R&D for Safety, Codes and Standards: Hydrogen Behavior

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Project Start Date: October 1, 2003
Project End Date: Project continuation and direction determined annually by DOE

Overall Objectives

- Develop a science and engineering basis for the release, ignition, and combustion behavior of hydrogen across its range of use (including high pressure and cryogenic).
- Facilitate the assessment of the safety (risk) of hydrogen systems and enable use of that information for revising regulations, codes, and standards (RCS) and permitting hydrogen fueling stations.

Fiscal Year (FY) 2018 Objectives

- Finalize validation of a cryogenic hydrogen dispersion model using data from lab-scale experiments.
- Develop a diagnostic that can measure large-scale and/or real-world cryogenic hydrogen dispersion including cryogenic hydrogen venting and vaporization from pools.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Safety, Codes and Standards section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration (MYRDD) Plan[1]:

- Safety Data and Information: Limited Access and Availability
- Insufficient Technical Data to Revise Standards.

Contribution to Achievement of DOE Milestones

This project will contribute to achievement of the following DOE milestones from the Hydrogen Safety, Codes and Standards section of the Fuel Cell Technologies Office MYRDD Plan:

- Milestone 2.13: Develop and validate simplified predictive engineering models of hydrogen dispersion and ignition. (4Q 2015)
- Milestone 2.19: Validate inherently safe design for hydrogen fueling infrastructure. (4Q, 2019)
- Milestone 4.8: Revision of NFPA 2 to incorporate advanced fueling and storage systems and specific requirements for infrastructure elements such as garages and vehicle maintenance facilities. (3Q, 2016)

FY 2018 Accomplishments

- Completed validation of the ColdPlume model with model comparisons to data collected using a unique, world-first, cryogenic hydrogen imaging diagnostic for 15 experimental release conditions, including five conditions with simultaneous velocity data. The validated model can be used to predict hazard distances from liquid hydrogen system leaks.
- Developed an optical design for light collection for a large-scale diagnostic enabling the measurement of hydrogen concentration for real-world releases from a stand-off distance of at least 20 ft. This first-of-its kind diagnostic will be used to measure liquid hydrogen vent stack dispersion and vaporization profiles from liquid hydrogen pools. The data will be used to validate models and enable reductions to liquid hydrogen fueling station footprints.

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[1] https://www.energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22

INTRODUCTION

Fire codes govern the required distances between hydrogen sources (e.g., a liquid hydrogen tank at a fueling station) and hazards (e.g., ignition sources). Revisions to the fire code distances require justification, which is facilitated by analysis that include physical models. These models must be validated by carefully controlled experiments, under relevant conditions, which can include high pressures (10,000 psi) or cryogenic temperatures (20 K). Over the course of this project, a range of experiments have been designed, developed, and executed to provide validation data for models. Models have been developed and exercised to inform the fire codes. This work has enabled quantitative risk assessments of hydrogen systems and subsequent reduction of setback distances from high-pressure hydrogen sources. More recently, our efforts have focused on developing a scientific basis for modeling dispersion and flames from cryogenic (liquid) hydrogen sources. There are currently large distances required by the fire codes around liquid hydrogen tanks, hindering the development and construction of hydrogen fueling stations with liquid hydrogen on site, an economically viable station design for large-capacity stations needed in urban areas. Validated models and targeted experiments from this project will be exercised to provide a technical basis for the revision of fire codes related to liquid hydrogen.

APPROACH

The goals of this work are to develop and validate scientific models to accurately predict hazards and consequences from hydrogen releases and combustion/flames. In this project, we previously developed one-dimensional and engineering models of hydrogen dispersion and flames that can run quickly on a PC. While these models are one dimensional, they include enough physics (e.g., the effect of buoyancy) to be accurate under a wide range of scenarios. These models are able to characterize the hazards from hydrogen releases and flames and are fast enough that they can be run multiple times and incorporated into a quantitative risk assessment framework that includes probabilities of leak frequency and size, and probabilistic harm models. While the models we used to inform fire codes have been validated, carefully controlled experiments are required to validate and develop new models for cryogenic hydrogen to have an impact on liquid hydrogen separation distances. Advanced optical and laser diagnostics are used, along with more conventional diagnostics (e.g., thermocouples) to characterize the dispersion and flame properties of releases, at a lab scale. The temperature, pressure, and orifice of the unignited releases and flames are controlled while characteristics are measured (e.g., concentration, flame temperature, radiative heat flux). For liquid hydrogen, some phenomena, such as releases from vent stacks and measurements of vaporization and pooling rates, require larger-scale experiments, and we are currently developing diagnostics and experimental platforms to measure these phenomena.

