as Eq. (3), except with exergy substituted for lower heating value.

Efficiencies		
η_{Thermal}	67.57	%
η_{Exergy}	63.55	%
Molar Flow Ratios		
H_2 Produced	2.28	mole / mole_{CH4}
Air Combustor	4.11	mole / mole_{CH4}
CH_4 Added	0.0	mole / mole_{CH4}

Table 2. Base-case global efficiencies and flow ratios.

The hydrogen molar flow ratio given in Table 2 represents the molar yield of hydrogen per mole of total methane into the system. Using the base-case S/C ratio, no additional methane was required by the system. Therefore, the hydrogen molar flow ratio in Table 2 is simply the hydrogen yield per mole of methane into the reformer. In order to put the 2.28 hydrogen yield ratio into perspective, it should be compared against the results of a global reaction analysis. A global reaction step for a hydrocarbon fuel is given in Eq. (11), adapted from Lutz et al [9]. Operating S/C ratio ≥ 3, the hydrogen yield ratio is 4. If this yield was actually achieved, both the thermal and exergy efficiencies of the system would improve. The difference between the hydrogen yield ratios calculated using the SMR model and the global analysis illustrates the impact of using the chemical equilibrium constraint. Global analysis of a SMR system over-estimates the hydrogen yield and system efficiency.

$$C_1H_4 + S/C \cdot H_2O(l) \longrightarrow 4H_2 + CO_2 + (S/C - 2)H_2O(g) \qquad (11)$$

Table 3 lists the global exergy flows of the SMR system. The third column of breaks-down the global exergy flows by their percentage of the total exergy into the system; Fig. 3 displays these percentages graphically. The compression and pump work represent a small fraction of total exergy into the system. Methane is the dominate exergy input. The majority of the exergy out of the system is carried by the hydrogen. The un-used exergy is mostly destroyed exergy, due to irreversibilities within the system.

	Exergy (kJ / mole$_{CH4}$)	**Percent of Total E $_{In}$ (%)**
Exergy In	838.12	100.00%
E_{CH4}	*827.54*	*98.74%*
$W_{compressor}$	*10.53*	*1.26%*
W_{pump}	*0.06*	*0.01%*
Exergy Out	588.04	70.16%
E_{H2}	*532.63*	*63.55%*
$E_{Exhaust}$	*55.41*	*6.61%*
Exergy Destroyed	250.14	29.84%
Exergy Un-Used	305.55	36.46%

Table 3. Base-case global exergy flows.

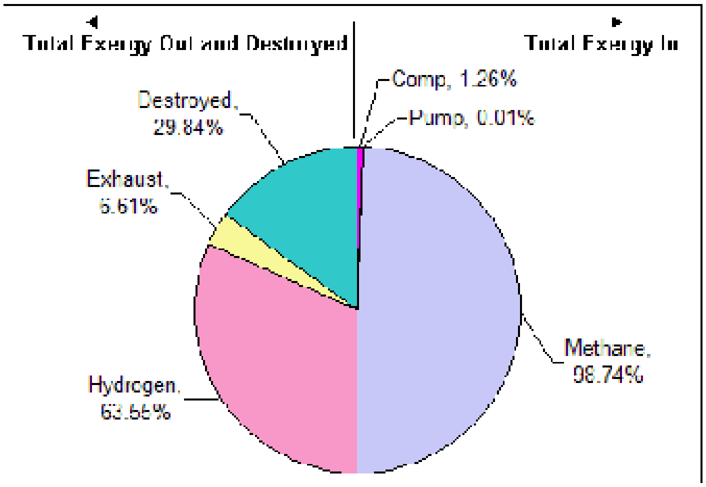

Fig. 3. Distribution of exergy flows into and out of the modeled SMR system.

