VIII.1 Hydrogen Safety, Codes and Standards R&D – Release Behavior

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Project End Date: Project continuation and direction determined annually by DOE

Fiscal Year (FY) 2012 Objectives

- Present results of reduce order model development efforts to the Hydrogen Industry Panel on Codes (HIPOC)
- Development and publication of new and validated source models for dispersion from high-source pressure releases
- Map ignition and light-up boundaries for multiple nozzle diameters and pressure ratios using laser spark apparatus

This project addresses the following technical barriers from section 3.8 of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Safety Data and Information: Limited Access and Availability
(F) Enabling national and international markets requires consistent RCS
(G) Insufficient Technical Data to Revise Standards
(L) Usage and Access Restrictions – parking structures, tunnels and other usage areas

Contribution to Achievement of DOE Safety, Codes & Standards Milestones

This project will contribute to achievement of the following DOE milestones from the Safety Codes and Standards section of the 2011 Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

- Milestone 2.1: Provide critical understanding of hydrogen behavior relevant to unintended releases in enclosures. (4Q, 2013)
- Milestone 2.2: Understand flame acceleration leading to transition to detonation (4Q, 2014)
- Milestone 2.3: Develop and validate simplified predictive engineering models of hydrogen dispersion and ignition (4Q 2015)
- Milestone 2.5: Develop holistic design strategies (4Q, 2017)
- Milestone 2.6: Validate inherently safe design for hydrogen fueling infrastructure (4Q, 2019)
- Milestone 4.1: Identify and evaluate failure modes (3Q, 2013)
- Milestone 4.2: Develop supporting research programs (round robins) to provide data and technologies (2Q, 2012)
- Milestone 4.3: Complete determination of safe refueling protocols for high pressure systems (1Q, 2015)
- Milestone 4.4: Complete risk mitigation analysis for advanced transportation infrastructure systems (1Q, 2015)
- Milestone 4.5: Revision of National Fire Protection Association 2 to incorporate advanced fueling and storage systems and specific requirements for infrastructure elements such as garages and vehicle maintenance facilities (3Q, 2016)

FY 2012 Accomplishments

- Created benchmark data set to evaluate the optimum distribution functions used to model mixture ignitability in support of milestones 2.1, 2.3, 2.5, 2.6, and 4.4.
- Performed comprehensive review of notional nozzle models for compressed hydrogen releases in support of milestones 2.1, 2.2, 2.3, 2.5, 2.6, 4.1, 4.2, and 4.4.
- Developed measurement apparatus necessary to experimentaly investigate flame light-up probability, which is the probability that an incipient ignition kernel will lead to a sustained flame. The probability of flame light up is integral to determining the overall hazard of a release (no flame is less hazardous). This accomplishment is critical to milestones 2.1, 2.2, 2.3 and provides validated simulation support for milestones 2.5, 2.6, 4.1, 4.2, 4.3, 4.4.
- Applied flame radiation models and experimental results to industry partner collected data set for large hydrogen flame releases. This collaborative effort supports ongoing advancement of milestones 2.1 and 2.3 while contributing to milestones 2.5, 2.6, 4.1, 4.2, and 4.4.

- Completed phase 1 of composite overwrapped pressure vessel (COPV) testing in support of milestones 2.3, 2.5, 2.6, 4.2 and 4.3. Data collected from laboratory testing used to validate three-dimensional, dynamic finite element model of COPV during fill process. This validation effort is part of an international 'round robin' effort by the International Partnership on Hydrogen Energy. Dynamic modeling of tank response to various fill protocol scenarios is critical to improving hydrogen fill protocols and tank construction.

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Introduction

Safety is critical to enabling the use of hydrogen as an energy carrier. While hydrogen has been used for industrial purposes for many years bringing industrial technology to a retail setting such as a refueling station involves many unknowns with regard to safety. Understanding release behavior of hydrogen is fundamental to performing quantitative risk assessments (QRA) – the use of past failures to predict the likelihood of future failures and thereby estimate the risk of harm from an accident. The hydrogen specific QRA approach is incorporated in the development of model codes and standards to appropriately regulate the retail/commercial use of hydrogen.

