Development of a high-efficiency hydrogen generator for fuel cells for distributed power generation

K. Duraiswamy a,*, Anand Chellappa a, Gregory Smith b, Yi Liu b, Mingheng Li b,*

a Intelligent Energy, 2955 Redondo Ave., Long Beach, CA 90806, USA
b Department of Chemical and Materials Engineering, California State Polytechnic University, Pomona, CA 91768, USA

1. Introduction

As a result of more stringent environmental regulations, hydrogen has attracted much interest as a potential clean energy carrier. Among various methods, steam reforming of hydrocarbons accounts for 95% of the hydrogen produced in the United States [1]. It is expected that steam reforming will play an important role in America’s transition to a hydrogen economy.

Conventional hydrogen generation by steam methane reforming (SMR), employing a high temperature reformer (~800 °C), a water gas shift (WGS) reactor (~300 °C) and multiple pressure swing adsorbers, operates at an efficiency around 65–67% based on lower heating value (LHV) of feed and product [2,3]. This conventional SMR system is not very easy to scale down cost-effectively for supplying 35–150 slpm H2 (to produce 3–13 kW electricity). In recent years, adsorption enhanced reforming (AER), a novel low-temperature reforming technique, has intrigued significant interest for potential low-cost hydrogen production [4–12]. Thermodynamic analysis conducted by the authors indicates that AER holds the promise of higher hydrogen yield and purity as well as suppressed coke formation [13,14]. Ongoing industrial development effort is being made by Chevron and Intelligent Energy to commercialize this novel technology [15,16]. Hybrid Adsorbent-Membrane Reactors (HAMRs) are also being explored in academia to enhance the process efficiency of hydrogen generation [17].

A collaborative effort between Intelligent Energy and Cal Poly Pomona has recently developed a bench-scale AER-based hydrogen generator for use in conjunction with fuel cells in the small sizes. The hydrogen generator has four beds operated alternately at a lower temperature (~500 °C) than the SMR. It employs potassium-promoted hydrotalcites...
(KHTC) as the carbon dioxide capturing material [18–20] and ceria supported rhodium as the reforming catalyst. The removal of CO\textsubscript{2} from the product favors the reforming and the WGS reactions so that H\textsubscript{2} is produced in one step with little CO and CO\textsubscript{2} impurities. In addition to steam which is typically used in bed regeneration, this work shows that the CO\textsubscript{2} purge can also be done using the off gas from the cathode of the fuel cell, which can potentially reduce steam usage. Moreover, it is developed in this work a novel pulsing feed approach to enhance the yield of hydrogen in the production stream. Continuous production of near fuel-cell grade hydrogen has been successfully demonstrated using various feedstocks. In AER of methane, the hydrogen/methane ratio in the product stream is as high as 125 while the CO and CO\textsubscript{2} are on the ppm level. The overall conversion of methane to hydrogen is around 92%.

2. Experimental setup

The experimental AER test assembly was constructed with four reaction tubes with a nominal ID of 1.8 inches and a length of 24 inches (see Fig. 1). An external electrical furnace heats the tubes to maintain the proper operating temperatures for the reforming reaction. Solenoid valves under the control of a programmable logic control (PLC) switch the tubes in sequence from a feed of hydrocarbon and steam for the reforming reaction to a purge flow of simulated cathode off gas (COG) or pure steam. At any specific time, one reaction tube would produce hydrogen that flows from the top to the bottom of the bed. The remaining three tubes would have a purge flow in the reverse direction to remove the adsorbed carbon dioxide from the adsorbent. Figs. 2 and 3 show the basic process flowsheet for the experimental unit with the corresponding state diagram for the flow through the tubes. The overall cycle is divided into 24 steps to allow flexibility in controlling the flows through the tubes. For a particular tube the reforming cycle (state P on the diagram) uses six steps (one quarter of the total time) for hydrogen production. Regeneration follows the production cycle in order to remove the adsorbed carbon dioxide. Regeneration takes place in a number of steps. First, a pure steam flows for 10 s (state E on the diagram) in order to sweep excess hydrogen from the tube. A simulated COG then flows (state R on the diagram) for the majority of the regeneration cycle. The oxygen in the simulated COG oxidizes any coke build up. In addition, it shifts the oxidation state of the ceria in the catalyst [21]. A pure steam flow follows the COG (state S on the diagram) to remove any excess oxygen before returning the tube to production. Finally, a backfill flow from the currently producing reactor (state B on the diagram) takes place to minimize the dilution of the hydrogen product when the given reactor resumes hydrogen production.

Fig. 1 – Four-tube AER reactors.

Fig. 2 – A piping and instrumentation diagram of the AER process.
3. Results and discussion

The hydrocarbon feedstocks used for the experimental studies included ethanol, methane and liquefied petroleum gas (LPG). Parametric analysis was also made to study the effect of reaction temperature, feed rate and steam to carbon ratio (S/C) on the process performance. A list of the main process parameters are listed in Table 1.

