XI.12 Fuel Quality Effects on Stationary Fuel Cell Systems

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Fiscal Year (FY) 2011 Objectives

- Study the effects of impurities on fuel cell systems for stationary applications.
- Correlate the cost of electricity to impurity concentrations in the fuel feedstock.

Technical Barriers

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/feedstocks, their conversion to reformate, and subsequent purification to meet the tolerance levels of the fuel cell stacks in stationary fuel cell systems. The analysis results in estimates of the differential cost of hydrogen attributable to gas clean-up.

FY 2011 Accomplishments

- A database, started in the last FY, to document the impurities encountered in stationary fuel cell systems by reviewing the literature and other public domain information has been extended to include halocarbons, volatile organic compounds (VOCs), and organosilicon compounds.
- The tolerance limits of various types of fuel cells to fuel impurities have been documented.
- A model of a stationary fuel cell-based combined heat and power system has been developed to estimate the effect of impurity levels on the cost of hydrogen:
  - Fueled by anaerobic digester gas cleaned through available technologies.
  - Power generated with a molten carbonate fuel cell.

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Introduction

Fuel cell systems are being deployed in stationary applications for the generation of electricity, heat, and hydrogen. These systems use a variety of fuel cell types, 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 to operate on reformate 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 attenuating these effects requires additional components to reduce, if not eliminate, the impurity concentrations to tolerable levels. These impurity management options increase the complexity of the fuel cell system, and they add to the capital and operating costs (regeneration, replacement and disposal of spent material, maintenance, etc.).

This project reviews the public domain information available on the impurities encountered in stationary fuel cell systems and their effects on fuel cells. A database has been set up which classifies the impurities, especially in renewable fuels such as landfill gas and anaerobic digester gas. It documents the deleterious effect on fuel cells and the maximum allowable concentrations of select impurities suggested by manufacturers and researchers. A generic model of a stationary fuel cell-based power plant is being developed; it includes a gas processing unit followed by a fuel cell system. The model is being used to conduct an economic analysis to estimate the effect of impurities (according to the class of materials, such as siloxanes) on the cost of electricity. The model identifies the key relevant design and process parameters, and their effects on the capital and operating costs, as a function of the impurity content in the fuel feedstock.

Approach

The project evaluated the fuel feedstocks used in the stationary fuel cell power plants and identified the impurities and their concentrations that are typically present. The effect of these impurities on the fuel cell stack and suggested tolerance limits have been documented. The literature review helped identify the impurity removal strategies that are available and their effectiveness, such as capacity, cost, etc. A system model has been set up to consolidate the information and correlate the interactions and demands on the system. The key impurity removal steps are being modeled to enable predictions of impurity breakthrough, component sizing, and utility needs. The energy needs and process efficiency results from the model will be entered into the H2A model to calculate the cost of electric power. Sensitivity analyses will be conducted to correlate the concentrations of key impurities in the feedstock to the cost of electric power.

Results

Biogas from a waste digester contains 50-60% methane, with the balance of the biogas being mostly carbon dioxide, and is a viable fuel for fuel cell systems. It also contains trace contaminants some of which are produced by biological digestion while others are volatilized from the waste stream being digested. The contaminant matrix can be rather complex, containing many species that can be harmful to the fuel cell. The nature and amounts of such contaminants depend on the type and age of the waste, temperature, pressure, etc.

In general, while many contaminant species are present in biogas, three classes of impurities are of particular concern for its use in fuel cell systems.

- Reduced sulfur compounds are common in all biogas sources. The primary reduced sulfur compound of concern is hydrogen sulfide (H_2S), which may be present in biogas at concentrations up to several thousand parts per million by volume. While H_2S represents the bulk of sulfur in the biogas, organic sulfur, such as mercaptans and dimethylsulfide, is also present although typically in much lower concentrations (~1 ppm or less).
- Siloxanes emanating from personal hygiene products are generally present in landfill gas and wastewater treatment plant sludge digester gas in concentrations of 10 ppmv or less. Siloxanes (**sil**icon, **ox**ygen, alk**ane**) are organo-silicon compounds with the formula R_2SiO, where R is H or a hydrocarbon group. Siloxanes can be cyclic (e.g., hexamethylcyclotrisiloxane [D3], etc.) or linear (e.g, hexamethyldisiloxane [L2], etc.). Out of all the hundreds of different siloxanes in use, the most commonly occurring ones in landfill and biogases are L2-L5 and D3-D6 [1]. Siloxanes are converted to solid silica in flames. The solid silica may accumulate on surfaces inside power generation equipment and it can prematurely deactivate the catalytic surfaces in reformers and fuel cells.
- VOCs include alkanes, alcohols, aromatics and halogenated species. Of primary concern are halogens that can deactivate the catalytic surfaces in reformers and react with the electrolytes in fuel cells. Halogens from landfill gas generally originate from discarded refrigerants, plastic foams, etc. Many compounds are stable and slowly evaporate to maintain significant levels of halogens for many years. The concentrations of halogenated species from waste water treatment plants (WWTP) are typically below 1 ppm, while landfill gas may contain halogenated species up to about 40 ppm.

