

On the Physical and Combustion Properties of Hydrogen and the Feasibility and Characteristics of Hydrogen Fuel-Cell Vessels

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*Sandia HQ:
Albuquerque NM*

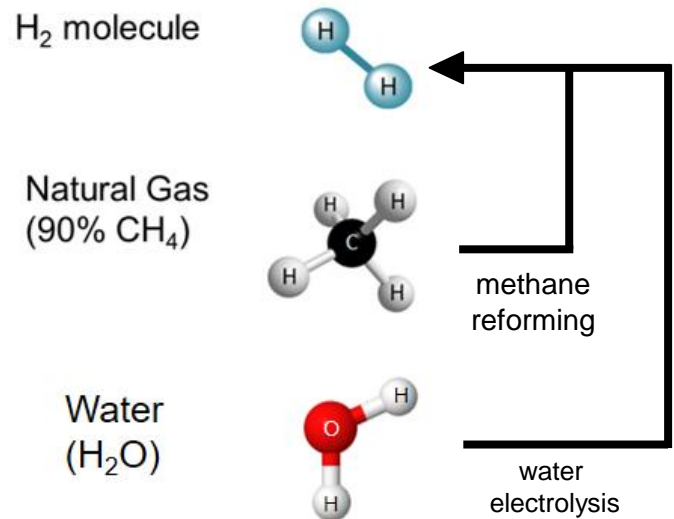


*Livermore CA
(SF Bay Area)*

- Sandia is the largest National Lab in the U.S.
 - U.S. Department of Energy (DOE) ~13,000 employees
 - ~ US \$3.2B/yr from DOE, other federal agencies, and private industry
 - H₂ Program in Livermore, CA (SF Bay Area)
- Hydrogen program: 60+ years of work, in a wide range of areas (H₂ storage, production, delivery, development of regulations, **market transformation**), which we apply to enable impactful clean energy solutions
- **Market Transformation: Zero Emission H₂/Fuel Cell Maritime Program:**



Hydrogen Properties:



- Is typically a gas, but can be a liquid (LH₂) if made very cold (20 K).
- LH₂ evaporates very fast (4,000 gallons will evaporate in ~7 seconds)
- More buoyant than helium. Goes straight up at ~40 mph.

Overall, H₂ is very similar to natural gas (which is ~ 90% methane, CH₄).

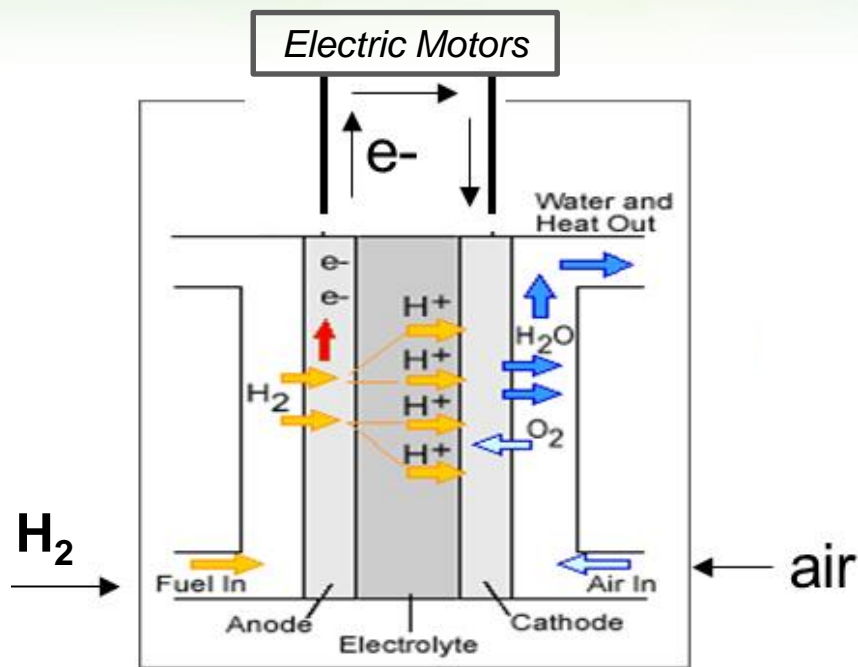
H₂ is NOT a Greenhouse Gas, unlike natural gas which is a potent GHG.

If spilled, LH₂ evaporates from the water leaving no residue.

H₂ can be ignited given an ignition source and the right H₂/air mixture.

Energetically, a kg of H₂ has about the same energy as a gallon of diesel fuel.

When hydrogen is used in a *Fuel Cell* it produces ZERO pollution or greenhouse gas at point of use



- commercially available
- more energy efficient than diesel generators
- eliminates emissions at the point of use
- eliminates fuel spills, greatly reduces noise
- emissions can only arise from H₂ production/delivery
- no "thermal runaway" possible



Photos Courtesy Ryan Sookoo, Hydrogenics

Going In:
H₂ and air

Going Out:
Electricity
Waste Heat
Warm humidified air

Physical Properties of LH₂ and LNG

LH₂:

Note: 75 °F = 297 K

Liquid Normal Boiling Point = 20 K (-253 °C).

Liquid Density = 71 g/L

Lower Heating Value = 120 MJ/kg

LNG (LCH₄):

Liquid Normal Boiling Point = 111 K (-162 °C).

Liquid Density = 422 g/L

Lower Heating Value = 45 MJ/kg

LH₂ has 0.38 times the mass of LNG, but has 2.4 times the volume, per unit of energy (LHV).

LH₂ has 0.36 times the mass of diesel, but has 4.2 times the volume, per unit of energy (LHV).

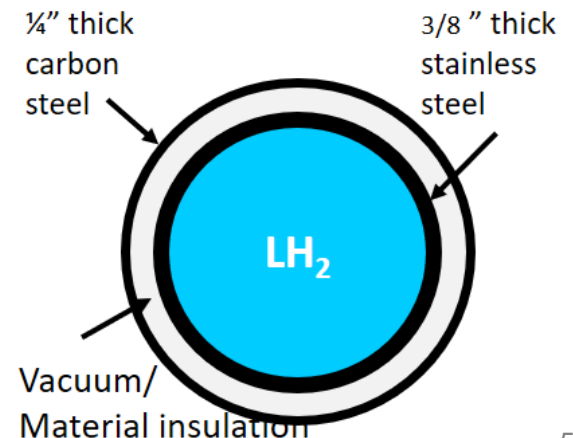
LH₂ and LNG are stored in similar ways:



LH₂ Storage Tank on Trailer

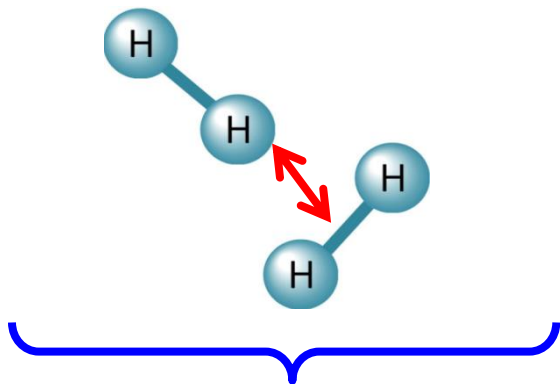


LNG Storage Tank on Trailer



LH₂ Evaporates Faster than LNG, Cools Surfaces Less (Spill)

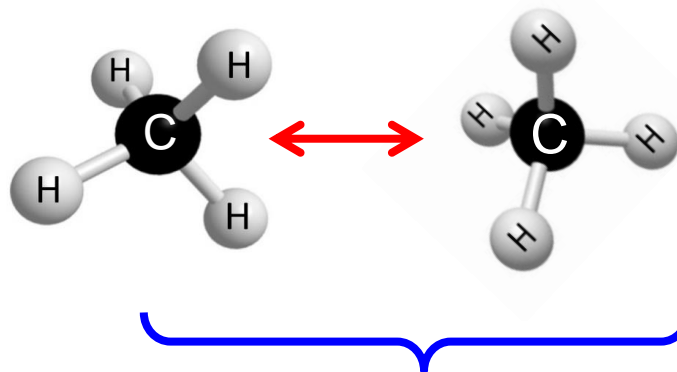
LH₂:



H₂ molecules barely interact at all

Heat of Vaporization = 0.922 kJ/mole

LNG (CH₄):



CH₄ molecules interact a bit more

Heat of Vaporization = 8.5 kJ/mole

-- For equal amounts of stored energy, LH₂ takes 3 times less energy than LNG to evaporate. In a spill, LH₂ will cool surroundings much less than LNG.

