Simulation of hydrogen production for mobile fuel cell applications via autothermal reforming of methane

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Abstract

This paper presents a simulation of catalytic autothermal reforming (ATR) of methane (CH4) for hydrogen (H_2) production. ATR is essentially an oxidative steam reforming, which combines the exothermic partial oxidation (PO) with the endothermic steam reforming (SR) under thermally neutral conditions. A model is developed using HYSYS 2004.1 to simulate the conversion behavior of the reformer. The model covers all aspects of major chemical kinetics and heat and mass transfer phenomena in the reformer. The ATR and preferential oxidation (PrOx) processes is modeled using conversion reactor, while the water gas shift (WGS) process is modeled using equilibrium reactor within HYSYS environment. The conditions used for high CH_4 conversion and high H_2 yield are at air to fuel ratio of 2.5 and water to fuel ratio of 1.5. Under this condition, CH_4 conversion of 100% and H_2 yield of 44% on wet basis can be achieved and the system efficiency is about 87.7%.

Keywords: Methane; Autothermal reforming; HYSYS simulation; Fuel cell

1.   Introduction

Production of pure hydrogen for use in downstream polymer electrolyte membrane fuel cells (PEMFC) for mobile applications is gaining increasing interest in recent years. The PEMFC is an adequate system for the power sources of the zero-emission vehicles, as its current density is higher compared to other types of fuel cells, the stack structure is rather simple, and there is no leakage or loss of electrolyte during the operation. It has also advantages of rapid start-up and response, long endurance, and flexibility of fuel usage from pure hydrogen to methanol and natural gas [1]. In addition, because of the various ranges of power, PEMFC can be applied to various fields, such as power sources for stationary generators, space shuttles, road vehicles, and military apparatuses. However, there are various disadvantages to be overcome, too. It can not utilize waste heat and cannot be directly connected to the fuel processor, because the operating temperature of the PEMFC is too low. The platinum catalyst is too expensive and the CO tolerance limit for platinum is also too low. For the PEMFC to be commercialized in mobile and stationary power supplies, above disadvantages have to be overcome.

A PEMFC can be powered directly by hydrogen or by hydrogen that is produced on site from a suitable hydrocarbon and alcohol feedstock [2]. Use of pure hydrogen as the energy carrier requires an expensive hydrogen-fuelling network leading to high costs in the fuel delivery system. Moreover, the low volumetric energy density of hydrogen at ambient conditions

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makes hydrogen storage uneconomical. Therefore, on site hydrogen generation from a hydrocarbon feedstock is preferred.

Hydrogen is traditionally produced via multiple reaction steps as a primary product from steam reforming of hydrocarbons such as methane, naphtha oil or methanol [2-4]. For the production of pure hydrogen for mobile applications using PEMFC, the process must be integrated and intensified with higher overall energy efficiencies, at lower temperatures and lower CO concentration.

Three major thermo-chemical reforming techniques are used to produce hydrogen from hydrocarbon fuels i.e., steam reforming (SR), partial oxidation reforming (POR) and autothermal reforming (ATR). The steam reforming of methane has been studied extensively [5–6]. It is probably the most common and traditional method for producing hydrogen on an industrial scale. Though this process can yield high a concentration of hydrogen (up to 70% on a dry basis), it is strongly endothermic and, hence, requires a substantial supply of external heat. Therefore, a reforming system with a heat-exchanger becomes very bulky and heavy, and it has high thermal inertia for frequent start-up and shutdown operation. As a result, it is not so suitable for mobile fuel cells. Partial oxidation [7–9] does not have the disadvantage of being endothermic, but it produces a high carbon monoxide concentration [7] that is undesirable for polymer electrolyte membrane fuel cells.

Autothermal reforming [10–13] combines the thermal effects of the oxidation and SR reactions by feeding the fuel, water and air together into the reactor. The thermal energy generated from oxidation is absorbed by SR and hence the overall temperature is lower. This is favourable for the water-gas shift reaction which consumes carbon monoxide and produces more hydrogen. Hence, the autothermal reactor is more compact and practical for use with mobile fuel cells.