The requirements for gas cleaning will vary, depending on the type of biogas, impurity concentrations in the biogas and the tolerance limits to the impurities of the specific fuel cell system. A single gas purification step is seldom sufficient to clean the biogas; rather, a combination of methods is used to ensure a fuel quality that matches the tolerance limits for the fuel cell system. Reviewing the literature that includes case studies for fuel cell systems operating both on landfill gas and digester gas [2-5], it was found that the general gas cleaning strategies involve several steps, which can be broken down to a) primary clean-up of bulk impurities (e.g., H_2S with iron oxide) and b) gas polishing (i.e. adsorption) of trace contaminants of concern before the gas is delivered to the fuel cell system.

A generic model of a stationary fuel cell-based power plant has been developed to determine the overall electrical efficiency and costs of clean-up and maintenance, as a function of the biogas impurity matrix. A schematic of the fuel cell power plant is shown in Figure 1. A base case system considers a fuel cell system operated on digester gas from a waste water treatment plant. Major sections of the system include the gas processing system, fuel processor/fuel cell stack, and thermal management system. First the bulk impurity H_2S is removed using an appropriate sorbent, such as iron oxide media or impregnated activated carbon. The gas is further cooled to condense the water as moisture can significantly reduce the adsorption capacity in subsequent clean-up steps. The gas can even be deeply cooled to below -20°C to condense some of the siloxanes and heavier VOCs.

The dry gas is further passed to the secondary polishing equipment that can contain a series of adsorbents and removes organic sulfur, siloxanes, and halogens. The cleaned gas enters the fuel cell system where it is converted to electricity and usable heat. The heat generated by the electrochemical reaction is removed to an external heat rejection system, where it is recovered for use by the sewage treatment plant, in particular, to meet the energy needs for