-- We estimate that if we spilled 1200 kg of LH₂, it would take ~ 6 seconds to evaporate

Let's Pause for Some Combustion Definitions

Explosion or Detonation: Extremely fast combustion where the flame propagates through the unburned fuel/air mix at supersonic speeds (~ 1000 m/s). Explosions produce loud bangs and very damaging overpressures. **Explosions are very, very bad.**

Deflagration: Fast combustion where the flame propagates through the unburned fuel/air mix at subsonic speeds (~ 100 m/s). Deflagrations are not as loud, and have 10x less damaging overpressures than explosions. **Deflagrations are very bad.**

Fire: Ordinary combustion where the flame propagates through the unburned fuel/air mix at slow speeds (~ 10 m/s). Fires are not loud, have negligible overpressure. **Fires are bad. If we work to prevent fires, we also prevent explosions and deflagrations.**

Weak (Thermal) Ignition Sources: Matches, sparks, hot surfaces, open flames (< 50 mJ). These are typically the ignition sources that cause accidents.

Strong (Shock Wave) Ignition Sources : blasting caps, TNT, high-voltage capacitor shorts (exploding wires) , lightning (> 4 MJ). Strong sources are $\sim 10^8$ stronger than weak initiators.

Gaseous Flammability of H₂ vs NG

Both H₂ and NG (methane) mixtures with air are easily ignited by “Weak (Heat) Ignition Sources” such as: sparks, hot surfaces, open flames (< 50 mJ).

Fire regulations reference the “Lower Flammability Limit” (LFL) because the greatest fire risk comes from building up gas in initially clean air:

Definition: % by volume = [Volume (Fuel)/Volume (Fuel + Air)] x 100.

The LFL to upper flammability limit (UFL) for H₂ = 4.0 – 75.0 % at RT. The LFL to UFL of methane is = 5.3 – 15.0 % at room temp. **Note: the LFL for diesel fuel is 0.6%.**

The minimum ignition energy for CH₄ = 0.29 mJ; That for H₂ is 0.02 mJ. Static discharges from human beings are ~ 10 mJ, **so both CH₄ and H₂ ignite easily.**

H₂ and NG are both easily ignited by weak ignition sources, and start to burn at similar lower flammability limits

Direct Explosions/Detonations of H₂ vs NG

The lower explosion limit (LEL) of H₂ at room temperature (% by volume) - upper explosion limit (UEL) = 18.3 – 59.0 % at RT. The LEL to UEL of methane is = 6.3 – 13.5 % at room temperature.

Experiments show that both H₂ and CH₄ require three things to directly detonate:

- 1. The fuel/air mix in the LEL – UEL range.**
- 2. A strong ignition source**
- 3. Confinement . Unconfined vapors of H₂ and CH₄ WILL NOT directly detonate, explode or deflagrate.**

A.D. Little study of LH₂ for the U.S. Air Force: For a series of LH₂ spills up to 5,000 gallon (1342 kg), igniting the unconfined vapor above the pool with spark, flame, or explosive charges produced only fire.

-- A.D. Little, Inc., Report to the U.S. Air Force, C-61092, (1960).

-- L.H. Cassutt, Report to the U.S. Air Force, Report No. 61-05-5182, (1964).

Sandia “Phoenix” Tests of LNG: Ignition of unconfined vapors above a 30,000 gallon pool of LNG produced only fire.

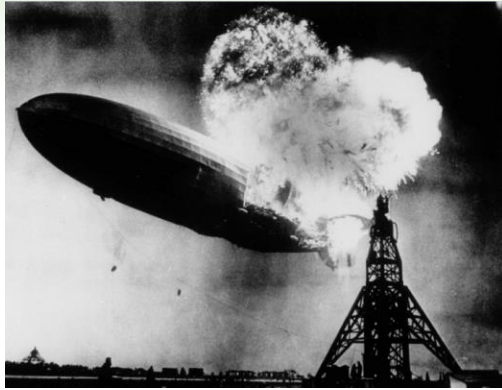
Deflagration to Detonation Transition (DDT)

In a confined environment with a lot of obstacles or internal structures, it is possible to get an explosion or detonation even with weak ignition sources.

Unlike direct detonation, which requires a strong ignition source, this type of explosion can start with a normal fire. In the confined/obstructed environment, the speed of the combustion accelerates over time and distance to a deflagration. With further acceleration, the deflagration transitions to a detonation because of turbulent mixing of the confined gases caused by the obstructions. We have a Deflagration to Detonation Transition (DDT).

For H₂, DDT can only occur for 12% fuel /air mix or higher. Both H₂ and NG can experience DDT, although it is easier for hydrogen. For hydrogen, ~ 10 m of run-up distance is required for the DDT.

Hindenburg Accident (1937)



It was a fire, NOT an explosion. Explosions are fast (think firecracker). The airship initially stayed aloft while burning. But fires are bad too and need to be prevented!

The method of storing hydrogen for the airship (rubberized gas bags) bears no resemblance to the highly engineered DOT-approved stainless steel LH₂ tanks in use today.



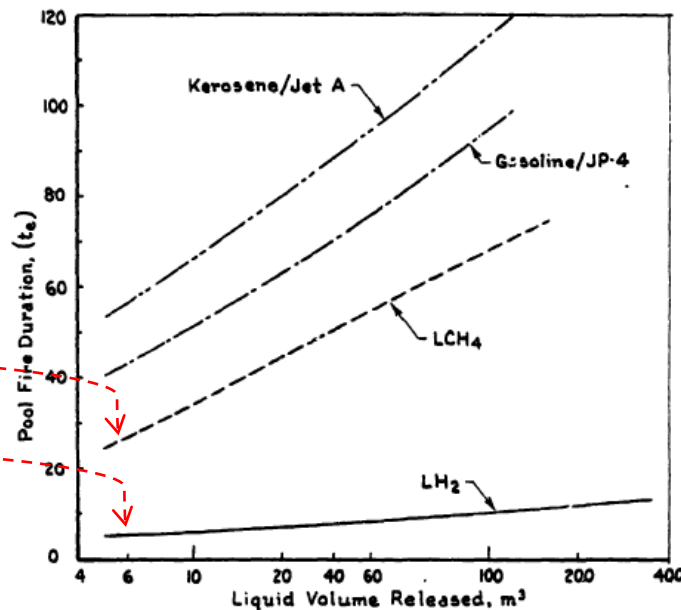
Improved to:



NASA mastered hydrogen, the “signature fuel” of the American Space Program since the 1960s.

The Nature of Fires: LH₂ vs. LNG

NASA funded a model study of the fire safety aspects of LH₂ and LNG as part of their program in alternative-fuel aircraft in the 1980s.



COMPARISON OF THE FIRE DURATIONS FOR POOL FIRES RESULTING FROM THE INSTANTANEOUS RELEASE OF THE FOUR FUELS

6 m³ = 6,000 L = 1587 gallons

= 426 kg of LH₂

= 2532 kg of LNG

A.D. Little, Inc., "An assessment of the crash fire hazard of liquid hydrogen fueled aircraft." Final Report to the National Aeronautics and Space Administration, NASACR-165526. 1982.

Pool Burn Times :

LNG = 25 s

LH₂ = 5 s

LH₂ pool fires burn out faster than LNG pool fires due to the much lower heat of vaporization of LH₂. But both fuels, if spilled, burn themselves out rapidly.