The total exergy destroyed within the system can be calculated either by Eq. (6) or summing all the individual component irreversibilities. Table 4 lists the exergetic performance of each component within the SMR system operating with the base-case parameters. The third column breaks-down the component exergy destructions by their percentage of total exergy destruction. The majority of the exergy destruction occurs in the reformer, mostly due to the high irreversibility of combustion, and in the water-to-steam heat-exchangers. The membrane heat-exchanger, membrane, and shift reactor contribute a small percentage to the total exergy destruction. The exergy destruction in the adiabatic methane/steam mixer and expansion valve is entirely due to the entropy production within each component.

	Exergy Destroyed (kJ / mole$_{CH4}$)	**Percent of Total E_D (%)**	**Component η_{Exergy} (%)**
Pump	0.01	0.00	85.05
Compressor	1.83	0.73	99.78
Water/Steam HE	59.00	23.60	---
W/S HE 1	*5.00*	*2.00*	*99.08*
W/S HE 2	*23.68*	*9.47*	*97.67*
W/S HE 3	*30.31*	*12.12*	*83.93*
Reformer	131.87	52.69	90.04
M/S Mixing	*8.68*	*3.47*	*99.08*
Reformation	*33.66*	*13.46*	*97.26*
Combustion	*89.54*	*35.76*	*76.76*
Membrane HE	8.94	3.57	99.22
Membrane Separation	5.78	2.31	99.41
Shift - W/S HE	5.27	2.11	99.45
Expansion Valve	18.16	7.26	95.71
R/A/M Mixer	19.28	7.71	95.25
Total Exergy Destroyed	**250.14**		

Table 4. Exergy destruction break-down by component.

The fourth column in Table 4 lists each component's individual exergy efficiency calculated using Eq. (7). With the exception of the combustor, third water-to-steam heat-exchanger, and pump, the exergy efficiency of each component is high. The relatively low efficiency of 76.8% is typical of combustors due to the large amount of entropy produced during uncontrolled chemical reactions, in accordance with published data [6, 10]. The third water-to-steam heat exchanger has the worst heat-exchange component efficiency due to the larger temperature gradients between the inlet and outlet water/steam streams and the reformer combustion and exhaust streams. The low pump exergy efficiency is the result of defining water to have a zero exergy content at the environmental temperature and pressure. When Eq. (10) is used to evaluate the pump, it reduces to the exergy out of the pump divided by the work into the pump. The change in the exergy of the water through the pump is mostly due to its increase in enthalpy (its increase in entropy is small), which results in the pumps exergy efficiency being approximately equal to its isentropic efficiency.

The exergy efficiency of the system, as defined in Eq. (5), can be evaluated as a function of the un-used exergy within the system. Fig. 4 illustrates the un-used exergy break-down by component as a percentage of the total un-used exergy. Of the total un-used exergy, 82% is destroyed within the system and 18% is wasted in the exhaust stream. Strictly first-law analysis of the SMR system would lead to the misconception that most of the energy is wasted in the exhaust stream. The un-used exergy break-down illustrates the utility of exergy analysis. A design engineer could use these results to make design improvements that could decrease the amount of un-used exergy.

