

VII.3 Cost Implications of Hydrogen Quality Requirements

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Objectives

The objective of this project is to correlate the impurity concentrations in hydrogen dispensed at refueling centers to the cost of that hydrogen. The relationship is a function of the:

- Hydrogen production pathways, e.g., natural gas steam reforming followed by pressure swing adsorption (PSA).
- Process design and operating parameters, such as the choice of sorbents in the PSA, the system pressure, and temperatures at various locations, etc.

Technical Barriers

This project addresses the following technical barriers from the Systems Analysis section (4.5) of the Hydrogen, Fuel Cells, and Infrastructure Technologies (HFCIT) Program Multi-Year Research, Development and Demonstration Plan:

- (B) Stove-piped/Siloed Analytical Capability
 - Segmented Resources
- (A) Suite of Models and Tools
 - Macro-System Models

Contribution to Achievement of DOE Systems Analysis Milestones

This project will contribute to achieving the following DOE Systems Analysis milestones from the Systems Analysis section of the Hydrogen, Fuel Cells, and Infrastructure Technologies Program Multi-Year Research, Development, and Demonstration Plan:

- **Milestone 5:** Complete analysis and studies of resource/feedstock, production/delivery and existing infrastructure for various hydrogen scenarios. (4Q, 2009) Different hydrogen production and dispensing scenarios potentially entail different contaminants at different concentrations. In the current phase of our analyses, we have quantified the key fuel contaminants in three hydrogen production scenarios.
- **Milestone 6:** Complete analysis of the impact of hydrogen quality on the hydrogen production cost and the fuel cell performance. (4Q, 2010) We are developing models for the effects of contaminants on the performance and costs of hydrogen production and purification, and for the degradation in the performance and durability of fuel cell systems. These models will permit trade-off and sensitivity analyses of these effects on a life-cycle cost basis.
- **Milestone 9:** Complete analysis of the impact of hydrogen quality on the hydrogen production cost and the fuel cell performance for the long range technologies and technology readiness. (2Q, 2015) Analyses similar to the ones described here will be extended to longer term technologies for hydrogen production, purification, use in the fuel cells, and hydrogen analysis and quality verification as those technologies reach a suitable stage of development for such analyses.

Accomplishments

- A detailed component model (using Comsol Multiphysics) of the PSA process has been set up as part of a flexible MATLAB-based systems model.
- The hydrogen production pathway for natural gas steam reforming (NG-SR) followed by PSA has been studied over a broad range of key design and operating parameters.
- The system model results have been used to calculate the cost of hydrogen using H₂A for the NG-SR-PSA pathway. These results were used to plot the cost of hydrogen vs. impurity concentrations.
- A process model has been set up for the autothermal reforming of natural gas followed by PSA. Some preliminary calculations have been done for a coal gasifier followed by a PSA.



Introduction

Developing and implementing fuel quality specifications for hydrogen are a prerequisite to the widespread deployment of hydrogen-fueled fuel cell vehicles. Several organizations are addressing this fuel quality issue, including the International Organization for Standardization (ISO), the Society of Automotive Engineers (SAE), the California Fuel Cell Partnership, and the New Energy and Industrial Technology Development Organization/Japan Automobile Research Institute, and DOE's research projects at the national laboratories (Argonne National Laboratory, Los Alamos National Laboratory, Savannah River National Laboratory) and universities (Hawaii Natural Energy Institute, University of South Carolina, University of Connecticut, and Clemson University). These activities have focused on the deleterious effects of different potential contaminant on the automotive fuel cell or on-board hydrogen storage systems.

While it is possible to provide extremely pure hydrogen to the fuel cell vehicle, the production, purification, delivery and dispensing costs determine the type and concentration of the impurity or contaminant initially present when the hydrogen is generated by a given production pathway. It is the objective of this task to study the effect of the production pathway and the choice of process (design and operating) parameters on the impurity concentrations in and, ultimately, the cost of, the dispensed hydrogen.

The distributed production of hydrogen (for a system capable of producing 1,500 kg H₂ per day) based on the SR of NG and followed by purification using the PSA process has been identified as the most likely near-term solution for refueling fuel cell vehicles. Therefore, this pathway was the first to be modeled and studied, and some of the results are included in this report.