It was desired to construct a simulation of a methane autothermal reforming system to identify potential design issues and obtain a preliminary estimate of the expected system efficiency. Significant operating conditions could than be identified, and their effect on the overall system performance or efficiency could be evaluated. Therefore, the objective of this study is to model and simulate a methane autothermal system for mobile fuel cell applications using Aspen HYSYS 2004.1 and can be used to guide the design of an autothermal reformer. The remainder of this paper is organized as follows, Section 2 describes the process and steady-state modeling of the fuel processor. Simulated ATR operating parameters are explored in Section 3 and lastly, the conclusion and recommendations for future works are drawn in Section 4.

2.   Overall description of a fuel processor

In order to generate a hydrogen-rich stream from a mobile fuel processor, fuel is converted in a reforming unit that involves autothermal reforming (i.e. feed is fuel, steam, and air). In Figure 1, a schematic drawing of the overall process is shown for the case of autothermal reforming. A fuel processor consists of several reactors and heat exchangers. It can be viewed as a small chemical plant with a series of reactors for reforming and gas cleaning. The fuel processor is simplified to a reformer (ATR), three water gas shift reactors [high temperature shift (HTS), medium temperature shift (MTS) and low temperature shift (LTS)] and one preferential oxidation (PrOx) reactor for the modeling purpose.
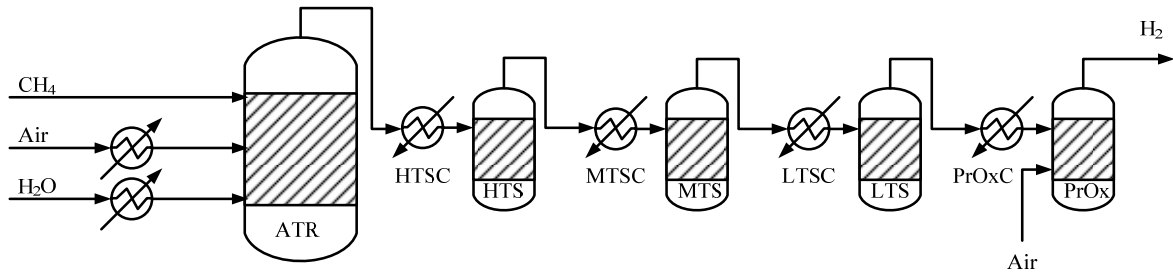
Figure 1   Principle of a scheme of an autothermal reforming process.
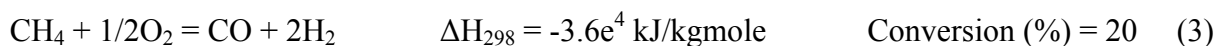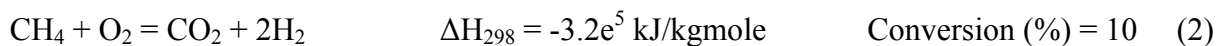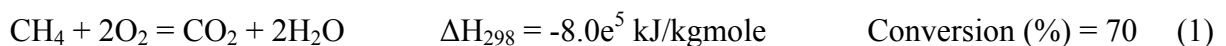
Air and water feeds are heated using external heater to the desired conditions, and together with methane are fed to the ATR with suitable ratios. The effluent of the reformer is passed through the heat exchanger HTSC to cool it down to the desired HTS inlet temperature. The hydrogen-rich syngas contains large CO quantities, a poison for the electro-catalysts of actual PEMFCs anode, able to operate with no more than 10 ppm of CO (50 ppm as pick levels). For this purpose it is necessary to adopt, immediately after the ATR, a CO clean-up system. The hydrogen-rich syngas goes through a series of reactors to perform the water gas shift reaction (HTS, MTS and LTS) in which CO was removed to meet the specification. In MTSC, the effluent of the HTS reactor will be cooled down to the desired MTS inlet temperature, and the same process happened to LTSC and PrOxC. Generally, the CO concentration out of the LTS was still too high, so the preferential oxidation reaction (PrOx) was performed. Air was injected to the PrOx reactor, and then CO was oxidized to CO_2, while, simultaneously, H_2 was oxidized to H_2O. Both reactions in the PrOx are exothermic reactions.
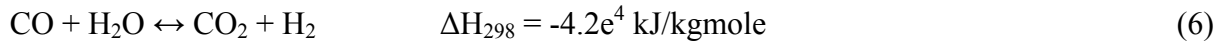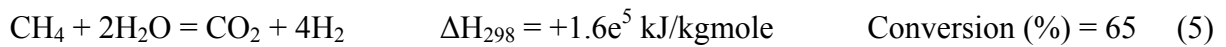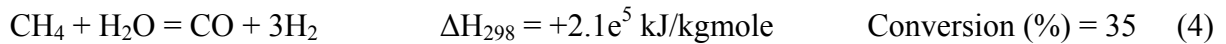
2.1   Chemical reaction scheme

