U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

# Gas Clean-Up for Fuel Cell Applications Workshop

March 6-7, 2014

Sponsored by U.S. Department of Energy
Fuel Cell Technologies Office (FCTO)

Organized and hosted by Argonne National Laboratory

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Workshop held March 6–7, 2014
Argonne National Laboratory
9700 S. Cass Avenue
Argonne, IL 60439

Sponsored by
U.S. Department of Energy (DOE) – Fuel Cell Technologies Office (FCTO)
Organized and hosted by
Argonne National Laboratory (ANL)

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# Executive Summary

On March 6-7, 2014 Argonne National Laboratory hosted a workshop addressing gas clean-up for natural gas (NG), liquefied petroleum gas (LPG), renewable bioliquids and biogas, and associated petroleum gas (APG) for fuel cell applications. The main objectives of the workshop were to identify the impurities that had the largest effect on system cost and performance, and to identify research and development (R&D) that can have the greatest impact on impurity removal and reducing the cost of fuel cell generated power. Workshop attendees identified sulfur impurities, siloxanes, and halogenated materials as the impurities that have the greatest impact on gas cleanup system reliability, capital and operating costs. They pointed that R&D to develop real time online sensors and sorbents (with lower cost, higher capacity, and maintainability) is the most impactful in the short term. The sorbents should preferably be insensitive to water, carbon dioxide, and hydrocarbons.

The main issues with gas clean-up systems are poor reliability, high capital and maintenance costs. Current technologies that remove the fuel contaminants of concern and provide purity requirements for fuel cell systems are costly and need to be custom-designed for the type of fuel. Field data show that the cost of removing impurities from natural gas is about 10 % of the operation and maintenance (O&M) cost while this cost for an anaerobic digester gas in an MCFC plant can vary between 20-40% depending on the size of the plant. Out of these costs 25% is solely the cost of the media used for impurity capture. Cost analysis models indicate that in a digester gas fueled molten carbonate fuel cell (MCFC) plant, gas clean-up contributes 14-22% of the cost of electricity or approximately 2 cent/kWh. The participants indicated that the near term cost targets for the clean-up system should be less than $500/kW (CapEx) and 1 cent/kWh (OpEx). In the long term, additional reduction to <$200/kW and <0.5 cent/kWh would further increase the fuel cell market share in highly competitive global markets. A study[1] showed that at <$200/kW capital cost of fuel-flexible clean up system, the world-wide market for fuel cells is expected to increase to >100,000 MW. Analysis suggests the need to reduce the fuel cell power plant cost to lower than $2000/kW (installed), with advances in clean-up technology and fuel flexibility.

The participants discussed several reasons for the high costs associated with gas clean-up. The low tolerance of fuel cells to some of the impurities and the varying levels and types of impurities in the feed gas contribute to the high capital cost. At the required parts per billion (ppb) level, reliable and cost-effective detection of impurities such as sulfur is a challenge. There is a lack of inexpensive online analytical techniques which would allow accurate determination of impurity levels entering into or breakthrough from the clean-up system. This makes it difficult to determine the remaining capacity of the removal system and leads to over-designing the systems and replacing the adsorbent beds before reaching their full capacity. Another factor contributing to the high cost is the presence of water in the fuel gas, especially for biogas feeds. Co-adsorption of water and other gas components decreases the adsorption bed capacity. The lack of adsorbents with high selectivity for the contaminants and low water adsorption leads to requirements for larger beds, more frequent media replacement, or additional equipment (dryers, chillers/condensers) that increases system complexity and associated costs. There is also cost associated with sorbent bed disposal as the spent media may contain flammable and hazardous components. Early and unpredicted breakthrough of impurities through the clean-up system leads to unplanned maintenance costs that tarnishes customer satisfaction and adversely impacts market share.

Development of real time online sensors and higher capacity sorbents were identified as very important near term goals. The sorbents should be fuel-flexible, environment friendly and insensitive to water and hydrocarbons. The short-term R&D recommendations also include:

- establishment of impurity specifications for the fuel streams;
- development of fuel flexible reforming catalysts;
- generation of sorbent properties that will enable process design;
- and, development of accelerated test protocols to determine the effectiveness of the clean-up steps.

Development of a single clean-up system capable of operation on multiple fuels such as natural gas, biogas, landfill gas (LFG) and other opportunity fuels will help increase fuel cell deployment.

[1] Based on an internal study by Fuel Cell Energy (FCE) Inc.

Stakeholders ranked development of next generation sorbents with even larger capacity and higher selectivity as a high priority research area in long-term. Development of methods to convert fuel impurities or spent sorbents into useful byproducts to convert disposal to a revenue source was also recommended.  Developing scalable, modular, environment friendly, portable, low cost clean-up systems with high selectivity for multiple impurities was also deemed a desirable long-term R&D goal. Replacing fuel odorants with non-sulfur containing odorants was also suggested. There are very few fuel cell plants, consequently limited data are available on fuel quality, management and their effect on downstream components. It was proposed to have more deployment projects on fuel cell power plant to enrich the current database.

# Workshop Objectives and Organization

The Gas Clean-up for Fuel Cell Applications Workshop was held at Argonne National Laboratory on March 6-7, 2014, and featured 43 participants from industry (fuel cell, process solution providers, material suppliers), government agencies, advocacy groups, universities, and national laboratories with expertise in the relevant fields. The objective of the workshop was to identify and prioritize the:

- impurities that have the greatest impact on the complexity and performance of the fuel cell plant;
- R&D strategies that can alleviate the cost for onsite removal of impurities;
- R&D strategies that will simplify the plant and reduce product cost (heat, power, hydrogen);
- fuel processors and gas clean-up systems that facilitate modularity and fuel flexibility for a range of fuel cell technologies;
- and, opportunities to avoid APG flaring by using fuel cells.

The workshop began with an introductory session by Dimitrios Papageorgopoulos (FCTO-DOE), Mohammad Farooque (FuelCell Energy), and Gabriel Phillips (GP Renewables & Trading). The session featured opportunities of using fuel cells to generate power using a variety of fuels ranging from natural gas, liquefied petroleum gas, renewable bioliquids and biogas, and associated petroleum gas. The session continued on the current state of the technology, the opportunities and challenges, while Gabriel Phillips presented arguments in favor of using APG for fuel cell power generation.

The main activities of the workshop were arranged in three sessions to (i) discuss the impurities, (ii) discuss the clean-up technologies, and (iii) discuss the R&D needed to advance the clean-up technologies. Each session began with a plenary session with 4-5 speakers presenting on the topic and then serving on the panel leading an open discussion. The panel discussion was followed by the breakout session, where the participants split into three groups of approximately 14 participants to address the questions posed for that breakout session. At the end of the session the representative of each breakout group summarized the outcome of the discussions.

# Introduction and Overview Session

Fuel cells generate electric power more efficiently than competing technologies by virtue of the electrochemical conversion of chemical energy to electrical energy. Introduction of these highly efficient systems into the many power generation applications in the US and globally can have an enormous impact on fuel savings and greenhouse gas emissions reduction. The Department of Energy's Fuel Cell Technology Office (FCTO) plays a leading role in supporting the research, development and demonstration of fuel cells in both transportation and stationary applications. Fuel flexibility will amplify the stationary applications of fuel cells. This includes infrastructure fuels (e.g., natural gas), renewable fuels (e.g., biogas), and recovery and reuse of waste streams with significant calorific value such as LFG and APG. Fuel flexibility poses a common challenge of dealing with impurities that can sharply diminish the efficiency of the fuel cell systems by poisoning the functional elements (e.g., fuel processing catalyst and electrocatalyst).

During the introductory session the potential of fuel cells and the growth of this technology in past and future were highlighted. Also the opportunities that can result from expanding the fuel base and challenges of dealing with fuel impurities were identified. Natural gas with its wide infrastructure can be used to fuel stationary fuel cell systems in remote, distributed, or central power generation applications. The use of APG in fuel cells can provide power while significantly reducing greenhouse gas emissions at the fuel extraction / production sites. GP Renewables presented a case study showing how government incentives can translate to large cost savings for a fuel cell plant fueled by APG. Renewable fuels such as liquid bio-fuels and biogas from landfills, etc. can power nearby residential areas or offset the power demands of industry.  Experience operating fuel cell plants with these fuels has affirmed the need for improved, less expensive clean-up technologies.  Currently each type of fuel requires a custom designed clean-up system because of the limited operating range for different contaminants. Few lessons learned from operating these plants are:  difficulty of removing some sulfur species, e.g., carbonyl sulfide (COS); complexity and high cost of small scale hydrodesulfurization (HDS); and simplicity of cold clean-up options.