Simulations and models, validated with experimental data, are the cornerstone of the hydrogen specific QRA. These simulations and models provide critical input to the overall risk evaluation. While risk is classically defined as the product of frequency and consequences, a more detailed definition specific to hydrogen hazards is shown in Equation 1. For hydrogen systems, analysis has identified the major hazard surrounds the release of hydrogen gas with subsequent ignition. Equation 1 characterizes the various factors of risk for ignition of a hydrogen release as a function of probability of a release, probability of ignition given the release type, probability of a hazard given a specific release and ignition type and finally the probability of harm given the associated hazard. Release behavior models and experiments provide insight to factors (shown in red in Equation 1) for predicting risk.

The goal of the Fast Fill project is to develop a set of high quality experimental results for rapid filling and venting of Type-III and Type-IV hydrogen storage tanks that can be used for model validation and the development of refueling protocols for 35 MPa and 70 MPa hydrogen refueling stations and consumption during aggressive driving cycles. Material temperature is the primary barrier for hydrogen fueling. Extreme material temperatures are achieved through interactions between the tank (at a given "soaked temperature" at the start of fueling (hot and cold) and the gas flow rate and gas temperature.

Approach

Isaac Ekoto, Bill Houf, and Daniel Dedrick, developed a five-year roadmap with the explicit goal of addressing short-, medium-, and long-term hydrogen behavior safety research needs. The plan was based on an analysis of the current knowledge base, key SNL contributions to this knowledge base, and critical outstanding gaps that serve as barriers to the creation of future standards but can be informed by leveraging unique SNL capabilities. Research topics were divided into five main areas:

1. General release behavior (relevant release geometries, storage states, jet dynamics)
2. Ignition mechanisms (diffusion ignition, electrostatic discharge, conduction)
3. Necessary ignition conditions (minimum ignition energy, mixture ignitability)
4. Necessary flame light-up conditions (ignition characteristics, flow strain rates)
5. Light-up consequences (flame radiation, pressure, flame impingement).

Development of a comprehensive risk assessment tool that couples arbitrary system failure mode analysis with quantifiable consequence modeling obtained from improved hydrogen behavior understanding remains the overarching goal. Ultimately this tool would be used to inform standards creation processes. Highlights from the research roadmap were condensed into a presentation to be given at the International Energy Agency (IEA) Task 31 Subtask A Coordination Meeting held in Oslo, Norway, on January 10 by Daniel Dedrick. As a result of this presentation, Sandia will be coordinating with the IEA task 31 Subtask to develop and disseminate models developed. A workshop with H2CAN collaborators (Pierre Bernard, et al. of Université du Québec à Trois-Rivières) was held April 11 and 12 in Livermore, CA to identify common research areas. Collaborative research topics ranging from risk assessment methodologies, flow dispersion, ignition mechanisms, and flame radiation characterization and modeling were identified, with ongoing data sharing occurring between both entities. User input and institutional expertise has likewise

$$Risk \propto \sum_{i,j,k} P(\text{Release}_i)P(\text{Ignition}_j|\text{Release}_i)P(\text{Hazard}_k|\text{Ignition}_j \cap \text{Release}_i)P(\text{Harm}|\text{Hazard}_k)$$

EQUATION 1. Risk as a function of probability of a release, probability of ignition given a release, probability of a hazard given a release and ignition and finally the probability of harm given the hazard.

been solicited from relevant industrial and regulatory partners (HIPOC, National Fire Protection Association, etc.).

Regarding COPV safety Sandia started the first phase of this project using a Type-IV 39-L 70 MPa tank provided by Lincoln Composites. Sandia then instrumented the tank with thermocouples fully characterize the gas and composite tank wall temperatures during dynamic H2 filling and vent. Five thermocouples spaced along the tank axis are used to measure the gas temperature in the tank. At four locations on the wall of the tank there are sets of four thermocouples that measure, from inside to outside, the liner temperature, the composite/liner interface temperature, a mid-wall composite temperature, and an outer composite temperature. Three of the locations are spaced along a parallel to the tank axis. The fourth location is centered along the tank axis and clocked 90 degrees around the tank circumference from the other three. That provides a total of 21 temperature measurements. The tank is mounted and attached to a H2 manifold in one of Sandia's high pressure hydrogen labs. The manifold is currently limited to 2,000 psi (14 MPa) hydrogen pressure, but future plans will increase the pressure capacity to 70 MPa. Although the maximum pressure is limited, the computer controlled manifold allows for significant experimental flexibility. For hydrogen filling, the tank pressure can be linearly ramped from 20 psi to 2,000 psi or any pressure combination in between. The ramp time can be varied from tens of seconds to tens of minutes. The hydrogen flow rate is measured by a high accuracy Coreolis mass flow meter and the pressure is measured at the inlet to the tank as well as at the opposite dead-ended fitting. We use an infrared camera to capture tank surface temperature gradients and compare to thermocouple measurements.