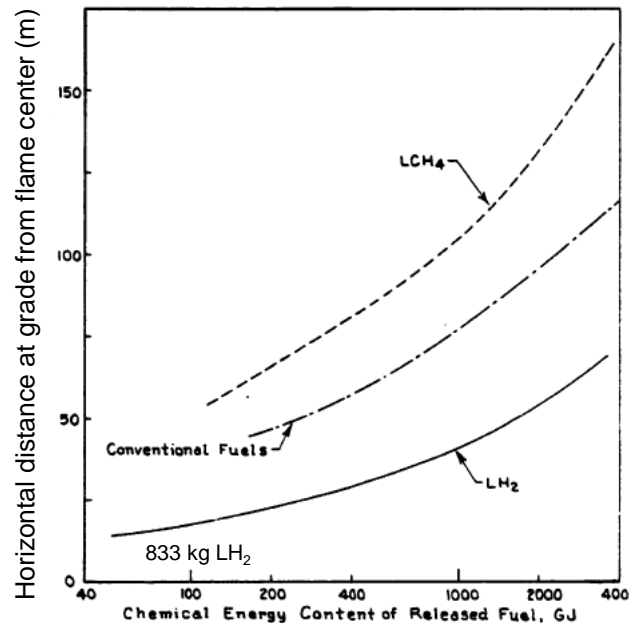
LH₂ Fires Pose Less Safety Risk Than LNG Fires

Results from the NASA-funded study:

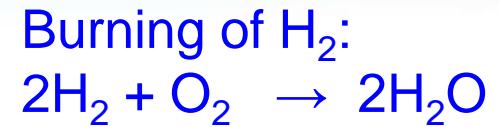
Note:
5 kW/m² is the threshold for skin thermal injury.

Approach limit
for LNG fire = ~54m

Approach limit
for LH₂ fire ~ 18m



Comparison of fire thermal radiation hazard distance (5kW/m²) as a function of the heat content of the released fuel.

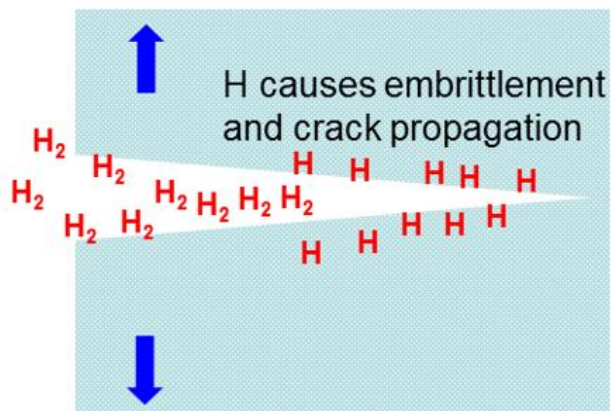
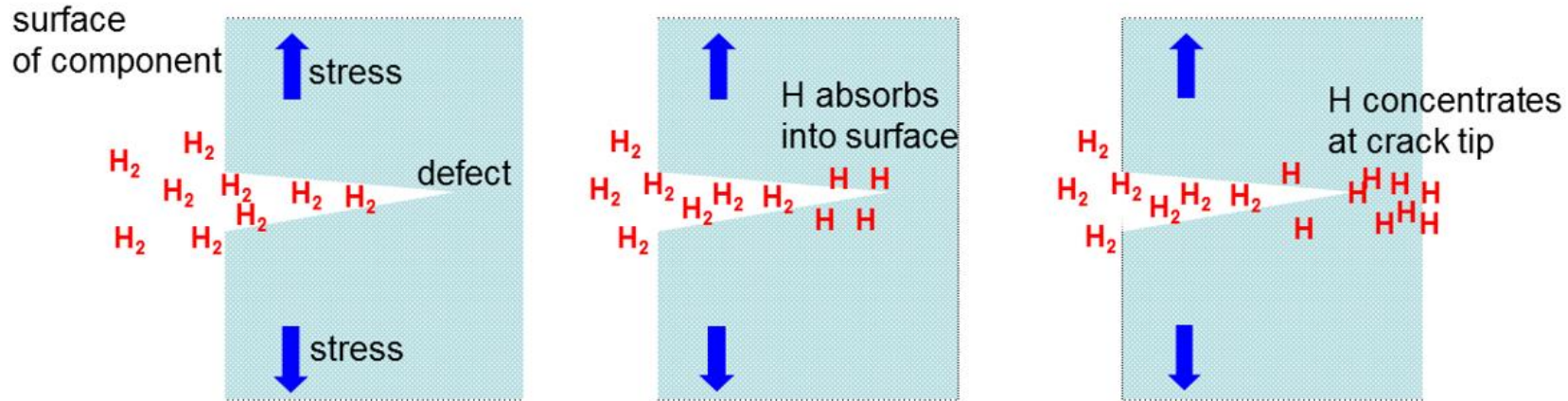


You can be 3x closer to a H₂ fire than a NG fire for the same safety factor.

LH₂ fires are radiatively much less hazardous than LNG fires for two reasons:

- 1. They don't contain carbon, and so radiate less than NG flames.**
- 2. Since the product of H₂ combustion is H₂O, the flame radiation is strongly absorbed by H₂O in the air.**

Hydrogen Embrittlement



H can accumulate at crack points, promoting crack propagation and eventual material failure in certain high-strength alloys and steels.

Solved Problem: The industry practice is to use 304 or 316 stainless steel in all H₂ plumbing, which is satisfactory.

But it is very important to ensure these alloys are used!

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Comparison of the safety-related physical and combustion properties of liquid hydrogen and liquid natural gas in the context of the SF-BREEZE high-speed fuel-cell ferry

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ABSTRACT

We review liquid hydrogen (LH₂) as a maritime vessel fuel, from descriptions of its fundamental properties to its practical application and safety aspects, in the context of the San Francisco Bay Renewable Energy Electric Vessel with Zero Emissions (SF-BREEZE) high-speed fuel cell ferry. Since marine regulations have been formulated to cover liquid natural gas (LNG) as a primary propulsion fuel, we frame our examination of LH₂ as a comparison to LNG, for both maritime use in general, and the SF-BREEZE in particular. Due to weaker attractions between molecules, LH₂ is colder than LNG, and evaporates more easily. We describe the consequences of these physical differences for the size and duration of spills of the two cryogenic fuels. The classical flammability ranges are reviewed, with a focus on how fuel buoyancy modifies these combustion limits. We examine the conditions for direct fuel explosion (detonation) and contrast them with initiation of normal (laminar) combustion. Direct fuel detonation is not a credible accident scenario for the SF-BREEZE. For both fuels, we review experiments and theory elucidating the deflagration to detonation transition (DDT). LH₂ fires have a shorter duration than energy-equivalent LNG fires, and produce significantly less thermal radiation. The thermal (infrared) radiation from hydrogen fires is also strongly absorbed by humidity in the air. Hydrogen permeability is not a leak issue for practical hydrogen plumbing. We describe the chemistry of hydrogen and methane at iron surfaces, clarifying their impact on steel-based hydrogen storage and transport materials. These physical, chemical and combustion properties are pulled together in a comparison of how a LH₂ or LNG pool fire on the Top Deck of the SF-BREEZE might influence the structural integrity of the aluminum deck. Neither pool fire scenario leads to net heating of the aluminum decking. Overall, LH₂ and LNG are very similar in their physical and combustion properties, thereby posing similar safety risks. For ships utilizing LH₂ or LNG, precautions are needed to avoid fuel leaks, minimize ignition sources, minimize confined spaces, provide ample ventilation for required confined spaces, and to monitor the enclosed spaces to ensure any fuel accumulation is detected far below the fuel/air mix threshold for any type of combustion.

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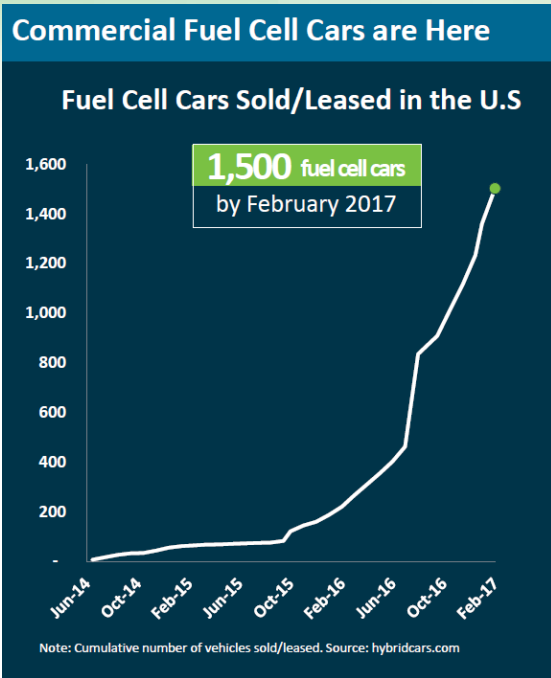
<http://dx.doi.org/10.1016/j.ijhydene.2016.11.024>

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More information about hydrogen gas (H₂) and liquid hydrogen (LH₂) can be found in:

L.E. Klebanoff et al., International Journal of Hydrogen Energy **42**, 757 (2017).