## DIMITRIOS PAPAGEORGOPOULOS, U.S. DOE

The Fuel Cell Technologies Office (FCTO) in the Office of Energy Efficiency and Renewable Energy (EERE) at the U.S. Department of Energy manages an integrated effort, structured to address all the key challenges and obstacles facing widespread fuel cell commercialization. More than 200 projects are currently funded in industry, national laboratories, and universities/institutes.  The projects cover a wide range of R&D, demonstration, and deployment.  At the time of the presentation nearly 1600 fuel cell systems have been deployed in applications such as material handling and critical load backup as a result of DOE funding.

Dr. Dimitrios Papageorgopoulos, the fuel cell program manager in FCTO presented the workshop's overview and purpose. The presentation highlighted applications and benefits of fuel cells such as high efficiency and fuel flexibility.  Fuel cell market penetration and acceptance were demonstrated by the 48% increase in global megawatts of electricity shipped and the 62% increase in North American fuel cell systems shipped in 2013.  Several worldwide automakers have announced plans for commercial fuel cell electric vehicles (FCEVs) within the 2015-2017 timeframe.

Natural gas, biogas, and APG resources provide opportunities for stationary fuel cell powers, such as distributed generation and combined heat and power (CHP), as well as for transportation.  It is estimated that approximately 11 million FCEVs could be fueled by hydrogen from biogas and 3 million FCEVs from landfill gas. The amount of APG currently being flared in the US have the potential to generate approximately 8 GW fuel cell powered CHP, and it could reduce the greenhouse gas emissions significantly.

The main issue with renewable resources is their impurities.  The effect of these impurities on fuel processors and fuel cells can be severe and the cost and system complexity associated with removal can be substantial, as highlighted in a key report in this area[2], where it is estimated that the clean-up of biogas costs 14-22% cost of electricity or approximately 2 cents/kWh.

## GABRIEL PHILLIPS, GP RENEWABLES

GP Renewables & Trading presented a general overview of natural gas fuel cell technology, its benefits and potential applications. After an introduction on how fuel cells work presenter made an economical case that natural gas drillers should deploy fuel cells on-site at drilling locations and man camps.

To make this case, the presentation explored the issue of excess, low-value natural gas that is produced through the hydraulic fracturing process resulting in the practice of flaring at the well head. Given the environmental consequences of the high amounts of flaring going on in the US at various drilling sites, fuel cells can be used to reduce various types of emissions by capturing the wasted gas. By placing fuel cells at drilling sites, low-cost electricity can be generated to support operations. A basic Levelized Cost of Electricity (LCOE) analysis presented to show the points at which fuel cells can reach parity with the cost of getting grid supplied electricity to the drilling sites.

[2] http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/fuel_quality_stationary_fuel_cells.pdf

For example, a 10-year grid supplied power would cost $9M, compared to $4.8M from an onsite fuel cell generation plant after incentives. In summary, the presentation advocated the use of fuel cells as a distributed power source to be put on-site across drilling locations.

## MOHAMMAD FAROOQUE, FUEL CELL ENERGY

FuelCell Energy, Inc. (FCE) has been selling commercial fuel cell power plants since 2003. These plants are based on its internal-reforming molten carbonate fuel cell (MCFC) technology dubbed the Direct Fuelcell® (DFC). The DFC fleet (consisting of 300 kW, 1.4 MW, 2.8 MW size plants) has attained a field capacity over 300 MW (installed + backlog) globally operating on various types of fuels including pipeline natural gas, liquefied natural gas, and biogas. The clean-up system design has been an important consideration for plant reliability and cost-of-electricity. The commercial DFC power plant comes with a standard gas clean-up system for operation on US pipeline natural gas fuel. For dual fuel operation on biogas, additional custom-designed clean-up system is used.

Hydro-desulfurization (HDS) is a proven technology widely used in large scale chemical and refining industries. However, it needs hydrogen for efficient operation, which is not readily available for clean-up systems. The very first Santa Clara demonstration fuel cell power plant (1.9 MW) in 1995 used a HDS process that was found to be more complex, more costly, and less reliable than a similarly sized cold clean-up system. FCE recognizes that the optimum choice for a fuel clean-up design (the cold clean-up vs. the high temperature hydro-desulfurization approach) may depend on fuel type, plant size, fuel cell system design, and other considerations.

FCE focused on the adaptation of cold clean-up for its fleet primarily for system simplicity. The FCE experience with the cold clean-up design for its fleet was presented. FCE currently uses a two-adsorbent mix in two chambers in a lead-lag configuration. FCE believes the current design performs technically but further cost reduction is desired. Some cost data were presented, showing that cleaning up of the natural gas represented 10% of the operations and maintenance (O&M) cost, where spent sorbent disposal was approximately 30% of the clean-up cost. In comparison, the clean-up of anaerobic digester gas (ADG) represented 30% of O&M costs. Depending on the plant size, biogas quality and variability in its contaminants, this number can vary from 20 to 40%. This is a significant opportunity for R&D investment by DOE.

Continuous operation of biogas fueled plants demands the availability of an additional fuel such as natural gas. This is due to the fact that the supply of biogas is unreliable and highly variable in quality. Also, the high moisture content in biogas makes it harder to remove non-$H_2S$ sulfur and halogen compounds.

FCE believes that further simplification of the clean-up design will enhance system reliability and significantly reduce the cost. Specific suggestions include:

- development of an efficient, low cost media or system that can clean non-$H_2S$ sulfurs, such as trace COS, $CS_2$, and organic sulfides (fuel moisture tolerant and applicable to both natural gas and biogas);
- development of an efficient, low cost media or system that can remove trace halogens, especially organic fluorides and chlorides (very important for landfill applications);
- design of a gas clean-up system that is fuel flexible, and cleans both biogas and pipeline gas (one system for multiple fuels);
- and, development of online monitoring of cleaned gas stream for sulfur to maximize use of adsorbents and increase reliability of fuel cell protection.

# Plenary-1: Fuel Opportunities and Impurity Issues

In addition to cost, the primary global issue concerning gas clean-up for fuel cells is the variability of the contaminants present and their concentrations that vary with the type of fuel (NG, LPG, ADG, APG, LFG, etc.) and the consistency of the source of the fuel. The most important contaminants include sulfur compounds (hydrogen sulfide, carbonyl sulfide, carbon disulfide, di-methyl sulfide, methyl-ethyl sulfide, odorants), siloxanes, halogens, and, to a lesser extent, ammonia. Fuel cell systems have low tolerance for these compounds, showing significant degradation at concentrations in the parts per million (ppm) range or lower. Secondary issues include the lack of low-cost accurate sensors for online real time monitoring of contaminants, and the lack of low cost options for disposal of spent adsorption materials.

Contaminant effects include chemical degradation of fuel cell components (catalysts, electrolytes) and fuel processor equipment (catalysts, materials of construction). For a given contaminant, the degradation mechanism and the severity/reversibility vary with fuel cell type and are influenced by temperature and humidity. The presence of water in the fuel stream can reduce the capacity of sorbent beds by blocking sites.

Removal technologies exist for the contaminants of interest although they add cost and complexity to the system, especially when multiple (competing) contaminants are present. Improved capacity and selectivity (or the ability to handle multiple contaminants without loss of capacity) are needed to alleviate the cost of clean-up.

The lack of accurate low-cost sensor/detection technologies results in overdesign of the beds and preemptive early replacement to prevent contaminant breakthrough. Siloxane detectors based on a Fourier Transform Infrared (FTIR) analyzer and novel analysis method which provides accurate onsite siloxane measurements in real time was presented by MKS Technologies. Validation of the method is complicated by the difficulty of securing reliable calibration standards.

## PLENARY-1 PRESENTATIONS

### RICK KERR, DELPHI

One of the challenges for a solid oxide fuel cell (SOFC) powered auxiliary power unit (APU) for trucks is to utilize the same ultra-low sulfur diesel (ULSD) fuel already onboard in the truck's main fuel tank. However, ULSD contains a maximum of 15 parts per million by weight (ppmw) sulfur, which is a known poison for many SOFC anodes. In order to utilize (up to) 15 ppmw ULSD, the APU would need hot desulfurization or perhaps a control strategy to operate on the sulfur-containing reformate and manage the resultant power loss.

The performance of an SOFC APU operated on ULSD reformate without a desulfurizer was presented. The effect of sulfur on SOFC performance at high fuel utilization is significantly more pronounced in ULSD reformate than in hydrogen-based fuels alone. Sulfur has a significant impact on the water gas shift reaction and the ability of the SOFC to utilize the CO fraction of the ULSD reformate. SOFC stack performance decrease has been measured at sulfur levels as low as 25 ppbv.