Results

Improved Accuracy of Turbulent Jets

To accurately assess the ignitability of given hydrogen releases the simulation must be accurate. Current computational fluid dynamics simulations treat intermittency (the presence of a concentration at a particular location) as linearly proportional to the ratio of the first and second order statistical moments. High fidelity experiments conducted at Sandia National Laboratories, however, demonstrate that this relationship is in fact non-linear, which contradicts current modeling approaches. The collection of these data provide new benchmarks for the evaluation of optimum distribution functions used to model mixture ignitability (Figure 1).

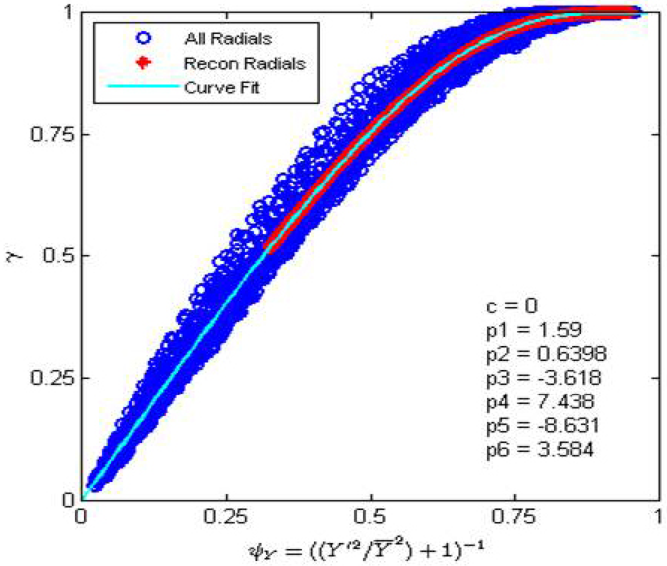


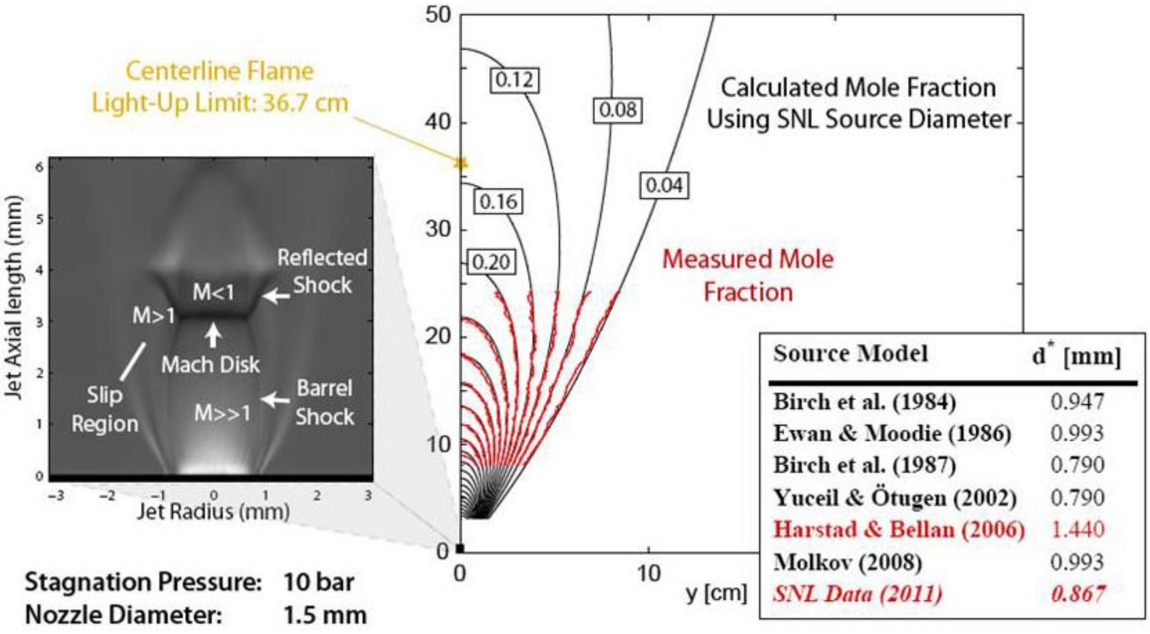
FIGURE 1. Intermittency plotted against the ratio of the first and second turbulent concentration moments. Commonly used intermittency models assume a linear fit between the first and second statistical moments of the scalar concentration field, but these data indicate a highly non-linear correlation, particularly for intermittency values (γ) greater than ~0.75.