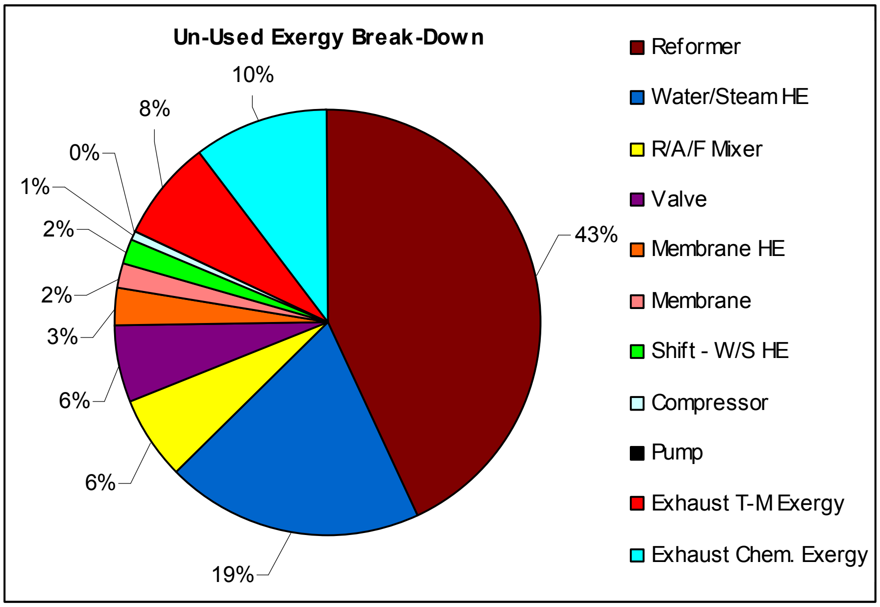

Fig. 4. Un-used exergy break-down. Total un-used exergy = 305.55 kW/mole$_{CH4}$.

The majority of the exergy destruction occurs in the reformer, heat-exchangers, expansion valve, and retentate/air/fuel mixer. To reduce the amount of exergy destroyed within the reformer, a more advanced combustor could be utilized to minimize entropy production and a more efficient catalyst with better heat-exchange characteristics could be implemented. Heat-exchangers inherently destroy exergy due to heat-transfer across a finite temperature difference. To minimize the exergy destruction within a heat-exchanger, the temperature differences between the two streams should be as small as possible. Heat-exchangers could be used in the SMR system to better match the inlet and outlet temperatures of the streams. In place of an expansion valve, a turbine could be used to extract work, which could then be used to provide power for the fuel compressor and water pump. The addition of a turbine was considered in this SMR system, but neglected under the assumption that the capital costs would not out-weigh the exergetic benefits. Adiabatic stream mixing is highly irreversible, resulting in exergy destruction. The retentate/air/fuel mixer destroys more exergy than through entropy production alone, because the inlet retentate stream enters the mixer at an elevated temperature (the membrane operating temperature), which results in further exergy destruction due to heat transfer. This could be remedied by better matching the temperatures of the two streams. These design recommendations based on exergy analysis would not be identified by first-law analysis alone.

In Fig. 4, the exergy of the exhaust is separated into two forms: thermo-mechanical (T-M) and chemical. The thermo-mechanical exergy associated with the exhaust stream is due to the temperature being higher than the environmental temperature. Some of thermo-mechanical exergy could be utilized by adding a bottoming cycle to the system, although the exergetic benefits would most likely not be worth the capital investment. If all of the thermo-mechanical exergy was recovered from the exhaust stream, the system exergy efficiency would increase from 63.5% to 66.5%.

The chemical exergy of the exhaust stream is the amount of work that could be extracted from the stream if it was brought into chemical equilibrium with the environment. Although the exhaust stream is in equilibrium with itself and comprised of stable species, the extraction of its chemical exergy is difficult, if not impossible. Theoretically, a reactor could be used that would produce only environmental species while extracting work. Each species would then need to be brought to their environmental concentrations (partial pressures). This could theoretically be achieved though a series of species-specific membranes that would diffuse each species to its environmental partial pressure while extracting diffusive work. If both the thermo-mechanical and chemical exergy of the exhaust stream were utilized, the exergy efficiency of the system would increase to 70.2%.

The thermal and exergy efficiencies presented in this paper are lower than those given in the limited number of other thermodynamic SMR analysis papers. Table 5 summarizes the thermal and exergy efficiencies determined in literature. The variance in reported thermal and exergy efficiencies can be attributed to a number of differences between the models and their operating parameters. The present paper is unique for combining an equilibrium reformer model with detailed heat-integration. The implementation of an equilibrium reformer with detailed heat exchange significantly influences the performance of a SMR model through the amount of hydrogen produced and the amount of additional methane required in the combustor.

