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On the Feasibility and Characteristics of Hydrogen Fuel-Cell Vessels

Lennie Klebanoff

Sandia National Laboratories

Livermore, CA 94551

Naval Post Graduate School

Monterey, CA

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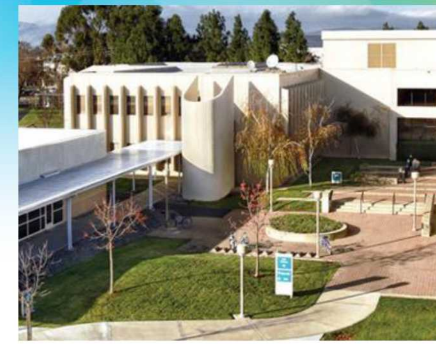
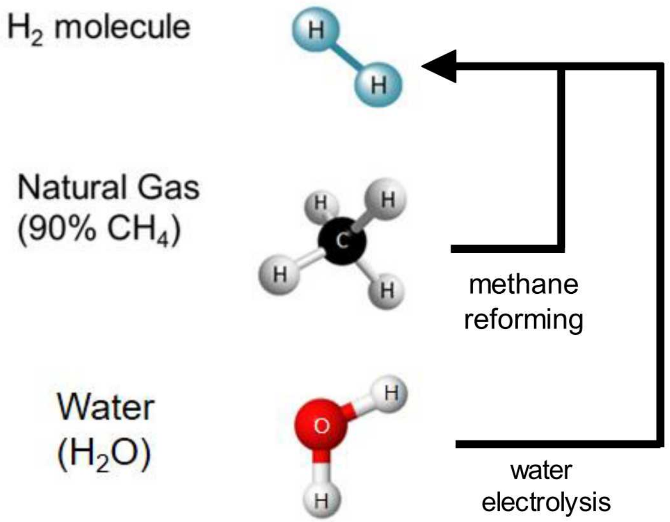


Livermore CA
(SF Bay Area)

- 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
  - H_2 Program in Livermore, CA (SF Bay Area)
- Hydrogen program: 60+ years of work, in a wide range of areas (H_2 storage, production, delivery, development of regulations, market transformation), which we apply to enable impactful clean energy solutions
- Market Transformation: Zero Emission H_2/Fuel Cell Maritime Program:

Hydrogen Properties:



- Is typically a gas, but can be a liquid (LH_2) if made very cold (20 K).
- LH_2 evaporates very fast (4,000 gallons will evaporate in ~7 seconds)
- More buoyant than helium. Goes straight up at ~40 mph.

Overall, H_2 is very similar to natural gas (which is ~ 90% methane, CH_4).

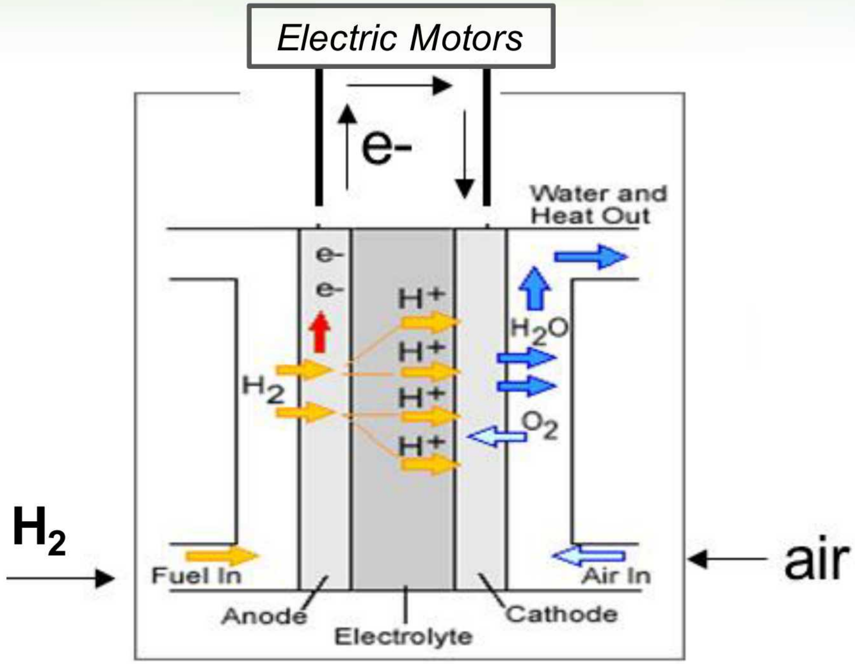
H_2 is NOT a Greenhouse Gas, unlike natural gas which is a potent GHG.

If spilled, LH_2 evaporates from the water leaving no residue.

H_2 can be ignited given an ignition source and the right H_2/air mixture.

Energetically, a kg of H_2 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



$$2\,H_2 + O_2 \rightarrow 2\,H_2O$$

-- 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 H_2 production/delivery

Photos Courtesy Ryan Sookoo, Hydrogenics

Going In:
H_2 and air

Going Out:
Electricity
Waste Heat
Warm humidified air

Physical Properties of LH_2 and LNG

Note: 75 ºF = 297 K

LH_2:

Liquid Normal Boiling Point = 20 K (-253 ºC).
Liquid Density = 71 g/L
Lower Heating Value = 120 MJ/kg

LNG (LCH_4):

Liquid Normal Boiling Point = 111 K (-162 ºC).
Liquid Density = 422 g/L
Lower Heating Value = 45 MJ/kg

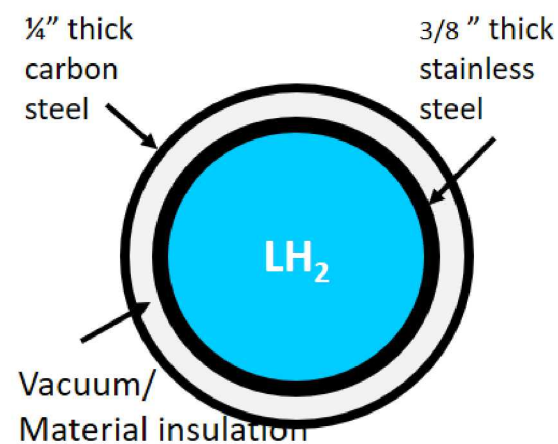
LH_2 has 0.38 times the mass of LNG, but has 2.4 times the volume, per unit of energy (LHV).

LH_2 has 0.36 times the mass of diesel, but has 4.2 times the volume, per unit of energy (LHV).