While operating without a desulfurizer does result in lower power output, it could offer some advantages, including lower initial hardware cost, lowered overall system pressure drop, and lowered thermal mass during startups.

### ANTHONY LITKA, ACUMENTRICS SOFC CORPORATION

With the support of DOE and the Department of Defense (DOD), Acumentrics has been developing small tubular SOFCs for 14 years as part of its portfolio of ruggedized power electronics products. The small tubular design is very forgiving of large thermal gradients enabling rapid start-up and shutdown, reaching their operating temperature between 700° and 800°C within 30-40 minutes.

The anode supported fuel cell coupled with an integrated reforming technology will operate on all logistic fuels of interest, including JP8 and diesel; however, initial commercialization has focused on natural gas and LPG fuels for the remote power market. These commercial units have been successfully deployed in remote areas where grid electricity is unavailable and the fuel efficiency, reliability and environment friendliness of the fuel cell is of greatest benefit to the client. Acumentrics has deployed hundreds of fuel cells in inhospitable environments, with the earliest commissions approaching 20,000 hours of operation with near 100% availability. The cumulative fleet operation is in excess of 1 million hours.

The nature of these markets requires that the SOFCs run on the fuels that are conveniently available: well head and liquid petroleum gas. Associated gas is also a possibility and is similar in chemical makeup to non-associated gas. The gas cleaning in these applications still centers on sulfur removal. The presentation showed data on sulfur species observed in LPG tanks and non-associated gas. Sulfur species and concentrations in these gases vary significantly, with location and time. This variability has ramifications for the life cycle cost of gas cleaning. An example is the presence of Carbonyl Sulfide (COS) which while not an odorant, is not uncommon in LPG, with concentrations as high as 150 parts per million by volume (ppmv) observed. The clean-up bed must be sized for the worst case (150 ppmv). Since online monitoring is expensive, and the cost of COS breakthrough into the fuel cell can result in SOFC failure, the beds are changed on schedule assuming the worst case scenario. This results in an under-utilized bed for most situations. Low cost sulfur sensors will allow better utilization of the bed capacity and help commercialize fuel cells for remote applications by decreasing costs.

## OLGA MARINA, PACIFIC NORTHWEST NATIONAL LABORATORY (PNNL)

An assessment of the tolerance to impurities present in biogas and other fuel types is necessary to project lifetimes of fuel cell systems operating on those fuels. PNNL has developed a significant base of knowledge, equipment, expertise, and experiences relevant to testing fuel gases containing single or multiple impurities. PNNL has the capabilities to extend those studies to address the role of impurities by identifying degradation mechanisms, establishing tolerance limits, and by developing recommendations for the clean-up. Few related studies presented by PNNL are:

*The interaction of phosphorus in synthesis gas with the nickel-based anode of solid oxide fuel cells.* Two primary modes of degradation were observed. The most obvious was the formation of a series of bulk nickel phosphide phases, of which $Ni_3P$, $Ni_5P_2$, $Ni_{12}P_5$ and $Ni_2P$ were identified. Phosphorus was essentially completely captured by the anode, forming a sharp boundary between converted and unconverted anode portions. These products partially coalesced into large grains, which eventually affected electronic percolation through the anode support. From thermodynamic calculations, formation of the first binary nickel phosphide phase is possible at phosphorus concentrations < 1 ppb in synthesis gas at typical fuel cell operating temperatures. A second mode of degradation is attributed to surface diffusion of phosphorus to the active anode/electrolyte interface to form an adsorption layer. Alkali carbonates were found to be especially effective in the capture of phosphorus from synthesis gas.

*HCl interaction with both MCFC and SOFCs.* For SOFCs, exposure to up to 800 ppm HCl resulted in reversible poisoning of the Ni/zirconia anode by chlorine species adsorption, the magnitude of which decreased with increased temperature. Performance losses increased with the concentration of HCl to 100 ppm, above which losses were insensitive to HCl concentration. Neither cell potential nor current density had any effect on the extent of poisoning. No evidence was found for long-term degradation that can be attributed to HCl exposure. Similarly, poisoning of MCFC anodes was insignificant. Loss of the molten carbonate electrolyte in MCFCs over very long exposure times is anticipated, due to volatilization of alkali chlorides. Effective clean-up options for chloride in synthesis gas exist, including absorption by calcium oxides/hydroxides.

*Exposure of Ni/YSZ anodes to hydrogen sulfide.* Such exposure resulted in a rapid but minor power output loss for both MCFCs and SOFCs. The extent of poisoning was dependent on sulfur concentration, temperature and current density, and was essentially completely reversible. The mechanism of sulfur poisoning appeared to be due to adsorption on active sites at the triple-phase boundary, affecting the rate of the electrochemical reaction. For MCFCs, dissolution of sulfur compounds into the molten carbonate electrolyte is possible.

## BARBARA MARSHIK-GEURTS, MKS INSTRUMENTS

The prevalent siloxane analysis for a biogas sample is a laboratory-based gas chromatographic method that includes a gas sample collection and transportation to an analytical laboratory to be analyzed for siloxanes. This process could takes anywhere from 3 to 7 working days to accomplish. MKS Instruments has a Fourier Transform

Infrared (FTIR) analyzer and novel analysis method which provides accurate onsite siloxane measurements in real time for use at landfill and digester plants for on demand or continuous siloxane measurements directly on the gas sample. This system uses a patented analysis method which is capable of analyzing the presence of low level (<0.2 $mg/m^3$) total Si from siloxanes and employs a total siloxane number rather than speciation of the siloxanes. Testing of the FTIR method was performed at several landfill sites where numerous gas samples (as well as duplicates) were taken and sent to several siloxanes detection laboratories for analysis. The laboratory analyses were to be used as the "golden standard" by which the FTIR results would be scaled against (if needed) in order to produce a total Si number that would be on the same order as those reported by the laboratory.

However, there were issues with the laboratory results even amongst duplicate samples that were run, so that it was unclear as to what value should be used to scale the FTIR data. There are a number of reasons for the inconsistent results seen at the various laboratories which were analyzing the same gas sample such as: sample collection; shipping and handling issues; siloxane conversion during the shipping process; as well as the fact that there are no gas standards available to make accurate siloxane calibrations. Issues were found when trying to generate high siloxane concentrations with permeation devices. At first there were no gas suppliers to provide cylinders with such concentration of siloxane that were available at the start of this testing. However once a gas supplier had been found that could produce blended siloxane gases, it was decided to validate the FTIR directly in the field using an analyte recovery method. This is similar to American Society of Testing Materials (ASTM)[2] Test Method D6348-12, since the cylinder was accurate only to ± 20% of the stated values and there were no long term stability data available. Validation of the FTIR can therefore be accomplished by using the analyte spike recovery test which shows that the system is truly responding to the analyte of interest while in the actual background gas sample. This method also minimizes the error due to the cylinder concentration and long term viability as the gas is run on the FTIR prior to the spike into the biogas so any changes in concentration are captured.

## PLENARY-1 PANEL DISCUSSION

For natural gas, diesel and APG, the panel members agreed that the principal concern was sulfur. Hydrodesulfurization was not very attractive to the fuel cell developers.

Siloxanes present in the fuel can be tolerated by the surface active components downstream at very low levels, but the effect builds with time. Even 1 ppm of siloxanes show a significant effect on a button cell of the solid oxide fuel cell. Elaborating on the siloxane issue, the panel explained that the problem with these species is that they form $SiO_2$ (silica) on oxidation which then deposits on critical surfaces as a fine glassy layer.

Delphi's SOFC operating on sulfur-containing fuels shows a sharp initial drop in performance which then levels off. Removal of the sulfur in the fuel recovers most of the performance that was lost.

Analysis of the siloxane concentration is currently determined by sending off gas samples to a laboratory, and typically requires 2-3 samples for a reliable analysis.

In addition to FTIR, gas chromatography – mass spectroscopy (GC-MS) can be used for analysis. Unfortunately, GC columns degrade in the presence of chlorinated hydrocarbons giving false siloxane readings.

## PLENARY-1 BREAKOUT SESSION

The following questions were posed to the participants.

