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FIRE HAZARDS OF SMALL HYDROGEN LEAKS

N.R. Morton[1], P.B. Sunderland[1], B.H. Chao[2], R.L. Axelbaum[3]

This study examines the types of hydrogen leaks that can support combustion and the corrosive effects of hydrogen flame exposure to aluminum, galvanized steel, stainless steel, and SiC fibers. Hydrogen, methane, and propane diffusion flames on round burners were observed. Measurements included limits of quenching and blowoff for burners with diameters of 0.36 — 1.78 mm. The measured mass flowrates at the quenching limits were found to be independent of burner diameter. In terms of mass flowrates, hydrogen had the lowest quenching limit and the highest blowoff limit of the fuels considered. Hydrogen flames were found to be more corrosive than methane flames to aluminum, galvanized steel, and SiC fibers.

1. Introduction

Concerns about the emissions of greenhouse gases have led to extensive consideration of hydrogen as an energy carrier. Hydrogen presents several unusual fire hazards, including high leak propensity, ease of ignition, and invisible flames. The scenario of interest in this work is that a small leak in a hydrogen system might ignite, support a flame that is difficult to detect, and degrade containment materials to the point of a catastrophic failure. This study includes experiments and analysis to identify which hydrogen leaks can support flames. Material degradation by hydrogen and methane flames also is examined here.

A Department of Energy report [1] found that hydrogen containment was the chief safety concern associated with using hydrogen as a transportation fuel and documented several catastrophic hydrogen fires.

Quenching and blowoff limits bound the leak flowrates that can support combustion. Measurements of propane quenching and blowoff flowrates were made by Matta et al. [2]. Quenching limits for methane were performed by Cheng et al. [3].

Research has been done in evaluating leak flow rates of hydrogen, methane, and propane. Swain and Swain [4] modeled and measured leak rates for diffusion, laminar, and turbulent flow regimes. They found that combustible mixtures in an enclosed space resulted more quickly for propane and hydrogen leaks than for methane leaks. Their supply pressures were the same for all fuels.

Khan et al. [5] examined the effects of raised temperatures on carbon fabric/epoxy composites, a likely material for high pressure storage tanks. Pehr [6] discusses

[1]Dept. of Fire Protection Engineering, Univ. of Maryland, College Park MD
[2]Dept. of Mechanical Engineering, Univ. of Hawaii, Manoa HI
[3]Dept. of Mechanical and Aerospace Engineering, Washington Univ., St. Louis MO

some of the issues associated with hydrogen containment. Utgikar and Thiesen [7] discuss the impact of hydrogen on materials, and the safety of hydrogen fuel tanks.

Thus motivated, the objectives of this work are to (1) measure limits of flaming (at quenching and blowoff) for hydrogen, methane, and propane issuing from circular burners of various sizes, and (2) examine material degradation arising from exposure to hydrogen and methane diffusion flames.

2. Flame Quench Scaling

A scaling analysis was developed to interpret measured flame quenching limits. These limits are the minimum flow rates required to support a diffusion flame. This analysis also yields a dimensionless crack parameter that indicates how close a given leak is to the quenching limit.

The stoichiometric length L_f of laminar gas jet diffusion flames on round burners is:

$$L_f / d = a\,Re = a\,\rho\,u_0\,d / \mu\ , \qquad (1)$$

where d is burner inside diameter, a is a dimensionless fuel-specific empirical constant, Re is Reynolds number, u_0 is the average fuel velocity in the burner, ρ is fuel density, and μ is fuel dynamic viscosity. The scaling of Eq. (1) arises from many theoretical and experimental studies, including Roper [8], Sunderland et al. [9], and references cited therein. Constant a here is assigned values measured by Sunderland et al. [9], as listed in Table 1.

Table 1: Selected fuel properties of hydrogen, methane, and propane. Values for *a* are from Sunderland et al. [9], L_q and S_L are from Kanury [10], and μ is from Weast and Astle [11].

