HYDROGEN QUALITY

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1. ABSTRACT

As hydrogen fuel cell vehicles move from demonstration to commercialization, early customers expect safe, convenient, customer-friendly fueling. Customers also require assurance that the fuel they receive is of appropriate quality and accurate quantity. Hydrogen quality affects fuel cell stack performance and lifetime, as well as other factors such as valve operation. If fuel quality is inadequate the vehicles will not perform to customer expectations. However, requirements for exceedingly high fuel quality may increase the cost of producing the hydrogen beyond what customers are willing to pay.

Developing appropriate hydrogen quality standards requires balancing vehicle and fuel cell requirements with hydrogen production methods and costs. To support standards development, the hydrogen industry needs validated cost-effective test and sampling procedures, which in turn, requires real-world data from existing hydrogen stations.

The California Fuel Cell Partnership, with support from its automotive, energy, technology and government member organizations, collected real-world hydrogen quality data from existing stations and vehicles operating in California. CaFCP shares this data with standard development organizations, such as SAE and ASTM, to help them develop hydrogen quality standards.

CaFCP's efforts in gathering and analyzing real-world hydrogen quality data and facilitating the collaboration between the members and standard development organizations is a key component to creating market foundations for hydrogen fuel cell vehicles.

2. INTRODUCTION

To ensure fuel cell vehicle readiness for commercialization the U.S. Department of Energy (DOE) set program goals for the year 2015 that include a 60% peak-efficient, durable, direct hydrogen fuel cell power system for transportation at a cost of $30/kW and a fuel cell lifetime of 5000 hours. In addition, DOE set a 2015 goal for fuel providers to supply hydrogen at a price equivalent to a gallon of gasoline at $2-3 [1]. Hydrogen quality plays a key role in achieving all of these targets. To balance performance and costs, fuel providers and automakers must collaborate to assess real-world fuel quality, causes of fuel impurities, impacts on fuel cell system performance and cost of producing fuel to meet proposed standards.

The California Fuel Cell Partnership (CaFCP) is actively engaged in codes and standards development to support realistic, appropriate standards that enable the developing industry. Specifically, if hydrogen quality standards are too stringent, fuel providers will not be able to price hydrogen competitively with gasoline. Higher quality hydrogen requires greater technology—and thus more money—to create. On the other hand, if hydrogen quality is too poor, the vehicles will have decreased performance and durability and will not meet consumers' expectations. Poor quality hydrogen can impede the electrochemical reaction in a fuel cell or cause mechanical failure in the vehicle. For example, one hydrogen station in California was delivering water to a fuel cell vehicle during fueling. The vehicle could not operate with the water contamination and the station was temporarily shut down until the source of the water was diagnosed and contained.

Hydrogen quality is defined by the level of impurities in hydrogen fuel, specifically constituents and particulates. Impurities in the hydrogen stream can absorb into the platinum surface, the carbon support, the ionomer, or the gas diffusion layers. Hydrogen sulfide, or sulfuric acid, from sulfur in the fuel can cause irreparable damage to the fuel cell stack. Impurities may also block reaction sites for chemisorption, charge transfer, and proton conduction [2], thus causing irreparable damage to the stack or reduced power output. Particulate matter in the hydrogen stream can cause valve failure and seal leakage.

Research on the effects of the hydrogen impurities on fuel cell stack performance continues at major labs including Los Alamos National Lab, University of Connecticut, and Clemson, as well as within automaker research and development efforts. The National Renewable Energy Lab recently initiated particulate research to support the automaker efforts. CaFCP provides a forum where automakers, technical developers, and fuel providers can collaborate and share information. CaFCP aids in collecting samples from California hydrogen stations, having the samples analyzed and then providing the resulting data to standards development organizations in a confidential and objective manner.

3. STANDARDS DEVELOPMENT

The California Fuel Cell Partnership is not a standards development organization, but we support the development of standards necessary for fuel cell commercialization. CaFCP works with hydrogen quality standards organizations such as the Society of Automotive Engineers (SAE), the California Division of Measurement Standards (DMS), and the American Society for Testing and Materials (ASTM). SAE is addressing the issues of hydrogen quality through publication of the Technical Information Report (TIR) J2719. SAE TIR J2719 is not a standard, but a technical guidance document written in advance of a final recommended practice. The document was prepared as a collaborative activity by stakeholders including automakers and energy providers. It specifies a quality of 99.97% hydrogen with allowable limits of specific common impurities including particulates.

