

VII.9 Fuel Quality in Fuel Cell Systems

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Project Start Date: October, 2006
Project End Date: Project continuation and
direction determined annually by DOE

Objectives

- Study the impact of impurities on fuel cell systems.
- Identify the key impurities of concern.
- Recommend research and development (R&D) strategies to mitigate the effect of the impurities.

This project addresses the following technical barriers from the Systems Analysis section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (B) Stove-piped/Siloed Analytical Capability
- (D) Suite of Models and Tools

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 Fuel Cell Technologies Program Multi-Year Research, Development, and Demonstration Plan:

- Milestone 8: Complete analysis and studies of resource/feedstock, production/delivery and existing infrastructure for technology readiness. (4Q, 2014) The study described here analyzes the quality of resources/feedstock, their conversion to reformat, and subsequent purification to identify the technology readiness and ability to sustain the operation of reformat-based fuel cell systems.

Accomplishments

A database has been set up to document the impurities encountered in stationary fuel cell systems by reviewing the literature and other public domain information:

- The impurities encountered in these systems have been identified.
- The effect of the impurities on the fuel processor components and their management options are being studied.
- The tolerance of the various fuel cells to the impurities is being documented.



Introduction

Fuel cell systems are being deployed in stationary applications for the generation of electricity, heat, and hydrogen. These systems comprise a variety of fuel cells ranging from the low temperature polymer electrolyte fuel cell (PEFC) to the high temperature solid oxide fuel cell (SOFC). Depending on the application and location, these systems are being designed for, or operate on reformat or syngas produced from various fuels that include natural gas, biogas, coal gas, etc. All of these fuels contain species that can potentially damage or pose a hazard for the fuel cell anode or other unit operations and processes that precede the fuel cell. These effects include loss in performance or durability and require additional components to reduce, if not eliminate, the impurity concentrations to tolerable levels. These impurity management options increase the complexity of the process and add to the capital and operating costs (regeneration, replacement and disposal of spent material, maintenance, etc.)

This project reviews the various impurities encountered in fuel cell systems with the objective of identifying which components (e.g., reformer, heat exchanger, fuel cell, etc.) in the system are affected, the extent of the deleterious effect, the impurity management options being practiced in the field and their effectiveness. For example, the presence of sulfur can lead to poisoning of the reforming catalyst which then results in coke formation and rapid failure of the reformer. To avoid this scenario the plant manager will install a sulfur-removal process. The decision on the desulfurization process (e.g., hydrodesulfurization or ambient sorbent bed and its size, etc.) will be made by considering the tradeoffs between the cost and complication of the process against the loss in productivity (hydrogen yield, power output) and other

considerations (e.g., deactivation rate, cost of disposing the spent sorbent, frequency of maintenance, etc.).

Approach

- Information relating to impurities and their impact on fuel cell systems are being collected from the literature and through personal communication with fuel cell developers. Data from the literature and from other public domain sources are being incorporated into a database, which classifies the information in terms of type of application, the type of impurity species encountered and their effect on the system, the technologies that are used for their removal or abatement, and the level at which a fuel cell can tolerate the impurity.
- The data will be analyzed to identify the impurities with respect to their pervasiveness, the difficulty of removal, and cost burdens. Ideally, it will be preferable to translate these factors in terms of cost impact, since this will allow a comparison across different systems and applications.

Results

A database has been set up to document and study the effect of fuel quality on fuel cell systems. Table 1 shows data from a demonstration project at the Penrose Power Station in Sun Valley, CA [1], where landfill gas was cleaned, reformed and then fed into a phosphoric acid fuel cell (PAFC) to generate 137 kW of electric power.

TABLE 1. Data from a Landfill Gas Fueled Fuel Cell Demonstration at Penrose Power Station, CA

Category	Information
Type of Application	Commercial Demonstration
Type of Fuel Cell	PAFC
Output	137 kW
Feedstock	Landfill Gas
Impurities	Sulfur, Halides, Siloxanes, Non-Methane Organic Carbons (NMOC)
Feedstock Purification	1. Claus Reaction on Carbon 2. Refrigerated Condensation 3. Desiccant 4. Activated Carbon
Feedstock Conversion	Reformer Water-Gas Shift Reactor
Reformate/Syngas Purification	Not Available
Concentration entering Fuel Cell	Sulfur as H ₂ S ~0.4 ppm Halide as HCl ~0.01 ppm Siloxane ~0.08 mg/dscm NMOC ~14 ppm
Effect on Fuel Cell	Not Available
Impurity Tolerance	Sulfur 3 ppm Halide 3 ppm

Landfill gas contains sulfur, halides, siloxanes, and hydrocarbons. For the Penrose plant, a number of clean-up units were installed to reduce the impurity concentrations to acceptable levels, which were reported to be 3 ppm for sulfur and halides. In order to understand the impact of the impurities and compare them against other applications, it is desirable to know what the clean-up process adds to the cost of the electric power that is generated.

A closer look at landfill gas [1-6] shows (Table 2) that the impurity species that are present at low concentrations can be classified into paraffins, sulfur, cyclics, aromatics, halides, and organic silicon. Hydrogen sulfide is the predominant sulfur species with concentrations that can approach 400 ppm. The organic silicon species include a large number of species each of which can be as high as 15 mg/Nm³.