1. ***What are the impurities that have the greatest impact on the cost, complexity and performance of the fuel cell plant? What impurities are common across fuels? Which are unique?***

   The participants identified the most detrimental impurities for the fuel cell system including fuel processing equipment, as carbonyl sulfide, dimethyl sulfide (DMS), hydrogen sulfide ($H_2S$) and thiophenes. They indicated sulfur impurities are common across fuels, and are found in fossil fuels, APG and all biogas. Siloxanes were indicated as being common impurities in landfill gas, digester gas, and gasified biomass. Metal impurities were indicated as a concern in gasified biomass, while selenium impurity concerns were restricted to biogas. Phosphorus and halocarbon impurities were concerns unique to biodiesel and landfill gas respectively.

[2] http://www.astm.org/Standards/D6348.htm

2. ***What are the issues associated with the use of APG as a fuel for fuel cells?***

   The participants indicated that the variability in APG composition, both geographically and temporally, make it difficult to design generic clean-up equipment and protocols. In addition, the combination of sulfur impurities and hydrocarbons other than methane make it difficult to remove the sulfur and siloxanes. The sulfur sensitivity of most reforming catalysts (sensitive to S at ppb levels) requires that sulfur is removed before the reformer.

3. ***Is there a need to establish/develop a purity spec for the FC plant (reformer and fuel cell) operating on biogas? Other "raw" fuels?***

   It would be beneficial to FC companies to know the level of impurities in the fuel gas supply. There can be a minimum standard which limits the levels of impurities allowed; while suppliers and fuel cells companies can design 'cleaner' fuel if that is needed.

4. ***For which impurities are there no completely satisfactory removal technologies; for which do solutions exist but the solutions have technical shortcomings such as poor selectivity; and for which are the technical solutions adequate but the current cost is too high and system simplification would be desirable?***

   The solutions for the removal of $H_2S$, siloxanes, and metals such as copper and heavy metals, are adequate, but the costs were deemed too high. There are technical shortcomings in the systems for removal of sulfur impurities (other than $H_2S$), siloxanes, halides, ammonia, and heavy hydrocarbons. There are also technical shortcomings dealing with the variability in APG impurity composition. No completely satisfactory (low cost and technically effective) technology exists for removal of sulfur impurities (COS, DMS, $CS_2$, etc.) and siloxanes. Siloxane tolerance levels have not been definitively established, and the current approach involves complete removal by cooling the fuel stream. Affordable online monitors for all impurities would be beneficial and would decrease operating cost by reducing the need to overdesign clean-up systems.

- ***Other Issues***

  Poor sorbent selectivity for the impurities is a common issue. Water and oxygen interact with many of the sorbents to reduce capacity, or produce unintended compounds. This reduces bed capacity and increases costs. As stated above, there is also a need for inexpensive analytical devices with better resolution. A good online analyzer for sulfur impurities would be very beneficial, but even inexpensive off-line analysis at the appropriate concentration levels would be an improvement. Sample rates around once per week would be acceptable.

  The participants did not think a purity spec was needed and one may not be beneficial because different fuel cell types have different tolerances to impurities. If one were developed, it should be a minimum standard, which would allow companies to design a gas clean-up process that generates a "cleaner" fuel if that is needed for a particular fuel cell type.

  The presence of water and some hydrocarbons is not harmful to the fuel cell system but they strongly adsorb on the media, thereby blocking adsorption of the deleterious impurities. A surge of water vapor / moisture in the fuel stream has been shown to displace / release some of the trapped sulfur species from the media. Moisture removal upstream of these sorption media is beneficial in that the full capacity of the media can be used for the removal of the deleterious species and prevents any release of previously trapped sulfur.

# Plenary-2: Industry Experience with Management of Fuel Impurities in Real World Applications

Impurity removal technology is available and is greatly affected by the scale of the application. Sulfur removal in large scale applications is dominated by the Claus ($H_2S+1/2O_2=S+H_2O$) process or hydrodesulfurization. The latter is effective but is complicated since it requires gas compression (high maintenance), hydrogen recycle (not available at start-up), and should be preceded by moisture removal as moisture content reduces $H_2S$ absorption. Since fuel cells require sulfur content to be limited to parts per billion, bulk sulfur removal is usually followed by polishing steps using sorption media. Siloxanes are removed with sorption media sometimes in combination with chilling. The siloxane removal capacities of the media are relatively low and decrease even further if the gas contains higher hydrocarbons and/or moisture. Some halogen species can be removed in low temperature media beds, while others require hydrolysis at elevated temperatures followed by getters (e.g., ZnO).

Pressure swing adsorption is a very effective method and is popular as a separation device in large scale chemical and petrochemical plants.  However, these systems are not cost-effective for the smaller fuel cell systems and not much developmental work has been pursued for smaller units.

Demonstration plant operation has shown potential in meeting targeted impurity concentrations after clean-up. Occasional breakthrough of the impurities past the clean-up system have been caused by factors such as spikes in the impurity concentrations in the feed gas and the lack of online sensors to detect the spike or breakthrough of the impurities.

Gas analysis to determine impurity concentrations is available by using GC-MS (offsite), x-ray fluorescence or energy dispersive systems. Smaller fuel cell systems are hard pressed to justify the investment and may resort to overdesign of the clean-up system. Since the impurity in the final gas to the fuel cell is targeted in the parts per billion, sampling and quality assurance of the analysis are important.

The unit cost of media used in the gas clean-up system is not very high, although the removal capacities of the media tend to be low so the final cost is high. The cost and complications of the clean-up system arise from the need to use multiple processes in a customized train, which may require ramping (or cycling) of pressure and temperature, humidity control, bed overdesign, and spent media disposal (labor intensive and hazardous). The custom design applied to each of the demonstration projects, where the fuel and clean-up targets have varied, suggests that a broader market demand can facilitate the development of generic systems with the desired economy of scale.  For the near term, cost targets for the clean-up systems should be $500/kW for CapEx and less than 1 cent/kWh for OpEx. For the long term, additional reduction to <$200/kW and 0.5 cents/kWh will promote fuel cell deployment.

## PLENARY-2 PRESENTATIONS

### ELLART DE WIT, HYGEAR B.V.

Most of the sulfur in European natural gas is removed at the well. NG from Russia and the North Sea contain some $H_2S$ and COS, while most overseas supply of NG arrives as liquefied NG and thus contains no sulfur. Most of Europe adds tetrahydrothiophene (THT) to their natural gas, with some regions using mercaptans as the odorant. Industry suggested the use of non-sulfur based odorants, which is used in a few German cities, but HyGear does not expect a wide use in the near term. Plasma cleaning and catalytic candles were mentioned as two promising technologies.

$H_2S$ removal is primarily based on the Claus process in large applications, while scavengers are used where the sulfur removal load is low. The scavengers reduce the sulfur to ppm levels, and have to be followed with polisher beds to get down to the ppb levels. HDS is hardly used in small fuel cell systems since there is no hydrogen available at start-up and the presence of water in the reformate diminishes the capacity of the ZnO sorbent.

The technology to remove each of the contaminants is available, but the market for cost effective solutions is not mature. Hygear studies have shown that combinations of zeolites, metal-based sorbents are proving effective. Besides the cost and complexity of clean-up, the problem is aggravated by sorption competition from water and higher hydrocarbons. A major issue in household applications is that the spent cartridges become toxic and flammable, leading to a hazardous material inventory and disposal problem that is difficult and expensive.

Some European organizations are exploring the use of gasifier for use with fuel cells. One contentious issue is that tar present in the gas condenses and polymerizes to deposit on critical surfaces and thus their use hinges on effective tar removal. The cost of tar removal has been identified as a major cost component, and thus more cost effective solutions are being sought.

## MICHAEL MITARITEN, GUILD ASSOCIATES

Siloxanes are a fairly recent and growing challenge in the beneficial use of biogas. Increasing market use of siloxane containing components has led to an increase in the presence of siloxanes in the vapor phase biogas generated by landfills and wastewater treatment plant digesters. In combustion processes siloxanes form hard particles of silica on boiler tubes, gas engine and turbine internals, and in fuel cell and post-combustion catalysts. For these reasons interest and implementation of siloxane removal systems is on an increase.

The purification of biogas to pipeline quality is a growing market, with many dozens of systems in operation throughout the world. Some of the purification methods for biogas are pressure swing adsorption (PSA), water wash scrubbing systems, membranes and solvent systems such as amine or physical solvents. Each of these systems has advantages and disadvantages and there is no universal answer for a specific project. However, it is universally true that production of pipeline gas largely removes siloxanes in these gas clean-up systems or through associated additional processing.