Fuel	a	L_q [mm]	S_L [cm/s]	μ [g/m-s]	m_{fuel} [mg/s] predicted	m_{fuel} [mg/s] measured
H_2	0.236	0.51	291	8.76e-3	0.008	0.021
CH_4	0.136	2.3	37.3	1.09e-2	0.085	0.112
C_3H_8	0.108	1.78	42.9	7.95e-3	0.063	0.031

The base of an attached jet diffusion flame is quenched by the burner. Its standoff distance can be approximated as one half of the quenching distance of a stoichiometric premixed flame. Such quenching distances typically are reported as the minimum tube diameter, L_q, through which a premixed flame can pass. It is assumed here that a jet flame can be supported only if its stoichiometric length is greater than half this quenching distance:

$$L_f \geq L_q / 2 \text{ to support a flame.} \qquad (2)$$

Measurements of L_q, shown in Table 1, are taken from Kanury [10]. When combined, Eqs. (1) and (2) predict the following fuel flowrate, m_{fuel}, at the quenching limit:

$$m_{\mathrm{fuel}} = \pi \rho u_0 d^2 / 4 = \pi L_q \mu / (8 a) . \quad (3)$$

Equation (3) indicates that the fuel mass flow rate at the quenching limit is a fuel property that is independent of burner diameter. When values of L_q, μ, and a from Table 1 are inserted into Eq. (3), the predicted fuel flowrates at quenching shown in Table 1 are obtained.

A crack parameter can now be derived. Assuming fully-developed, incompressible laminar flow in the burner,

$$u_0 = d^2 \Delta p / (32 \mu L_b) , \quad (4)$$

where Δp is the pressure drop across the burner and L_b is the burner flow passage length [12]. Equation (4) is valid for many laboratory burners. However, compressed hydrogen storage systems at pressures of up to 350 bar require more advanced models of leak flowrates such as those in [4].

Combining Eqs. (1), (2), and (4) yields, for leaks that are fully-developed, incompressible and laminar,

$$CP = a \rho d^4 \Delta p / (16 \mu^2 L_b L_q) \geq 1 \text{ to avoid flame quenching,} \quad (5)$$

where CP is the dimensionless quenching crack parameter.

3. Experimental

3.1 Quenching and Blowoff

Quenching and blowoff limits of hydrogen, methane, and propane diffusion flames were measured. These tests involved five burners with inside diameters of 0.356, 0.711, 0.838, 1.397, and 1.778 mm. All tests were performed in quiescent air at 1.01 bar.

The burners were stainless steel nozzles that are manufactured for spray generation. The top of each burner is a curved surface with a hole passing through its axis. Fuel was delivered to each burner via a pressure regulator, a metering valve, and a rotameter.

For the quenching limit measurements, a flame approximately 5 mm long was ignited. The flow was then reduced until the flame extinguished. This was done several times for each burner and each fuel. The flames were small enough, and the experiments were done quickly enough, that there was no noticeable increase in the temperature of the burners. Measurement of the hydrogen quenching limits required special care, as small hydrogen flames are nearly invisible even in a darkened lab. Methods to identify quenching for hydrogen flames included passing paper above the burner and increasing the flowrate.

Also measured were the blowoff limits of each fuel for each burner. Blowoff limits were measured by igniting a flame and then increasing the flow rate until the flame lifted off and extinguished. The tests were performed quickly to ensure burner temperatures remained close to ambient.

Blowoff occurs when velocities in the flammable regions exceed the burning velocity. For laminar flames the relevant burning velocity is the laminar flame speed, which is shown in Table 1, however most of the present flames were turbulent just before blowoff.

3.2 Materials Degradation

Materials degradation tests were performed on specimens of six different materials: aluminum alloy 1100, galvanized 1006-1008 carbon steel, 304 stainless steel, 316 stainless steel, SiC yarn and SiC filament. These materials were chosen owing to their common use in gas storage systems. The specimens were approximately 100 mm long, with diameters as given in Table 2.

Table 2: Wire and fiber specimen diameters.

Material	Diameter (mm)
Aluminum Alloy 1100	1.01
Galvanized 1006-1008 Carbon Steel	1.04
304 Stainless Steel	1.04
316 Stainless Steel	1.01
SiC yarn	1.14
SiC filament	0.015

The burners for these tests were stainless steel tubes with inside diameters of 2.43 mm. The flames were approximately 15 mm long, and are shown in Fig. 1. These images were recorded using a Nikon D100 Digital Camera with a 60 mm focal length lens, and with ISO 1600, direct sunlight white balance, 50 ms shutter time, and f/3.8.