Approach

The cost of hydrogen is dependent on many factors at the various stages in the production pathway. It begins with (1) the feedstock that is used for its production, e.g., NG, water, coal, etc., followed by (2) the conversion of the feedstock, e.g., SR, electrolysis, gasification, etc., followed by (3) the purification of the hydrogen produced in the conversion step, e.g., PSA, hydrogen transport membranes, etc. Finally, (4) the cost of compression and delivery of the product hydrogen is determined by the pressures at which the hydrogen is available in step (3) and the storage pressure on-board the vehicle.

This project is assessing the cost of the product hydrogen by setting up a pathway model using MATLAB, which integrates the results of more detailed component models (e.g., for PSA) set up using Comsol Multiphysics. These models are then exercised to study the effect

of key process design and operating parameters on the performance measures such as process efficiency, concentrations of non-hydrogen species at various points in the process, hydrogen recovery in the PSA unit, etc. The process efficiency (for a particular set of conditions) calculated from our model can then be entered into the H2A spreadsheet, which contains the relevant assumptions for the financial calculations, to arrive at the cost (\$/kg) of hydrogen.

A final cost item is due to the composition analysis needed to ensure that the product hydrogen meets the regulatory quality standards (yet to be established). In consideration of the highly specialized analysis that is needed for the trace levels of some contaminants (e.g., ammonia and sulfur), some preliminary cost estimates have been published [1].

Results

The process models have been set up for three production pathways during Fiscal Year 2009. The NG-SR-PSA process was the first studied and is shown in Figure 1, where the process conditions are specified for the reference or "base" case. The NG, assumed to be available at the plant gate at 3 atm absolute pressure, is compressed to the process pressure (the reformer, shift reactor, and the PSA are assumed to operate at the same pressure) before it reacts with steam in the reformer. For the base case, the reformat exits the reformer and the shift reactors at 750°C and 435°C, respectively. The reformat enters the PSA at 25°C containing 76.5% hydrogen, 2.8% CO, 0.4% N₂, 2.8% CH₄, and 17.5% CO₂. The product hydrogen from the PSA is then compressed to the final delivery pressure of 430 atm. The tail gas from the PSA, which contains the impurities (CO₂, CO, CH₄, N₂) as well as significant amounts of H₂, is burned to generate the heat for the reforming process.

The model is set up to track up to nine species through the pathway, including inerts (N₂, Ar, He), H₂S, and NH₃. Helium passes through the process unreacted, although its concentration in the final product hydrogen is diluted considerably, as shown in Figure 2 for the process conditions shown in the figure. The H₂S and NH₃ are removed very effectively by the sorbents in the PSA – their concentrations in the final product are calculated to be considerably lower than 10⁻¹²%. Under the base case set of conditions, the two species with the highest concentrations in the product hydrogen are N₂ and CO. Figure 3 (top) plots their concentrations in parts per million (ppm) as a function of the hydrogen recovery, which is defined as the molar flow of purified hydrogen in the product as a percentage of the molar flow of hydrogen entering the PSA unit. At a recovery of 74% the concentrations of CO and N₂ are 0.2 and 10 ppm, respectively, and meet the guideline values suggested by ISO and SAE. At higher recoveries, the CO concentration exceeds the recommended 0.2 ppm,