The fuel processor is simplified to a reformer, three water gas shift reactors and a preferential oxidation reactor for the modelling purpose. The model includes detailed reactions associated with total oxidation reforming (TOR), partial oxidation reforming (POR) and steam reforming (SR). The detailed analysis of chemical reactions in these processes to determine the reaction scheme for ATR has been presented elsewhere [10-13].

ATR sometimes referred to as oxy-steam reforming, combines the effects of both the exothermic POR and the endothermic SR by feeding the fuel, oxidant, and water together into the reaction vessel normally containing a nickel catalyst bed. In the catalytic process, the catalyst can be tailored to control the reaction pathways, namely, the relative rates of POR and SR reactions, thereby resulting in a controlled product yield and a lower-temperature process than POR and SR. The reforming temperature and product composition are affected by the Air/CH_4 and H_2O/CH_4 molar ratios in the feed, CH_4 inlet flowrate, and CH_4 inlet temperature.

ATR for methane, the oxidation reactions involve the following:

$$CH_4 + 2O_2 = CO_2 + 2H_2O \qquad \Delta H_{298} = -8.0e^5 \text{ kJ/kgmole} \qquad \text{Conversion (\%)} = 70 \quad (1)$$

$$CH_4 + O_2 = CO_2 + 2H_2 \qquad \Delta H_{298} = -3.2e^5 \text{ kJ/kgmole} \qquad \text{Conversion (\%)} = 10 \quad (2)$$

$$CH_4 + 1/2O_2 = CO + 2H_2 \qquad \Delta H_{298} = -3.6e^4 \text{ kJ/kgmole} \qquad \text{Conversion (\%)} = 20 \quad (3)$$

and methane may react with steam by SR and Water Gas Shift (WGS) reactions

$$CH_4 + H_2O = CO + 3H_2 \qquad \Delta H_{298} = +2.1e^5 \text{ kJ/kgmole} \qquad \text{Conversion (\%) = 35} \quad (4)$$

$$CH_4 + 2H_2O = CO_2 + 4H_2 \qquad \Delta H_{298} = +1.6e^5 \text{ kJ/kgmole} \qquad \text{Conversion (\%) = 65} \quad (5)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H_{298} = -4.2e^4 \text{ kJ/kgmole} \qquad (6)$$

In order to reduce the CO concentration out of the LTS, the preferential oxidation reaction (PrOx) was performed.

$$CO + 1/2O_2 = CO_2 \qquad \Delta H_{298} = -2.8e^5 \text{ kJ/kgmole} \qquad \text{Conversion (\%) = 50} \quad (7)$$

$$H_2 + 1/2O_2 = H_2O \qquad \Delta H_{298} = -2.4e^5 \text{ kJ/kgmole} \qquad \text{Conversion (\%) = 50} \quad (8)$$
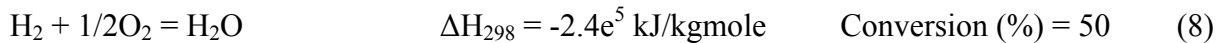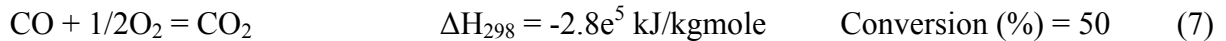
Thus, the model takes into account eight reactions (1)-(8) and seven gas species, i.e., methane (CH_4), oxygen (O_2), carbon dioxide (CO_2), carbon monoxide (CO), water (H_2O), hydrogen (H_2) and nitrogen (N_2).