LH_2 and LNG are stored in similar ways:

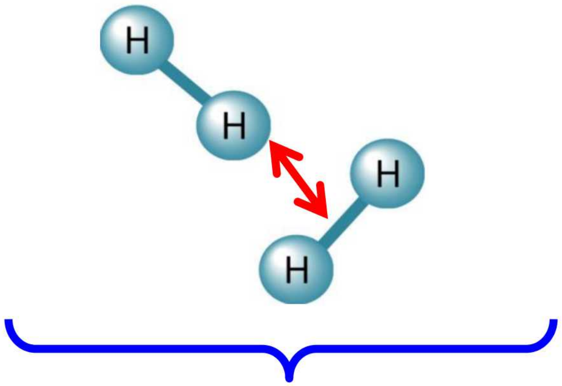
LH_2 Storage Tank on Trailer

LNG Storage Tank on Trailer



LH_2 Evaporates Faster than LNG, Cools Surfaces Less (Spill)

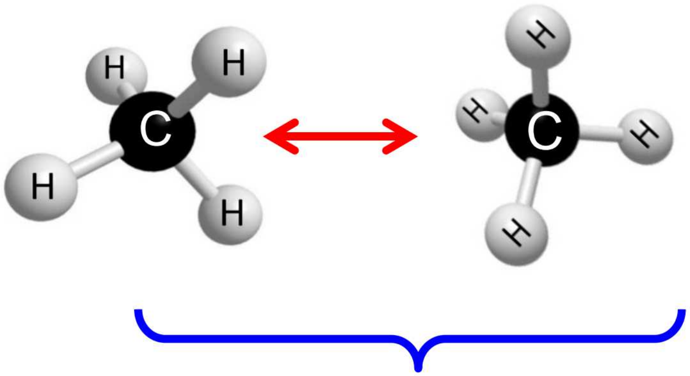
LH_2:



H_2 molecules barely interact at all

Heat of Vaporization = 0.922 kJ/mole

LNG (CH_4):



CH_4 molecules interact a bit more

Heat of Vaporization = 8.5 kJ/mole

-- For equal amounts of stored energy, LH_2 takes 3 times less energy than LNG to evaporate. In a spill, LH_2 will cool surroundings much less than LNG.

-- We estimate that if we spilled 1200 kg of LH_2, 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 ~ 10^8 stronger than weak initiators.

Gaseous Flammability of H_2 vs NG

Both H_2 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 H_2 = 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 CH_4 = 0.29 mJ; That for H_2 is 0.02 mJ. Static discharges from human beings are ~ 10 mJ, **so both CH_4 and H_2 ignite easily.**

H_2 and NG are both easily ignited by weak ignition sources, and start to burn at similar lower flammability limits

Direct Explosions/Detonations of H_2 vs NG

The lower explosion limit (LEL) of H_2 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 H_2 and CH_4 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 H_2 and CH_4 WILL NOT directly detonate, explode or deflagrate.**

A.D. Little study of LH_2 for the U.S. Air Force: For a series of LH_2 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.

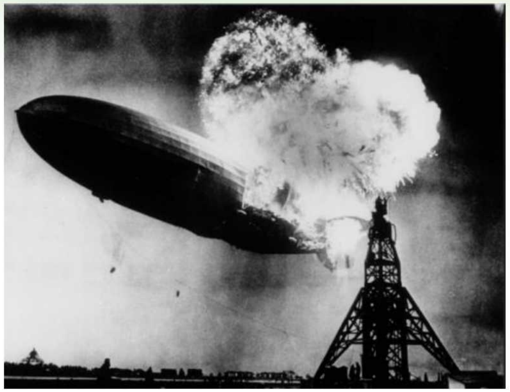
Deflagration to Detonation Transition (DDT)

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 H_2, DDT can only occur for 12% fuel /air mix or higher. Both H_2 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 Disaster (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 LH_2 tanks in use today.

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

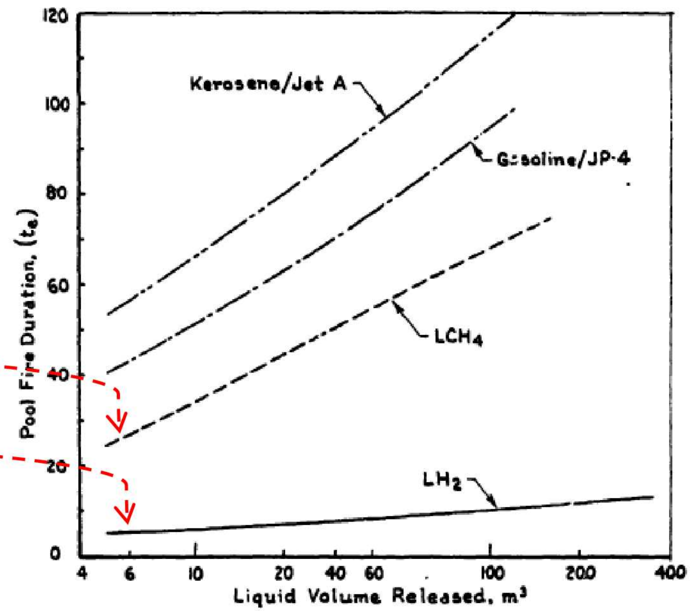
The Nature of Fires: LH_2 vs. LNG

NASA funded a model study of the fire safety aspects of LH_2 and LNG as part of their program in alternative-fuel aircraft in the 1980s.

Pool Burn Times :

LNG = 25 s

LH_2 = 5 s



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

6 m^3 = 6,000 L = 1587 gallons

= 426 kg of LH_2

= 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.

LH_2 pool fires burn out faster than LNG pool fires due to the much lower heat of vaporization of LH_2. But both fuels, if spilled, burn themselves out rapidly.

LH_2 Fires Pose Less Safety Risk Than LNG Fires

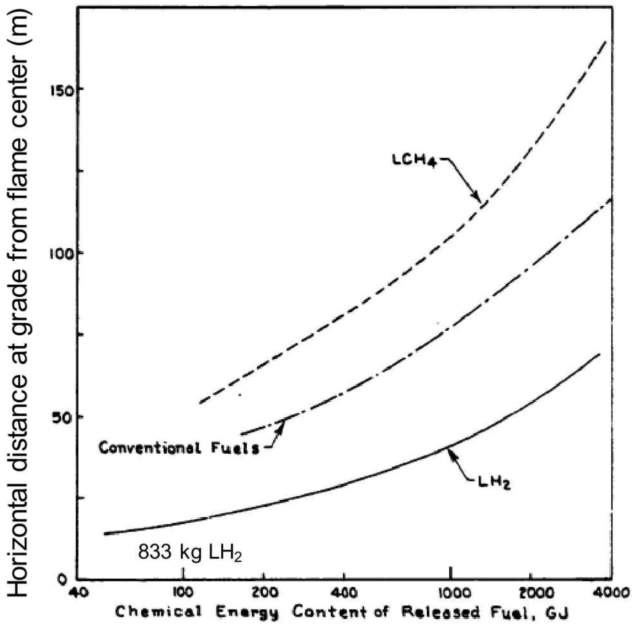
Results from the NASA-funded study:

Burning of H_2:
$2H_2 + O_2 \rightarrow 2H_2O$

Note:
5 kW/m^2 is the threshold for skin thermal injury.