RESULTS

With the focus on developing a large-scale diagnostic, one of the first tasks this fiscal year was surveying the literature for diagnostics capable of measuring hydrogen concentration with reasonable resolution suitable for model validation. One option is using sensors, either within the flow or on samples extracted from the flow. Sensors are reasonably low cost and straightforward to implement. However, there are several drawbacks to sensors. Placing either the sensors or sampling probes in the flow can disturb the flow field of interest. Sensors lead to point measurements of concentration making it challenging to get spatial resolution, and most sensors have poor temporal response (and hence poor temporal resolution). Finally, depending on the technology (e.g., electrochemical, thermal conductivity, catalytic), sensors are often not specific to hydrogen and can be affected (e.g., drift, have reduced accuracy) by other environmental factors (e.g., temperature). Optical diagnostics, on the other hand, can provide high spatial and temporal resolution and are nonintrusive, but optical methods of detecting hydrogen are very challenging (i.e., there are no strong absorption features or fluorescence transitions). Nonetheless, due to the perceived benefits, and our experience using optical hydrogen diagnostics in the laboratory, we decided to pursue the scale-up of our lab-scale method of measuring Raman scattering.

Raman scattering is inelastic scattering of light off molecules. Different molecules have different Raman transitions and hence different Raman bands. In the laboratory, we reshape a high-powered laser beam into a sheet and image Raman scattered light off hydrogen and nitrogen molecules to calculate the two-dimensional hydrogen concentration and temperature fields of turbulent jets, as shown in Figure 1. We have specific light filters to only collect Raman shifted light that is scattering off of the molecules of interest and can reduce the signal due to ambient light (a serious issue when trying to measure in the sunlight) and light scattered at the excitation wavelength (the laser wavelength—a large signal for cryogenic plumes where there is condensed moisture scattering a lot of light).