2.2 Simulation development

Aspen HYSYS 2004.1 simulation program has been utilized for simulation studies. Mass and energy balances have established for all cases. The Peng-Robinson equations of state were used to calculate the stream physical and transport properties. The autothermal reforming of methane developed using HYSYS 2004.1 is shown in Figure 2.
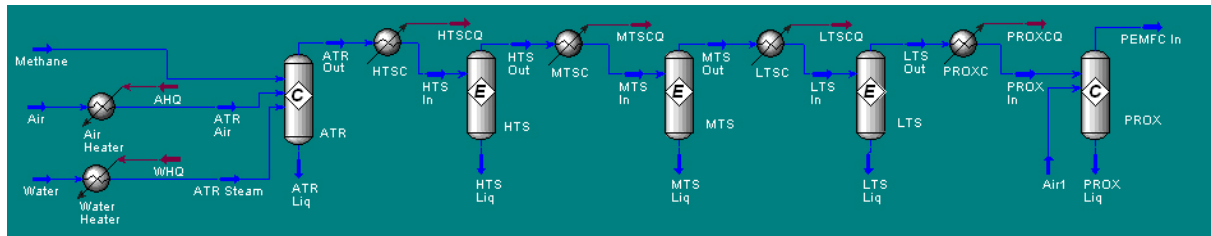
Figure 2 Fuel processor plant developed using Aspen HYSYS 2004.1.

2.2.1 Simulation of the autothermal reformer

To operate the autothermal reformer, the methane and air are first fed to the reformer for combustion to heat up the catalyst of the reformer. When the catalyst temperature reaches about 300°C [10], at which the autothermal reaction can be self-activated (known as lightoff), the predetermined mixture of methane, air, and water is fed to the reformer. The aim is to convert as much as the methane into hydrogen gas at acceptable yields in an efficient manner while decreasing CO formation. Lower water to fuel (W/F) ratios favour soot and coke formation, which is not desired in autothermal reforming process. A considerably wide W/F ratio (0.5-2.0) range has been selected to see its effect on hydrogen yield and CO formation [14]. A similar approach has been adopted for air to fuel (A/F) ratio which is changed between 2.0 and 3.5. In brief, this model takes into account five principal reactions (Eqs. (1)-(5)) and six gas species including methane (CH_4), oxygen (O_2), carbon dioxide (CO_2), water (H_2O), carbon monoxide (CO), and hydrogen (H_2) in chemical kinetics. Nitrogen (N_2) present in inlet air is considered as a diluent, which affects only the gas property. Since the

stoichiometry of all the reactions and the conversion of the base component are known, the reformer was set up as a conversion reactor. By using conversion reactor, HYSYS will calculate the composition of the outlet stream.

2.2.2   Simulation of water gas shift reactor

The equilibrium CO concentration at a temperature of 750°C and W/F ratio of 2.0 is about 12 mol% according to Lattner and Harold [15]. The CO content can be reduced to about 0.5% by reacting it with water at lower temperatures to produce additional hydrogen according to the WGS reaction (Eq. 6). Commercial hydrogen plants generally perform the WGS in two stages: (i) High-temperature shift at 300-450°C using a Fe-chrome oxide catalyst, and (ii) low-temperature shift at 160-270°C using copper–zinc oxide [16]. Heat exchangers are required between shift reactors to provide cooling, and the conversion in an adiabatic reactor is limited because the reaction is exothermic and the temperature increases as the reaction proceeds. In this study, WGS reactors are modeled using equilibrium reactor. By using equilibrium reactor, HYSYS will determine the composition of the outlet stream given the stoichiometry of all reactions occurring and the value of equilibrium constant (or the temperature dependant parameters that govern the equilibrium constant) for each reaction.