Approach limit for LNG fire = ~54m

Approach limit for LH_2 fire ~ 18m



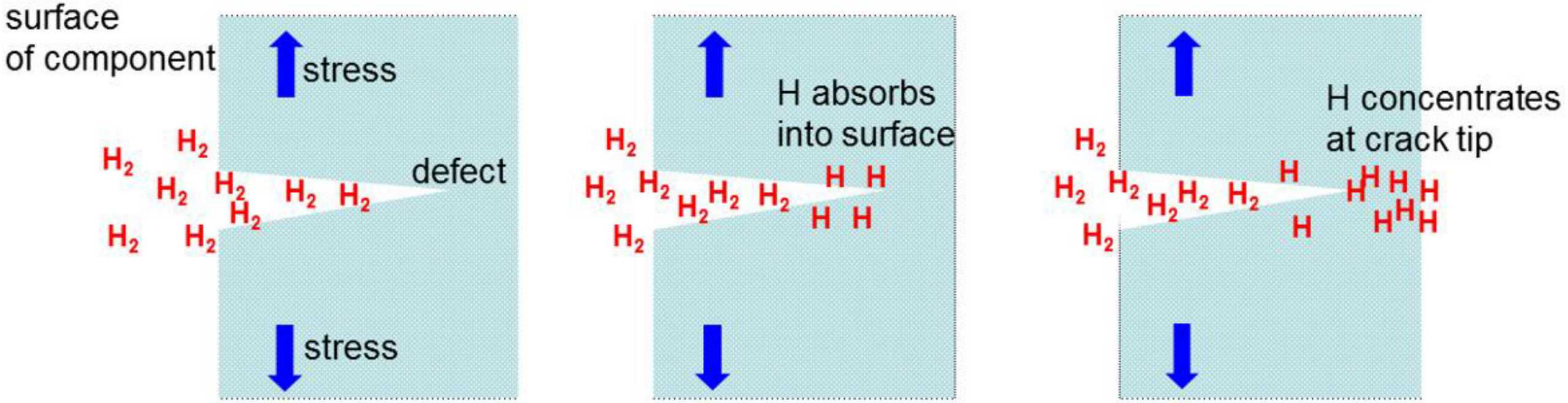
Comparison of fire thermal radiation hazard distance (5kW/m^2) as a function of the heat content of the released fuel.

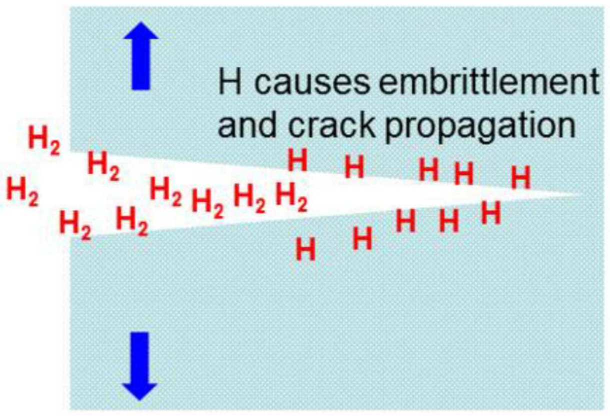
You can be 3x closer to a H_2 fire than a NG fire for the same safety factor.

LH_2 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 H_2 combustion is H_2O, the flame radiation is strongly absorbed by H_2O 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.

<u>Solved Problem:</u> The industry practice is to use 304 or 316 stainless steel in all H_2 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

L.E. Klebanoff [a,*], J.W. Pratt [a], C.B. LaFleur [b]

[a] Sandia National Laboratories, Livermore, CA 94551, USA

[b] Sandia National Laboratories, Albuquerque, NM 87185, USA

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ABSTRACT

We review liquid hydrogen (LH_2) 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 LH_2 as a comparison to LNG, for both maritime use in general, and the SF-BREEZE in particular. Due to weaker attractions between molecules, LH_2 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). LH_2 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 LH_2 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, LH_2 and LNG are very similar in their physical and combustion properties, thereby posing similar safety risks. For ships utilizing LH_2 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.

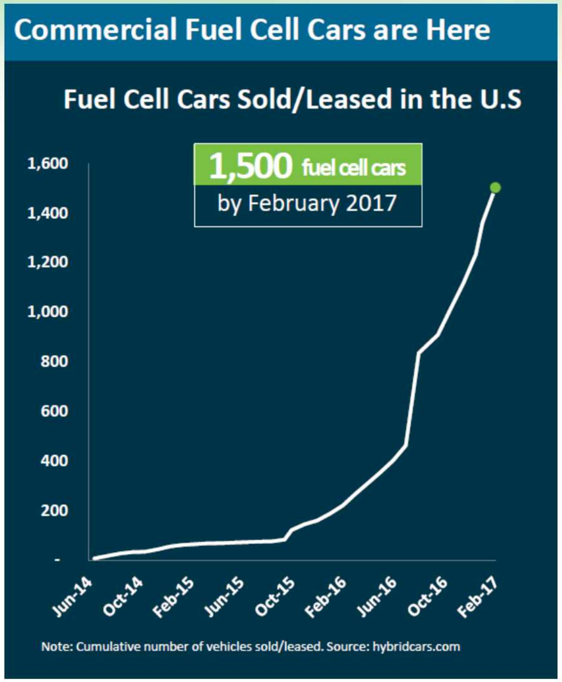
* Corresponding author.
E-mail address: lekleba@sandia.gov (L.E. Klebanoff).

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

More information about hydrogen gas (H_2) and liquid hydrogen (LH_2) can be found in:

International Journal of Hydrogen Energy **42**, 757 (2017).

Hydrogen Technology is Here and Growing



Fuel Cell Electric Vehicles Can:

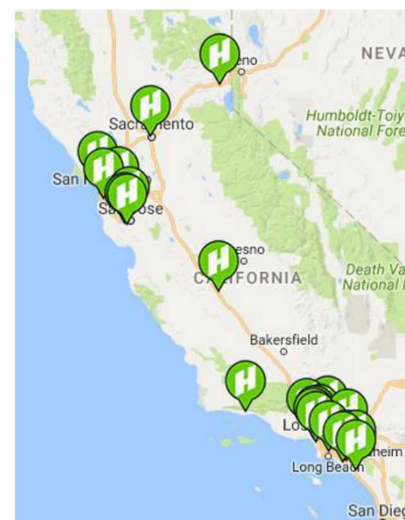
- ✓ Refuel in 5 minutes
- ✓ Have a 366 mile driving range (limited by H_2 storage)
- ✓ Only clean water vapor as the tailpipe emissions
- ✓ No need to plug in.

And it's not just fuel cell cars:

Fuel Cell Forklifts

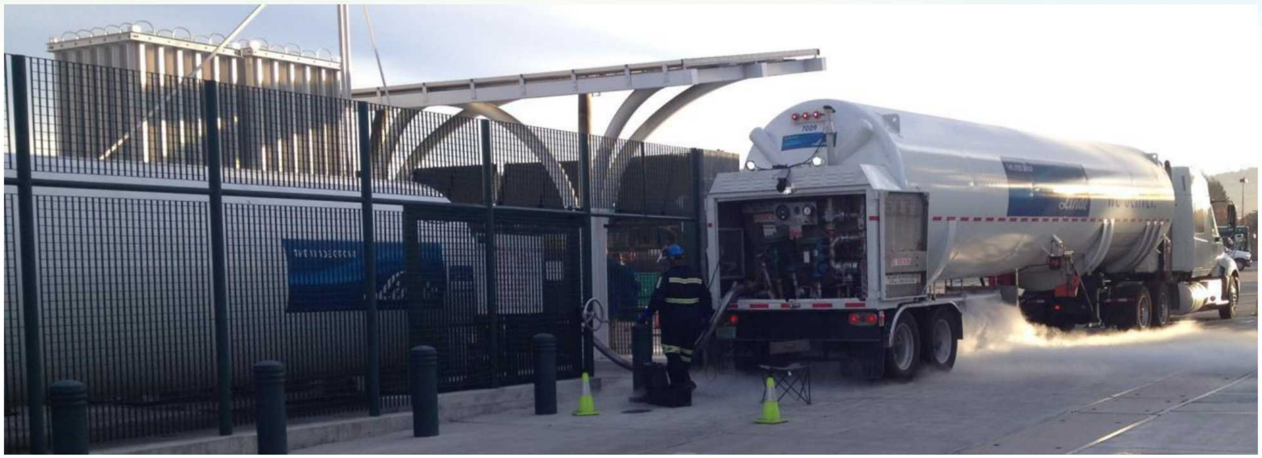
Fuel Cell Buses

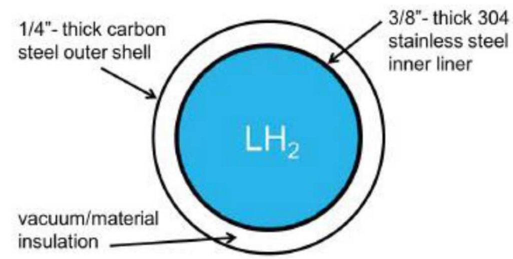
Fuel Cell Lighting



H_2 Stations are Being Built

H_2 Has Been Delivered and Used for Decades





Today: AC Transit Bus Station, Emeryville CA

1964 - 1973

1981 - 2011

A typical LH_2 trailer can deliver 4000 kg (~15,000 gallons) at a time.
(1 kg LH_2 = 3.72 gallons)

Trailer LH_2 tanks are DOT-approved and have never been breached in a road accident.

Toyota Mirai

700 bar,
~ 10,000 psi
compressed H_2

Densities of Hydrogen:

700 bar gas = 40 g/L

LH_2 (at 1 bar pressure) = 71 g/L

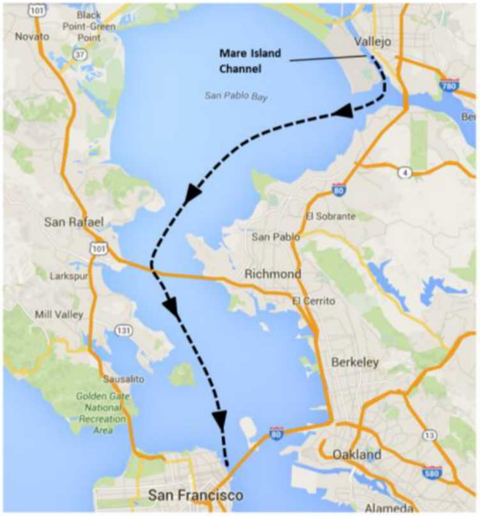
Solid AlH_3 = 149 g/L

The low density of even high pressure H_2 limits the range of fuel cell vehicles. Solid-state H_2 storage could be better!

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

SF-BREEZE: The first study to show that H_2 fuel cells can be used in maritime propulsion, and how to do it.

High-speed H_2 Ferry



Route:
San Francisco
to Vallejo, CA

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

Project Integrates Ship Designers, Regulators, H_2 Experts and End Users

USCG MSC and Design and Eng. Stds.

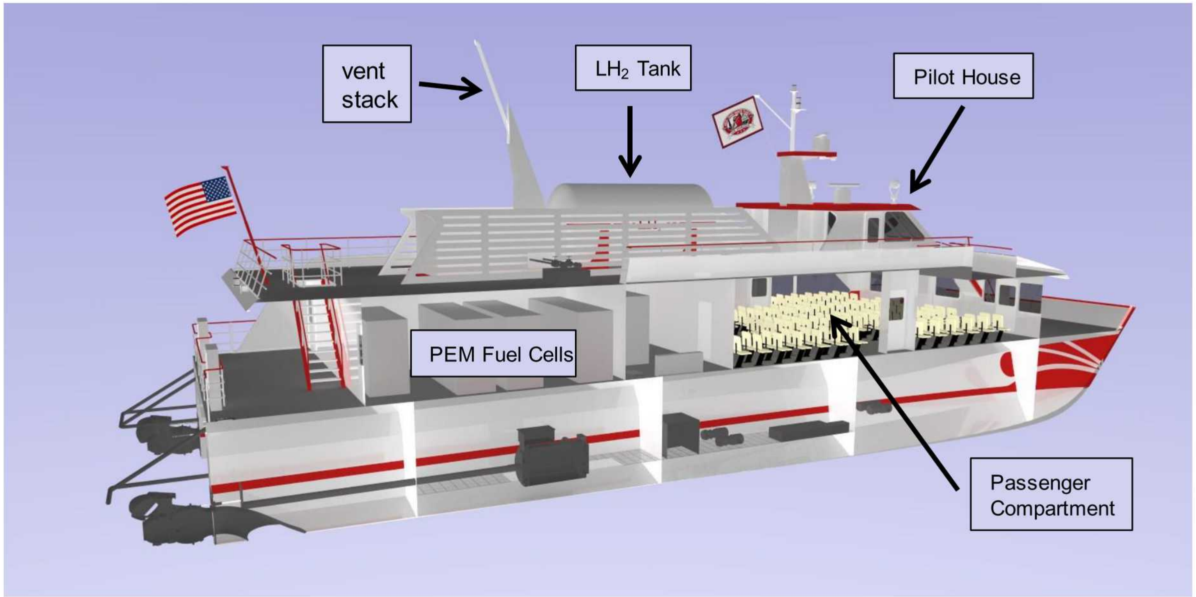
USCG Sector San Francisco

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.

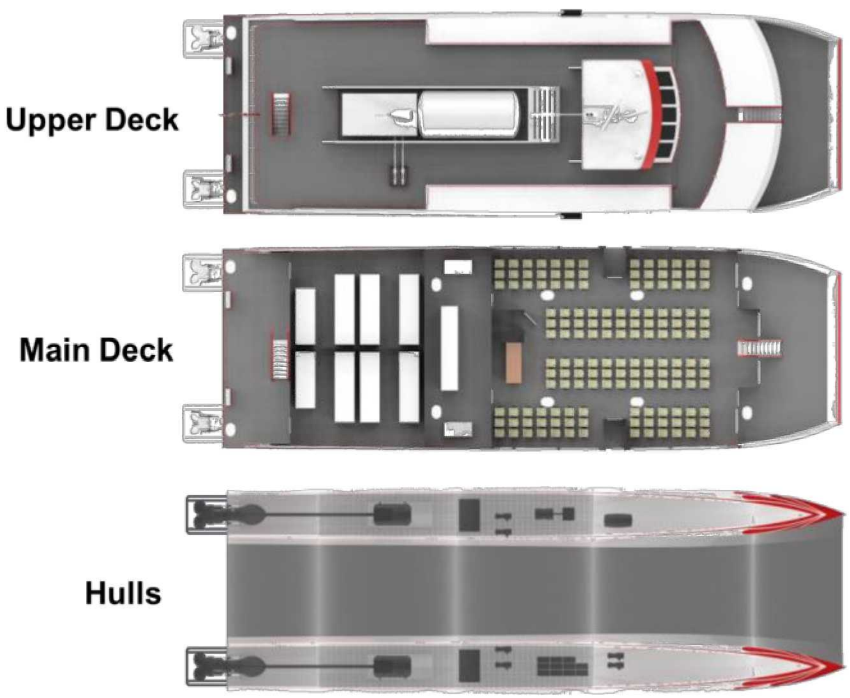
SF-Breeze Design



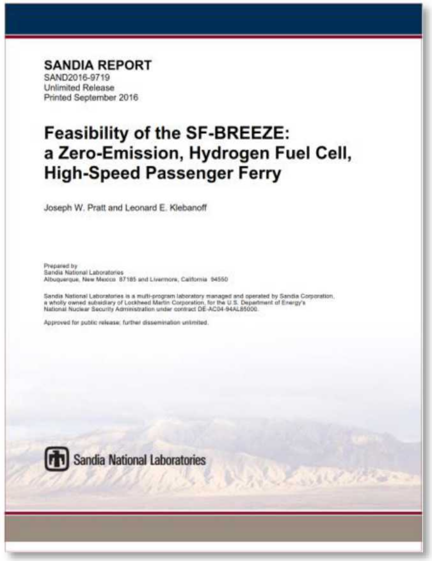
Elliott Bay Design Group

Design generated by Elliott Bay Design Group

SF-BREEZE details



- Fuel: ~2,000 kg LH_2 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**



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SAND2016-9719
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Feasibility of the SF-BREEZE:
a Zero-Emission, Hydrogen Fuel Cell,
High-Speed Passenger Ferry