In 2007, California became the first state to recognize hydrogen as a transportation fuel. Senate Bill 76, signed into law by Governor Schwarzenegger on July 21, 2005, directed the California Department of Food and Agriculture, Division of Measurement Standards, to adopt regulations governing hydrogen fuel quality and dispensing. DMS is the California agency responsible for regulating all fuel dispensing and quality within the state. The legislation required DMS to adopt a hydrogen quality guideline or ANSI-approved standard by January 1, 2008. In the absence of an ANSI-approved standard the State had no choice but to move forward with an interim standard, even though most stakeholders believed it was too soon to specify fuel quality requirements.

CaFCP began meeting with DMS representatives to craft an interim standard to use until the final SAE recommended practice is adopted. Table 1 shows the specifications based on SAE TIR J2719 and listed in the DMS hydrogen fuel interim standard.

Table 1. DMS hydrogen fuel quality specification [3]

Specification	Value
Hydrogen Fuel Index (minimum, %) (1)	99.97
Total Gases (maximum, ppm v/v) (2)	300
Water (maximum, ppm v/v)	5
Total Hydrocarbons (maximum, ppm v/v) (3)	2
Oxygen (maximum, ppm v/v)	5
Helium (maximum, ppm v/v)	300
Nitrogen and Argon (maximum, ppm v/v)	100
Carbon dioxide (maximum, ppm v/v)	2
Carbon monoxide (maximum, ppm v/v)	0.2
Total Sulfur Compounds (maximum, ppm v/v)	0.004
Formaldehyde (maximum, ppm v/v)	0.01
Formic acid (maximum, ppm v/v)	0.2
Ammonia (maximum, ppm v/v)	0.1
Total Halogenated Compounds (maximum, ppm v/v)	0.05
Particulates Size (maximum, µm)	10
Particulate Concentration (maximum, µg/L @ NTP)	1

1. The hydrogen fuel index is the value obtained with the value of total gases (%) subtracted from 100%
2. Total Gases = Sum of all impurities listed on the table except particulates
3. Total Hydrocarbons may exceed 2 ppm v/v only due to the presence of methane, provided that the total gases do not exceed 300 ppm v/v.

By working with CaFCP's members in a consensus-building manner, DMS considerably shortened the process of developing the interim standard. CaFCP hosted meetings with all parties to hear ideas and address concerns, acting as a liaison for DMS and industry stakeholders. As a result of the collaborative work, industry stakeholders voiced only support for the interim standard during the regulatory hearing.

4. TEST METHOD DEVELOPMENT

Test methodologies to detect acceptable limits of impurities in hydrogen are under development. ASTM International Committee D03 is aggressively working to standardize and publish test methods needed to determine hydrogen impurities at the current or lower concentration levels. CaFCP participates in the committee, bringing our members' real-world data and designs to the working group.

One test method under development in this ASTM committee is the physical field sampling of the hydrogen from the station. Testing hydrogen at the nozzle is vital to standards development and to the industry in general, as it mimics the hydrogen fuel seen by the fuel cell vehicles. Therefore, in 2004, CaFCP developed a prototype hydrogen quality sampling adapter (HQSA) to collect samples from the nozzle. (Figure 1).

Figure 1. CaFCP HQSA

CaFCP designed the HQSA for safe field sampling incorporating a nozzle, regulator, filter, and canister to: 1) collect the gaseous hydrogen into a high-pressure rated collection vessel and allow for return of the sample to the lab for analysis, and 2) collect particulates onto a filter for weight, count, and elemental analysis. The HQSA developed at the partnership has since been donated to California DMS to support their efforts. Improved designs have been built and are incorporated into the ASTM test procedures currently in progress.

5. RESULTS

CaFCP members have used the HQSA to test five hydrogen stations, including several station design types: electrolysis, natural gas reformation, and delivered liquid hydrogen. These tests yielded valuable hydrogen quality data for automakers and station owners, as well as valuable lessons learned related to design, operation, and analysis methodologies.

Table 2 is the aggregated hydrogen quality results sponsored by the CaFCP and conducted by Dr. J.P. Hsu of Smart Chemistry. The table shows the SAE recommended limits from TIR J2719, Smart Chemistry detection limits, and results from Dr. Hsu's sampling. The results are shown as "<DL" or "Less than Detection Limit" and numerical values, in most cases depicted in parenthesis to indicate the value being a single outlier or range of outliers differing from the majority. The particulates were measured differently, so the results of the particulate sampling are depicted in a range of sizes and concentrations.