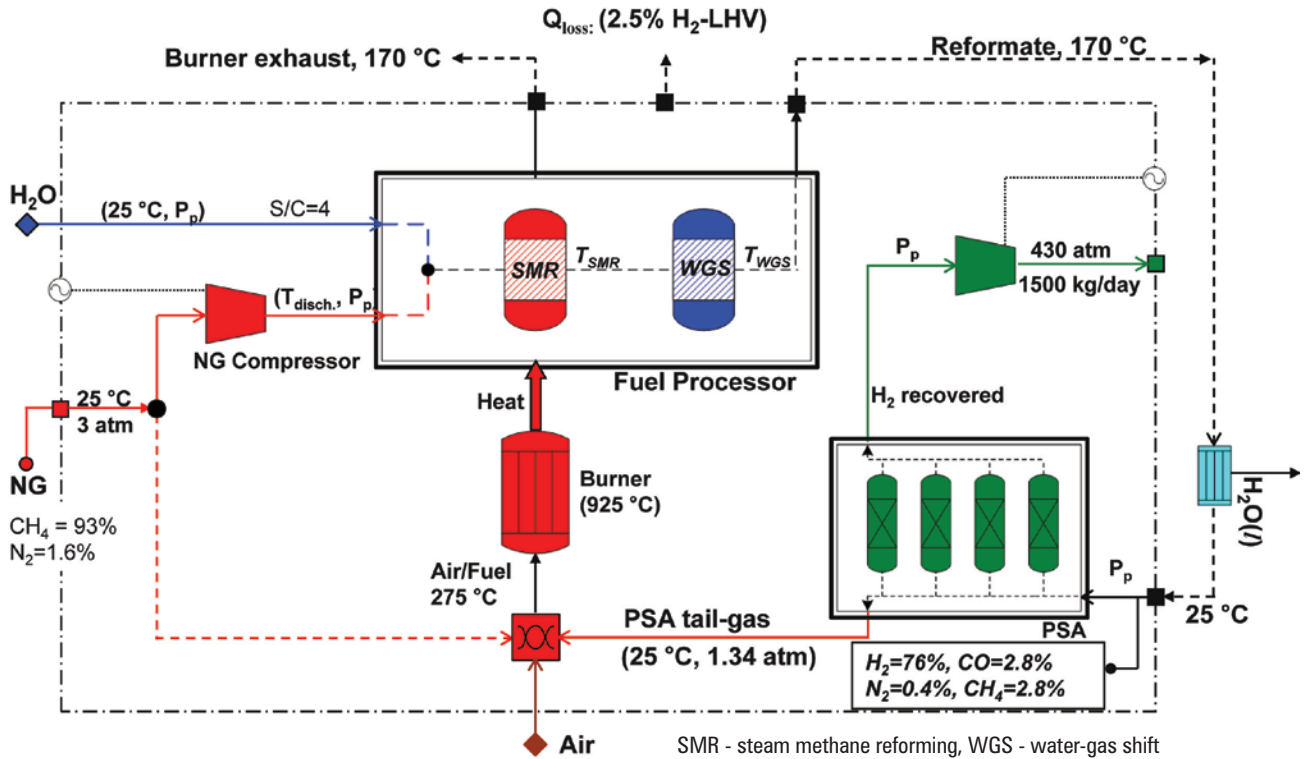


FIGURE 1. Schematic of the SMR-PSA System (Base Case)

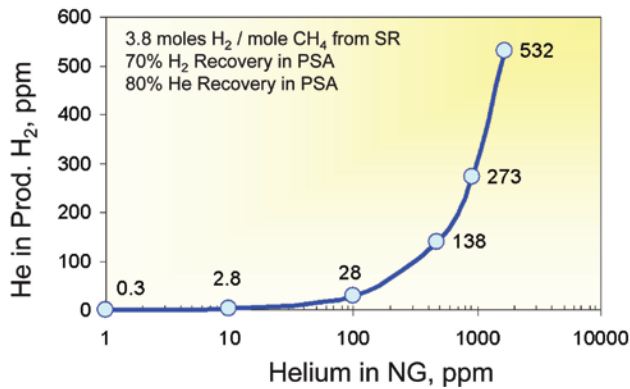


FIGURE 2. The concentration of helium in natural gas gets diluted in the product hydrogen.

even though all the other contaminant species are at concentrations below the ISO/SAE suggested limits. Thus CO can be referred to as the (recovery-) limiting species. The plot at the bottom shows the efficiency of the process (at a steam-to-carbon ratio of 4) at the base case conditions to be approximately 66%, where the efficiency [1] is defined as the lower heating value (LHV) of the purified product hydrogen leaving the PSA unit as a percentage of the LHV of the natural gas entering the system. The electrical energy requirement (e.g., compression) are calculated and then entered into the H2A spreadsheet.

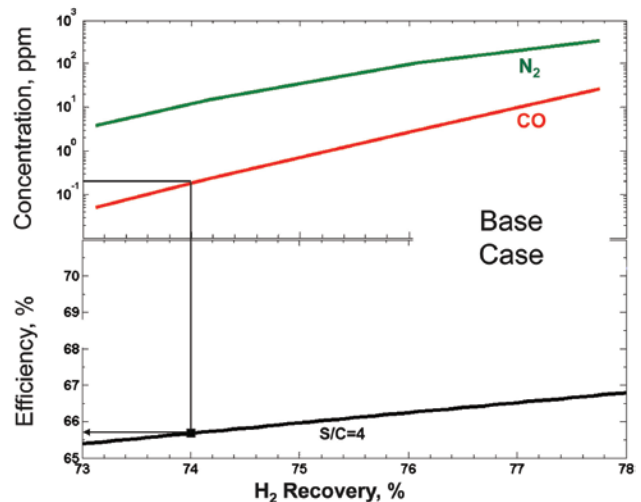


FIGURE 3. A CO specification of 0.2 ppm limits the H₂ recovery to 74% and the efficiency to ~66%.