Joseph W. Pratt and Leonard E. Klebanoff

Prepared by
Sandia National Laboratories
Albuquerque, New Mexico 87185 and Livermore, California 94550

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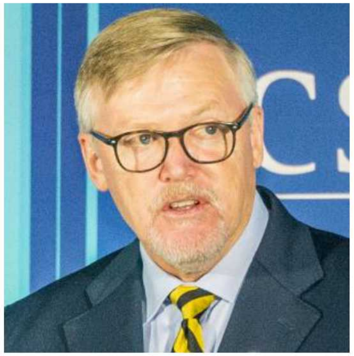
The SF-BREEZE Project Led to the Zero-V Hydrogen Fuel Cell Research Vessel

Overall Feasibility Question: Is it technically and economically possible to create a zero-emissions H_2 fuel cell research vessel that meets or <u>exceeds</u> the requirements of such vessels operating along U.S. coastlines?

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

Lennie Klebanoff
Sandia National Laboratories

Bruce Appelgate
Scripps Institution of Oceanography



Zoltan Kelety
Scripps Institution of Oceanography

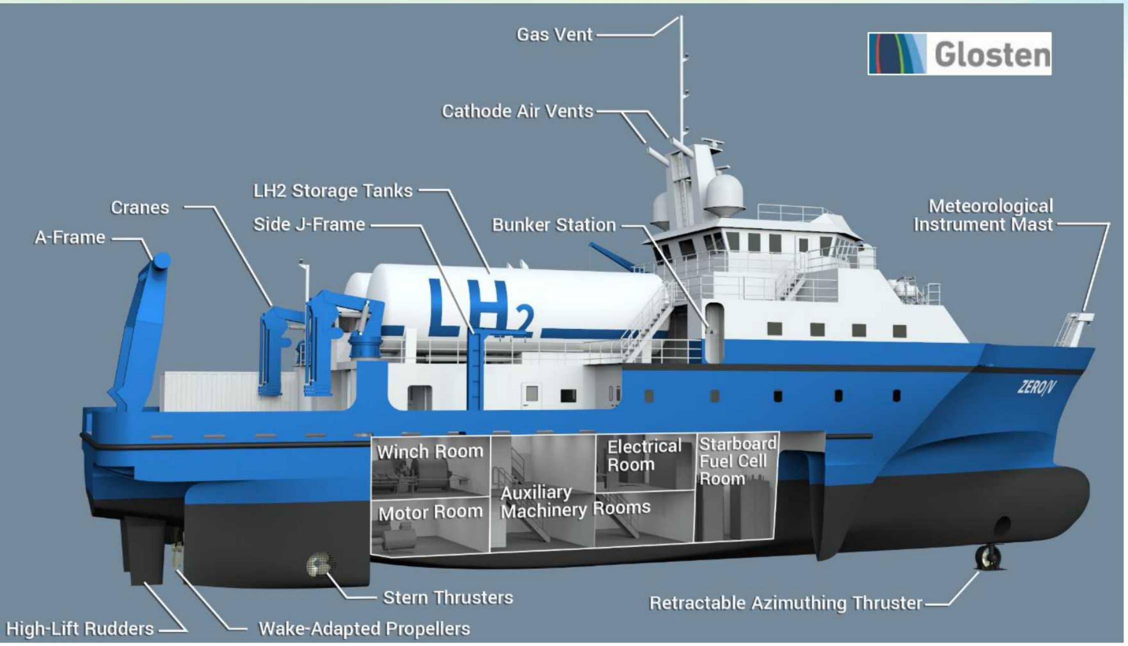
Glosten Participants: (L-R) Ian McCauley, Sean Caughlan, Robin Madsen and Catherine Farish.

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

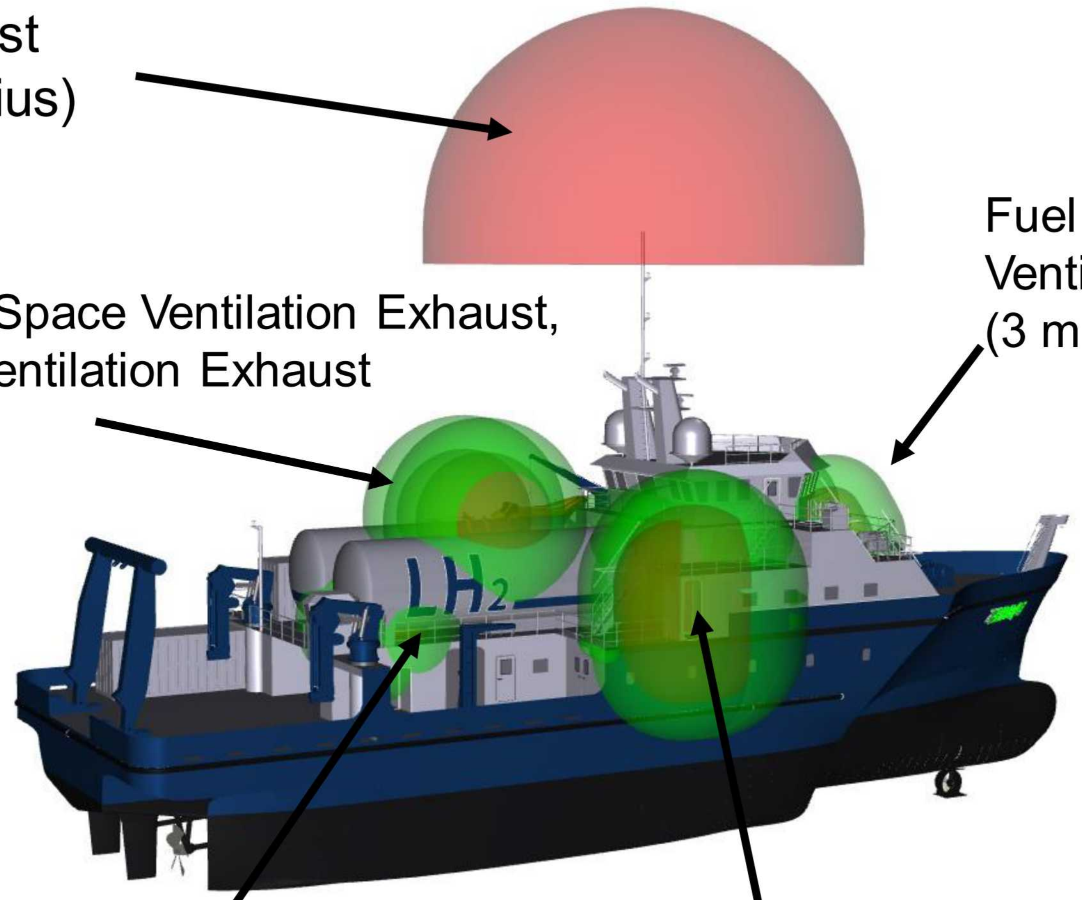


- Oceanographic research vessel for coastal / regional operations
- Uses clean hydrogen: **No fossil fuels!**
- Zero emissions: **Clean/no GHGs!**
- Carries no diesel: **No oil spills!**
- All-electric propulsion: **Quiet!**
- **FEASIBLE** with existing technology
- Outstanding scientific capabilities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