Since upgrading to pipeline quality is expensive, less expensive systems targeted at siloxane removal are becoming common. These systems are generally based upon siloxane adsorption on a fixed bed of media which can either be disposed when saturated or through a cyclic process where the media is regenerated on site. Development efforts have focused upon better media for siloxane removal and this remains as a logical future R&D activities. Better media can lead to lower cost systems, longer life between bed changes for non-regenerated systems or can reduce cost and improve operations in regenerated systems. This presentation outlined the current status for siloxane removal with a focus on media-based systems, which can be broadly categorized as: (i) non-regenerative adsorption systems that are appropriate for smaller flows and lower concentrations, and (ii) regenerative adsorption systems for large flows and higher concentrations, with hot air regeneration and flaring. Some recommendations include the development of higher capacity (loading per unit mass) of the media and balancing the capacity with regenerability, lower cost siloxane measurement options, media optimization for co-removal of $H_2S$ or reduce $H_2S$ interference on removal of other impurities.

## MARK RILEY, UOP

The level of fuel contaminants decreases as the fuel is cleaned up to meet commercial specifications, used to produce hydrogen, and fed to the fuel cell to produce electricity. Trace levels of impurities are typically removed using fixed beds of adsorbents. While the specifics may vary with the technology providers and the fuel, commercially proven technology exists at each stage of the transformation of fuel into electricity. Various technologies are available for the removal of impurities; however, from an economic/business point of view the fuel cell manufacturers would like to see less expensive technology that can clean-up fuels to their standards.

## GOKHAN ALPTEKIN, TDA RESEARCH

Conventional gas clean-up systems do not meet the gas purity requirements of bio-fueled fuel cells. Presence of high concentrations of moisture and in some instances high concentrations of oxygen (0.1 to 2% vol.) reduces the sulfur removal capacity of conventional adsorbents. Contaminants such as dimethyl sulfide and carbonyl sulfide are particularly difficult to remove from high moisture gas. The gas compression and refrigeration options to reduce the moisture content of the gas significantly increase the parasitic power loss and the cost of electricity. TDA Research/SulfaTrap LLC is developing high capacity ambient temperature sorbents that can reduce the sulfur concentration to ppbv levels. SulfaTrapTM–R7 has a capacity of over 25 mg-S/g sorbent for the removal of $H_2S$. Data was also presented on the capacity of their sorbents with other sulfur species such as methyl ethyl sulfide, tetrahydrothiophene, dimethyl sulfide, COS, and methyl mercaptan. Field studies at the ADG-fueled fuel cell plant in Tulare, CA have shown the ability to remove siloxane. TDA believes that a useful supplement to the high performance sorbents is an inexpensive sulfur sensor that will indicate the end-of-life to ensure maximum utilization of the sorbent and any sulfur slippage that may occur as a result of the high fluctuations in the inlet sulfur concentration.

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## ALAKH PRASAD, QUADROGEN POWER SYSTEMS

Biogas (from landfills, wastewater treatment plants, or agricultural digesters), a source of renewable energy, is derived from the decomposition of organic waste matter into methane and $CO_2$. Typically, raw biogas also contains many harmful contaminants that require removal prior to utilization in fuel cells, turbines, or reciprocating engines. Current conventional gas clean-up systems have limited capability to consistently remove contaminants that can be harmful to downstream power generating equipment.

Quadrogen Power Systems has developed a high performance biogas clean-up solution that can remove all sulfur species, siloxanes, chlorides, water, oxygen, and other impurities to the ppb level. Quadrogen recently completed a successful demonstration of its biogas clean-up system with Air Products and Chemicals, and FuelCell Energy at the Orange County Sanitation District's Wastewater Treatment Plant. Ongoing independent testing has shown that all sulfur and halogen species at the outlet of Quadrogen's clean-up system have remained below the 25 parts per billion detection limit of the gas analysis instruments since May 2011. Siloxane species have also remained below the 100 ppbv siloxanes detection limit.

Currently, Quadrogen is leading another demonstration project – "Quad-generation from landfill gas at Village Farms" in Delta, BC, Canada, where landfill gas is cleaned to co-produce renewable electricity, heat, hydrogen, and ultra-clean carbon dioxide for use in greenhouses. The Quad-generation project will demonstrate Quadrogen's

Biogas Clean-up System and $H_2$ Booster technology (which is combined with FuelCell Energy's Direct FuelCell and hydrogen separation technology) to meet the project objectives.

Quadrogen is also developing a novel clean-up and conversion process for APG. APG is typically flared or capped at drilling sites because the heating value of APG (due to the presence of heavier hydrocarbons) prohibits its utilization in fuel cells and engines. By converting the heavier hydrocarbons present in APG into methane using Quadrogen's proprietary hydrogen assisted reformation process, natural gas is produced and can be used for on-site power generation at remote drilling wells.

Quadrogen has a proprietary biogas clean-up system, named the C3P technology that consists of four steps beginning with condensing, followed by conversion of the sulfur species into fewer species that are then adsorbed on high capacity media. The remaining impurities are then brought down to specified limits with the help of a polishing medium. Quadrogen recommends studies to validate the performance of clean-up technologies with APG and to determine the lifecycle of these technologies.

## PLENARY-2 PANEL DISCUSSION

The panel discussion after plenary 2 focused on the different types of clean-up systems, their applicability to fuel cell systems, and their effectiveness. Panel members agreed that current custom-designed, clean-up systems can be effective, and cost of the clean-up systems is the main issue. Panel members thought a universal gas clean-up system for multiple fuel gases would be highly desirable as it would benefit from economies of scale. Since cleaning landfill gas is the most challenging, developing a generic system for landfill gas clean-up would work for most systems. However, that system would have components that may not be required for some applications.

The potential for PSA systems for fuel cell applications was discussed. PSA is very popular in large plants for the extraction of high purity hydrogen from a reformate stream, but has found limited use in fuel cell applications to date. One reason is scaling. The cost of PSA decreases to half with a fourfold increase in size, making their use in smaller systems less cost effective. The offgas from the PSA contains heating value (flammable components) that is used to generate heat for other endothermic processes. This is useful in refineries, where the heat can be readily utilized. Since fuel cells, especially high temperature fuel cells, generate surplus heat, these systems are unable to recover the energy content of the PSA offgas. There also has not been sufficient interest in the development of PSA for the small and medium sized fuel cell applications, contributing to high costs due to a lack of economies of scale. Some panel members expressed the opinion that there should be an effort to develop PSA systems for small and medium size fuel cell applications.

The non-sulfur odorant Gasodor, being tried in Europe, is nitrogen based and has no detrimental effect on the fuel cell. While the nitrogen can form ammonia, tests have shown that this is not an issue.

Strategies for determining sorbent bed saturation were discussed. Different organizations use different strategies. Guild monitors $CO_2$, taking the bed offline when the $CO_2$ concentration in the outgas rises. Small CHP applications do not regularly monitor impurities, and instead swap their beds long before they anticipate saturation. TDA and UOP make a determination based on the cost trade-off between sensors and overdesigned / unused media. Considering that siloxane monitoring is expensive, the use of sensors is more difficult to justify for small systems.

There was significant discussion surrounding clean-up costs. Costs for biogas clean-up systems were estimated to be approximately \$600K for 100 standard cubic feet per minute (scfm) and \$800K for 300 scfm at one-off price. Volumes of 50 can reduce cost by ~ 20% and volumes of 1,000 can reduce cost by 50%. Using one material/adsorbent versus two could save ~ 10% in cost. In Europe there are a lot of smaller (50 kW and smaller) applications. At 50 kW, clean-up becomes a high fraction of cost, and handling and labor costs become significant, with current sulfur removal material cost being estimated at as much as ~\$1/kWh. The current materials for bulk contaminant removal are produced in large volumes and are cheap. However, some of them have high costs of removal and disposal. Size and numbers for market are important factors in new materials development. Since the sorbent material cost is so cheap the development focus should be on better performance.

Halogens and halogenated compounds can be a concern. Quadrogen's field experience shows the inlet streams to their media beds contained 50-100 ppbv of halogens. This is relatively low when compared to other landfill gas that reportedly contain much higher (ppm levels) concentrations of refrigerants (halocarbons).

## PLENARY-2 BREAKOUT SESSION

The following questions were posed to the participants.

1. ***How close do current clean-up technologies get to targets (including cost)?***

   Workshop participants concluded that the current technologies can meet the technical targets in terms of removing impurities to the desired levels, but clean-up costs are too high. Cost targets for clean-up systems were identified to be: CapEx < $500/kW, OpEx < 1 cent/kWh. Larger systems are able to approach the total cost targets to within 50%. For smaller systems, the cost targets are ~30% of current costs, i.e., 70% cost reduction is desirable.