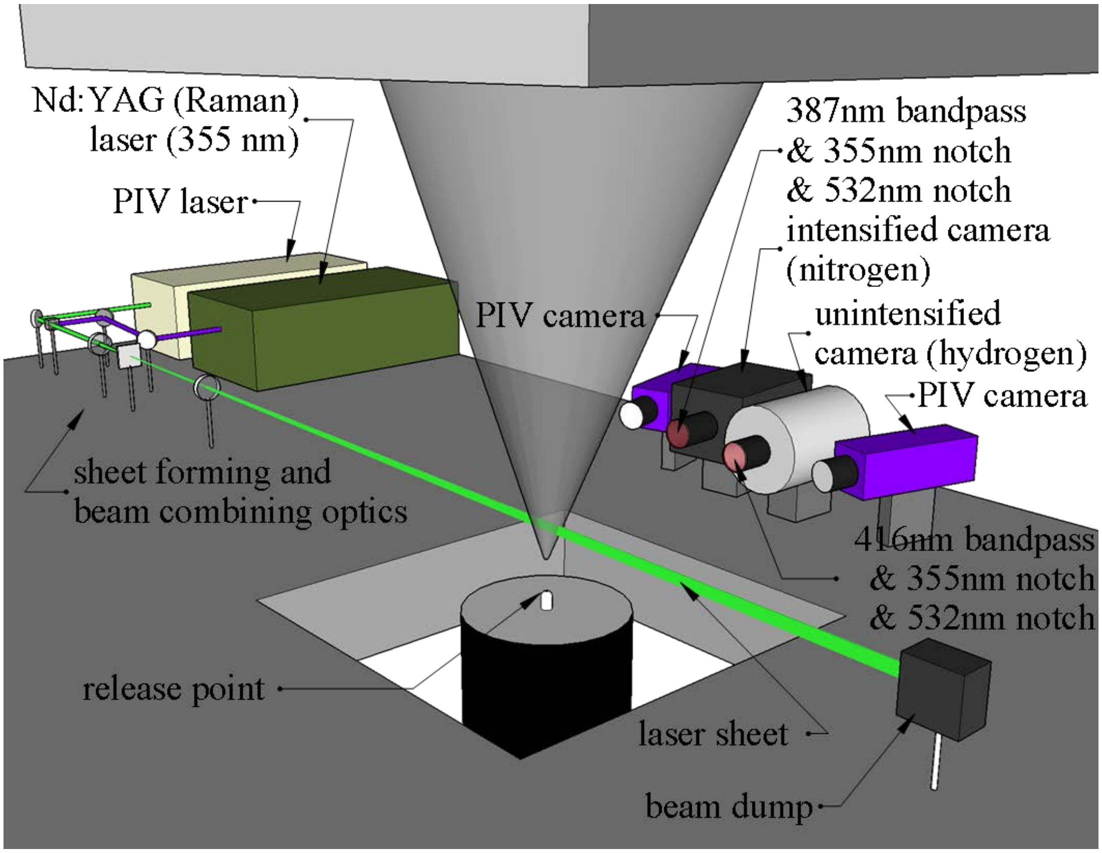

Figure 1. Laboratory setup for simultaneous Raman scattering measurements and particle imaging velocimetry measurements of cryogenic hydrogen jets. This setup enables the measurement of two-dimensional fields of species concentrations, temperatures, and velocity.

The intensity of Raman scattered light is inversely proportional to the wavelength of light to the fourth power and therefore the intensity increases greatly when smaller wavelengths of light are used to excite the molecules. However, the sensitivity of detectors (e.g., cameras, diodes) is often poorer at lower wavelengths and if using a laser, converting the higher wavelengths to lower wavelengths reduces the laser power output. Nonetheless, moving to the ultraviolet wavelengths can boost the signal-to-noise ratio, both in the lab and in moving toward the large-scale diagnostic. Figure 2 demonstrates this relationship using the laser system in the laboratory and several camera options that we currently have in the laboratory. As shown, by using the same cameras, we expect to achieve over 3 times the current signal-to-noise level by using the third harmonic of our Nd:YAG laser at 355 nm instead of the second harmonic at 532 nm.

Efforts toward experimentally demonstrating this signal-to-noise boost in the lab were delayed by several challenges. Ultraviolet light at 355 nm, even at lower laser energy, is much more damaging to optical coatings than visible light at 532 nm. This required us to develop a more even distribution of laser energy from the oscillator cavity by replacing optics and develop less temporal energy fluctuations by seeding the laser. We also determined a maximum laser power, less than the peak power, to prevent damage to optics. To maintain the total power needed to achieve the signal boost shown in Figure 2, we are adding a second laser that will temporally lag the first laser, but it will still produce spontaneous Raman scattering that will be captured by our cameras. Although the laser energy at 355 nm was lower than the energy at 532 nm, the photon energy is higher, and we found that we were igniting the flows when using the ultraviolet light. For this reason, we reduced the peak energy by temporally stretching the laser pulses by constructing delay cavities.