Hydrogen Technology is Here and Growing



Fuel Cell Electric Vehicles Can:

- ✓ Refuel in 5 minutes
- ✓ Have a 366 mile driving range (limited by H₂ storage)
- ✓ Only clean water vapor as the tailpipe emissions
- ✓ No need to plug in.

And it's not just fuel cell cars:



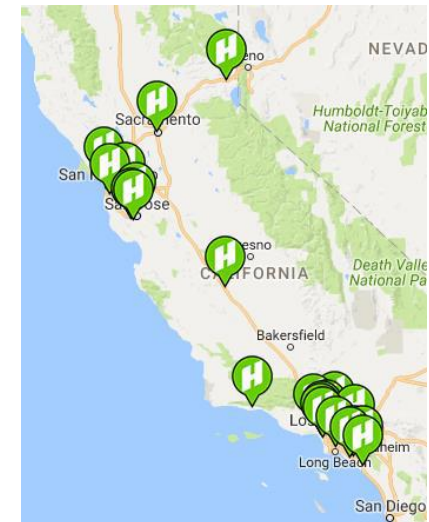
Fuel Cell Forklifts



Fuel Cell Buses

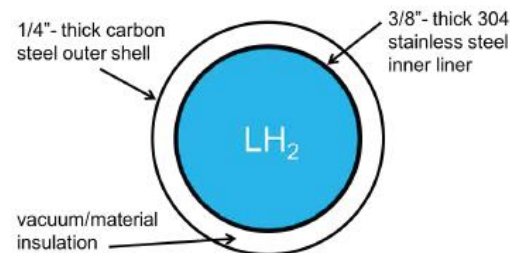


Fuel Cell Lighting



H₂ Stations are Being Built

H₂ Has Been Delivered and Used for Decades



Today: AC Transit Bus Station, Emeryville CA



1964 - 1973



1981 - 2011

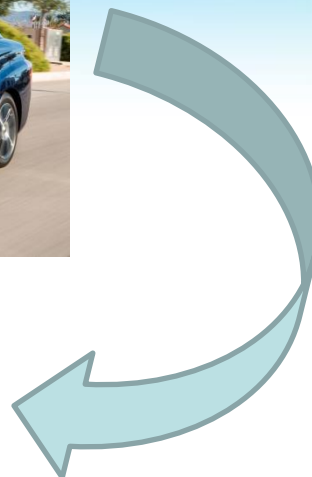
A typical LH₂ trailer can deliver 4000 kg (~15,000 gallons) at a time.
(1 kg LH₂ = 3.72 gallons)

Trailer LH₂ tanks are DOT-approved and have never been breached in a road accident.

Toyota Mirai



700 bar,
~ 10,000 psi
compressed H₂



Densities of Hydrogen:

700 bar gas = 40 g/L

LH₂ (at 1 bar pressure) = 71 g/L

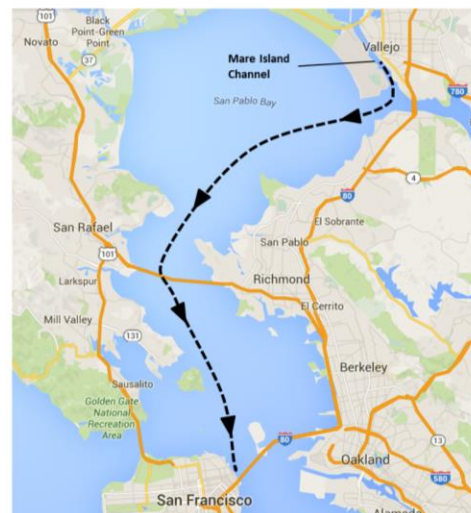
Solid AlH₃ = 149 g/L

The low density of even high pressure H₂ limits the range of fuel cell vehicles. Solid-state H₂ storage could be better!

But solid-state hydrogen storage is still a R&D area.

SF-BREEZE: The first study to show that H₂ fuel cells can be used in maritime propulsion, and how to do it.

High-speed H₂ Ferry



Route:
San Francisco
to Vallejo, CA

	Ferry	Hydrogen Station
Technical	✓	✓
Regulatory	✓	✓
Economic	<i>Higher than conventional now, today's market acceptance to be determined</i>	

Project Integrates Ship Designers, Regulators, H₂ Experts and End Users



USCG MSC and Design and Eng. Stds.



USCG Sector San Francisco



USCG Liquid Gas Carrier NCOE

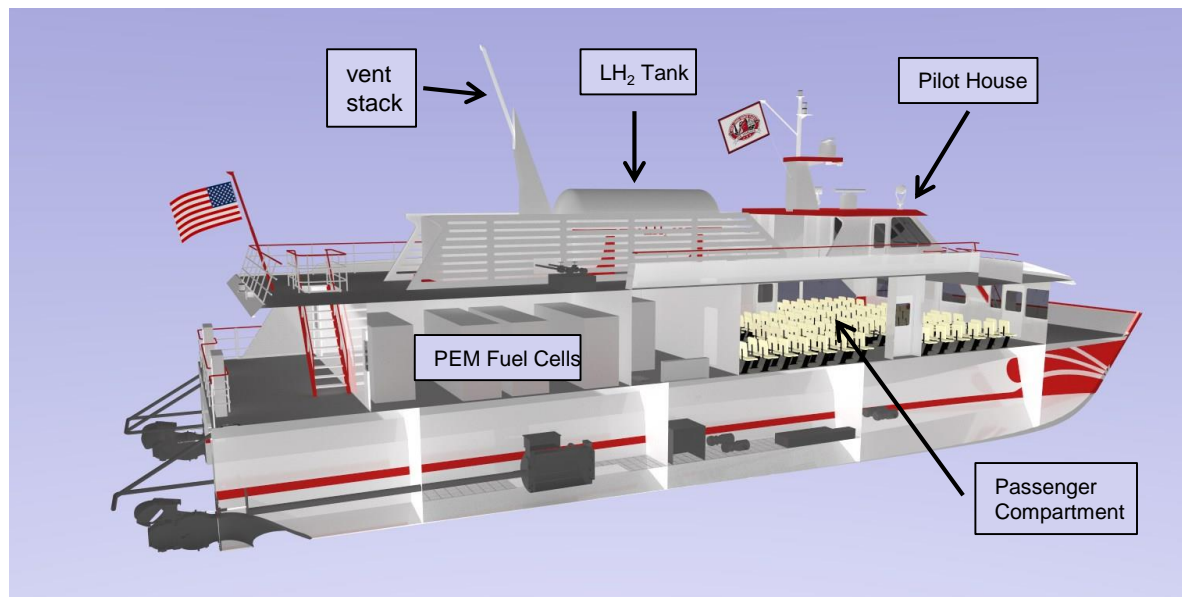


American Bureau of Shipping



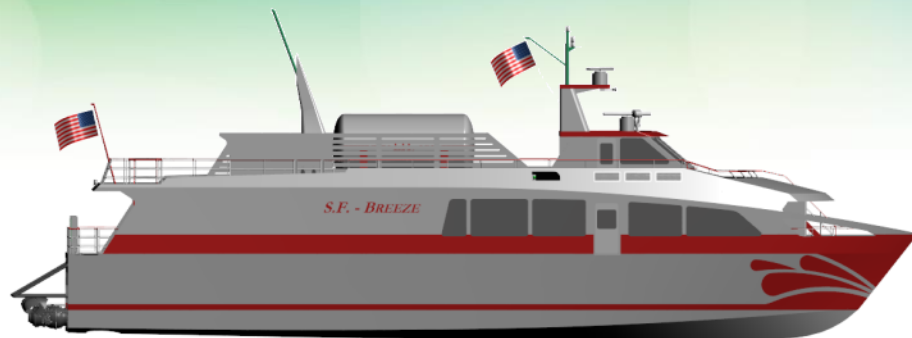
Work Funded by The U.S. Department of Transportation (DOT), Maritime Administration (MARAD) through MARAD's Maritime Environmental and Technical Assistance (META) program.