The effect of several process parameters on performance (efficiency, impurity concentrations, etc.) have been studied for the NG-SR-PSA system described in Figure 1. These include the effect of the steam-to-carbon molar ratio, the effect of pressure, the effect of the PSA inlet temperature, and the effect of the proportion of carbon in the PSA beds. For example, a bed with 80% carbon (and 20% Zeolite) is much more

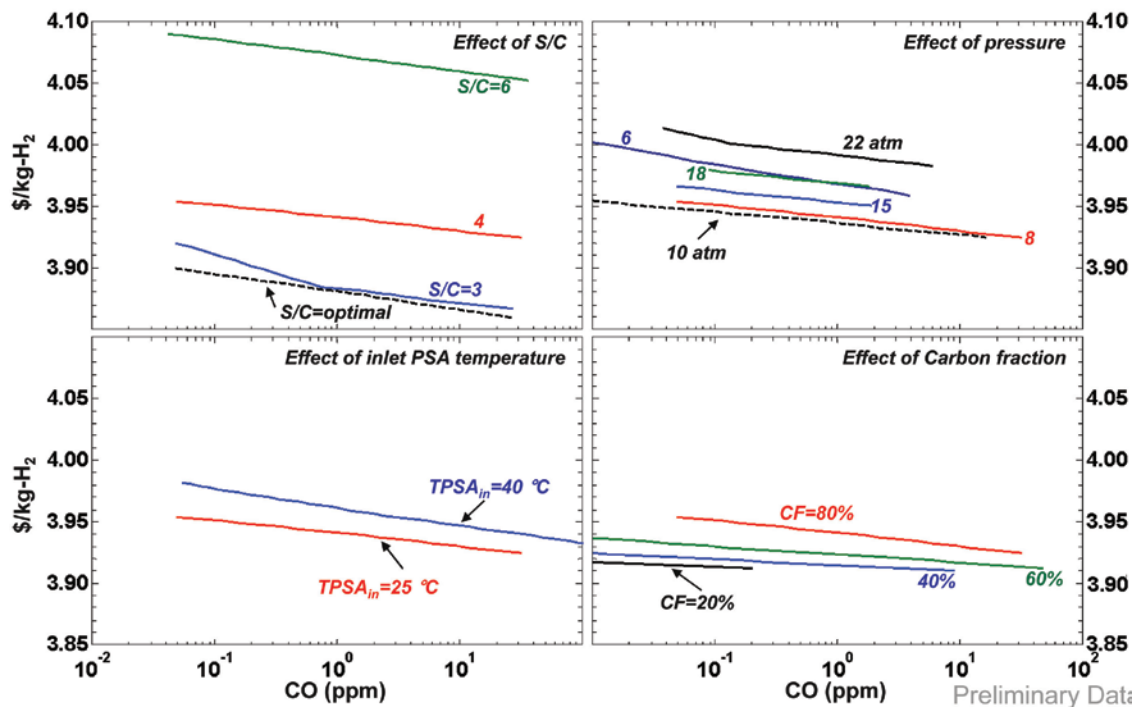


FIGURE 4. Hydrogen cost is a weak function of CO concentration (based on NG price of \$7.6/1,000 ft³ or \$7.8/MMBTU)

effective in removing methane, while a bed with 20% carbon (80% Zeolite) is more effective in removing CO. Our models calculated the process efficiency for each set of process conditions. Entering them into DOE's H2A spreadsheet generated the corresponding cost of hydrogen. These cost results are plotted in Figure 4, which shows the cost of hydrogen (\$/kg) vs. the concentration of CO in the hydrogen. Each subplot shows the effect of a different parameter. The curves in the figure show that there is a significant effect of these parameters on the cost of hydrogen. However, the cost is only slightly affected by the change in the CO concentration in the hydrogen. Reducing the CO from 10 to 0.1 ppm shows a difference of 3 cents in the cost per kg of hydrogen. The parametric sensitivity studies were conducted by changing only one variable at a time and did not attempt to optimize the parameters with respect to any objective function. The results presented in the figures are more significant with respect to the trends (slopes), rather than the absolute values (\$/kg).