The samples were installed horizontally in hydrogen and methane diffusion flames at a height of 7 mm. This height was near the flame mid-height and was low enough in the methane flame to avoid soot deposition.

4. Results

The images of Fig. 1 show sample hydrogen and methane diffusion flames. The methane flame exhibits the familiar blue and yellow regions of hydrocarbon diffusion flames. The hydrogen flame is much dimmer and is visible only in a darkened room.

4.1 Quenching and Blowoff Limits

The measured fuel mass flowrates at quenching and blowoff are presented in Fig. 2. Results are shown for hydrogen, methane, and propane and are plotted as a function of burner diameter.

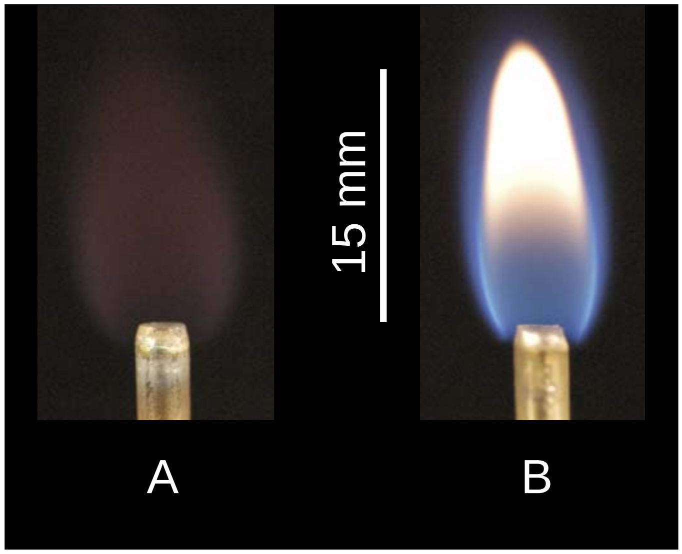

Figure 1: Color images of (A) hydrogen flame and (B) methane flame.

Figure 2 shows that burner mass flowrate at the quenching limit is independent of burner diameter. This finding is supported by the prediction of Eq. (3). Mass flowrates at the quenching limits increase from hydrogen to propane to methane. Results averaged for all burner diameters are shown in Table 1. The predictions of Eq. (3), also given in Table 1, capture the trends of the quenching experiments. It may be possible to improve the agreement by using different published values of quenching distances of premixed flames. The prediction may also be improved by using the available standoff distances of these fuels, instead of quenching distance, as the length scale in the analysis.

Matta et al. [3] measured quenching limits for propane, and found that flowrate is nearly independent of burner tube diameter. The prediction [3] uses to correlate the quenching data uses the standoff distance as the length scale for the analysis. Ref. [3] also noted that the predicted flow velocity for the flammable mixtures will be larger than the local flame speed at blowoff. The measurements from the present study were found to be lower for the quenching regime, but similar for blowoff.

Cheng et al. [2] measured quenching velocities for methane, and makes use of flame length correlations and measurements of standoff distance to predict when quenching will occur. The measurements from the present study were found to be smaller then the quenching measurements and predictions from [2].

The blowoff measurements in Fig. 2 show that mass flowrate at blowoff increases with burner diameter. Blowoff mass flowrates increase from methane to propane to hydrogen. This is qualitatively supported by the laminar flame speeds shown in Table 1.

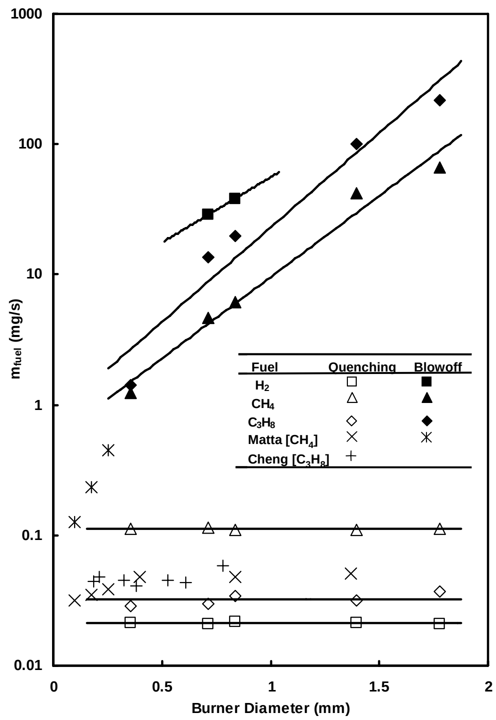

Figure 2. Measured fuel mass flowrate at the quenching and blowoff limits versus burner diameter. The lines are the fits of the present experiments.