Author	Reference Number	η_{Thermal} (%)	η_{Exergy} (%)	Notes
Rosen	[6]	86	78.5	Detailed system analysis with heat-integration. Uses global reformation model with PSA CO_2 separation and methanation.
Lambert et al.	[11]	---	76.62[a]	Purpose of paper was to analyze SMR with oxygen enriched combustion. Uses equilibrium reformer model. Separation method is not described.
Sorin et al.	[12]	---	79.88	Only analyzes natural gas reformation to syngas. Reformation heat is provided by combustion of extra fuel.
Simbeck	[1]	65.3, 76.2	---	Purpose of paper was to determine hydrogen production costs. Details of SMR were not described.
Lutz et al.	[9]	89[b], 81[c]	---	First law based analysis. Analyzes both a global and equilibrium reformer. Reformer heat is provided by combustion of retentate stream exiting membrane. Does not use detailed heat-integration.
Bargigili et al.	[13]	77[d]	71[d]	Purpose of paper was to use a multi-criteria approach to compare hydrogen production pathways through energy, exergy, and emergy analysis.

Table 5. Comparisons of SMR thermal and exergy efficiencies from literature. [a] Uses slightly different exergy efficiency definition. [b] Maximum thermal efficiency using global reaction model going to equilibrium. [c] Maximum thermal efficiency using equilibrium reformer model. [d] Values taken from National Renewable Laboratory report.

Parametric Study Results

This section examines the influence that the reformer operating temperature, pressure, and steam-to-carbon ratio has on system efficiencies and global exergy flows. The results were calculated by varying one operating parameter while holding all other parameters constant at their base-case values.

Fig. 5 illustrates the effects that the reformer temperature has on system efficiencies and global exergy flows. The thermal and exergy efficiencies of the system reach maximum values of 68.0% and 64.0%, respectively, when the reformer operates at 975 K. The behavior of the efficiency curves can be explained through evaluation of the global exergy flows. As the reformer temperature increases, the amount of hydrogen produced increases until it plateaus at approximately 1200K. This behavior is consistent Le Chatelier’s Principle, which states that if a dynamic equilibrium is disturbed by changing the conditions, the position of equilibrium moves to counteract the change. Since the global reaction is endothermic, Eq. (11), higher temperature shifts the equilibrium position towards the products in order to absorb more heat. The increase in hydrogen production increases the system efficiencies. However, at temperatures above 975 K, additional methane is required by the system to make up for the decreased heating value of the reformate stream. As the reformer temperature increases above 975 K, the amount of additional methane increases at a faster rate than the amount of hydrogen produced, which decreases the efficiency of the system. This effect was not shown in Lutz et al. [9], because the heat-integration in their model did not include a prescribed heat-exchanger effectiveness or minimum inlet/outlet stream temperature difference.

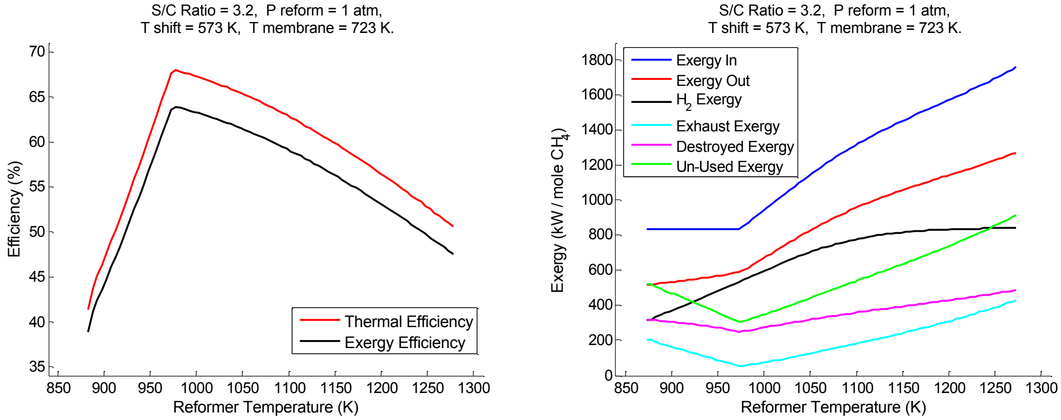

Fig. 5. Influence of reformer operating temperature on system efficiency and global exergy flows.