   Factors contributing to the high cost include absorption of water on absorbents, which reduces absorbent capacity for the impurities of interest and leads to a requirement for moisture removal equipment; incompatible temperature regimes for absorbents and other process equipment, which leads to requirements for chillers, compressors, and/or heat exchangers; high spent sorbent disposal costs due to the presence of flammable and/or hazardous materials; and oversizing of beds and equipment for worst case scenarios due to inadequate online analytical equipment.

   Sulfur removal technology is available, although multiple steps may be required to deal with the variety of sulfur species. Sulfides (Dimethyl sulfide/methyl-ethyl sulfide) are removed with ambient temperature sorbents at a cost of removal of up to $550 per pound of sulfur. The effectiveness of these sorbents is compromised by the presence of moisture, so moisture needs to be removed first. Other techniques such as membrane technology or oxidation are not considered promising alternatives. Some organic sulfur species are not effectively removed with sorbents, and need to undergo hydrodesulfurization to convert them to a more readily absorbed or adsorbed species. Likewise, carbonyl sulfide can be removed fairly easily at higher temperatures (>400°C) by hydrolysis to convert to $H_2S$, followed by reaction or adsorption on suitable media. High temperature media are better after reformers as this would avoid having to cool and then reheat the gas.

   Halogens and halogenated compound removal is similar to sulfur and sulfide removal. Halogens are removed via sorption on molecular sieve, carbon or zeolite based sorbents. Moisture interferes in halogen removal effectiveness. However, some halogenated compounds require high temperature hydrotreatment to convert them to readily absorbed species.

   Siloxane removal usually includes adsorption on carbon under chilled conditions, at temperatures around -20°F. This requires additional equipment such as compressors and chillers, and increases parasitic power demands and cost.

   Pressure Swing Adsorption that is cost effective for large refinery scale applications, is not considered to be a cost effective option in small- or medium-sized plants.

2. ***What is the major cost in current clean-up technologies (energy, materials, waste disposal, testing/sensing/sensor)?***

   Hydrodesulfurization, material disposal, and analytical costs were identified as the major costs in current clean-up technologies for stationary fuel cell plants, while the lack of economies of scale was identified as an additional reason for high costs for fuel clean up. HDS represents a major component of the balance of plant (BOP) capital cost. Although there is extensive experience utilizing HDS in refineries, there has been little work done towards the development of HDS for smaller systems. The high pressure desired for HDS requires use of a compressor which adds to the capital and maintenance costs. Integrating HDS into a stationary fuel cell system is challenging due to start-up issues (HDS utilizes $H_2$, which is not available at plant start-up) and the variable processing rates in the fuel cell duty cycle.

   Material disposal is also a major cost associated with fuel clean-up. Disposal of spent media is labor intensive and expensive. Some spent sorbents are classified as hazardous waste or flammable material, demanding additional safety considerations and disposal costs. Disposal costs are related to the unavailability of affordable online sensing equipment. Currently, beds are disposed of before they have reached their full capacity, because it is more cost effective to dispose of underutilized beds than to install online monitoring equipment. However, this leads to higher volumes of material to dispose.

The supply and calorific value of biogas is unpredictable, thus NG supply infrastructure is essential for fuel cell power plants.

Developing specifications for fuels at application / plant gate and that required for a fuel cell type would be beneficial for designing on-site clean-up equipment

Materials / media– The cost is the result of a combination of initial price and low impurity capture capacity of some sorbent materials. Often a sorbent has to be replaced because it reaches its capacity for a limiting species or its capacity is diminished by retention of a non-damaging species (e.g., some hydrocarbon species). Examples of some media that are currently used include iron oxides, activated carbon, activated carbon functionalized with Potassium (K), molecular sieves, silica gel, etc.

3. ***What type of clean-up system (generic, modular, integrated with reformer or fuel cell, drop-in, etc.) is best suited for low temperature (<300$^o$C) and high temperature (>300$^o$C) applications?***

Participants concluded that for low temperature fuel cells, regenerable sorbent based clean-up systems are most suitable. The system should be modular to allow for variations to accommodate different fuel feeds without total redesign of the system for each installation, and should be scalable, and sized appropriately for the gas feed stream quality. This eliminates paying for unneeded clean-up capacity and allows the elimination of components that aren't needed for a particular feedstream. Clean-up systems for high temperature fuel cells should be similar and be capable of thermal integration with other parts of the fuel cell system to enable a reduction in total part count.

4. ***What clean-up systems (if any) could benefit from increased volume/reduced cost by use across platforms?***

Sensors could benefit from increased volume/reduced cost by use across platforms. Low cost, 100 ppb sensors could be used across several platforms. Current sensors either don't have the sensitivity (X-ray fluorescence (XRF) sensors are available for measuring 300 ppb) or cost too much (energy dispersive systems can measure at higher sensitivity but cost about 10X more). Online sensors or regular and frequent analysis is essential for effective use of sorbent beds and to identify impurity breakthrough, especially in cases where the impurity level in the feed gas varies unpredictably. ADG from a waste water treatment plant (WWTP) has the potential to destroy a $1M fuel cell, so a $50K sensor would probably be acceptable for that case, but for residential CHP, the sensor cost is not viable. Offsite testing is also often not an option as testing can take two weeks at costs of about $3500/sample. For sources where impurity content varies unpredictably, a two week turnaround is too long. High threshold sensors that could cheaply identify a contaminant spike and protect the stack would be useful.

- ***Other Comments***

Common issues encountered in the gas clean-up system include: (i) thermal management since temperature control involves both heating and cooling, (ii) water management – usually water removal since its presence reduces sorbent capacity, (iii) parasitic energy losses including compression and chilling, and (iv) sensing to determine approach to bed saturation / capacity. Variability in fuel composition and impurity content also lead to increased costs by developing specifications for fuels at the application/plant gate and for a fuel cell type it is beneficial to design on-site clean-up equipment.

# Plenary-3: R&D Needs and Opportunities for Managing Impurities, Avoiding Gas Emissions and Flaring of APG

The session dedicated to identifying needs and opportunities was led by speakers from fuel cell companies, research institutions and universities with wide range of research and development in low and high temperature fuel cells, fuel gas clean-up and high temperature sulfur getters. The low temperature fuel cells which use natural gas and methanol are primarily challenged by sulfur impurities. On the other hand, the higher temperature fuel cell developers have explored a wider range of traditional and non-traditional fuels (NG, LFG, ADG, etc.) that contain the most contentious impurities, sulfur, siloxanes, and halogens. Several demonstration studies have been conducted with biogas, often complemented with natural gas for the production of hydrogen as well as reformate fueled fuel cells.

Although current removal technologies can be and have been adapted to resolve the clean-up of a particular fuel stream, the customized design approach leads to significant cost. The cost contribution comes from numerous factors. Current clean-up systems use multiple getters, usually with multiple temperature steps to remove all the impurities and require customization for the specific fuel stream. The removal capacity of the current generation of getters is low, requiring large heavy media beds. Lack of online sensors forces designers to overdesign the media beds in anticipation of the maximum expected impurity levels. The resultant excess mass and underutilization adds to the cost of the plant and its products. Managing the moisture is an important consideration since the removal of bulk sulfur requires water but the water reduces the capacity of other media. Downstream, water is again necessary in the reformer. Similarly, heavier hydrocarbons which are acceptable in the reformer and the fuel cells sharply reduce the capacity of the media. Thus the sequencing of the removal process and the temperature ramping contribute to the complexity of the plant and the cost. Media that is saturated with hydrocarbons are flammable, while some other impurity content such as sulfur in the spent media classifies it as hazardous waste and imposes a high disposal cost. Some of the recommendations included: developing fuel quality standards; developing sorption media (getters) that combine the ability to capture multiple impurities and high removal capacities that are not affected by moisture or hydrocarbons; developing sensors that enable better management of media capacities; identifying environmentally friendly regeneration techniques for spent media or converting them to useful products to eliminate the high cost of disposal; and conducting more plant demonstration studies. Development of generic modular processes that can be scaled and used in multiple plants and with different fuels will allow cost reductions through economies of scale in clean-up module manufacturing. Fundamental R&D was recommended to develop new media, develop high-temperature high-capacity media, study of the properties of the media, and develop sulfur resistant catalysts.