A bold, transformative game-changer

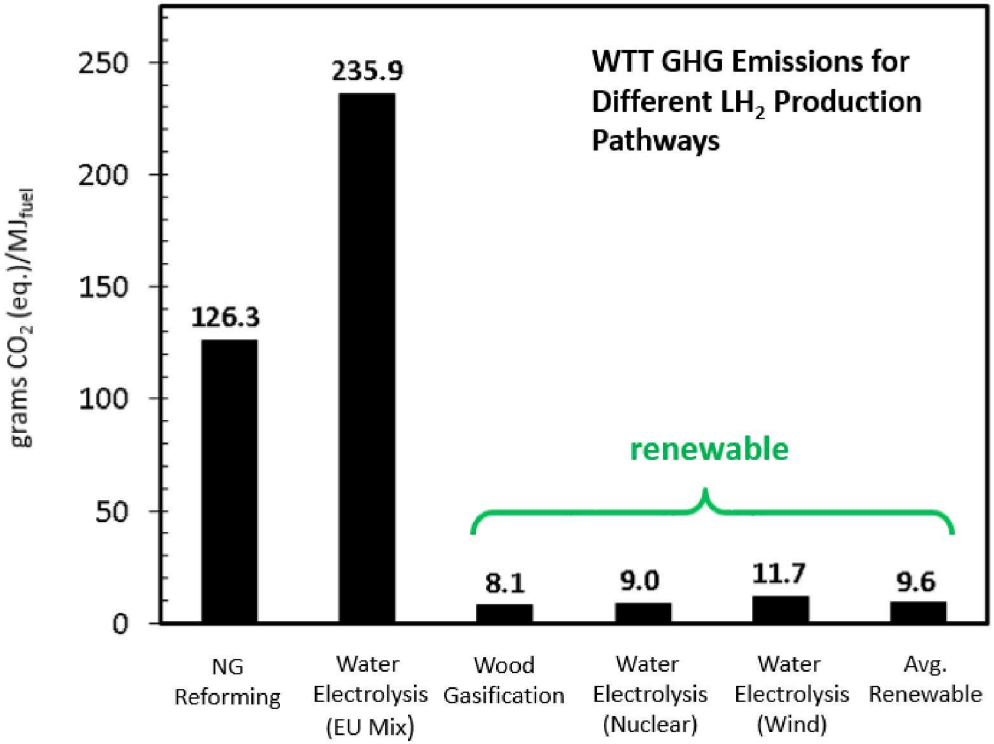
The zero-emission research vessel (Zero-V) concept vessel has a range of 2,400 nm, speed of 10 knots, with berths for up to 20 scientists, supporting general-purpose missions. Anticipated cost to build: $80 million.

Hazardous Zone Plan for the Zero-V Drives The Design



Locations where H_2 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.

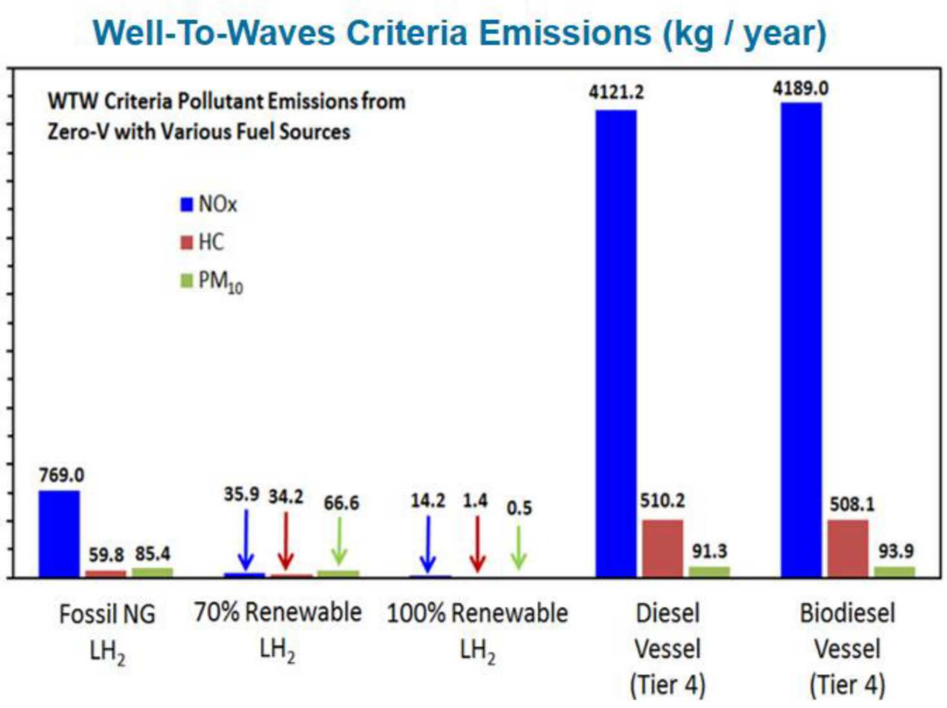
The GHG Reduction from Using H_2 technology REALLY depends on How the H_2 is Made

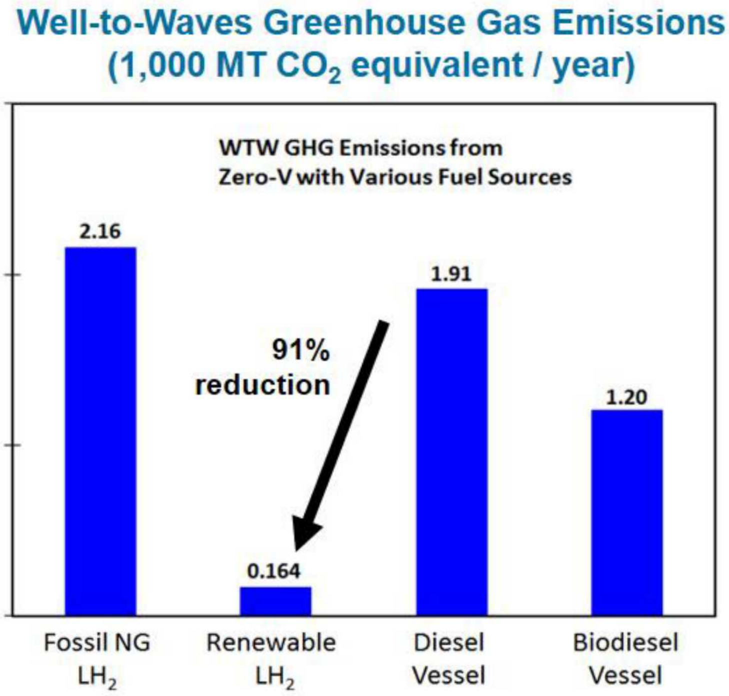


-- the equivalent GHG emissions for diesel fuel is 87.4 grams CO_2 (eq.)/MJ_{fuel}