Fig. 6 compares the parametric thermal efficiency results presented by Lutz et al. [9] to the present results. Both models use the same reformer operating pressure, however Lutz el al. [9] used a S/C ratio of 3.5 and a membrane and water-gas-shift temperature of 573 K. The two efficiency curves exhibit the same behavior until 975 K. The horizontal shift in thermal efficiencies reported by Lutz el al. [9] is due to the difference in operating parameters. The departure of the two curves above 975 K illustrates the effects of using detailed heat-integration.

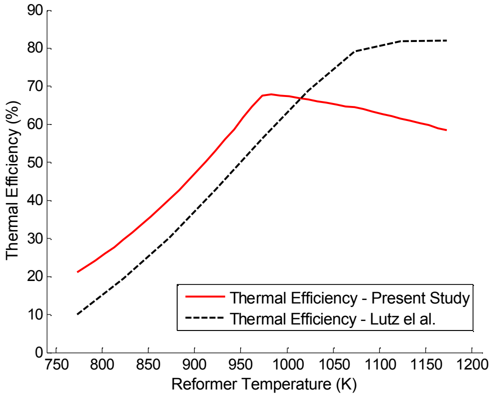

Fig. 6. Comparison between the results presented by Lutz et al. [9] and the present paper.

The influence that reformer operating pressure has on system efficiencies and global exergy flows is shown in Fig. 7. The thermal and exergy efficiencies of the system decrease as the reformer operating pressure is increased. This is due to a combination of the equilibrium syngas composition shifting to lower concentrations of hydrogen and the amount of additional methane required by the system. As the pressure is increased, the increase in compression and pump work is negligible compared to the change in hydrogen yield. At pressures between 2 and 10 atm, the decrease in efficiencies is caused by the equilibrium concentration shift, and at pressure above 10 atm, the addition of methane to the system dominates the efficiency calculations. The syngas equilibrium composition is consistent with Le Chatelier's Principle. Since the global reaction in Eq. (11) increases the total number of moles, higher pressure shifts the equilibrium towards reactants. While operating at lower pressure is theoretically advantageous from the equilibrium analysis, reaction kinetics require high pressure to ensure enough molecular collisions with the catalyst.

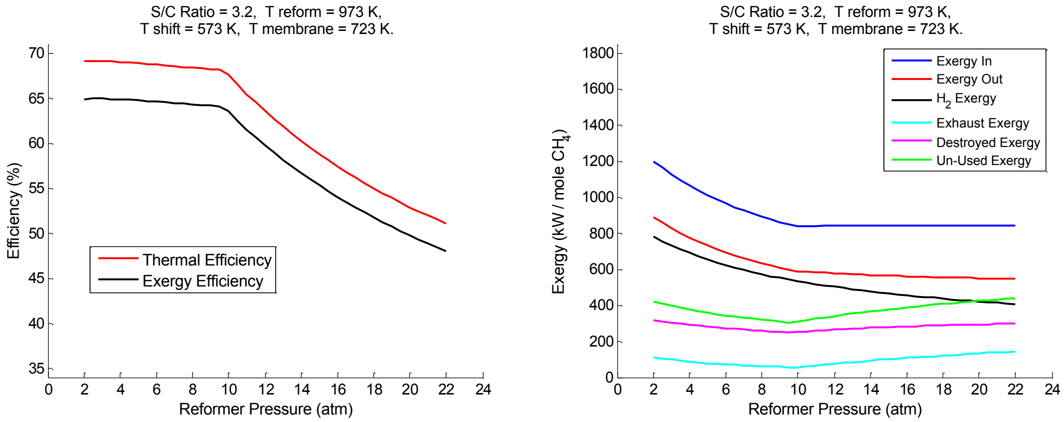

Fig. 7. Influence of reformer operating pressure on system efficiency and global exergy flows.

