X.11 Hydrogen Quality Issues for Fuel Cell Vehicles

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Objectives

- Assess how fuel quality influences the life-cycle costs and performance of the overall "hydrogen system" – production, purification, use in fuel cell vehicles, and analysis and quality verification.
- Develop models to evaluate the quantitative effects of fuel quality on the costs of the hydrogen system components.
- Identify information gaps and the research and development (R&D) needed to fill those gaps.
- Develop a roadmap that defines the significant cost elements, identifies challenges to reducing those costs, and makes recommendations on how to address those challenges.

Technical Barriers

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

(B) Stove-piped/Siloed Analytical Capability
- Segmented resources

(D) Suite of Models and Tools
- Macro-system models

Contribution to Achievement of DOE Systems Analysis Milestones

This project will contribute to achievement of the following DOE 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 are working to identify and quantify these fuel contaminants in several distributed 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

- Conducted a fuel quality modeling workshop at Argonne to discuss pressure-swing adsorption (PSA) and fuel cell impurity effects modeling (Aug-07).
- Participated in International Standards Organization (ISO) WG12 meetings and held in-depth discussions on modeling impurity effects on fuel cell systems (Nov-07, Apr-08).
- Presented and discussed Hydrogen Quality Working Group (H2QWG) work at several FreedomCAR and Fuel Partnership's Technical Team meetings and at other forums (May-07, Jun-07, Oct-07, Nov-07, Jan-08, and Apr-08).
- Developed PSA performance models for different design and operating conditions and levels of various contaminants in product H_2.
- Developed methodology to evaluate effect of impurity level on hydrogen production cost using H2A.

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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, among others, the 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. All of these activities, however, have focused on the deleterious effects of different potential contaminants on the automotive fuel cell or on the on-board hydrogen storage systems. While it is possible for the energy industry to provide extremely pure hydrogen, such hydrogen could entail excessive costs. It is the objective of this task to develop a process whereby the hydrogen quality requirements may be determined based on life-cycle costs of the complete hydrogen fuel cell vehicle "system". To accomplish this objective, the influence of different contaminants and their concentrations in fuel hydrogen on the life-cycle costs of using that hydrogen in a fuel cell vehicle must be assessed. Some of the contributing factors include the life-cycle costs of production, purification, gas analysis and quality verification, effect on the performance and cost of the fuel cell, etc.

Approach

We have assembled a DOE H2QWG to obtain input from a broad spectrum of involved groups and organizations. Members of the H2QWG include DOE Hydrogen Program's Technology Development Managers from the Fuel Cells, Hydrogen Storage, Hydrogen Production, Delivery, Systems Analysis, Codes and Standards, and Cross-Cutting teams; U.S. automobile companies and fuel cell developers (Chrysler, Ford, General Motors, UTC Power); energy companies (BP, Chevron, ConocoPhillips, ExxonMobil, Shell); and DOE National Laboratories (Argonne, Los Alamos, National Renewable Energy Laboratory). Argonne coordinates the activities of the H2QWG.

To develop the process for assessing the effects of hydrogen quality specifications on costs and energy usage of the fuel cell vehicle over its life-cycle, we have:

- developed a draft Roadmap to identify what R&D and/or data are needed;
- initiated a database of critically assessed relevant literature;
- worked with model developers at Argonne and other organizations to help develop and validate performance and life-cycle cost models;
- held a workshop on modeling hydrogen purification processes and effects on fuel cell performance; and
- provided briefings and updates to various FreedomCAR Technical Teams and other groups involved in related work.

Results

The draft Roadmap lists major recommendations for continued work by the H2QWG. In the area of hydrogen production and purification, the recommendations are to determine the ranges of concentrations of N_2, CH_4, CO, and other species as a function of the production process design and operating conditions. Since hydrogen purification by the PSA process is the widely accepted commercial practice today, the recommendation is to develop quantitative models for the PSA process, which models can then be used to analyze trade-offs in H_2 quality, H_2 recovery, and production efficiency. In the area of the use of H_2 in fuel cells, if appropriate models can be developed and validated, the recommendation is to evaluate design and operating parameters (e.g., electrocatalyst loading, recirculating anode gas purge rates) to enable fuel cell operation on various levels of the different contaminants. Such analyses can correlate design parameters with life-cycle costs of automotive fuel cell systems. In the area of hydrogen analysis and quality verification, the recommendations are to develop and validate (e.g., ASTM International certified) analytical techniques to sample, monitor, and analyze dispensed H_2, and to develop standardized methods (even if they are expensive), which can be used to calibrate simpler, less expensive methods and instrumentation for field use.