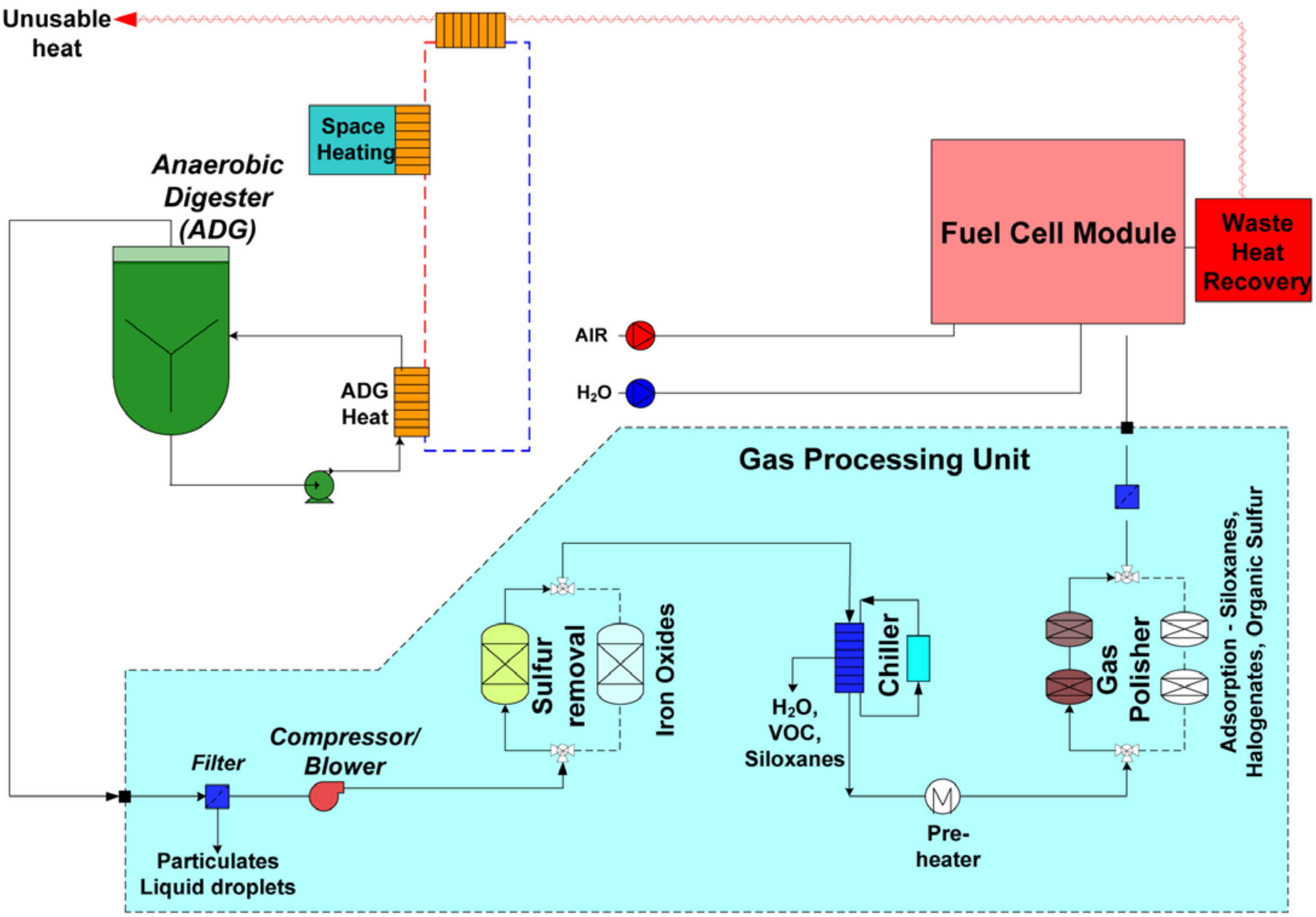

FIGURE 1. A Base Case Fuel Cell System Operating on Anaerobic Digester Gas

the anaerobic digestion process and, possibly, for other uses, e.g., space heating.

The overall process model has been set up initially for a molten carbonate fuel cell, and various component models are being developed to determine the utilization of the adsorbents (and, ultimately, the replacement costs) as function of impurity concentrations in the raw gas. For example, Figure 2 shows the adsorption capacity of activated carbon on some select trace impurities typically found in digester gas from WWTPs. The lines are modeled adsorption isotherms on pure organic components as a function of concentration (partial pressure) [6-7], and have been calibrated with available experimental data on activated carbon [8]. The shaded region in the graph is a range of concentration limits on a) the lower impurity tolerance limits for a fuel cell, and b) the typical maximum concentrations of individual trace impurities entering the gas polisher. Unsupported activated carbon has a rather low adsorption capacity for hydrogen sulfide, and so H_2S must be removed prior to the gas polisher. Some species, such as chlorobenzene and aromatics (e.g., toluene), show very high adsorption affinities for carbon, even at low

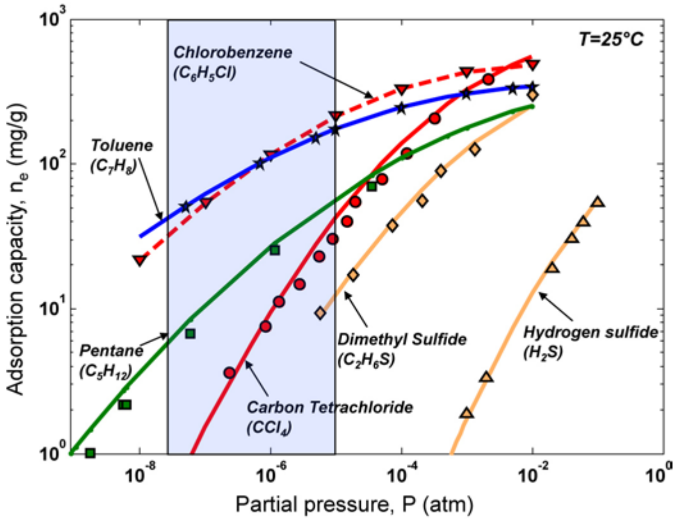

FIGURE 2. Adsorption isotherms on activated carbon (BPL) on some of the most frequent encountered trace impurities in digester gas. Solid lines are modeled pure component isotherms and symbols corresponding experimental data from the literature.

concentrations. Aromatics at ppm levels will not pose any hazard to the fuel cell system as such, but they will compete with available adsorption space and reduce the adsorption capacity for halogens and siloxanes – species of concern for the durability of the fuel cell system.

Conclusions and Future Directions

- Data available on biogas sources with respect to trace contaminant matrix and clean-up options and performance has been collected into a database. This information, along with the effects and removal of the various species that have significant deleterious effects on fuel cell performance or lifetimes, is categorized in classes of impurities, biogas source, and unit operations of the systems.
- Impurities of particular concern for the fuel cell system are sulfur, siloxanes, and halogens, which vary in concentration and speciation, depending on the biogas source of interest. Higher hydrocarbons, aromatics, and alcohols are also present in the biogas. While their concentrations may not be of direct threat to the fuel cell, they can greatly reduce the capacity of the various adsorbents to remove siloxanes and halides.
- A base case system has been set up for economic analysis and initially considers a molten carbonate fuel cell system operating on digester gas from waste water treatment plants. A generic model of a stationary fuel cell-based power plant has been developed, including component models of typical gas processing units, to determine the utilization of various adsorbents as a function of the biogas impurity type and concentration matrix.
- Cost data are being gathered for the various components in the power plant to complete the cost analysis for the base-case system. Further work will determine costs for different fuel cells, bio-gas sources, and clean-up technologies. Trade-off analyses between cost of clean-up versus degradation and power loss of fuel cell system are also important to determine life-cycle costs. Ultimately, these models and results will need to be validated with data from operating plants.

FY 2011 Publications/Presentations

1. "Fuel Quality in Fuel Cell Systems," Presented at the 2011 DOE Hydrogen Program and Vehicle Technologies Program Annual Merit Review and Peer Evaluation Meeting, Arlington VA, May 9–13, 2010.

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