High Source Pressure Hydrogen Release Behavior

Turbulent hydrogen releases, both ignited and unignited, are typically treated and canonical expanded free-jets using similarity arguments based on the jet exit diameter. For underexpanded jets with choked flow releases and complex jet-exit structure past the release point a notional nozzle, modeled from thermodynamic variables, is used to create a pseudo source jet exit diameter, and the dispersion characteristics of the downstream flow is solved for with the use of the incompressible jet-similarity relations. These release types are important, since most hydrogen is stored at a compressed state that is above the critical pressure ratio. The optimum method to model the pseudo source term, however, had not yet been determined for hydrogen. A schlieren image of the underexpanded jet is provided at the left in Figure 2. Using the planar laser Raleigh scatter technique to measure statistical dispersion fields of mole fraction, a comprehensive comparison of measured data to model results using six separate notional nozzle formulations was performed. For each notional nozzle model, both ideal and non-ideal equations of state were analyzed. The evaluation showed poor correlation for all existing models, with the most comprehensive model (Harstad & Bellan) substantially and unexpectedly overpredicting the size of the mass weighted effective diameter (d*). Nonetheless, the measurements indicate better ways to more accurately model these release types; refined model development is ongoing.

Applied Flame Radiation Evaluation

Previous radiation experiments conducted by Sandia National Laboratories provided a universal correlation for small and mid-size flames regardless of fuel gas type. Recent experiments, conducted by Air Products and Chemicals has revealed larger than expected radiative emission values from larger flames. The results of this work are still pending,



Source Model	d^* [mm]
Birch et al. (1984)	0.947
Ewan & Moodie (1986)	0.993
Birch et al. (1987)	0.790
Yuceil & Ötugen (2002)	0.790
Harstad & Bellan (2006)	1.440
Molkov (2008)	0.993
SNL Data (2011)	*0.867*

FIGURE 2. Left, schlieren image of hydrogen under-expanded jet. Center, calculated mole fraction in black using the measured effective nozzle diameter compared to the measured mole fraction in red; the centerline light-up limit is also shown for comparison. Right, table comparing the predicted mass weighted effective diameter based on various notional nozzle models relative to the 'true' measured result.

however, several hypothesis have been tested using Sandia National Laboratories using the high source pressure flame capabilities previously developed to analyze notional nozzle models from choked flow releases. Figure 3 shows images of the flames used in the experiment, which are reproduced with the permission of the industry collaborator.

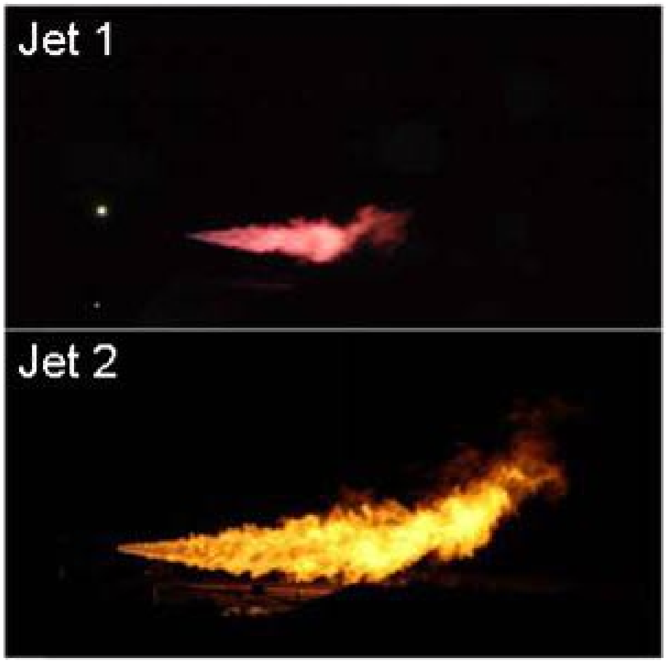


FIGURE 3. Images of Large-Scale Hydrogen Flames

COPV Testing and Characterization

The experimental results met the target accuracy (<1% error, mass balanced). In addition the qualitative information gained in the thermography reinforced the choice of temperature measurement locations. Images from thermography are shown in Figure 4.