SF-Breeze Design



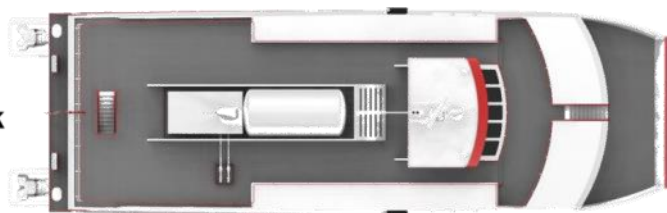
Design generated by Elliott Bay Design Group

SF-BREEZE details

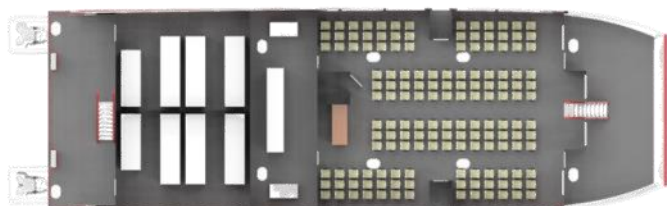


- Fuel: ~2,000 kg LH₂ per day
- Propulsion power 4.4 MW, installed: 4.92 MW
- Passengers: 150
- Service Speed: 35 knots
- Length 109' x Beam 33' x Depth 11.25'
Full Load Draft ~ 4.6'
- **Emissions: Zero**
- **Fuel Spills: Zero**

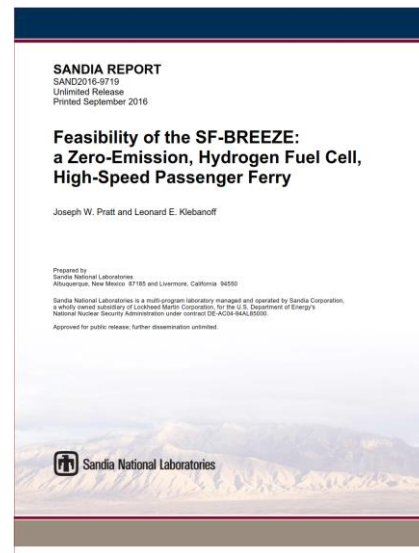
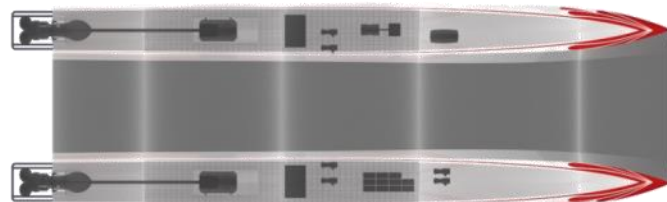
Upper Deck



Main Deck



Hulls



The SF-BREEZE Project Led to the Zero-V Hydrogen Fuel Cell Research Vessel

Overall Feasibility Question: Is it technically and economically possible to create a zero-emissions H₂ fuel cell research vessel that meets or exceeds the requirements of such vessels operating along U.S. coastlines?



Lennie Klebanoff
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Bruce Appelgate
Scripps Institution of Oceanography



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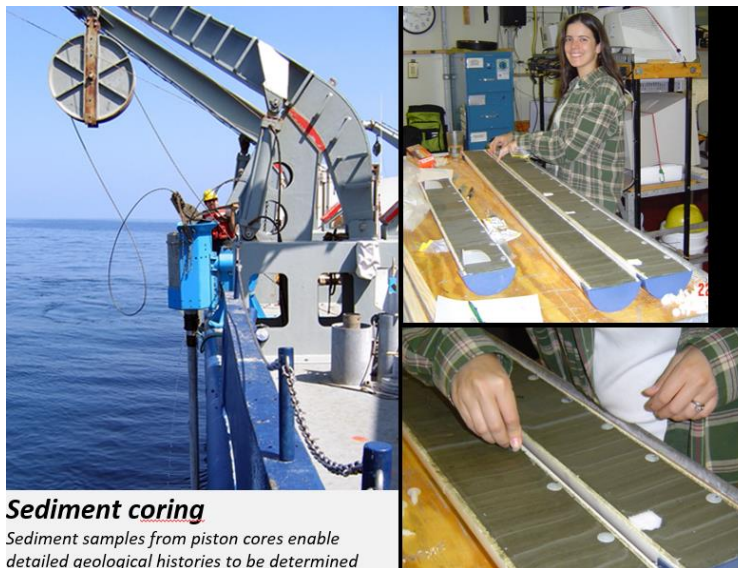
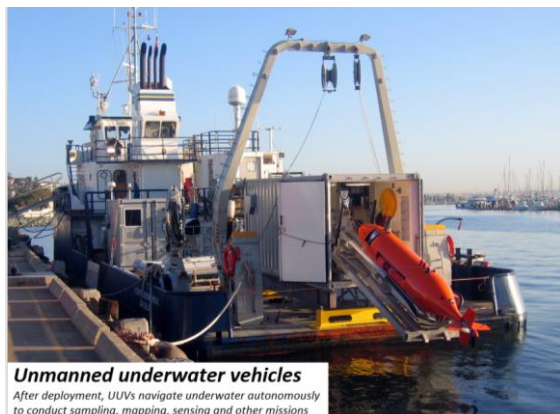


Gerd Petra Haugom (L) Hans-Christian Wintervoll
DNV GL



Glosten Participants: (L-R) Ian McCauley, Sean Caughlan, Robin Madsen and Catherine Farish.

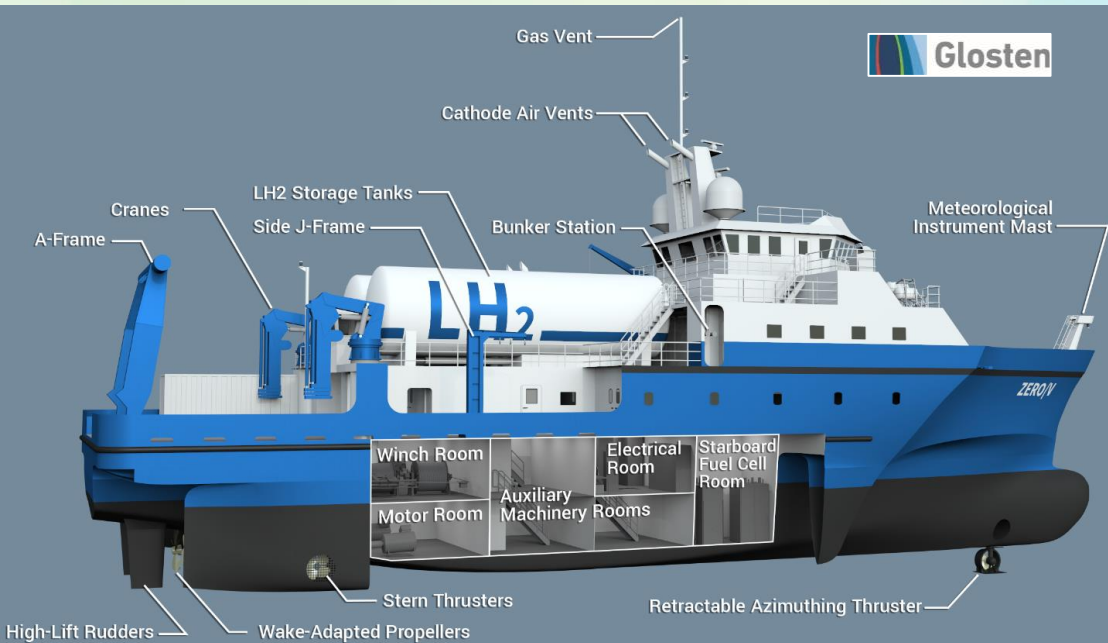
Scripps Missions Define the Zero-V Performance



The Zero-V has very different performance needs:

- Desired calm water speed: 10 knots (instead of 35 knots for the SF-BREEZE)
- Desired range: 2,400 nautical miles (instead of 100 nm for the SF-BREEZE)
- Endurance: 14 days (instead of 4 hours for the SF-BREEZE).