Several valuable pieces of data can be observed from this table. First, in the two years of testing Dr. Hsu was able to lower his detection limit for several constituents. Oxygen lowered from a detectable limit of 5 µmol/mol to 3µmol/mol, total sulfur decreased from 0.001 µmol/mol to 0.0005 µmol/mol, formaldehyde decreased from 0.004 µmol/mol to 0.002 µmol/mol, formic acid from 0.06 µmol/mol to 0.02 µmol/mol, and hydrogen chloride and bromide from 10 µmol/mol to 0.05 µmol/mol, a substantial advance in analysis technology. His work is assisting ASTM in creating the test methodologies necessary for SAE and DMS' hydrogen quality standards development. Understanding the actual ability to measure the levels defined in their tables and the actual quality of the hydrogen in real world applications is crucial.

Second, there are four instances where the quality of the hydrogen does not meet the SAE TIR limits. One test returned a nitrogen content of 762 µmol/mol when the recommended limit is 5 µmol/mol. Another test yielded a CO_2 concentration of 1.2 µmol/mol when the recommended limit is 1 µmol/mol. The third instance is the test that resulted in 0.0046 µmol/mol of carbonyl sulfide, part of the total sulfur constituents recommended at less than 0.004 µmol/mol. Finally, all tests yielded particulate sizes that exceeded the SAE recommended <10 µm. Occasional variance from SAE recommended limits may be expected in this stage of development, but for all stations to fail to meet a recommended limit in the same category calls for further research.

Finally, although the detection limits are constantly improving, they are not at the level they need to be to accurately test for the levels called for in SAE TIR J2719, nor the DMS hydrogen fuel interim standard. Thus further research is still required.

Table 2. Aggregated hydrogen quality results (all units in µmol/mol unless specified otherwise).

Constituent	SAE TIR J2719 Limits	Previous Smart Chemistry Detection Limits	Updated Smart Chemistry Detection Limits	Concentration (Outliers)
Water	5	1	1	**< DL (2.2)**
Total Hydrocarbons (C_1 Basis)	2			
Methane		0.1	0.1	**< DL**
Ethane, Ethene, Ethyne		0.6	0.6	**< DL**
Other Hydrocarbons		0.1	0.1	**< DL (0.14)**
Oxygen	5	5	3	**< DL**
Helium, Nitrogen, Argon	100			
Helium		10	10	**< DL (78)**
Nitrogen		5	5	**< DL (762)**[1]
Argon		0.8	0.8	**< DL**
Carbon Dioxide	1	0.4	0.4	**< DL (1.2)**
Carbon Monoxide	0.2	0.1	0.1	**< DL**
Total Sulfur	0.004			
Hydrogen Sulfide		0.001	0.0005	**< DL**
Carbonyl Sulfide		0.001	0.0005	**< DL (0.0018 – 0.0046)**
Methyl Mercaptan		0.001	0.0005	**< DL**
Carbon Disulfide		0.001	0.0005	**< DL**
Formaldehyde	0.01	0.004	0.002	**< DL**
Formic Acid	0.2	0.06	0.02	**< DL**
Ammonia	0.1	0.04	0.04	**< DL**
Total halogenates	0.05			
Chlorine		0.05	0.05	**< DL**
Hydrogen Chloride		10	0.05	**< DL**
Hydrogen Bromide		10	0.05	**< DL**
Organic Halides		0.02	0.02	**< DL**
Particulate Size	< 10µm	1µm	1µm	
Number of Particulate Found with size more than 1 cm				**(1)**[2]
Number of Particulate Found with size within 1 mm and 1 cm				**19**
Number of Particulate with size within 100 µm and 1000 µm				**39**
Number of Particulate with size within 10 µm and 100 µm				**3**[3]
Particulate Concentration	1µg/L	Balance	0.0025µg/L	**0.0025 – 0.019 µg/L**

[1] Underlined numbers indicate outliers from the majority results that exceed SAE recommended limits.

[2] Underlined numbers in the "Particulate Size" section indicate particulate sizes that exceed the SAE recommended sizes.

[3] The three smallest particulates found are not considered outliers. If large particulates were found during sampling the smaller particulates may have been overlooked.

Particulate sampling yielded a wide range of results, as seen in Table 1. We observed varying quantities, sizes, and composition of particulates. Figure 2 is an image of a particulate filter after sampling. The filter had 22 particulates, 18 had sizes greater than 100µm (0.1mm). The SAE limit is 10µm (0.01 mm).