## PLENARY-3 PRESENTATIONS

### CHUCK SISHTLA, GAS TECHNOLOGY INSTITUTE

The Gas Technology Institute has been involved in four biogas projects: 1) Gills Onions in Oxnard, California, in the clean-up of biogas derived from anaerobic digestion of agricultural waste for on-site fuel cell electricity generation; 2) Altamont Landfill in Livermore, California, in the clean-up of landfill gas to produce liquefied natural gas for vehicle fuel; 3) Ft. Lewis army base in Seattle, Washington, in the production of hydrogen from biogas as a fuel cell based material handling equipment (MHE) fuel and included a clean-up system for biogas generated by anaerobic digestion of waste water, a biomethane reformer system and hydrogen purification and 4) SCRA in South Carolina, in the clean-up of landfill gas and on-site reforming to generate hydrogen for MHE. GTI demonstrated hydrogen purity by compliance with Society of Automotive Engineers (SAE) J2719[3] specifications in the Ft. Lewis and SCRA projects.

The talk outlined the key challenges for biogas clean-up for fuel cells and recommended R&D work such as improving tolerance of fuel cells to contaminants in biogas, generation of database for adsorption properties of biogas contaminants on sorbents and catalysts, development of improved gas quality monitoring sensors, cost reduction of biogas clean-up systems and development of recycling technologies to reduce O&M costs.

[3] http://standards.sae.org/j2719_201109/

### CHRISTOPHER TESLUK, BALLARD

Ballard is working towards a highly compact, efficient and most importantly low cost fuel processor to further expand their telecom backup market as well as to enable fuel cell solutions for a wider range of small stationary and semi-mobile applications. There are two key requirements of this work, namely high durability and low cost, both of which are adversely affected by fuel contamination. The connection between contamination and durability is straightforward; however a quantitative understanding of a contaminant's impact on product life time is neither straightforward nor inexpensive. Even when that data is known, the actual quantity of a particular contaminant in the field can be far from certain, forcing the system to be over-designed to accommodate a wide tolerance, which tends to work directly contrary to the critical need to minimize cost.

From Ballard's experience, investments that could positively impact the success of methanol and natural gas / LPG fuel cell systems include:

1. Effort to determine the types, sources and quantities of contaminants in commercial methanol, NG and LPG in North America.
2. Development of broad-range liquid phase desulfurization.
3. Validation of accelerated contamination life test methods for reforming catalysts.
4. Low cost ppb-level sulfur detection.

### KERRY DOOLEY, LOUISIANA STATE UNIVERSITY

Researchers at LSU design rare earth/transition metal oxide systems using computation, synthesis and characterization to fulfill two functions related to gasifier effluent clean-up and conditioning. The first phase of the work focuses on materials capable of removing sulfur (primarily $H_2S$) at temperatures near those of the gasifier itself (>600$^oC$), and capable of air regeneration. The second phase focuses on catalytically reforming/cracking tars in typical syngas mixtures containing $H_2O$, $H_2$, CO, $CO_2$, $H_2S$ and light hydrocarbons. Naphthalene is the model "tar" compound used. These studies seek catalysts that can demonstrate stability for at least a week, with the primary reforming products as CO and $H_2$. The presentation showed data indicating that (i) the composition of the active phase in the sorbent is key to sulfur capture, with both the active phase and the support playing a role in thermal stability and redox capability, (ii) the combination of the gas species and the adsorbent composition determine the sulfur loading capacity.

### PINAKIN PATEL, FUEL CELL ENERGY

Fuel gas pretreatment systems are needed for cost effective operation of fuel cell power plants. Conventional systems are not fuel-flexible, requiring individual customized solution for each fuel gas. The gas pre-treatment systems are capital intensive and lack robustness. Unplanned maintenance costs are another area of concern. Overall, there is a need to reduce the fuel processing cost from >$2000/kW to <$200/kW to increase wide-spread penetration of fuel cell systems in multiple markets. At <$200/kW capital cost of the fuel-flexible clean-up system, the world-wide market for fuel cells will increase to >100,000 MW.

An impurity removal system that can service the needs of many fuels ranging from natural gas to biogas, to shale gas and coal bed methane is necessary. Some desirable attributes of such a system includes low cost (capital and operating), simple and reliable. Existing clean-up solutions are available and consist of discrete and customized components. Process intensification may offer the ability to approach or meet some of the desired attributes. There is also a need for inexpensive online sensors which will improve system reliability, and Fuel Cell Energy has developed a sulfur sensor with a detection limit of 100 ppb. Development of next generation media that are effective with non-$H_2S$ sulfurs with wet gas, and for the removal of trace halogens are needed.

The development of these gas clean-up systems will benefit from R&D on materials development and sensor technology. Multi-purpose demonstration, outreach to stakeholders, information exchange at national forums, financial incentives for early adopters will directly or indirectly aid the development of such a fuel clean-up system.

## PLENARY-3 PANEL DISCUSSION

Alternative solutions for the desulfurization of liquid fuels such as methanol, diesel, and gasoline are needed, since existing solutions are costly.

Biogas from various sources, such as an onion processing plant, can be hooked up to the natural gas grid if an appropriate clean-up solution can be set up.

There is a need to develop high temperature sorbents that have better stability and regenerability, preferably with air. There have been advances in academia, but major breakthroughs in capacity, etc. are needed to demonstrate commercial viability.

Gasification plants have been demonstrated at the pilot plant scale and need to be scaled up to larger plants to demonstrate commercial viability.

Sludge gasification technologies represent an opportunity and Fuel Cell Energy has looked at six types of gasification at small scales. The sludge gasification product is most attractive for power generation, followed by hydrogen production.

The term “pre-breakthrough” of impurities is the process where the impurity concentrations from a sorbent bed exceed those predicted by equilibrium when the bed has not reached saturation or equilibrium predicted loading capacity.

## PLENARY-3 BREAKOUT SESSION

The objective of the third breakout session was to identify, discuss, and prioritize the R&D that would help manage the removal of impurities from the various fuels in a cost effective manner. The following question was posed to the participants.

1. ***What R&D activities related to fuel clean-up would be most beneficial to advance the deployment of fuel cell systems?***

   The result of the deliberations can be summarized as follows. For the short term (1 to 5 years) the highest priority was assigned to developing real-time online low-cost sensors, as these devices will allow the operator greater control of their process. Knowing the breakthrough or media saturation times will allow full use of the media capacity and reduce the O&M costs. The second highest priority for the short term was the development of adsorbents that can retain their capacity to trap the targeted impurities in the presence of water. Other areas for pursuing short term R&D included the generation of adsorption property data to facilitate prediction of bed saturation / impurity breakthrough by process modeling; establishing impurity specifications (allowable limits) for biogas streams for fuel cell use; developing size exclusion membranes to separate impurity species from the main species of interest (methane); developing a list of key impurities that damage fuel cells and define tolerance limits for the different types of fuel cells; developing accelerated test protocols to quantitatively assess the relationship between impurities, their concentration, and the detrimental effect on different kinds of fuel cells; developing strategies for testing fuel gas slip streams to enable online monitoring; and developing sulfur tolerant reforming and shift catalysts.

   For the long term (> 5 years) the participants identified six strategies. The highest priority was given to the development of a new generation of sorbents (metal organic frameworks or MOFs, nanoscale materials, super hydrophobic, or microbial based materials) which can demonstrate capacities exceeding 10 wt.%, and are selective (water insensitive, super selective based on molecular imprinting). Other recommended technologies included developing “green” methods that can convert the trapped impurities into useful products or where the saturated / spent sorbent can be recycled for other uses, e.g., fertilizers; developing scalable, environment friendly, portable and low cost clean-up systems similar to the automotive catalytic converter; developing odorants that are not based on sulfur, thereby eliminating the need to remove any added sulfur from the fuel; improving the tolerance of the fuel cells to impurities as a way to reduce the extent of clean-up needed and thus lower the fuel cell plant operating costs; and improving the quality of biogas by treating it with sulfur consuming microbes.

   There were several other recommendations that were discussed. These included the development and demonstration of a rugged, modular, and universal clean-up system that could be applied in different fuel cell power plants and thus benefit from economies of scale; a demonstration / study of the use of APG in a fuel cell power plant was suggested; development of low cost sensors such as colorimetric sensors to indicate bed saturation and breakthrough; development of media regeneration methods that are environmentally acceptable; and development of accelerated test methods to evaluate the effect of contaminants on reforming catalysts.

# Conclusions

The sensitivity of the fuel processor and fuel cells to the impurities present in fuels of interest imposes a clean-up cost that adds to the burden of fuel cell systems in stationary applications. Estimates show the clean-up of biogas costs ~2 cents per kWh of electricity, and ~30% of the O&M costs in an ADG fueled power plant.

Sulfur, siloxanes, and halogens are the most damaging impurities or difficult to remove. Sulfur has an immediate detrimental effect on the fuel cell and reforming catalyst performance. Siloxanes have a slower effect by depositing a glassy layer on active surfaces. Halogens can form acid gases and can increase electrolyte loss rates in MCFCs, while other contaminants such as moisture and heavy hydrocarbons interfere with impurity removal because of their greater affinity for the sorbents.