A zero-emission research vessel is feasible NOW using existing technology



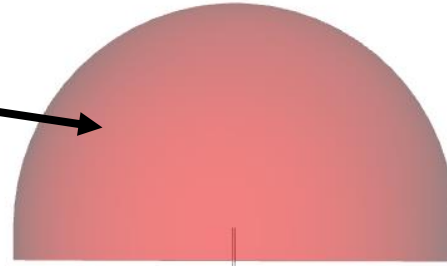
- Oceanographic research vessel for coastal / regional operations
 - Uses clean hydrogen: **No fossil fuels!**
 - Zero emissions: **Clean/no GHGs!**
 - Carries no diesel: **No oil spills!**
 - All-electric propulsion: **Quiet!**
 - **FEASIBLE** with existing technology
 - Outstanding scientific capabilities
 - Advanced instrumentation
 - Designed for California's educational and R&D needs
- A bold, transformative game-changer***



The zero-emission research vessel (Zero-V) concept vessel has a range of 2,400 nm, speed of 10 knots, with berths for up to 20 scientists, supporting general-purpose missions. Anticipated cost to build: \$80 million.

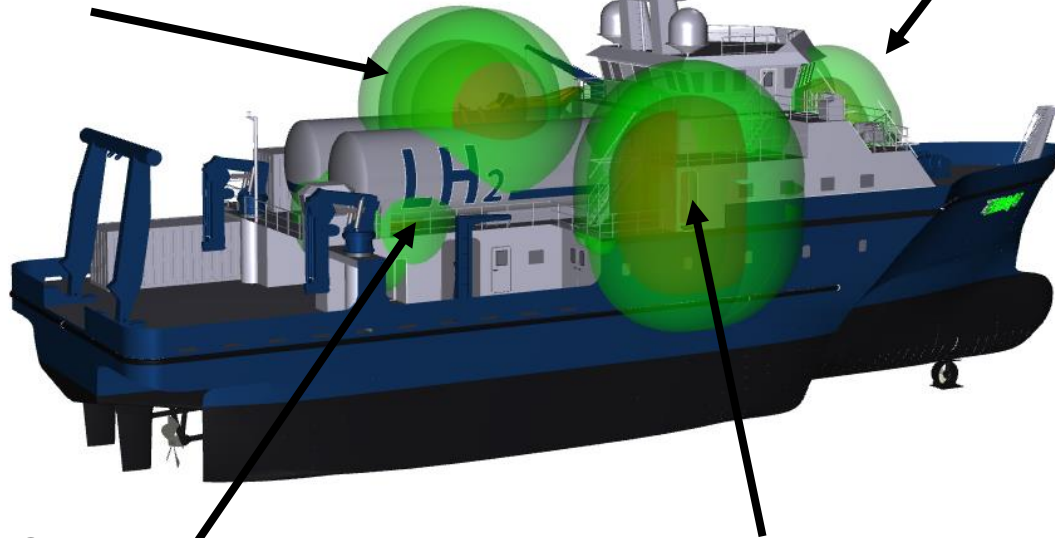
Hazardous Zone Plan for the Zero-V Drives The Design

Vent Mast
(10 m radius)



Fuel Cell Room
Ventilation Intake
(3 m radius)

Tank Connection Space Ventilation Exhaust,
Fuel Cell Room Ventilation Exhaust
(3 m radius)

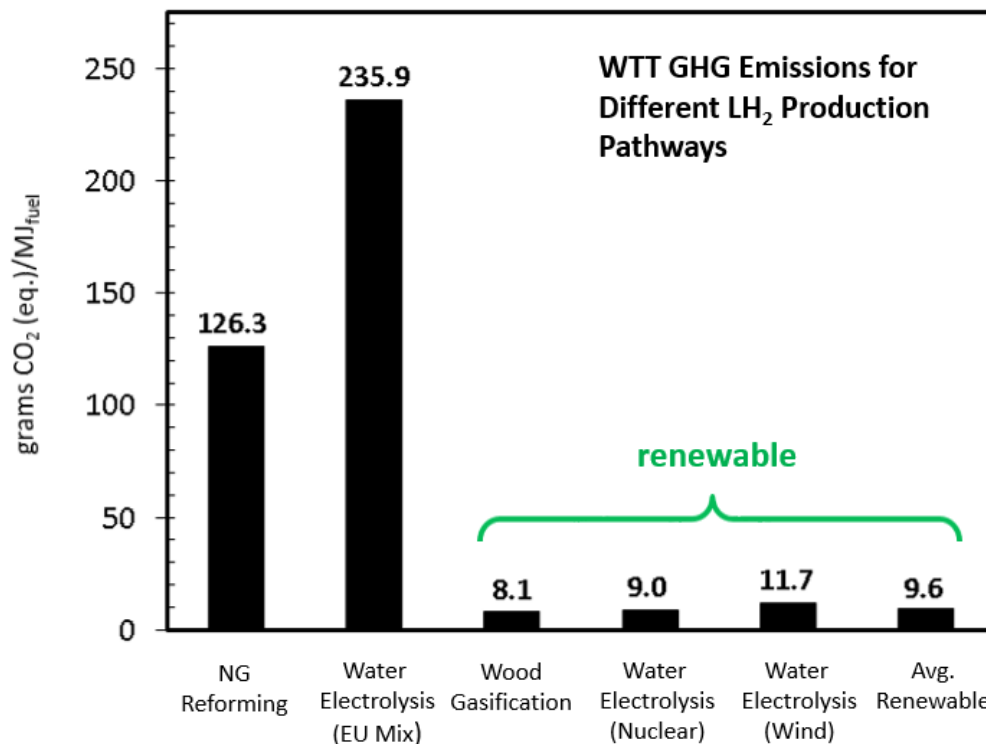


Locations where H₂ vapors are expected to exist or may exist under normal or abnormal conditions. These spaces cannot have ignition sources or gas paths to safe areas.

Tank Connection Space
Ventilation Intake
(1.5 m radius)

Bunkering Station
(3 m radius)

The GHG Reduction from Using H₂ technology REALLY depends on How the H₂ is Made

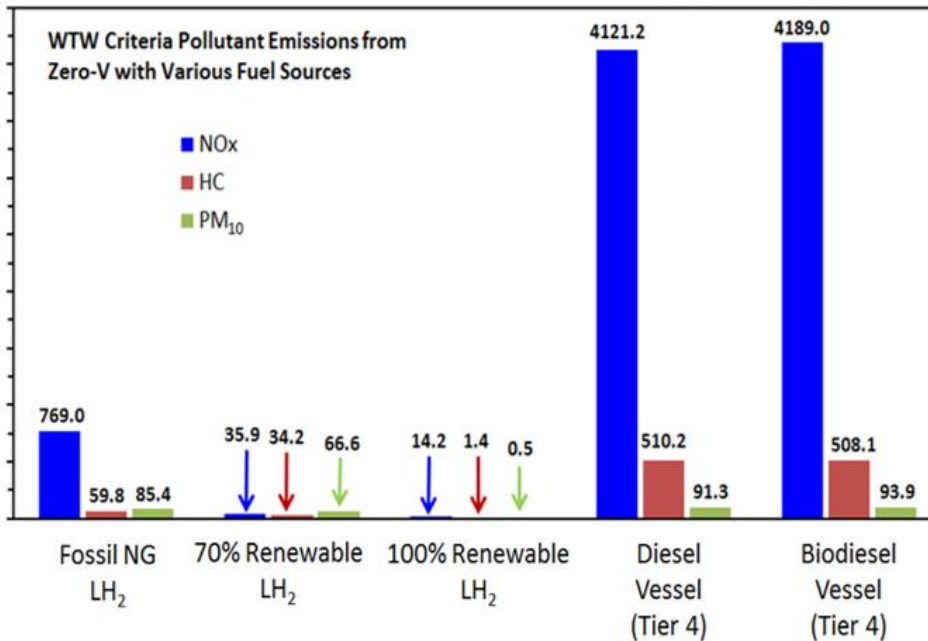


-- the equivalent GHG emissions for diesel fuel is 87.4 grams CO₂ (eq.)/MJ_{fuel}

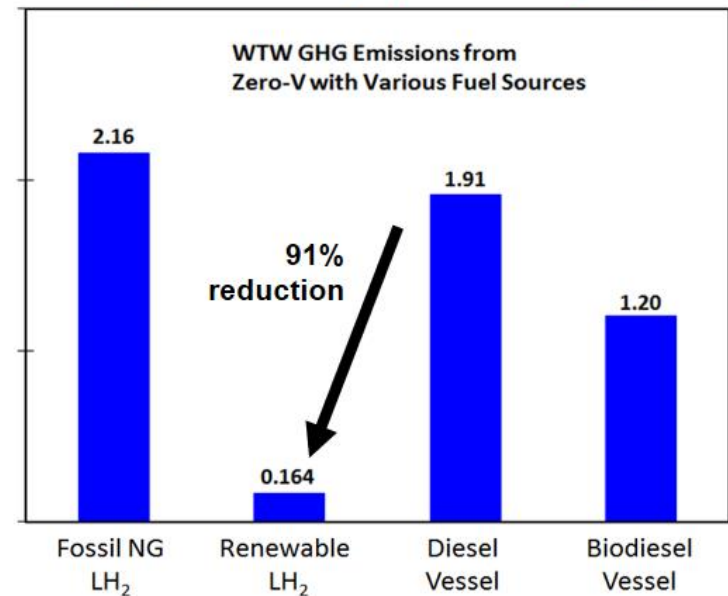
More information on the calculation of GHG emissions from H₂ fuel cell technology can be found at: L.E. Klebanoff, J.W. Pratt et al., Transportation Research D **54**, 250 (2017).