Fig. 8 illustrates the effects that reformer steam-to-carbon ratio has on system efficiencies and global exergy flows. The thermal and exergy efficiencies of the system increase significantly with the S/C ratio until approximately 3.2, because excess water shifts the equilibrium towards products. At S/C ratios above 3.2, the efficiencies increase only slightly with excess steam. There is an optimum S/C ratio, before the additional methane required reduces the efficiency; however, the profile is relatively flat and would be hard to identify in practice. The thermal and exergy efficiencies reach maximum values of 68.5% and 64.4%, respectively, when operating with a reformer S/C ratio of 4.4.

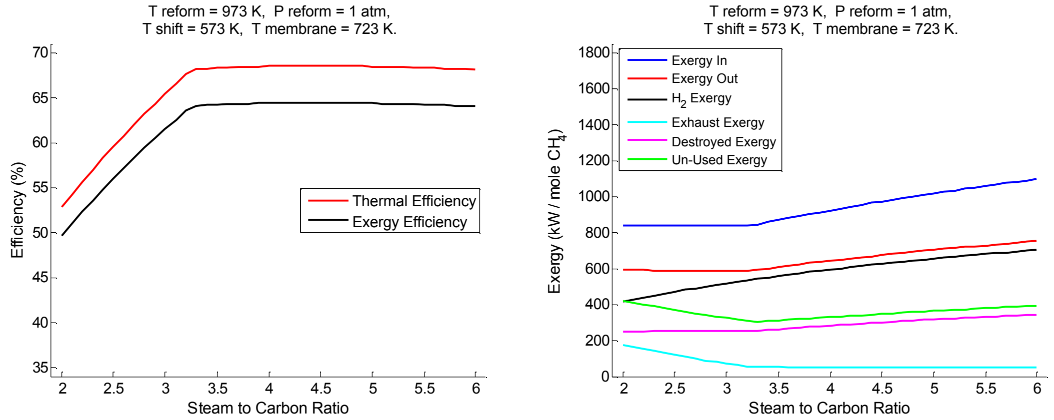

Fig. 8. Influence of reformer steam-to-carbon ratio on system efficiency and global exergy flows.

Conclusion

This investigation uses exergy analysis to evaluate the performance of hydrogen production via steam methane reforming. The key components of the SMR model are a chemical equilibrium reformer model, an expansion valve, a hydrogen separation membrane, and heat transfer components for detailed heat-integration. The global thermal and exergy efficiencies of the base-case system are 67.6% and 63.5%, respectively. The majority of the exergy destruction occurs within the reformer, mostly due to the high irreversibility of combustion and heat-transfer, and in the water-to-steam heat-exchangers. Of the 36.5% of exergy not utilized within the system (un-used exergy), 82% is destroyed within the system and 18% exits in the exhaust stream.

The variation of reformer operating parameters demonstrates the importance of using a chemical equilibrium model and detailed heat-integration. The model identifies optimal conditions for temperature and steam-to-carbon ratio. In general, the optimal efficiency maximizes hydrogen yield without requiring additional methane for combustion. This occurs at approximately 975 K for the nominal conditions. The efficiency increases with excess steam, but the benefit is marginal above a steam-to-carbon ratio of 3.2. The equilibrium model is less useful in determining the optimal pressure, except that above 10atm the efficiency drops significantly.

Exergy analysis provides insight into the performance of the modeled SMR system that would elude purely first-law analysis. Research and development efforts should be focused on reducing exergy destruction within the reformer and heat-exchangers, as well as utilizing the exhaust stream exergy.

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