The following terms are defined to evaluate the performance of different experiments. CH conversion is given as the fraction of carbon element in the feedstock that is converted to CO or CO2. H2 yield is the actual amount of H2 produced in the reactor divided by its theoretical maximum. H2 escaping ratio is the fraction of hydrogen that exits the reactor from the regeneration exhaust.

The compositions of the production gas and regeneration exhaust (both on dry basis) using ethanol (with nitrogen as the carrier gas) and water in one run are shown in Fig. 4. The average gas compositions (on dry basis) are provided in Table 2. In this case the CO and CO2 concentrations in the gas are about 1200 ppm and 600 ppm respectively. With CO2 adsorption, not only CO2 but also CO in the gas phase are reduced because the forward WGS reaction is favored [13]. However, a methanator may still be necessary to reduce the concentration of CO to the fuel-cell level. The hydrogen/methane ratio in the product stream is 22. If calculated on dry and nitrogen free basis, the hydrogen purity is about 95%. About 90% of the ethanol feed is converted to CO and CO2 while the rest is CH4. The overall hydrogen yield (including both the production stream and the regeneration exhaust) is about 51%.

The hydrogen/methane ratio in the product stream at various reforming temperatures and ethanol flow rates are shown in Fig. 5. This ratio is an indicator of the hydrogen purity and yield in the production stream. It is clear that AER has an advantage over conventional reforming reactors in that reasonable conversions of the feedstock can be obtained in the production stream even when the temperature goes below 500 °C. At increased temperatures, the CO2 adsorption is adversely affected. However, the reaction rate is higher and the reforming reaction is thermodynamically favored [13]. In most cases, the yield of H2 improves when temperature increases because the reforming reaction is enhanced. At a nominal ethanol flow rate of 0.024 mol/min, increasing temperature from 530 °C to 545 °C resulted in a decrease in the hydrogen/methane in the product. A tentative explanation is that CO2 adsorption becomes the limiting factor at this high temperature. Further investigations are required to validate this assumption. Fig. 5 also indicates that the ethanol feed rate has an effect on the conversion rate if S/C is kept at 3. Increasing the ethanol feed rate reduces the residence time of the reactants in the reactor. This implies that the process is kinetically limited and a larger reactor could improve the hydrogen yield under similar flow conditions.

The compositions of the production gas and regeneration exhaust (on dry basis) based on AER of methane are shown in Fig. 6. Even though no carrier gas is used in the feedstock, the
gas compositions in the production stream do not add up to 100%. This is mainly because part of the nitrogen trapped in the bed during the regeneration step is taken out by the production gas. The average gas compositions and conversions to hydrogen are shown in Table 3. If calculated on dry and nitrogen free basis, the hydrogen purity in the production stream is 98%. The overall conversion of methane to hydrogen is 56% accounting for both the production and exhaust streams. Recovery of hydrogen in the regeneration exhaust is important as it accounts for 34% of the total hydrogen generated in the reactor.

Our dynamic simulation of the AER process (to be published as a separate work) indicates that at the end of the reforming cycle, there is a fair amount of methane and hydrogen in the reactor. Along the flow direction, the methane concentration in the gas phase decreases while the hydrogen increases. If the flow is immediately reversed to state E from P (as shown in Fig. 3), most of the methane and hydrogen will go to the exhaust instead of the product. Moreover, because CO₂ is released from the adsorbent, the WGS reaction could shift backward and part of the hydrogen might be converted to CO in the exhaust stream. Recovering methane and hydrogen remaining in the bed in the product stream will improve the overall conversion. Based on this it is proposed a novel adsorption enhanced pulsing feed reforming (AEPFR) concept.

As shown in Fig. 7, the methane feed is turned off after the production cycle. However, the steam is still on and will continue to reform the methane remaining in the bed to generate hydrogen. Because the S/C ratio is boosted due to paused methane feeding, the reforming reaction is favored both thermodynamically and kinetically. This cycle is referred to as S₅ (or forward steam cycle) in Fig. 7. After the forward steam cycle when more methane is converted and more hydrogen is recovered in the production stream, the flow is then reversed with CO₂ purge.

The compositions of the production gas and regeneration exhaust (on dry basis) based on AEPFR of methane are shown in Fig. 8. The average gas compositions and methane conversion to hydrogen are shown in Table 4. It is seen that both the purity and conversion are improved when pulsing methane feed is used. The overall yield of hydrogen is about 76%, much higher than the previous case (with no pulsing methane feed) even when a lower reforming temperature is used. The CH conversion is also higher which implies more methane is converted. It is apparent that increasing the

| Table 2 – Average gas compositions (on dry basis) and conversions of ethanol to hydrogen in the AER. Ethanol flow = 0.0174 mol/min, carrier N₂ = 2.5 slpm, T = 530 °C, S/C = 3. |
|----------------------------------|----------------|----------------|
| 9/15/2009                        | Production     | Regeneration   |
| Flow rate (slpm)                 | 2.6            | 9.8            |
| H₂ (%)                           | 32.63          | 3.14           |
| CH₄ (%)                          | 1.46           | 0.38           |
| CO (%)                           | 0.12           | 0.46           |
| CO₂ (%)                          | 0.06           | 6.42           |
| CH conversion (%)                | 90             |                |
| H₂ escaping (%)                  | 27             |                |
| H₂ yield (%)                     | 51             |                |

As shown in Fig. 4, the compositions of (a) production gas and (b) exhaust gas based on AER of ethanol. Ethanol flow = 0.0174 mol/min, carrier N₂ = 2.5 slpm, T = 530 °C, and S/C = 3.
pulsing feed off period will further improve the yield of hydrogen. However, this requires more steam (or more energy for water vaporization) per unit amount of methane. There is room for process optimization. It is planned to systematically investigate the pulsing feed frequency on the effect of hydrogen yield and process efficiency in future development.