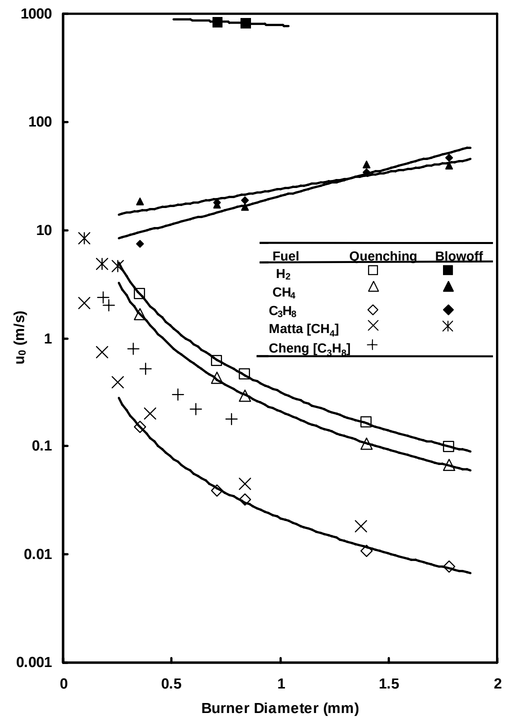

Figure 3. Measured fuel velocity at the quenching and blowoff limits versus burner diameter. The curves shown are fits of the present experiments.

Figure 3 shows the same measurements and correlations of Fig. 2 when the ordinate is changed to fuel velocity. This figure suggests a regime may exist at the smallest burner diameters where the blowoff limit is lower than the quenching limit. Burners smaller than those considered here will need to be tested to further evaluate this.

4.1 Material Degradation

Aluminum alloy 1100 showed very different effects when exposed to hydrogen and methane flames. Figure 4 includes images of the aluminum samples after the 8 hour exposure. The hydrogen flame caused severe warping, as well as noticeable oxidation of the aluminum wire, after one hour. As the test continued, the distortion became more and more severe, as did the degree of oxidation, until the aluminum wire failed. The wire in the methane flame for the same exposure time did not reveal these effects. There is some slight discoloration where some soot deposited from the methane flame, but nothing approaching what was observed for they hydrogen exposure.

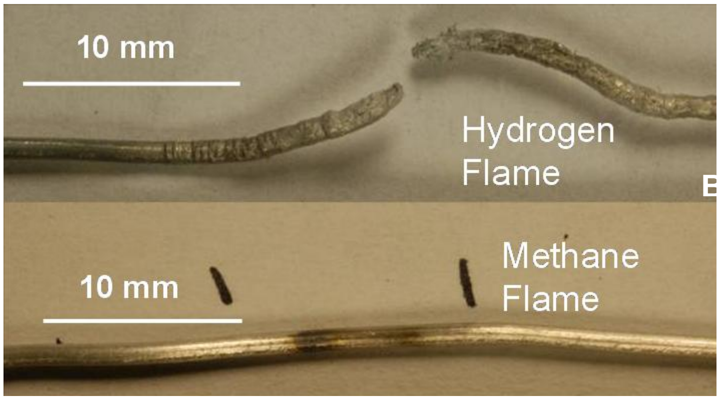

Figure 4: Aluminum wires following 8 hours of exposure to (A) hydrogen flame and (B) methane flame.

Another material that showed significant differences upon flame exposure is galvanized carbon steel. The sample exposed to a hydrogen flame showed more significant corrosion than the sample in the methane flame, see Fig. 5.

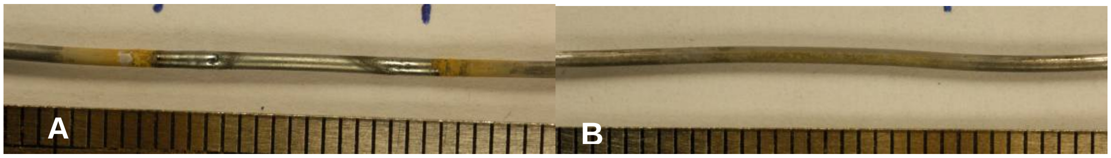

Figure 5: Galvanized 1006-1008 Carbon steel following one hour of exposure to (A) hydrogen flame and (B) methane flame. The scale markings are in mm.