The models developed and validated by this experiment are part of an international collaboration. Professor Jinyang Zheng conducts hydrogen storage research at Zhejiang University of China. Dr. Jianjun Ye, a member of the Zhejian University team, arrived at Sandia in November 2011. Dr. Ye completed the development of the three-dimensioinal model geometry and has optimized the finite element mesh for accuracy and minimum computational time. The model is running and several of the experimental conditions are being simulated.

In addition to Dr. Ye's work Sandia is developing a one-dimensional simulation of hydrogen dispensers using the Sandia-developed, multi-species compressible-flow, simulation program, Netflow.

Netflow calculations have been carried out for several of the H2 filling experiments conducted during the last two quarters and the comparison between simulation results and experimental data is currently being analyzed. These simulations are comparable to simulations currently underway by automotive original equipment manufacturers in support of hydrogen fueling protocol standard, SAE J2601.

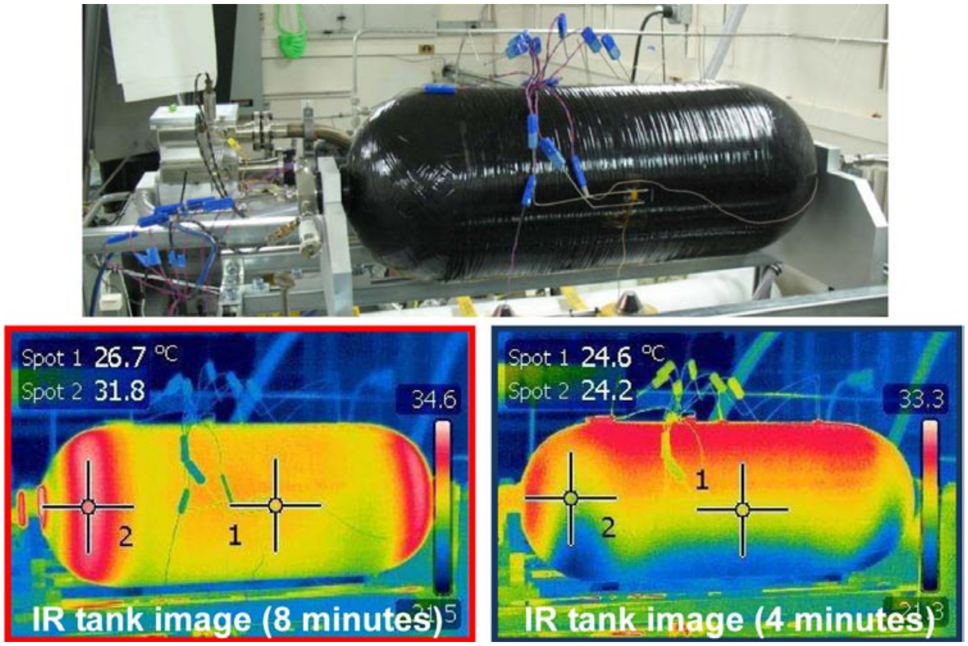


FIGURE 4. Above, instrumented tank in test facility, below left, thermal image of tank during fill – screen capture of video taken 8 minutes for a 90 sec, 13 MPa fill, below right, thermal image of tank during vent – screen capture of video taken at 4 minutes for a 1.9 g/sec vent from 9 MPa.