In accordance with these recommendations, we have developed a model for the hydrogen production-purification process based on steam methane reforming (SMR) for hydrogen production, followed by PSA for hydrogen purification. For a plant size of 1,500 kg/day of H_2, we have considered a range of the major operating parameters: a steam-to-carbon molar ratio of 3 to 6, SMR and PSA operating pressures of 8 to 22 atm, PSA inlet temperatures of 25°C or 40°C, and carbon fractions of 20% to 80% in the carbon/zeolite PSA beds. For the reference base case, the selected parameter values were: steam-to-carbon molar ratio of 4, 8 atm pressure, 750°C SMR exit (equilibrium) temperature, 435°C water-gas shift exit (equilibrium) temperature, 25°C PSA inlet temperature, and 80% carbon fraction in the PSA beds. For this base case, Table 1 shows the feed natural gas composition and the SMR product composition (feed to PSA), both on a dry basis. We arbitrarily added 100 ppmv of H_2S to the reformate to check for sulfur removal by the PSA beds.

The preliminary results of the PSA model are shown in Figure 1. Of the major impurity species considered, the purified hydrogen from the PSA unit is very low

TABLE 1. Base Case Natural Gas and Reformate Compositions

Natural Gas Composition		Reformate Composition	
CH_4	93.1%	H_2	76.4%
C_2H_6	3.2%	CO_2	17.5%
N_2	1.6%	CH_4	2.8%
CO_2	1.0%	CO	2.8%
C_3H_8	0.7%	N_2	0.4%
C_4H_{10}	0.4%	H_2S	100 ppmv

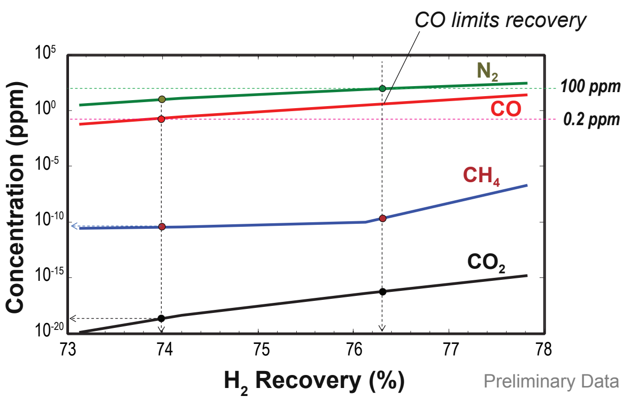

FIGURE 1. For the base case, CH_4, CO_2, and H_2S levels in the product hydrogen are very low.

in CO_2 (<10^{-15} ppm) and CH_4 (10^{-5} to 10^{-10} ppm). The concentration of H_2S in the purified hydrogen is extremely low. Thus, the main contaminant species of interest are CO and N_2, for which Figure 2 shows the concentration in the product H_2 as a function of the fractional recovery (fraction of the total H_2 fed to the PSA that is delivered in the purified H_2 product stream). The preliminary results shown in Figure 2 also include the corresponding overall efficiency of the SMR-PSA production-purification process.

The production costs of H_2 by the SMR-PSA process are greatly influenced by the cost of the feedstock natural gas. For the 2007 average industrial natural gas price of $7.60/million Btu, the corresponding (preliminary) H_2 costs are $3.50 and $3.70 for production efficiencies of 75% and 65%, respectively. These costs are only secondarily affected by the steam-to-carbon, PSA inlet temperature and pressure, and the carbon fraction in the PSA beds, for CO concentrations in the product H_2 ranging from 0.1 ppm to 1 ppm.

The performance of the automotive fuel cell, on the other hand, is significantly affected by the CO content in the fuel H_2, as shown in Table 2. While the calculated cost of H_2 decreases slightly from $3.630/kg to $3.617/kg as the permissible CO content increases from 0.1 ppm to 1 ppm, the corresponding fuel cell efficiencies decrease from 50.7% to 46.4%, resulting in

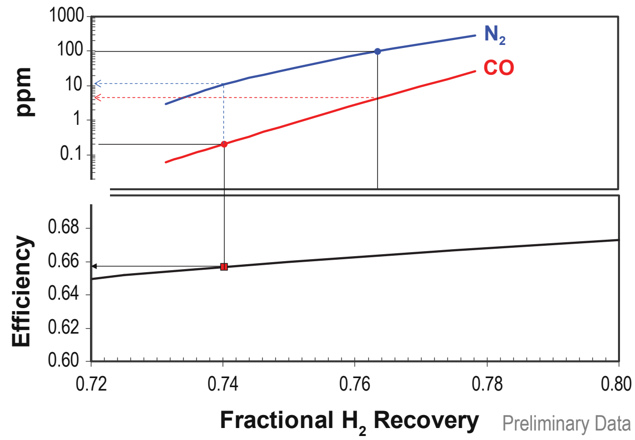

FIGURE 2. A CO specification of 0.2 ppm limits the H_2 recovery to 74% and yields an efficiency of 66%.