A test of one hour exposure of the fiber yarn showed that it performed similarly in both hydrogen and methane flames. Several individual filaments failed during both exposures, but most remained intact.

Individual SiC filaments were observed to burn through during exposure to either hydrogen or methane flames. Filaments in the hydrogen and methane flames were observed to fail in 15 and 116 minutes, respectively.

5. Conclusions

The quenching and blowoff limits for hydrogen, methane, and propane have been measured for small round burners. Materials degradation of exposure to hydrogen and methane diffusion flames was observed. The conclusions of this study are:

The measured fuel mass flow rate at the quenching limits is independent of burner diameter. This is consistent with a simple scaling analysis based on a premixed flame quenching distance.

Hydrogen has a lower mass flowrate at quenching and a higher mass flowrate at blowoff than either methane or propane.

Hydrogen flames caused faster corrosion than methane flames on aluminum alloy 1100, galvanized steel, and SiC filaments.

6. Acknowledgements

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7. References

[1] Cadwallader, L.C. and Herring, J.S., Safety Issues with Hydrogen as a Vehicle Fuel, Report INEEL/EXT-99-00522, prepared for U.S. Department of Energy (1999).

[2] Matta, L.M., Neumeier, Y., Lemon, B., Zinn, B.T., Characteristics of Microscale Diffusion Flames. Proceedings of the Combustion Institute v. 29. n.1, p 933-938 (2002).

[3] Cheng, T.S., Chen, C.P., Chen, C.S., Li, Y.H., Wu, C.Y., Chao, Y.C., Characteristics of Microjet Methane Diffusion Flames. Combustion Theory and Modeling v.10, n. 5, p. 861-881 (2006).

[4] Swain, M.R., Swain, M.N., A Comparison of H2, CH4, and C3H8 Fuel Leakage in Residential Settings, Int. J Hydrogen Energy 17:807-815 (1992).

[5] Khan, R., Kan, Z., Al-Sulaiman F., Merah, N., Fatigue Life Estimates in Woven Carbon Fabric/Epoxy Composites at Non-Ambient Temperatures. Journal of Composite Materials Vol. 36, No. 22, p. 2517-2535 (2002).

[6] Pehr, K. Aspects of Safety and Acceptance of LH2 Tank Systems in Passenger Cars. Int. J. Hydrogen Energy Vol. 21, No. 5, pp. 387-395 (2006).

[7] Utgikar, V.P., Thiesen, T., Safety of compressed hydrogen fuel tanks: Leakage from stationary vehicles. Technology in Society 27:315-320 (2005).

[8] Roper, F.G., The Prediction of Laminar Jet Diffusion Flame Sizes: Part I. Theoretical Model. Combust. Flame 29:219-226 (1977).

[9] Sunderland, P.B., Mendelson, B.J., Yuan, Z.-G., Urban, D.L., Shapes of Buoyant and Nonbuoyant Laminar Jet Diffusion Flames, Combust. Flame 116:376-386 (1999).

[10] Kanury, A.M., Introduction to Combustion Phenomena. Gordon and Breach, New York, p. 131 (1975).

[11] Weast, R.C., Astle, M.J., CRC Handbook of Chemistry and Physics, 59th edition, CRC Press, Inc. West Palm Beach, p. F-58 (1979).

[12] Munson, B.R., Young, D.F., Okiishi, T.H., Fundamentals of Fluid Mechanics, Wiley, Hoboken, NJ, p. 359 (2002).

[13] Odegard, Ben C., Thomas, George J., Testing of High Pressure Hydrogen Composite Tanks. Proceedings of the 2001 DOE Hydrogen Program Review. Livermore, CA, USA.

[14] Bahadori, M. Y., Hegde, U., Zhou, L., Liftoff and Blowoff of Jet Diffusion Flames, Paper AIAA-2002-1078, Aerospace Sciences Meeting, Reno, Nevada, January 14-17, 2002.