TABLE 2. Typical Species Present in Landfill Gas

Major Species	%	Aromatics	ppm
CH ₄	41-54	Isopropyltoluene	< 13
CO ₂	32-35	Benzene	< 10
O ₂	0.7-0.9	Toluene	< 69
N ₂	11-13	Xylene (and isomers)	< 22
Paraffins	ppm	Styrene	< 2
Ethane	< 220	Ethylbenzene	< 13
Butane	< 100	Trimethylbenzene	< 14
Pentane	< 970	Halides	ppm
Hexanes	< 390	Chlorobenzene	< 1
Sulfur	ppm	Dichloroethene	< 33
Hydrogen Sulfide	< 430	Dichloroethane	< 0.25
Methyl Mercaptan	< 3	Cis-1,2 Dichloroethane	< 5
Ethyl Mercaptan	< 0.5	Methylene Chloride	< 12
Dimethyl Sulfide	< 8	Dichlorofluoromethane	< 1.4
Carbon Disulfide	< 0.5	Trichloroethene	< 2.8
		Vinyl Chloride	< 1.4
Cyclics	ppm	Organic Silicon	mg/Nm ³
Pinene	< 14	(D3, D4*, D5, L2, L4)	< 15*
Limonene	< 35	Trimethylsilanol	< 12

The presence of siloxanes in landfill gas pose challenges for fuel processing since these species react at higher temperatures to produce silica which then deposits on the surfaces of catalysts and heat exchangers. Siloxanes can be removed with sorbents such as silica gel, bentonite, etc. However, the gravimetric capacity of these sorbents tends to be low and is adversely affected by the presence of other species. For example, silica gel's capacity for siloxane uptake [6] drops from 10%

for dry gas to less than 1% when the relative humidity is increased to 50%. Similarly, the presence of volatile organic compounds prevents the adsorption of siloxanes on carbon.

Sulfur is present in almost all the feedstocks used for power generation and plagues the fuel cell industry because of their ability to poison heterogeneous and electrochemical catalysts. Some sulfur species can be removed with sorbents such as activated carbon, while others require more reaction based processes such as the Claus process or hydrodesulfurization. The latter reaction produces H_2S and COS , which then have to be reacted with other reagents such as ZnO or other sorbents. These processes are complex because of the effects of temperature, competition of sorption sites with H_2O , kinetics, and low gravimetric capacities of the sorbents. Table 3 shows some of the media that are used for the removal of H_2S [7,8].

TABLE 3. Media Used for H_2S Removal

Medium	Regeneration	Capacity	\$/kg of H_2S
Iron Sponge (Iron Oxide)	2-3 X	2.5 kg- H_2S /kg- Fe_2O_3	0.35-1.35
Sulfa Treat [®] (Iron Oxide)	No	0.5-0.7 kg- H_2S /kg- Fe_2O_3	4.85-5.00
Sulfur Rite [®] (Iron Oxide)	No		7.95-8.50
Media G2 [®] (Iron Oxide)	15 X	0.5 kg- H_2S /kg- Fe_2O_3	2.90-3.00
Impregnated Activated Carbon	Yes	0.12 g-S/g-C	1.75-2.00

Other methods that are employed for the removal of impurities from the reformat stream include phase change to condense out species such as metal vapors from coal syngas, separation membranes, etc. The most comprehensive method for hydrogen enrichment is the pressure swing adsorption which can produce very high purity hydrogen and is very effective for the removal of sulfur and ammonia. Unfortunately, these units require pressurization of the gas stream which is energy intensive, and the operation of the multiple beds tends to be complex.

The data available in the literature on the effect of impurities on fuel cell systems covers a range of systems and conditions [9-13]. Although comparison on a common basis is difficult, some trends and contributing factors are evident. For example, the higher temperature fuel cells show greater tolerance to impurities – the SOFC can tolerate orders of magnitude higher concentrations of ammonia and sulfur than the low temperature PEFCs. Even for a particular type of fuel cell, the performance loss is affected by the nature and

concentration of the impurity, the current density, the composition of the fuel, the exposure time, etc.

As an example, introduction of 2 ppm H_2S into a natural gas reformed syngas causes the voltage in a button-size SOFC cell to drop sharply by 10%. Increasing the H_2S concentration to 5 ppm doubles the performance loss to 20% [13]. The database being assimilated in this project includes similar data on a host of impurities tested at various conditions in fuel cells with varying anode compositions. Analysis of performance data, however, can be much more coherent when the tests are coordinated to address specific questions on similar hardware under consistent conditions.

Conclusions and Future Directions

- A database is being set up to document the impurity levels and their management in stationary fuel cell applications:
 - The data are being classified on the basis of the unit operations and processes of the system.
- The key impurities in the feedstock fuel and the fuel gas to the anode have been identified:
 - The concentrations of these impurities are being documented.
- Sulfur and siloxanes have detrimental effects on fuel cells and components that precede them.
- The higher temperature fuel cells demonstrate higher tolerance to impurities such as sulfur, carbon monoxide, and sulfur.
- The database will be analyzed to identify trends and key technical challenges faced by the stationary fuel cell industry. This will be followed by recommendations on R&D needs.

FY 2010 Publications/Presentations

1. “Fuel Quality in Fuel Cell Systems,” Presented at the 2010 DOE Hydrogen Program and Vehicle Technologies Program Annual Merit Review and Peer Evaluation Meeting, Washington, D.C., June 7–11, 2010.

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