TABLE 2. Example: Effect of CO Concentration in Fuel H_2 on Fuel Costs for the Fuel Cell Vehicle*

CO in H_2, ppm	0.1	0.2	0.5	1.0
Cost of H_2, $/kg	3.630	3.627	3.621	3.617
Fuel cell efficiency, %	50.7	49.4	47.8	46.4
FCV/ICEV fuel economy multiplier	2.54	2.50	2.46	2.42
Fuel economy, mpgge	50.8	50.0	49.2	48.4
Total H_2 needed, kg	1,970	1,998	2,033	2.065
Total cost of H_2, $	7,152	7,246	7,361	7,467

*Sport utility vehicle driven 100,000 miles; Internal combustion engine vehicle achieving 20 mpg.
FCV - Fuel cell vehicle
ICEV - Internal combustion engine vehicle

an increase in H_2 consumption of 1,970 kg to 2,065 kg over 100,000 miles of driving. This results in an overall increase in fuel costs from $7,152 to $7,467 as the CO specification in the fuel is allowed to increase from 0.1 ppm to 1 ppm. These results are preliminary and subject to change as the various parameters used in the models are refined and validated. For example, the July 1, 2008, market price of natural gas is approximately $13.30/million Btu, representing a 75% increase over the $7.60/million BTU used in our analyses summarized above; the fuel costs for the 100,000 miles of driving would be correspondingly higher for the range of CO concentrations analyzed. Finally, hydrogen sampling, analysis, and quality verification is likely to add several ¢/kg per contaminant analyzed to the dispensed cost of H_2.

Conclusions and Future Directions

In summary, we have submitted a draft Roadmap to DOE that includes species-specific summaries in the Appendices, which have been used by SAE in their deliberations on revising their draft recommendations for hydrogen quality in their technical information report, TIR J-2719. We have organized workshops and other meetings to bring fuel cell developers and fuel providers together to discuss hydrogen quality issues. A PSA model has been set up to correlate impurity concentrations with H_2 recovery and production efficiency, using the steam-to-carbon ratio, pressure, PSA inlet temperature, and sorbent proportions as key parameters. The results were used with H2A hydrogen delivery cost model to evaluate the impacts of fuel quality requirements on hydrogen costs. We are conducting modeling of impurity effects on fuel cell performance to assess impacts of fuel impurities on fuel cell costs.

In future activities, we will:

- Further develop the PSA model and obtain results for
  - natural gas, ethanol, and other feedstocks of interest;
  - electrolysis-derived H_2; and
  - verifying CO or other species as viable canary species.
- Use fuel cell impurity modeling data to develop relationships between contaminant levels and fuel cell costs, including efficiency and durability for CO, CO_2, H_2S/COS, NH_3, condensable hydrocarbons.
- Update cost analyses with new data and validated modeling results for H_2 purification, drive-cycle fuel cell performance, and off-line and on-line analyses for quality verification.
- Continue working with H2QWG, ISO/SAE, etc., and organize related workshops to bring together fuel providers with fuel users to promote ongoing dialogue and identify key results and data needs.

FY 2008 Publications/Presentations

Since the 2007 Annual Merit Review meeting, we have made progress and update presentations and reports to:

1. Safety Codes and Standards Technical Team, 05/14/07.
2. Fuel Pathways Integration Technical Team, Naperville, IL, 06/13/07.
3. Delivery Technical Team, 06/21/07.
4. Submitted draft H2QWG Roadmap to DOE, 08/08/07 (Executive Summary, Text, Appendices).
5. Fuel Modeling Workshop, Argonne, IL, 08/30/07.
6. Fred Joseck presentation in China, 10/21/07.
7. DOE Bio-Derived Liquids WG, Laurel, MD, 11/06/07.
8. ISO TC 197, WG 12, Montecatini Terme, Italy, 11/06/07.
9. DOE Hydrogen Purification WG, Laurel, MD, 11/07/07.
10. Joint Tech Teams, USCAR, Southfield, MI, 11/14/07.
11. Fuel Pathways Integration TT, Fairfax, VA, 01/31/08.
12. ISO Meeting, San Francisco, CA, 04/02/08.