Emissions from LH₂ Production (the Zero-V itself is zero-emissions):

Well-To-Waves Criteria Emissions (kg / year)



Well-to-Waves Greenhouse Gas Emissions
(1,000 MT CO₂ equivalent / year)



Using H₂ from any source, dramatic reductions in criteria pollutants below Tier 4 are provided. Using renewable hydrogen, a 91% reduction in CO₂ (eq.) emissions is obtained.

SANDIA REPORT

SAND2018-4664 Unlimited Release | Printed May 2018

Feasibility of the Zero-V:

A Zero-Emission, Hydrogen Fuel-Cell, Coastal Research Vessel

Leonard E. Klebanoff, Joseph W. Pratt, Robert T. Madsen, Sean A.M. Caughlan, Timothy S. Leach, T. Bruce Appelgate, Jr., Stephen Zoltan Kelety, Hans-Christian Wintervoll, Gerd Petra Haugom and Anthony T.Y. Teo

Prepared by
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 Sandia National Laboratories



maritime.sandia.gov

Dr. Bruce Appelgate (Scripps) is currently seeking funding for further design and construction of the Zero-V.

Work Funded by The U.S. Department of Transportation (DOT), Maritime Administration (MARAD) through MARAD's Maritime Environmental and Technical Assistance (META) program.

A H₂ Fuel Cell Ferry Is Under Construction!

-- Funded by the State of California Air Resources Board (CARB)



The world's first commercial hydrogen fuel cell ferry, and first hydrogen fuel cell vessel in the U.S.

- Aluminum catamaran
- 70' long
- 84 passenger (reconfigurable)
- 22 knot top speed

Project Lead



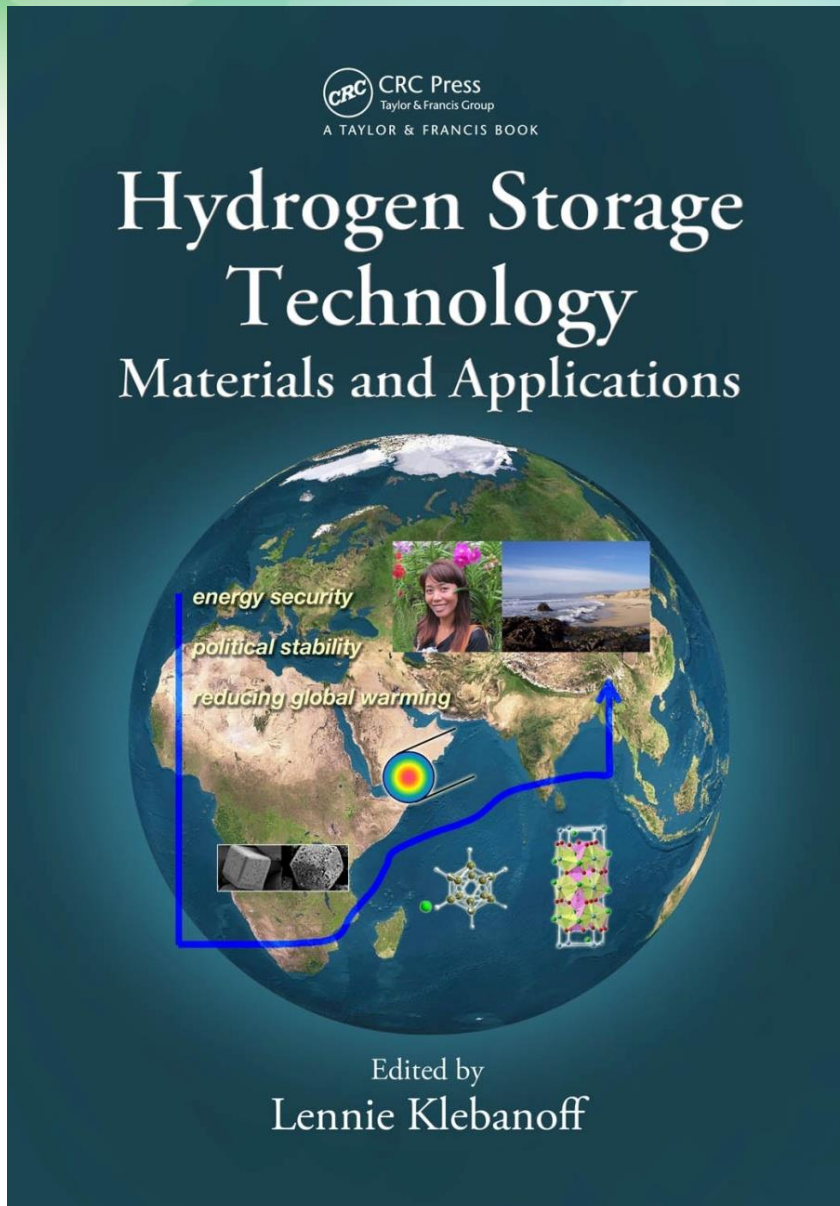
Funding & Administration



This project is supported by the "California Climate Investments" (CCI) program

H₂ Vessel Feasibility Questions Encountered and Passed

- Will they float? ✓
- Can they go fast enough, up to 35 knots? ✓
- Can they carry a decent number of people (~150)? ✓
- Do they have sufficient range before needing refueling? ✓
- Can the hydrogen suppliers provide 2500 kg of LH₂ per day? ✓
- Can the hydrogen suppliers provide renewable LH₂? ✓
- Can they be refueled fast enough for commuter service? ✓
- Would the technology be supported by Bay Area Ports? ✓
- Are there deep cuts in well-to-waves (WTW) GHG emissions? ✓
- Are there deep cuts in WTW criteria pollutant emissions? ✓
- Can they satisfy regulatory requirements to gain an Approval in Principal? ✓
- Would the U.S. Coast Guard find any “show stopping” issues? ✓
- Would it be commercially attractive? **TBD**
- Can suitable refueling sites be found for these vessels? ✓
- Would there be support from local government (City Hall, others)? ✓

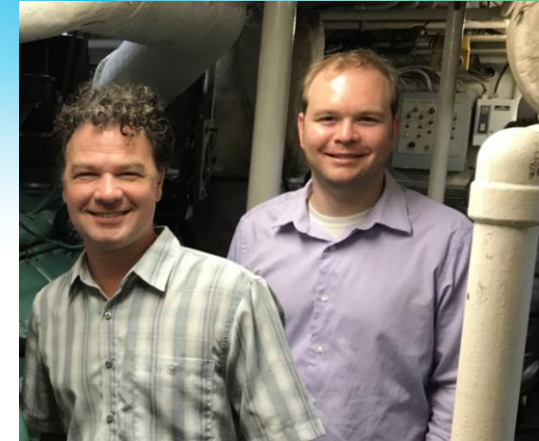


--published by CRC Press in 2012

Topics:

- Why we need H₂-based energy
- H₂ Energy Conversion Devices
- All methods of H₂ Storage
- Engineered H₂ Storage Systems
- H₂ Codes and Standards

-- available on Amazon



Thanks to all my friends and colleagues!



Sujit Ghosh, MARAD

An extra special Thank You to Sujit Ghosh and the US DOT / Maritime Administration (MARAD) for supporting these studies

For more information on H₂ Storage Projects, visit:
<https://hymarc.org/>

For more information on H₂/Fuel Cell Maritime Projects visit:
<https://maritime.sandia.gov>

- Past and current maritime projects
- Download reports

Thank You!