2.2.3   Simulation of preferential oxidation reactor

Carbon monoxide is a poison to the precious metal catalyst in the anode of the PEM fuel cell. Preferential oxidation (PrOx) is a reactive approach to destroy CO in the ATR reformate. PrOx of CO is typically used to reduce CO to the ppm levels required for the PEM fuel cell. The catalyst and conditions must be selected to minimize the oxidation of hydrogen. For the overall process model heat and material balance, 50% selectivity to CO oxidation is assumed [17], with the remainder of the oxygen reacting with hydrogen to form water. The PrOx reactor was modeled in HYSYS as a conversion reactor based on two reactions to oxidize CO (Eqs. 7-8).

3.   Results and Discussion

Table 1   Molar fractions of all components in the effluent of all reactors.

	CH_4	O_2	H_2O	CO_2	CO	H_2	N_2
ATR	0.0000	0.0000	0.1393	0.1000	0.0544	0.4012	0.3050
HTS	0.0000	0.0000	0.1225	0.1169	0.0375	0.4181	0.3050
MTS	0.0000	0.0000	0.1033	0.1361	0.0183	0.4373	0.3050
LTS	0.0000	0.0000	0.0854	0.1539	0.0005	0.4551	0.3050
PrOx	0.0000	0.0000	0.0904	0.1525	0.0000	0.4437	0.3134

In the following, the results obtained for an autothermal reforming of methane system which is shown in Figure 2 are presented. With the developed system models which are implemented in the HYSYS 2004.1 process simulator, effluents from all reactors are simulated. Table 1 shows the molar fractions of all components in the effluent of all reactors in the fuel processor system. In this model, the air to fuel ratio is set to 2.5 and the water to

fuel ratio is set to 1.5. In these conditions, 100% methane is converted to produce 40% hydrogen, 10% CO_2 and 5.4% CO. Also, under these conditions, oxygen is 100% consumed. As we know, WGS reaction will convert CO into CO_2 and hydrogen with the existence of steam. Therefore, the percentage of CO is decreasing from 5.4% to 0.05%, while the percentage of CO_2 and hydrogen is increasing from 10% to 15.4% and from 40% to 45.5%, respectively. In the same time, the percentage of steam is decreasing from 13.9% to 8.5%. Air was injected to the PrOx reactor, and then CO was oxidized to CO_2, while, simultaneously, H_2 was oxidized to H_2O.

3.1 Temperature profile of fuel processor system

The temperature profile of the fuel processor is illustrated in Figure 2. With 2.5 of A/F and 1.5 of W/F ratios, the outlet temperature of ATR reactor is about 434°C which is higher than lightoff temperature as mentioned in [10], where the autothermal reaction can be self-activated. The effluent is then cooled to 400°C, 300°C, 100°C and 50°C by passing it through HTSC, MTSC, LTSC and PrOxC, respectively and must be lower than outlet temperature of ATR, HTS, MTS and LTS to prevent reversible reaction happened in Eq. (6). In the HTS, the inlet temperature is 400°C, whereas the outlet temperature is about 420°C. The slightly increased in the outlet temperature is due to the exothermic nature of WGS reaction. The same profile is shown by MTS and LTS. There is also slightly increased in the outlet temperature of the PrOx reactor, but this is due to the exothermic of PrOx reaction (Eqs. 7-8).
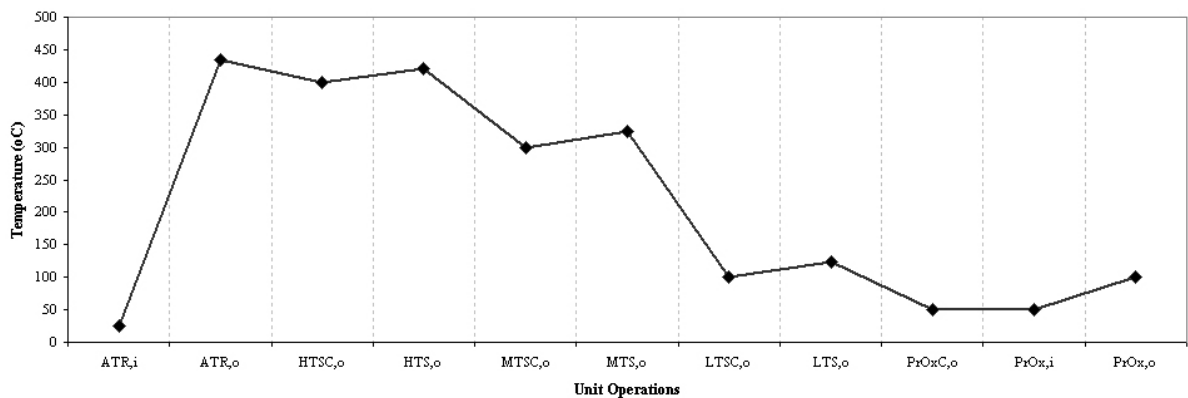
Figure 2   Temperature profile for fuel processor system.