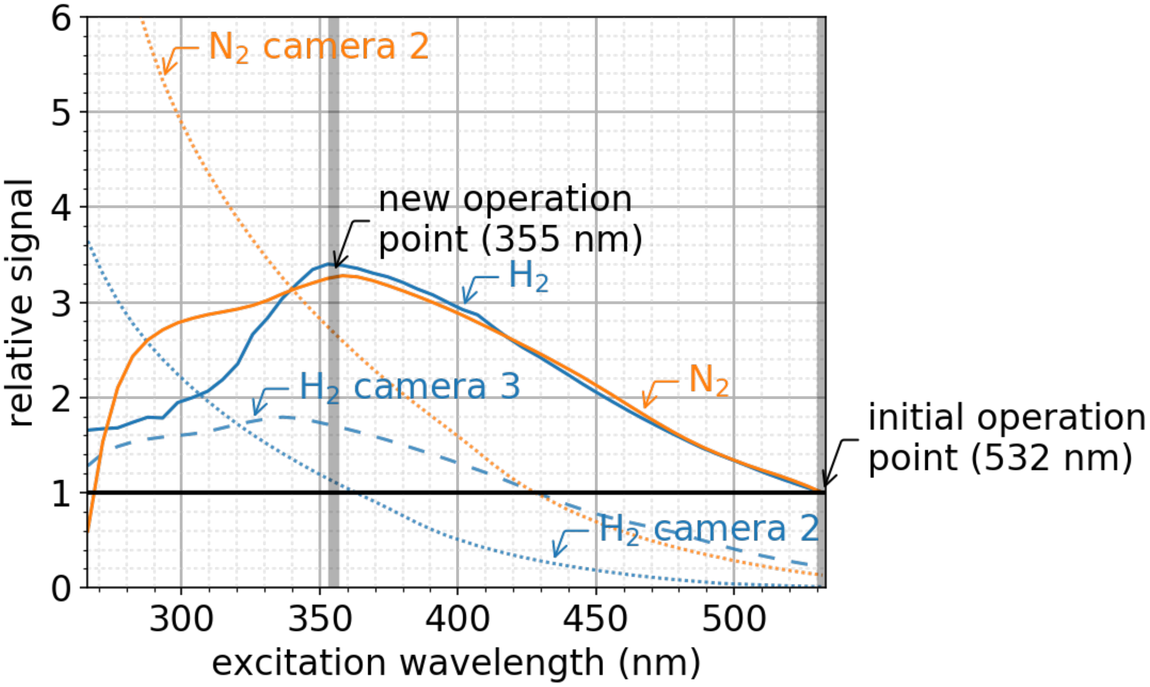

Figure 2. Relative signal that can be achieved for measuring Raman scattering from hydrogen and nitrogen molecules as a function of excitation light wavelength using several scientific cameras available in the laboratory

We developed plans for the light collection system of the large-scale diagnostic and proved several concepts in the lab this fiscal year. The goals of the large-scale diagnostic are extremely challenging to meet, and we used ray-tracing software to specify the necessary optics, as shown in Figure 3. There are several important characteristics of the system. First, we are using the full 10-in. (f/0.8) aperture afforded by a Fresnel lens (which reduces cost and time to develop large, custom optics) maximizing the solid angle of light collection. Second, there is a region of parallel light rays between the imaging lens and the achromatic focusing lens that enables placement of the wavelength filter, which has an angular response to light rejection/throughput. Finally, we have carefully chosen the focal lengths to reduce the image size so that it can fit on a small sensor. We used the system shown in Figure 3 to successfully measure Raman scatter off a pure 3-in. section of hydrogen from over 20 ft away. This proves that our light collection system has the potential to work in the field, measuring hydrogen concentration from a large standoff distance.

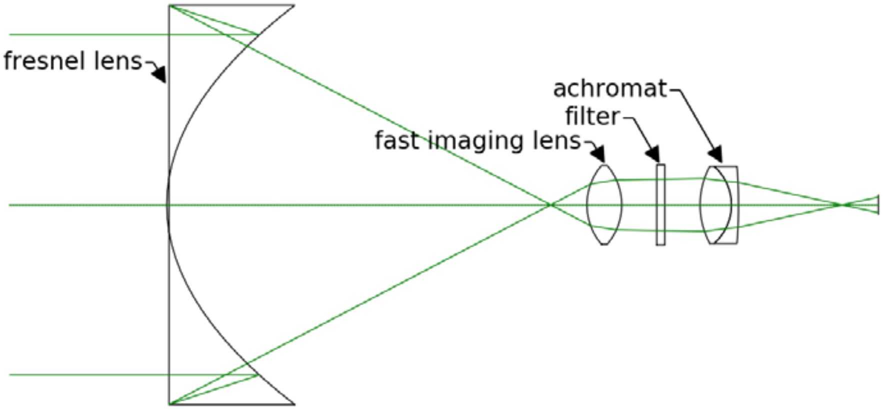

Figure 3. Ray trace diagram of large-scale cryogenic hydrogen dispersion diagnostic

A final result from this fiscal year was the completion of a lab-scale experimental campaign collecting simultaneous concentration, temperature, and velocity fields from cryogenic hydrogen releases. We then compared this new data, along with data collected last fiscal year, to a model of cryogenic hydrogen dispersion. The model and data showed very good agreement, validating the modeling approach. The model can now be used with confidence to predict the dispersion and mixing of cryogenic hydrogen jets and plumes with air. This model can be incorporated into our quantitative risk assessment toolkit and used to assess the safety of hydrogen fueling stations with liquid hydrogen.