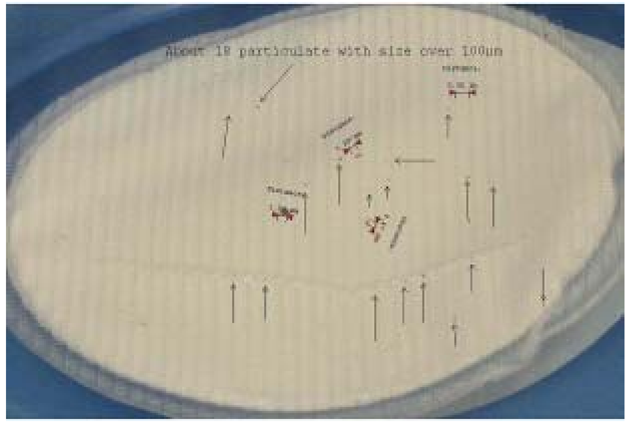

Figure 2. Post-sampling particulate filter

Overall, the particulates sampled from the five stations varied in size from 30µm to 28,000µm (Figure 3). Smaller particulates may have existed, but were overshadowed by the larger particulates. PG&E provided a scanning electron microscope analysis that indentified the composition of the particulates as polymers, organic compounds, stainless steel, aluminum, iron, and calcium (Figure 4).

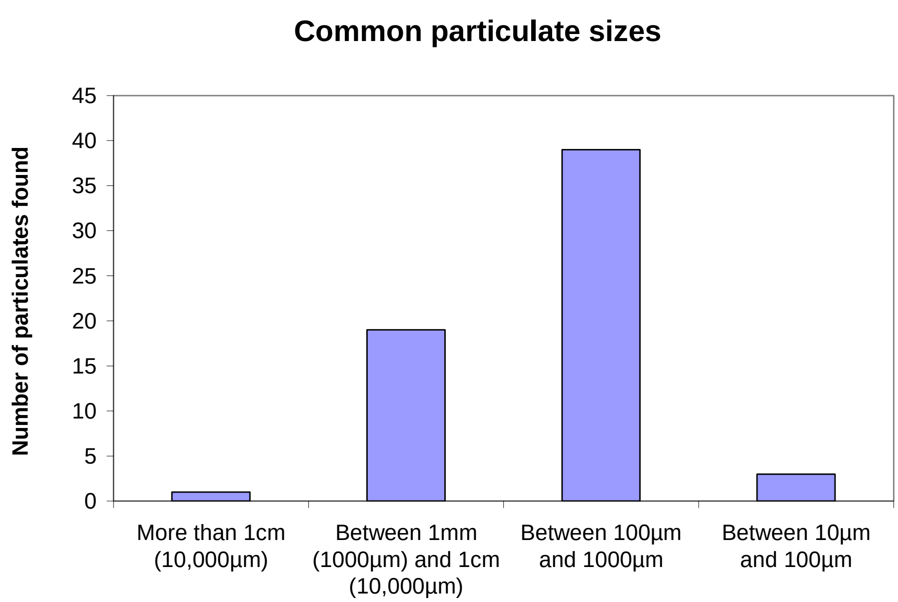

Figure 3. Sampled particulates sizes

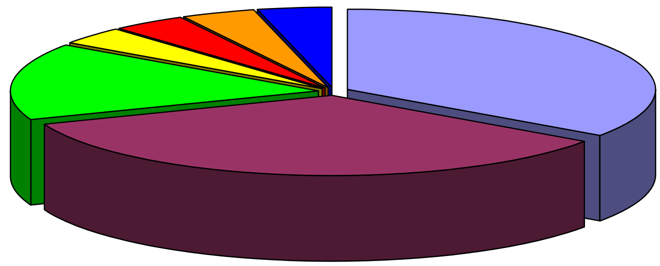

Figure 4. Composition of particulates found in sampling

This vast variation in composition and size of particulates indicates a need for further research into testing methodologies and specifications for acceptable size limits of particulates, as well as research into determination of particulate sources. This particulate testing may result in changes in testing procedures, allowable limits, or both. CaFCP supports ongoing research of hydrogen quality including funding additional tests, sharing results with key stakeholder groups, and developing new equipment and test methods.

6. CONCLUSIONS AND RECOMMENDATIONS

Developing appropriate codes and standards provides a technical foundation for commercial success. Unlike conventional fuels, for which the codes and standards were developed after vehicle commercialization, the fuel cell industry is working to develop hydrogen standards before commercialization to help ensure a safe and successful market introduction.

CaFCP and its members facilitate necessary testing and guideline development (the precursor to standards) in a manner that supports both technology and industry stakeholder requirements by ensuring these efforts proceed quickly, but not before they have properly matured. CaFCP will continue to work with SAE, DMS, ASTM and other standards development organizations to develop appropriate codes and standards, identify proper testing procedures, and allow the industry to move forward. Our collective goal is to support and facilitate the use of hydrogen as a fuel and move fuel cell vehicles closer to the commercial market.

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8. REFERENCES

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