3.2 Molar flowrate profile of fuel processor system

Figure 3 shows the behaviour of all components from ATR to PrOx reactors. The main objective of this study is to maximize the production of hydrogen and in the same time to reduce the concentration of CO as lower as possible. Therefore, it is important to monitor concentrations of hydrogen and CO. As shown Figure 3, the concentration behaviour of hydrogen and CO after the ATR is contrary. This is because, immediately after the ATR, is a CO clean-up system where the hydrogen-rich syngas goes through a series of reactors to perform the water gas shift reaction in which CO is converted into CO_2 and hydrogen with the existence of steam. For that, the concentration of CO is almost zero in the outlet of LTS.

3.3 Fuel processor system efficiency

We defined the efficiency of the fuel processor as

Efficiency % = 100 x (LHV of H_2 produced)/(LHV of fuel used)

The lower heating value (LHV) of the product hydrogen is expressed as

LHV of H_2 produced = H_2 yield x heat of combustion of H_2

In this study, with the A/F ratio of 2.5 and W/F ratio of 1.5, the calculated fuel processor system efficiency is about 87.7%.
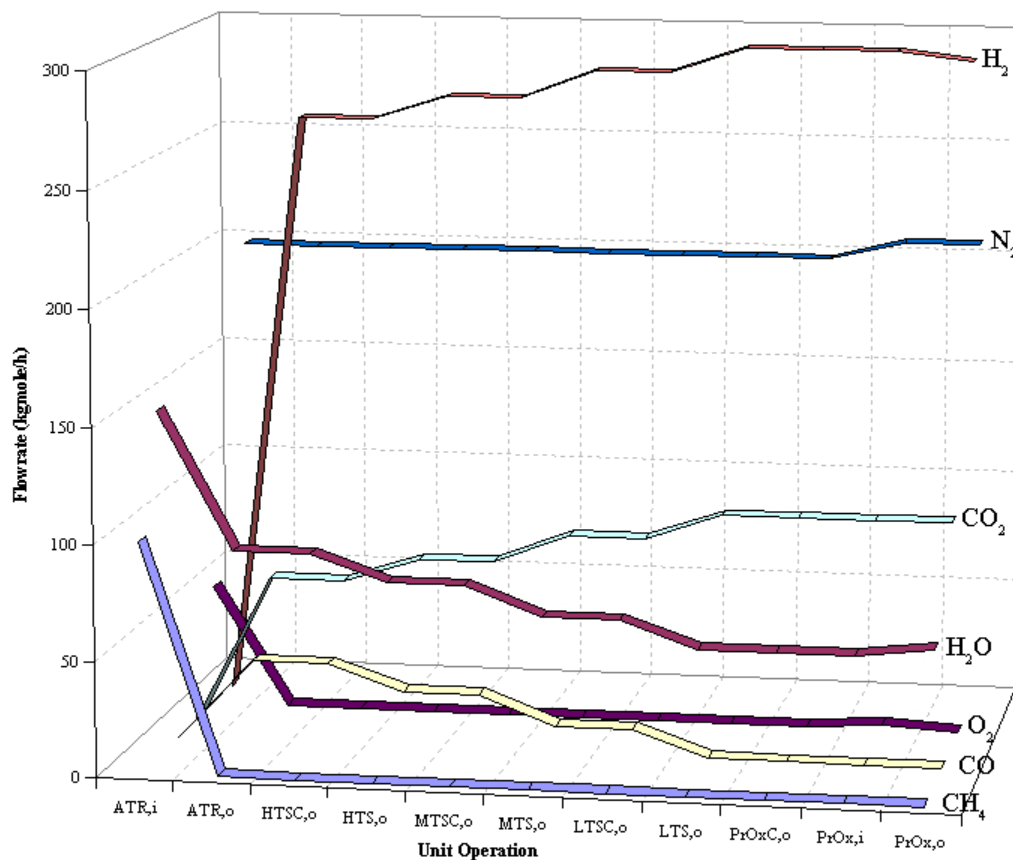
Figure 3 Steady-state flowrate (kmole/h) for fuel processor system.