The severity of the detrimental effects on the fuel cell system requires some impurities to be reduced to the parts per billion level, which adds to the cost of clean-up as well as fuel quality monitoring. Current solutions for the removal of impurities in natural gas, biogas (LFG and ADG), and APG are in the market place and can meet clean-up specifications, but these solutions are often overdesigned and costs are too high.

Uncertainties and variations in the impurity levels and the lack of affordable sensors for the impurities at low detection limits leads to overdesign and underuse of the sorbent capacities, which increases costs. Disposal of the spent sorbent which may contain flammable and hazardous material is expensive.

Each plant is designed with a customized gas clean-up system to match the fuel and its quality and the fuel cell application. This limits potential cost savings from volume production.

Fuel cells running on APG can be competitive with grid supplied electricity on a LCOE basis at remote sites. Using APG to generate power can reduce greenhouse gas (GHG) emissions from APG flaring.

Short-term R&D is needed in the following areas:

- Development of affordable analytical equipment and methods suitable for rapid onsite analysis.
- Development of higher capacity sorbents that are unaffected by moisture and hydrocarbons.
- Development of impurity specifications for fuels.
- Development of fuel flexible reforming catalysts.
- Generation of sorbent properties to enable process design.
- Development of accelerated test protocols to evaluate effective clean-up systems.

Long-term R&D recommendations include the following:

- Development of methods to convert fuel impurities or spent sorbents into useful byproducts – this would convert a disposal problem to a revenue source and improve economics.
- Development of scalable, modular, environmentally friendly, portable, low cost clean-up systems so that the clean-up system can benefit from volume production.
- Additional studies and plant demonstrations can provide much needed data for the industry.
- Replacement of fuel odorants with non-sulfur containing odorants.

# Acronyms

| | |
|---|---|
| ADG | Anaerobic digester gas |
| APG | Associated petroleum gas |
| APU | Auxiliary power unit |
| ASTM | American Society of Testing Materials |
| CapEx | Capital expense |
| CHP | Combined heat and power |
| COS | Carbonyl sulfide |
| DMDS | Dimethyl disulfide |
| DMS | Dimethyl sulfide |
| DOD | U.S. Department of Defense |
| DOE | U.S. Department of Energy |
| EERE | Energy Efficiency and Renewable Energy |
| FCE | Fuel Cell Energy, Inc. |
| FCEV | Fuel cell electric vehicle |
| FCTO | Fuel Cell Technologies Office |
| FTIR | Fourier transform infrared spectroscopy |
| GC-MS | Gas chromatography mass spectroscopy |
| GHG | Greenhouse gas |
| GW | Gigawatt |
| kW | kilowatt |
| kWh | kilowatt hours |
| HDS | Hydrodesulfurization |
| LCOE | Levelized cost of electricity |
| LFG | Landfill gas |
| LPG | Liquefied petroleum gas |
| MCFC | Molten carbonate fuel cell |
| NG | Natural gas |
| O&M | Operation and maintenance |
| OpEx | Operating expense |
| ppbv | parts per billion by volume |
| ppmv | parts per million by volume |
| ppmw | parts per million by weight |
| PSA | Pressure swing adsorption |
| R&D | Research and development |
| SAE | Society of Automotive Engineers |
| SCFM | Standard cubic feet per minute |
| SOFC | Solid oxide fuel cell |
| THT | Tetrahydrothiophene |
| ULSD | Ultra low sulfur diesel |
| WWTP | Waste water treatment plant |
| YSZ | Yttria stabilized zirconia |

# Follow-Up to the Workshop Report

## Key conclusions of the Gas Clean-up workshop:

- The sensitivity of the fuel processor and fuel cells to the impurities present in fuels of interest imposes a clean-up cost that adds to the burden of fuel cell systems in stationary applications. Estimates showed the clean-up of biogas costs ~2 cents per kWh of electricity, and ~30% of the O&M costs in an ADG fueled FC power plant.

- Sulfur, siloxanes, and halogens are the most damaging impurities or difficult to remove. Sulfur has an immediate detrimental effect on the fuel cell and reforming catalyst performance. Siloxanes have a slower effect by depositing a glassy layer on active surfaces. Halogens can form acid gases and can increase electrolyte loss rates in MCFCs, while other contaminants such as moisture and heavy hydrocarbons interfere with impurity removal because of their greater affinity for the sorbents.

- The severity of the detrimental effects on the fuel cell system requires some impurities to be reduced to the parts per billion level, which adds to the cost of clean-up as well as fuel quality monitoring.

- Uncertainties and variations in the impurity levels and the lack of affordable sensors for the impurities at low detection limits leads to overdesign and underuse of the sorbent capacities, which increases costs.

- Short term R&D is needed in the following areas to develop:

    - affordable analytical equipment and methods suitable for rapid onsite analysis

    - higher capacity sorbents that are unaffected by moisture and hydrocarbons

    - impurity specifications for fuels

    - fuel flexible reforming catalysts

    - accelerated test protocols to evaluate effective clean-up systems

- Long-term R&D is needed in the following areas to develop:

    - methods to convert fuel impurities or spent sorbents into useful byproducts – this would convert a disposal problem to a revenue source and improve economics

    - scalable, modular, environmentally friendly, portable, low cost clean-up systems so that the clean-up system can benefit from volume production

    - additional studies and plant demonstrations to provide much needed data for the industry

    - replacement of fuel odorants with non-sulfur containing odorants

## Request for Information (RFI)

The DOE posted the workshop report on their website and requested further information (June 1, 2015) to obtain feedback and opinions from industry, academia, research laboratories, government and other stakeholders on the workshop and the report. The report can be found at EERE Exchange website (https://eere-exchange.energy.gov/), also the presentations presented during the workshop are posted at http://www.energy.gov/eere/fuelcells/downloads/workshop-gas-clean-fuel-cell-applications.

The official Request for Information (RFI) was posted on EERE Exchange website (https://eere-exchange.energy.gov/) under DE-FOA-0001331. The following summarizes the responses received within the designated time (July 24, 2015).

# Responses to Request for Information Questions

1. ***Upon reading the workshop report, do you agree with the findings? Why or why not?***

   The responders collectively agreed on the workshop conclusion.

2. ***What is the basis of the opinion?***

   All respondents agreed on the importance of reducing the impurities in methanol, natural gas, biogas (e.g., landfill gas (LFG)). Impurities cause loss of performance and compromises durability by poisoning the catalytic surfaces. In particular, impurities containing sulfur and chlorine have been proven to poison low cost Cu/Zn catalysts.

   In addition to knowing the source of the impurities, quantifying the concentration of these contaminants is very important. It is crucial to develop low-cost analytical equipment to detect the type and quantity of the impurities.

   Development of low-cost adsorbent bed processes for impurity removal will directly impact system reliability and economics.

   There are large amounts of impurities in current sources of $H_2$ production. For the long term, it is necessary to identify and quantify the impurities likely in other sources of hydrogen, such as from the various thermochemical processes.

3. ***Please prioritize challenges and needs, if different from those in the report.***

   Although the challenges and needs have been considered important, other prioritizations have also been suggested:

   **Set one:**

   - Effort to determine the sources and quantities of contaminants in commercial Methanol, Natural Gas and LPG in North America.
   - Development of affordable analytical equipment and method suitable for rapid onsite analysis of sulfur and chloride.
   - Development of adsorbents for liquid phase desulphurization that retain their clean-up capacity in presence of water and hydrocarbons.
   - Development of accelerated test protocols to evaluate effective clean-up.
   - Development of re-generable and modular adsorbent bed and processes that can be scaled based on system economics.

   **Set two:**

   - Affordable analytical equipment and methods suitable for rapid onsite analysis
   - Higher capacity sorbents that are unaffected by moisture and hydrocarbons
   - Additional studies and plant demonstrations to provide much needed data for the industry

4. ***Are there other findings that are considered critical but were not included in this report? If so, please list them.***

   The following topics have not been highlighted in the report but are considered important by the RFI responders.

- Characterization of poisons for Copper-Zinc based reforming catalyst, other than Sulfides and Chlorides.
- Characterization of heavy hydrocarbons on performance of reforming catalysts, and their effect on the possibility of coke formation resulting in degraded catalyst performance.
- Development of analytical equipment and processes for removal of these heavy hydrocarbons.
- Development of sulfur-tolerant low-temperature methanol reforming and water-gas shift catalysts

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