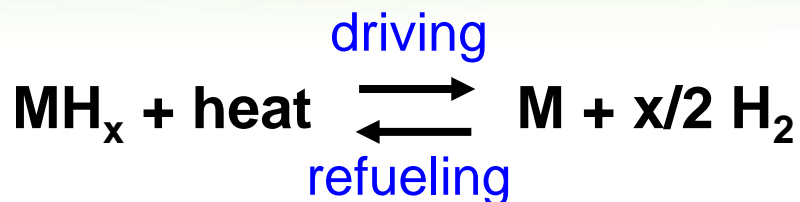
Lennie Klebanoff

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Extra Slides

Solid-State H₂ Storage Materials



MH_x: FeTi-H, LaNi₅-H, NaAlH₄

Benefits:

- ✓ Can reduce tank pressures from 10,000 psi to 100 psi (safer).
- ✓ Can triple the storage density of 700 bar H₂.

But, something is wrong with all of the MH_x, making this an R&D area:

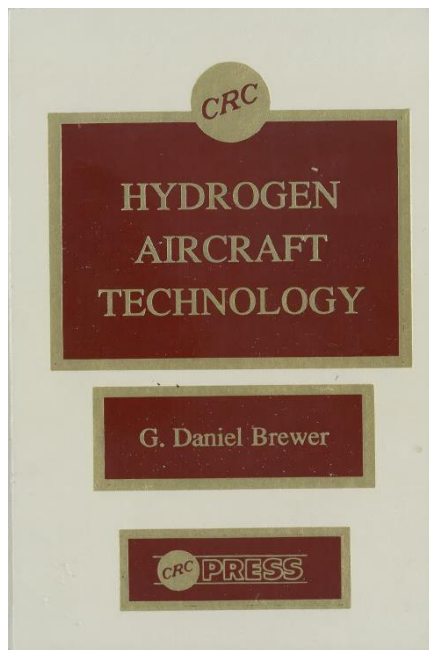
1. Too heavy
2. Don't release hydrogen fast enough (bad kinetics)
3. Don't re-absorb hydrogen fast enough (bad kinetics)
4. Bind hydrogen too tightly (bad thermodynamics)
5. The H₂ they release is contaminated with other species
6. Too expensive
7. Degrade when cycled



-- funded by DOE EERE FCTO to investigate the fundamental limitations of hydrogen storage materials.

H₂ Aircraft Technology

<u>Fuel</u>	<u>-$\Delta H^{\circ}_{\text{Combustion}}$ (kJ/g) (LHV)</u>
Hydrogen (H ₂)	120.0
Methane (CH ₄)	50.1
Jet-A (JP-4) (~C ₁₂ H ₂₆)	42.8

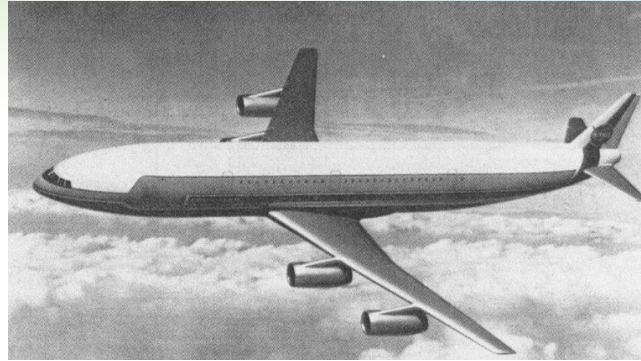


Prior Studies:

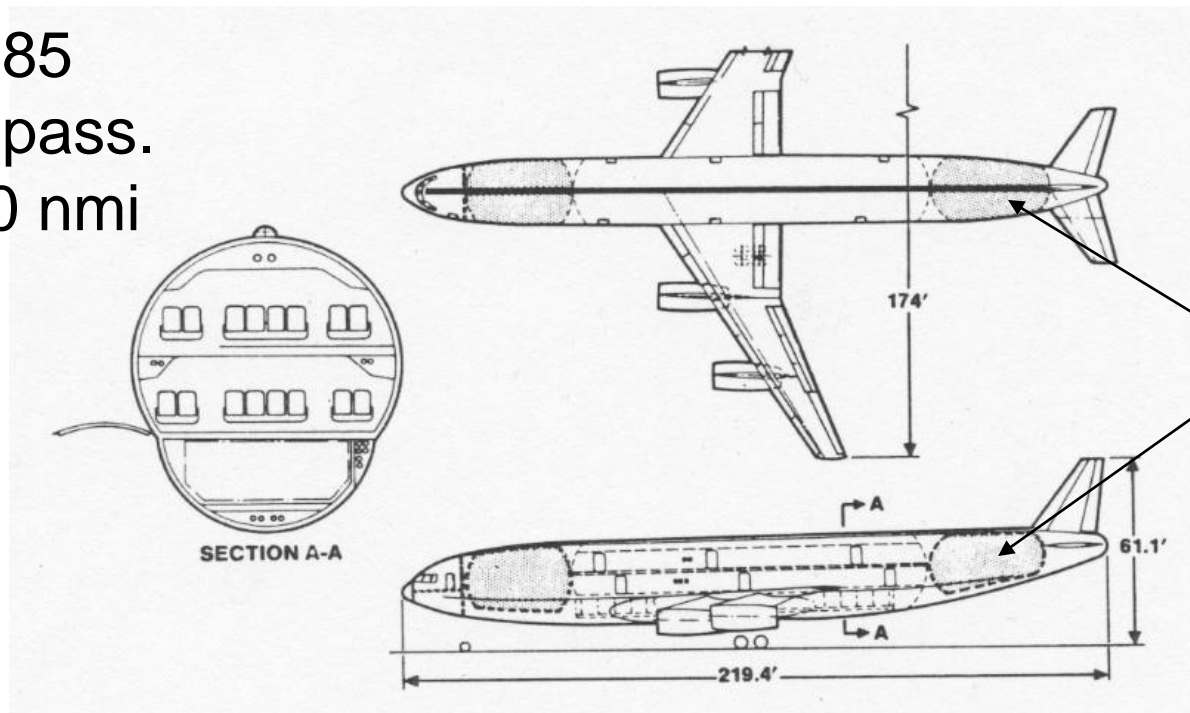
- Lockheed studies of the 1970's
- 2002 Airbus Study (Cryoplane)
- Boeing Study: (2006)

-- Published in Proceedings of the 25TH INTERNATIONAL CONGRESS OF THE AERONAUTICAL SCIENCES (2006)

Larger Fuselage Accommodates LH₂ Fuel, Cargo, People



M 0.85
400 pass.
5500 nmi



LH₂ tanks
(fore, aft)

Comparison of Jet-A vs. LH₂-Fueled Subsonic Passenger Aircraft (Mach 0.85, 400 passengers, Range = 5,500 nmi)

	Jet-A	LH ₂	Ratio (LH ₂ /Jet-A)
Takeoff Gross Weight (lb)	523,200	391,700	0.75
Operating Empty Weight (lb)	244,420	242,100	0.99
Fuel Weight (lb)	190,800	61,600	0.32
Wing Area (ft ²)	4,186	3,363	0.80
Take-off Distance (ft)	7,990	6,240	0.78
Energy Utilization $\left(\frac{Btu}{seatnmi} \right)$	1,384	1,239	0.89

Tables 3-11 and 3-12 from “Hydrogen Aircraft Technology”

Potential Military Uses of LH₂ Aircraft

Fighters: **No**, they only carry ~ 10,000 – 25,000 lbs of fuel,
-- performance penalties associated with larger fuselage.



F22

Large Transports: **YES**

Ex: Lockheed Martin C-5 A/B Galaxy
(M0.79, Range 2400 nmi with 263,000 lb payload)
C-5 Fuel Capacity = 332,500 lbs.



Note: Transport aircraft consume 80% of fuel used by the U.S. Air Force

High Altitude Long Endurance (HALE) Aircraft: **YES**

Satcom restoration, communications relay, persistent ISR
(Intelligence, Surveillance, Reconnaissance)

– Capabilities: 4 days, 14,000 miles, 450 lb payload, LH₂

Boeing
Phantom
Eye