4. Conclusions and Recommendations

Autothermal reforming of methane in a Ni-based catalytic reformer has been physically investigated. A reformer model has been successfully developed using HYSYS 2004.1 for the simulation study. The ATR and preferential oxidation (PrOx) processes is modeled using conversion reactor, while the water gas shift (WGS) process is modeled using equilibrium reactor within HYSYS environment. The conditions used for high CH_4 conversion and high H_2 yield are at air to fuel ratio of 2.5 and water to fuel ratio of 1.5. Under this condition, CH_4 conversion of 100% and H_2 yield of 44% on wet basis can be achieved and the system efficiency is about 87.7%.

In the future works, it is recommended to study and integrate the following aspects:

1. *Process optimization*
   It is important to study process optimization to determine the optimum operating conditions for the fuel processor system.

2. *Purification of hydrogen*
   It is obvious that the product gas mixture exiting the ATR reaction system contains appreciable amounts of water vapor, carbon dioxide, and nitrogen as well as the desired hydrogen product. In view of compactness requirements and the need for a robust hydrogen generation system to be integrated with the fuel cell system in the future proposed mobile applications, a hydrogen purification step becomes inevitable.

3. *Energy integration basis*
   Achievement of a high efficiency fuel processor system requires very good energy integration. An attempt was made to maximize the recovery of waste heat from various portions of the fuel processor, while minimizing the number of heat exchangers and complexity of the system. Waste process heat is utilized to generate the steam needed in the process. Steam is required for the autothermal reformer.

4. *Water management*
   One of the objectives of the fuel processor system is to maintain self-sufficiency with respect to water needs. In each of the systems, there is a single exhaust stream consisting of CO_2 and water vapor from the complete combustion of the fuel, a small amount of unused oxygen, and all of the nitrogen that originates with air feed streams. Recovery of sufficient water from the exhaust stream to meet the steam generation needs depends on the following four factors:

   - *Exhaust temperature.* The cooler the exhaust, the more water is recovered by condensation. The minimum temperature is limited by ambient temperature and the amount of heat transfer surface area.
   - *Exhaust pressure.* Higher pressures allow more water condensation, but require an increase in the fuel cell operating pressure.
   - *Air feed rate.* The more air that is fed to the system, the more nitrogen must be purged out with the exhaust. More exhaust nitrogen reduces the recovery of water condensed from the exhaust. There are two sources of air feed: (i) air to autothermal reformer, and (ii) air to the PrOx reactor. These air rates are determined by stoichiometric ratios, which are not varied for the sake of the water balance.
   - *Fuel processor efficiency.* As the fuel processor efficiency is reduced, the hydrocarbon feed rate to the processor is increased. This increases the production of water vapor, since all hydrocarbon is eventually combusted completely. With all else held constant, the additional water production will be recovered in the exhaust condenser.

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