Fuel Quality in Fuel Cell Systems

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Project Overview

Timeline

- Project Start: October 2007
- Project End: Open

Barriers

- B. Stove-Piped/Siloed Analytical Capability
- D. Suite of Models and Tools

Budget

- FY 07: $200 K
- FY 08: $350 K
- FY 09: $200 K
- FY 10: $200 K

Partners

- Energy Companies (BP, GTI)
- National Laboratories (NREL)
- Fuel Cell Companies
- International
  - Japan Gas Association
  - International Standards Org

Relevance - Impurities in hydrogen affect the performance, life, and cost of fuel cell systems

- Fuel Cell systems operate on hydrogen and H_2-rich reformates that contain impurities
  - Inerts / diluents, reversible / irreversible poisons
- The effect of impurities depends on the type of fuel cell
  - Electrolyte, anode, operating temperature, concentration of impurities
- The impurities usually enter the fuel cell system with the feedstock
  - Natural gas, landfill gas, bio-derived liquid, etc.
- The critical impurities are removed before the vulnerable component
  - e.g., sulfur before reforming catalyst, ammonia before fuel cell anode, etc.
- Impurity removal adds to the lifecycle cost of the fuel cell
  - Existing clean-up strategies are often expensive or burdensome
    - E.g., low sorbent capacity, regeneration or waste disposal
  - Newer clean-up technologies will accelerate deployment of fuel cell systems

Relevance - Objective

- Study the impact of impurities on fuel cell systems
  - Components affected
  - Performance loss
  - Degradation
  - Clean-up strategies and their cost factors
- Identify the impurity – system configurations that are most constrained by impurity effects
- Recommend R&D that can
  - Mitigate the deleterious effects
  - Provide alternative and less expensive clean-up options

Approach

- Track the pathway between the feedstock and the fuel cell through literature review and industry experience
- Assess the impact of the impurities on the fuel cell
  - e.g., sorbent capacity and associated cost, loss in performance
- Identify opportunities to enhance impurity removal or tolerance

Previous Years Technical Accomplishments

- Studied the effect of impurity concentrations on the process efficiency and cost of hydrogen
  - Produced at distributed production centers (1500 kg/day)
  - From Natural Gas
  - Based on Steam Reforming followed by Pressure Swing Adsorption (PSA)
  - In most cases, the allowable limit for CO (0.2 ppm) limited the H2-recovery of the PSA unit
  - The cost of hydrogen was marginally affected by the CO concentration
- Extended the study to include
  - Hydrogen from NG using Autothermal Reforming
  - Hydrogen for Central production plants using coal gasification

Technical Accomplishments and Progress - FY10
A database has been set up to document the effects

- The template classifies a fuel cell system in terms of
  - The type of fuel cell (e.g., PEFC, SOFC, …)
  - The feedstock / fuel that it uses (e.g., NG, landfill gas, biogas, …)
  - The impurities present in the fuel (e.g., sulfur, metals, …)
  - The fuel purification / impurity management strategies employed (e.g., HDS, sorbent, …)
  - Conversion to syngas / reformate (e.g., gasification, steam reforming, …)
  - Reformate purification (e.g., PSA, sorbent, …)
  - The type of application (e.g., stationary, remote, …)
  - Outputs (e.g., kWe, heat, hydrogen, …)
  - Impurities entering the fuel cell (e.g., sulfur, ammonia, metals, …)
  - Impact (on performance, durability, cost)

Technical Accomplishments and Progress Identified the fuel impurities*

- Natural gas impurities are few
  - Oxygen, sulfur, helium, nitrogen, light HCs, moisture
- Biogas contains many species that can be classified into
  - Sulfur, siloxane, hydrocarbons, halides, air, moisture, etc.
- Syngas from coal contains metal vapors and oxides

*Meets March 2010 milestone

Landfill gas contains a wide variety of species at concentrations of less than 0.05%

Major Species: %	
CH_4 :	**41-54**
CO_2 :	**32-35%;**
O_2 :	**0.7-0.9%;**
N_2 :	**11-13%**

Paraffins	ppm
Isobutane	<100
Isopentane	<970
N-Pentane	<180
Hexanes	<390

Sulfur	
Hydrogen Sulfide	<280
Methyl Mercaptan	<0.5
Ethyl Mercaptan	<8
Dimethyl Sulfide	<0.02
Carbon Disulfide	<0.5
Methanethiole	<0.5