CONCLUSIONS AND UPCOMING ACTIVITIES

Significant progress was made this fiscal year toward the development of an optical diagnostic that will be used to measure the dispersion from large-scale cryogenic hydrogen releases. The light collection system was developed and the concept was proved to measure Raman scattered light from hydrogen molecules from over 20 ft. This optical collection system needs some refinement, including additional light rejection at the excitation wavelength and the use of a field lens to increase the field of view. The illumination system for the large-scale diagnostic also still needs development before this diagnostic can be applied to a large-scale cryogenic hydrogen release. This is the thrust of our work moving forward; completing the assembly of the large-scale diagnostic and using this diagnostic to measure the real-world dispersion of cryogenic hydrogen. Next fiscal year, our first use of this diagnostic will be to measure the dispersion of cryogenic hydrogen from a liquid hydrogen vent stack. This information will be used to provide justification for the reduction of the 75 ft setback distance (in NFPA 2: Hydrogen Technologies Code) from liquid hydrogen bulk storage to air intakes and the general footprint for hydrogen fueling stations with liquid hydrogen.

FY 2018 PUBLICATIONS/PRESENTATIONS

1. E.S. Hecht. “October 2017 Codes and Standards Tech Team Update: Building Knowledge of Cryogenic Hydrogen Behavior.” Presented to the DOE Codes and Standards Tech Team, October 12, 2017. SAND2017-11032PE.
2. E.S. Hecht. “Hazard and Consequence Modeling Applicable to Safety Codes and Standards.” Presented at the US-Korea Joint Research Meeting, Long Beach, CA, November 6, 2017. SAND2017-12044 PE.
3. E.S. Hecht. “Current Research and Future Outlook for Behavior and Consequence Modeling.” Presented at the US-Korea Joint Research Meeting, Long Beach, CA, November 6, 2017. SAND2017-12045 PE.
4. E.S. Hecht. “November Update on the Separation Distance for Liquid Hydrogen Storage Project.” Presented to the Liquid Hydrogen CRADA contributors, November 28, 2017. SAND2017-12948 PE.

5. E.S. Hecht, B. Roy Chowdhury. “Experimental Validation of a Model for Cryogenic Hydrogen Jet Dispersion.” Presented at the 255th American Chemical Society National Meeting, New Orleans, LA, March 20, 2018. SAND2018-2834 C.
6. E.S. Hecht. “Hydrogen Behavior R&D for Safety, Codes and Standards at Sandia National Labs.” Presented to the NFPA 2 Hydrogen Storage Task Group, April 3, 2018. SAND2018-3518 PE.
7. E.S. Hecht, B. Roy Chowdhury, S.E. Bisson, A.H. McDaniel. “How to See and Quantify Hydrogen Concentration (and Cryogenic Hydrogen) using Optical Diagnostics.” Presented at the PreSLHy Kick-Off Meeting in Karlsruhe, Germany, April 16–20, 2018. SAND2018-4000 PE.
8. E.S. Hecht, B. Roy Chowdhury, A.H. McDaniel, S.E. Bisson. “R&D for Safety, Codes and Standards: Hydrogen Behavior.” Presented at the U.S. Department of Energy’s Hydrogen and Fuel Cells Program 2018 Annual Merit Review and Peer Evaluation Meeting, Washington, DC, June 13–15, 2018. SAND2018-4001 PE.
9. E.S. Hecht. “Safety, Codes and Standards and the HyRAM Toolkit.” Presented to representatives of the State Power Corporation of China Research Institute in Livermore, CA, August 6, 2018. SAND2018-5847 PE.
10. E.S. Hecht, P. Panda. “Mixing and Warming of Cryogenic Hydrogen Releases.” *International Journal of Hydrogen Energy*. In Press 2018. https://doi.org/10.1016/j.ijhydene.2018.07.058
11. E.S. Hecht. “Cryogenic Hydrogen Behavior and Research Priorities.” Presented at PreSLHy LH2 Research Priority Workshop in Buxton, England, September 17–21, 2018. SAND2018-10121 PE.
12. E.S. Hecht, B.D. Ehrhart, G.A. Bran Anleu. “Summary of Liquid Hydrogen Research at Sandia National Laboratories.” Presented by Jay Keller at the 2nd International Workshop on Liquefied Hydrogen in Kobe, Japan, October 24–25, 2018. SAND2018-10664 C.