Conclusions and Future Directions

- Computational fluid dynamics models for hydrogen ignitability should be evaluated against benchmark data.
- Characteristics of predictive choked flow dispersion models were examined against Sandia generated validation datasets:
  - Deficiencies identified and from the measurements, more accurate modeling methods have been proposed.
- Qualitative high-speed ignition imaging elucidated potential sustained flame light-up mechanisms:
  - Light-up boundaries for choked flow releases were experimentally mapped for several different source pressure ratios and nozzle diameters.
  - Enhanced flamelet models can be used to predict light-up boundaries–experimental apparatus needed to measure relevant flow and combustion variables was constructed.
- Measured radiative heat fluxes from large-scale H_2 flames were compared against model predictions:
  - Deficiencies identified and improved modeling methods have been proposed.
- Future Direction – develop simplified model for overpressure transient releases. A simplified model is necessary for risk assessment of deflagrations created from delayed ignition of hydrogen releases.
- Future Direction – Develop improved models of choked flow dispersion including notional nozzle deficiencies.
- Future Direction – Evaluate jet elongation due to surface effects for horizontal releases.
- Future Direction – Develop models to predict the reflection due to surfaces for various hydrogen flame scenarios.

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

FY 2012 Publications/Presentations

1. Ruggles, A.J., and Ekoto, I.W., "Ignitability and mixing of underexpanded hydrogen jets," 4th International Conference on Hydrogen Safety, San Francisco, CA, Sept. 12–14, 2011. (Accepted for publication in IA-HySafe special edition of *Int. J. Hydrogen Ener.*)

2. Houf, W.G., Evans, G.H., Ekoto, I., Merilo, E. and Groethe, M., "Hydrogen Releases and Ignition from Fuel-Cell Forklift Vehicles in Enclosed Spaces," 4th International Conference on Hydrogen Safety, San Francisco, CA, Sept. 12–14, 2011. (IA-HySafe special edition of *Int. J. Hydrogen Ener.*)

3. Houf, W.G. and Winters, W.S., "Simulation of High Pressure Liquid Hydrogen Releases," 4th International Conference on Hydrogen Safety, San Francisco, CA, Sept. 12–14, 2011. (IA-HySafe special edition of *Int. J. Hydrogen Ener.*)

4. Ekoto, I.W., Merilo, E.G., Houf, W.G., Evans, G.H., Groethe, M.A., "Hydrogen Fuel-Cell Forklift Vehicle Releases in Enclosed Spaces," 4th International Conference on Hydrogen Safety, San Francisco, CA, Sept. 12–14, 2011. (IA-HySafe special edition of *Int. J. Hydrogen Ener.*)

5. Merilo, E., Groethe, M., Adamo, R., Schefer, R., Houf, W., Dedrick, D., "Self-Ignition of Hydrogen Jet Fires by Electrification of Entrained Particulates," 4th International Conference on Hydrogen Safety, San Francisco, CA, Sept. 12–14, 2011. (IA-HySafe special edition of *Int. J. Hydrogen Ener.*)

6. Ekoto, I.W., Dedrick, D. E., Merilo, E., Groethe, M., "Performance-Based Testing for Hydrogen Leakage into Passenger Compartments," International Journal of Hydrogen Energy Vol. 36, Issue 16, 2011.

7. Dedrick, D.E., "Approach to establishing technical basis for Codes and Standards," IEA Task 31 Subtask A Coordination Meeting: Hydrogen Behavior Research, Oslo, Norway, Jan. 10, 2012.

8. Ekoto, I.W. "General Release Behavior R&D for H2 Safety, Codes & Standards," H2CAN/Sandia Workshop April 11, 2012.

9. Ruggles, A.J. "Summary of Hydrogen Release and Ignition Behavior at Sandia National Labs," H2CAN/Sandia Workshop April 11, 2012.

10. Ekoto, I.W. "Summary of Hydrogen Release and Ignition Behavior at Sandia National Labs IEA Task 31 Subtask A Coordination Meeting: Hydrogen Behavior Research, Oslo, Norway, April, 2012.

11. Ekoto, I.W., Houf, W.G., Ruggles, A.J., Crietz, L.W., Li, J.X., "Large-Scale Hydrogen Jet Flame Radiant Fraction Measurements and Modeling," 19th World Hydrogen Energy Conf., Toronto, Canada, June 16–21, 2012.

12. Ekoto, I.W., Houf, W.G., Ruggles, A.J., Crietz, L.W., Li, J.X., "Large-Scale Hydrogen Jet Flame Radiant Fraction Measurements and Modeling," International Pipeline Conference, Calgary, Canada, September 24–28, 2012 (Accepted).