Cyclics	
Pinene	<86
Limonene	<25

Aromatics	ppm
Isopropylbenzene	<6
Benzene	<5
Toluene	<21
Xylene (and isomers)	<45
Styrene	<0.5
Ethylbenzene	<13
Trimethylbenzene	<14

Halides	
Chlorobenzene	<1
Dichloroethene	<33
Dichloroethane	<0.25
Cis-1,2 Dichloroethane	<5
Methylene Chloride	<12
Trichloromethane	<0.6
Trichloroethene	<6.3
Vinyl Chloride	<1.4

Organic Silicon	
Siloxane (D3, D4*, D5, L2, L4)	<15*
Trimethylsilanol	<12

- Urban, W., Lohmann, H., Salazar Gomez, J.I., Journal of Power Sources, 193 (2009) 359-366.
- Speigel, R.J., Preston, J.L., and Trocciola, J.C., Energy 24 (1999) 723-742.

Technical Accomplishments and Progress Available information is being documented for each item in the database

- Identifies the impurities of concern contained in a feedstock and their effects, e.g.,
  - Coal contains metals that are volatilized during gasification
    - The metals react with active surfaces (catalyst, heat exchanger)
    - The metals condense out at various temperatures (locations within the system)
  - Landfill gas contains siloxanes
    - Siloxanes oxidize to form silica that deposits on surfaces
    - Siloxanes can be removed by sorbents (e.g., silica gel, bentonite, etc.)
    - Removal is affected by siloxane type, sorbent used, and the nature of the other impurities (e.g, water)
    - Sorbent beds are often staged
    - Life / capacity are generally low

Siloxane Uptake Capacity of Silica Gel*

Rel. Humidity, %	L2	D5
0	11	10
10	10	8.4
20	6.2	4.6
30	1.8	1.0
50	0.8	0.6

*Schweigkofler et al (2001), Journal of Hazardous materials B83 183-196

Technical Accomplishments and Progress
Impurity removal strategies are identified

- Sulfur is removed by HDS, Adsorption, Absorption, Oxidation

Example of medium used for H_2S and mercaptan removal*

Medium	Regeneration	Capacity	$/kg of H2S
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

- Pressure swing adsorption is very effective for most impurities
- Membrane permeation (H_2) is effective but the membrane is vulnerable to poisoning by sulfur
- Phase separation is used for the removal of moisture, ammonia, metals

*Zicari, S (2003). M.Sc Thesis - Cornell University; Spiegel et al (2003). Waste Management, 23, 709-717

Technical Accomplishments and Progress
The documented projects have been classified in terms of application and output

- The applications range from
    - Stationary – central, distributed, remote
    - Portable
    - Transportation – auxiliary power, forklifts, etc.
- With outputs that include
    - Electric power
    - Heat, steam, hot water
    - Hydrogen

Technical Accomplishments and Progress
Higher temperature fuel cells are less affected by impurities

- Manufacturers define tolerance limits based on degradation rate, cost of maintenance, maintenance schedule, life, etc.
  - Tolerance limits are affected by stack temperatures

Reported and (Tolerance Limits) of Fuel Cells* to Select Impurities
(The tolerance limits usually have constraints on exposure time)

	PEFC	PAFC	MCFC	SOFC
Sulfur		0.40 ppm (3)	0.1 ppm (?)	1 ppm (?)
Ammonia		0.25 ppm (?)		5000 ppm (?)
CO				
Total Halide		0.01 ppm (3)		
Tars				0.5 g/Nm^3 (?)
Silanes/Siloxanes		0.08 ppm (?)		

*Reformate/Syngas based systems

Collaborations

- We are grateful for the technical support and guidance from
    - Fuel Cell Energy
    - Versa Power
    - Acumentrics
    - Nuvera

Summary

- A database is being set up to document the impurity levels and management in 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 concentration levels of these impurities are being determined
    - Open literature, personal communications
- Sulfur, siloxanes, and halides are detrimental for all fuel cells
  - Ammonia, CO, hydrocarbons are less damaging for the higher temperature fuel cells
  - Metals are easier to remove for low temperature fuel cells

Proposed Future Work

- Available data will be organized within the database and analyzed to identify
  - The key impurity that is limiting a fuel cell system performance
    - Capital and operating costs, maintenance frequency, regeneration or waste disposal, life of components
- Identify the R&D needed to help resolve the limitations for each combination of fuel and fuel cell application
  - Report the results from this study (September 2010)