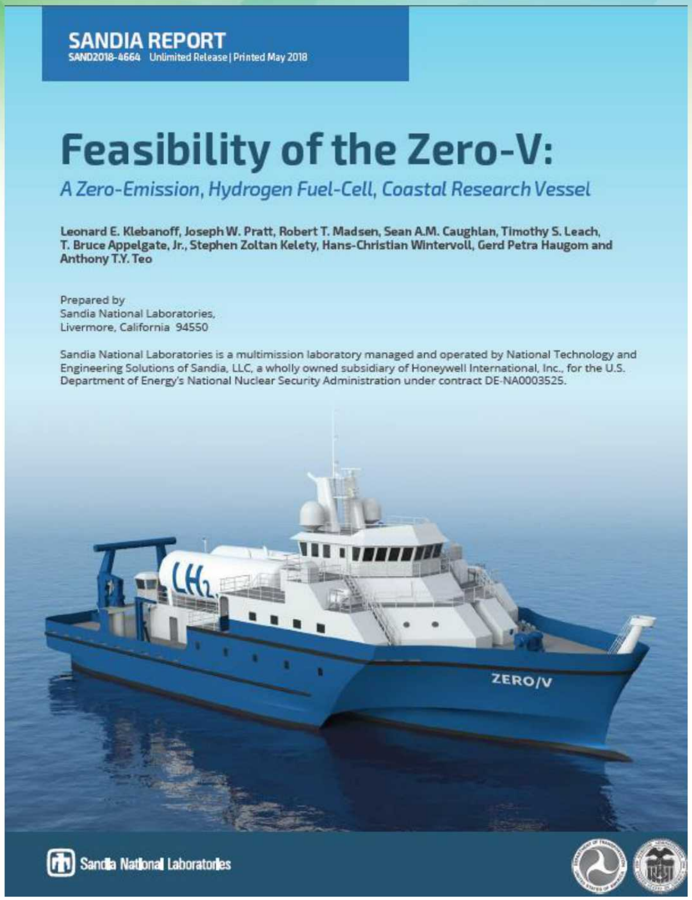
More information on the calculation of GHG emissions from H_2 fuel cell technology can be found it: L.E. Klebanoff , J.W. Pratt et al., Transportation Research D **54**, 250 (2017).

Emissions from LH_2 Production (the Zero-V itself is zero-emissions):





Using H_2 from any source, dramatic reductions in criteria pollutants below Tier 4 are provided. Using renewable hydrogen, a 91% reduction in CO_2 (eq.) emissions is obtained.



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

maritime.sandia.gov

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

A H_2 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

GOLDEN GATE ZERO EMISSION MARINE

Funding & Administration

CALIFORNIA AIR RESOURCES BOARD

BAY AREA AIR QUALITY MANAGEMENT DISTRICT

CALIFORNIA CLIMATE INVESTMENTS — Cap and Trade Dollars at Work

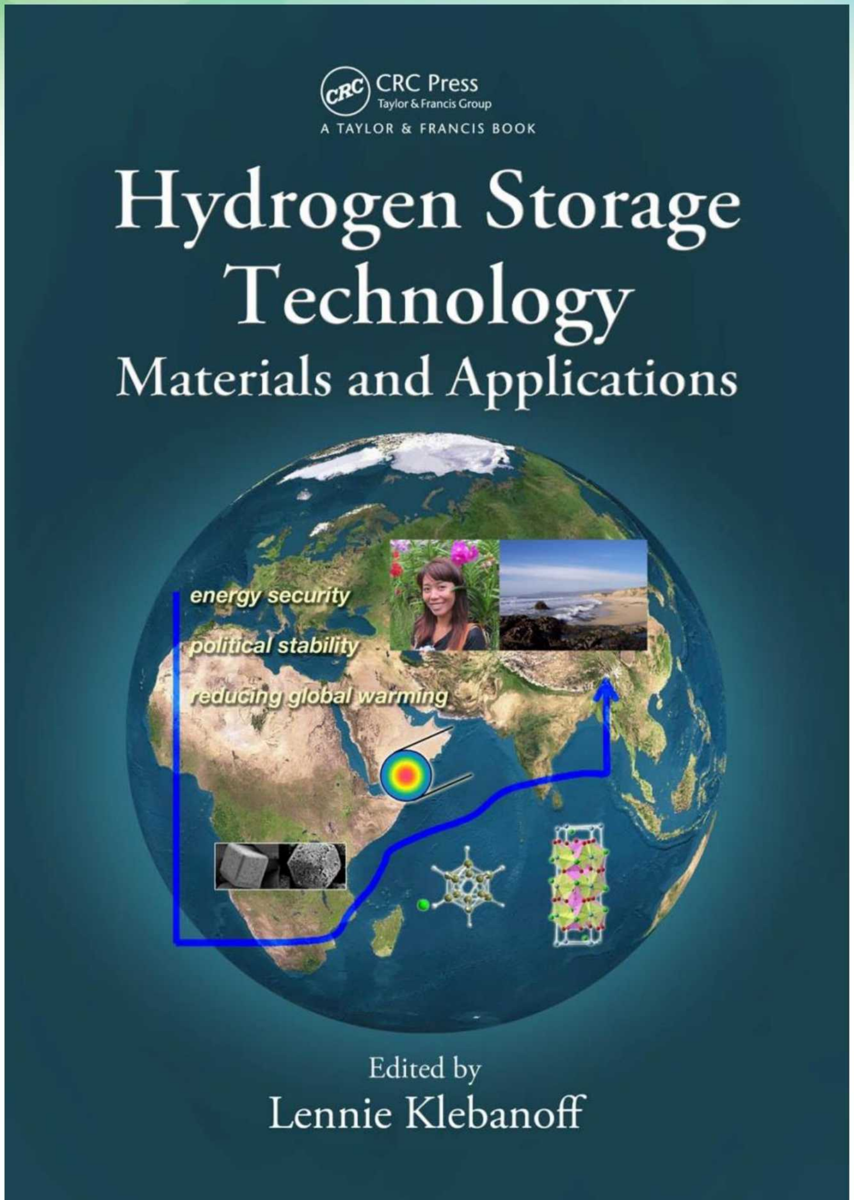
This project is supported by the "California Climate Investments" (CCI) program

H_2 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 LH_2 per day? ✓
- Can the hydrogen suppliers provide renewable LH_2? ✓
- 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)? ✓

Sandia National Laboratories

H_2FC Hydrogen and Fuel Cells Program

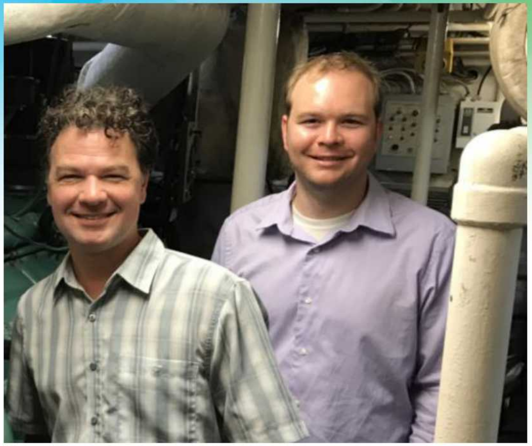


--published by CRC Press in 2012

Topics:

- Why we need H_2-based energy
- H_2 Energy Conversion Devices
- All methods of H_2 Storage
- Engineered H_2 Storage Systems
- H_2 Codes and Standards

-- available on Amazon



Thanks to all my friends and colleagues!