Two other models have also been set up for analysis. These are for the (1) autothermal reforming of NG followed by hydrogen purification using PSA, and (2) coal gasification followed by PSA. Preliminary results indicate that the hydrogen recoveries in the PSA will likely be limited by the inerts (N₂, Ar) that are introduced with the oxygen (from air) for these two hydrogen production pathways.

Conclusions and Future Directions

A process model was set up and used to correlate the cost of hydrogen with the impurity concentrations in the product hydrogen. The pathway consisting of natural gas steam reforming followed by the PSA process was studied, to generate a series of plots of the cost of hydrogen vs. the concentrations of impurities (N₂, CO, etc.) as functions of the key process parameters. The results showed that,

- For the NG-SR-PSA pathway, the cost of hydrogen is only slightly affected by the impurity concentration for given process conditions. Changing the key process parameters, however, can lead to sharp changes in the cost of hydrogen. There are significant opportunities for optimization of the plant.
- For most conditions in the NG-SR-PSA pathway, the CO specification limits the hydrogen recovery. Nitrogen may become the limiting species in certain cases, such as when the beds are loaded with high zeolite content, or when the natural gas feedstock contains high concentrations of nitrogen.
- Helium present in the natural gas will pass through the NG-SR-PSA process and will emerge in the product hydrogen, but at about one-fourth the concentration in the feed natural gas. Helium has a suggested 300 ppm upper limit in the product H₂; thus, any NG that contains 1,200 ppm or more of

helium would be unsuitable for producing H₂ for fuel cell vehicles.

- For the autothermal reforming (ATR) of NG followed by PSA purification, the Ar or N₂ specification may limit the maximum H₂ recovery achievable in the PSA.
- Similarly, for coal gas reforming followed by PSA, the H₂ recovery may be limited by the Ar or the N₂ specification.

For the future, we will:

- Evaluate the impurity concentrations likely from other hydrogen production pathways such as ATR, coal gasification, electrolysis.
- Validate the NG-SR model results with field data.
- Incorporate more complex PSA systems if needed.
- Incorporate our model results into H2A.

FY 2009 Publications/Presentations

1. D. Papadimas, S. Ahmed, R. Kumar, X. Wang, R.K. Ahluwalia, "Update on Hydrogen Quality: Modeling the Reformer/PSA System and Effect of H₂S on Fuel Cell Performance," presented to the Fuel Cell TT and Codes & Standards TT, Southfield, MI, August 2008.
2. Joseck, F., Papadimas, D., Ahmed, S., R. Kumar, "Fuel Quality Impacts on Hydrogen Production, Purification and Use in Fuel Cell Automobiles," 2008 Fuel Cell Seminar, Phoenix, AZ, October, 2008.
3. D. Papadimas, S. Ahmed, R. Kumar, "Modeling a Hydrogen Production Pathway – Natural Gas Steam Reforming followed by Pressure Swing Adsorption," presented at the Modeling Workshop, Golden, CO, November, 2008.
4. D. Papadimas, S. Ahmed, R. Kumar, F. Joseck, "Hydrogen Quality for Fuel Cell Vehicles – A Modeling Study of the Sensitivity of Impurity Content in Hydrogen to the Process Variables in the SMR-PSA Pathway," accepted for publication, International Journal of Hydrogen Energy, 2009.
5. R. Kumar, D. Papadimas, S. Ahmed, "Hydrogen Quality for Fuel Cell Vehicles," presented to the FreedomCar Joint Operations Group, December, 2008.
6. S. Ahmed, D. Papadimas, R. Kumar, "Modeling a Hydrogen Production Pathway – Natural Gas Reforming followed by Pressure Swing Adsorption," presented at the ISO-WG12 Meeting, Grenoble, France, February, 2009.

References

1. D. Papadimas, S. Ahmed, R. Kumar, F. Joseck, "Hydrogen Quality for Fuel Cell Vehicles – A Modeling Study of the Sensitivity of Impurity Content in Hydrogen to the Process Variables in the SMR-PSA Pathway," accepted for publication, International Journal of Hydrogen Energy, 2009.