If pure steam purge is used in conjunction with pulsing methane reforming, the overall conversion can be further improved. This is because when COG is used, oxygen in the COG would oxidize CO, CH₄ and H₂, resulting in a lower yield of hydrogen. The compositions of the production gas and regeneration exhaust (on dry basis) based on pulsing methane reforming and pure steam regeneration are shown in Fig. 9. The average gas compositions are shown in Table 5. In this case the CO and CO₂ concentrations in the product stream are only 10 ppm and 70 ppm, respectively. The H₂/CH₄ in the product is as high as 125. The overall CH conversion and hydrogen yield are both around 92%. Due to effective CO₂ adsorption, the ratio of CO₂ in the regeneration exhaust to the one in the product stream is on the order of 10³. The hydrogen yield solely based on the production stream is about 66% (equivalent to 80% of the LHV of the feed methane) if all the methane and hydrogen in the regeneration exhaust are burned to supply heat for reforming and steam generation.

In the operation of AER and AEPFR processes, the evolution of reactor temperature is dynamic due to endothermic reforming and CO₂ desorption and exothermic CO₂ adsorption and oxidation of hydrogen and methane by COG. Such temperature dynamics might pose a challenge on the performance and safety of the reactor. For this purpose, the temperature profiles at top, middle and bottom of the reactor are monitored real-time. As shown in Fig. 10, the temperature distribution along the reactor is not uniform, which is due to non-uniform external heat supply. During cyclic operation, it is consistently observed that the temperature of the reactor at the top (where reforming and CO₂ adsorption are prominent) shifts about 7°C. When COG is used for regeneration, the reactor temperature at the bottom (where oxidation of hydrogen and methane occurs) increases about 5°C. However, when steam is used, the temperature at the same location does not change much. The temperature does not vary too much probably because of the short cycle time as well as the heat transfer between different tubes. Because the temperature change is not significant, it can be concluded that the performance and safety of the reactor are not adversely affected.

The adsorbent exhibited excellent stability in the reforming tests. The same Pural Mg70/20 wt% K₂CO₃ KHTC adsorbent pellets in the beds have been used for over 10,000 cycles at
average bed temperatures between 450 and 550 °C for over 330 h. The adsorbent pellets have been unpacked, inspected and repacked in the reactor tubes three times. No fracturing or particle break up and no discoloration were observed. During each cycle the adsorbent is regenerated with oxygen and steam containing simulated cathode off gas. Hence, any carbon accumulation in the bed is avoided. We have avoided the failure of downstream equipment such as solenoid valves by the use of proper particle filters. The use of particulate filters is a standard operating procedure in most process plants that have packed beds.

Steam generation is one of the key issues that determine the economics of the AER process. For 1 mol methane feed, about 4–5 mol steam are required for reforming as well as regeneration. When COG from the fuel cell is used for regeneration, the steam contained in the COG displaces the CO₂ on hydrotalcites and later is released during reforming and adsorption of CO₂, thus the low pressure, low quality steam contained in the COG helps subsidize the overall steam demand in the AER. A heat integration has to be done in order
to recover waste heat as much as possible. One possible design is to burn fuel in the regeneration exhaust (which contains hydrogen, methane and CO2) and the anode off gas from the fuel cell (which contains methane and hydrogen) to supply heat for the reformer as well as steam generation. The combustion exhaust can be further used to preheat methane and water. With this type of heat recovery, the exhaust from the process to the environment will be cold enough. A detailed heat exchanger network design is undergoing.

4. Concluding remarks

The experimental results obtained in the AER bench-scale test unit confirm that near fuel-cell grade, high purity hydrogen can be produced by pulsing feeding, medium temperature reforming and CO2 adsorption in one step at a overall hydrogen yield of 92% for distributed power generation. The ratio of CO2 in the regeneration exhaust to the one in the product stream is on the order of 103. Scale-up and heat integration are being pursued to make it a viable, low-cost small-scale hydrogen generation system.

Acknowledgement

This work is supported by the Department of Energy (#DE-FG36-07GO17013). The authors would also like to thank the anonymous reviewers for valuable comments and suggestions.

REFERENCES

[18] Reijers HTJ, Valster-Schiermeier SEA, Cobden PD, van den Brink RW. Hydrotalcite as CO2 sorbent for sorption-enhanced