Sujit Ghosh, MARAD

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

For more information on H_2 Storage Projects, visit:
https://hymarc.org/

For more information on H_2/Fuel Cell Maritime Projects visit:
https://maritime.sandia.gov

- Past and current maritime projects
- Download reports

Thank You!

Lennie Klebanoff

(925) 294-3471

lekleba@sandia.gov

Extra Slides

Solid-State H_2 Storage Materials

$$MH_x + \text{heat} \underset{\text{refueling}}{\overset{\text{driving}}{\rightleftharpoons}} M + x/2\ H_2$$

MH_x: FeTi -H, $LaNi_5$-H, $NaAlH_4$

Benefits:

- ✓ Can reduce tank pressures from 10,000 psi to 100 psi (safer).
- ✓ Can triple the storage density of 700 bar H_2.

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

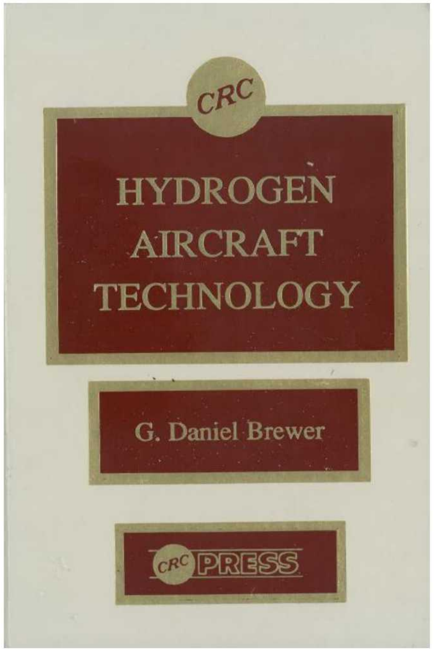
1. Too heavy
2. Don't release hydrogen fast enough (bad kinetics)
3. Don't re-absorb hydrogen fast enough (bad kinetics)
4. Bind hydrogen too tightly (bad thermodynamics)
5. The H_2 they release is contaminated with other species
6. Too expensive
7. Degrade when cycled

HyMARC Hydrogen Materials Advanced Research Consortium: Sandia National Laboratories, Lawrence Livermore National Laboratory, Berkeley Lab, NREL National Renewable Energy Laboratory, Pacific Northwest National Laboratory, NIST National Institute of Standards and Technology U.S. Department of Commerce

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

H_2 Aircraft Technology

Fuel	$-\Delta H^o_{Combustion}$ (kJ/g) (LHV)
Hydrogen (H_2)	120.0
Methane (CH_4)	50.1
Jet-A (JP-4) (~$C_{12}H_{26}$)	42.8

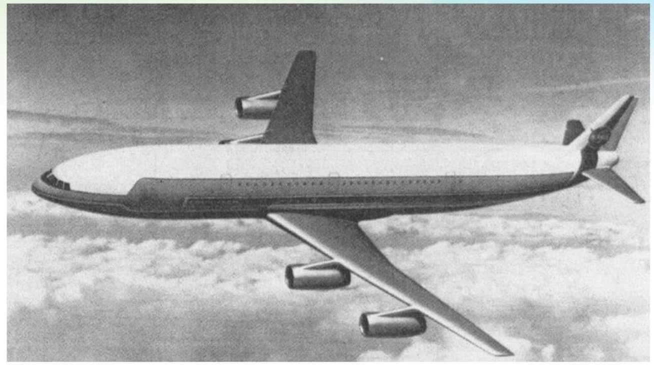


Prior Studies:

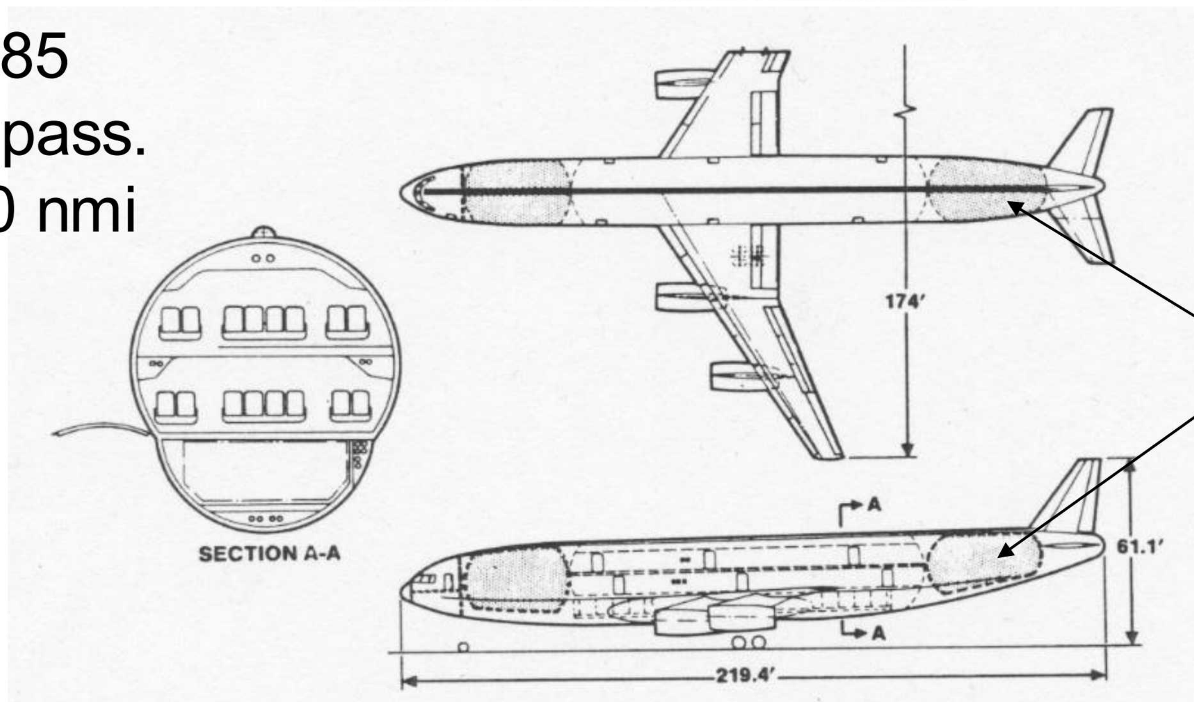
- Lockheed studies of the 1970's
- 2002 Airbus Study (Cryoplane)
- Boeing Study: (2006)

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

Larger Fuselage Accommodates LH_2 Fuel, Cargo, People



M 0.85
400 pass.
5500 nmi



LH_2 tanks (fore, aft)

- From "Hydrogen Aircraft Technology", pg. 46

Comparison of Jet-A vs. LH_2-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 LH_2 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, LH_2

Boeing Phantom Eye