

# **SAFETY CONSIDERATIONS ON LIQUID HYDROGEN (PART 1)**

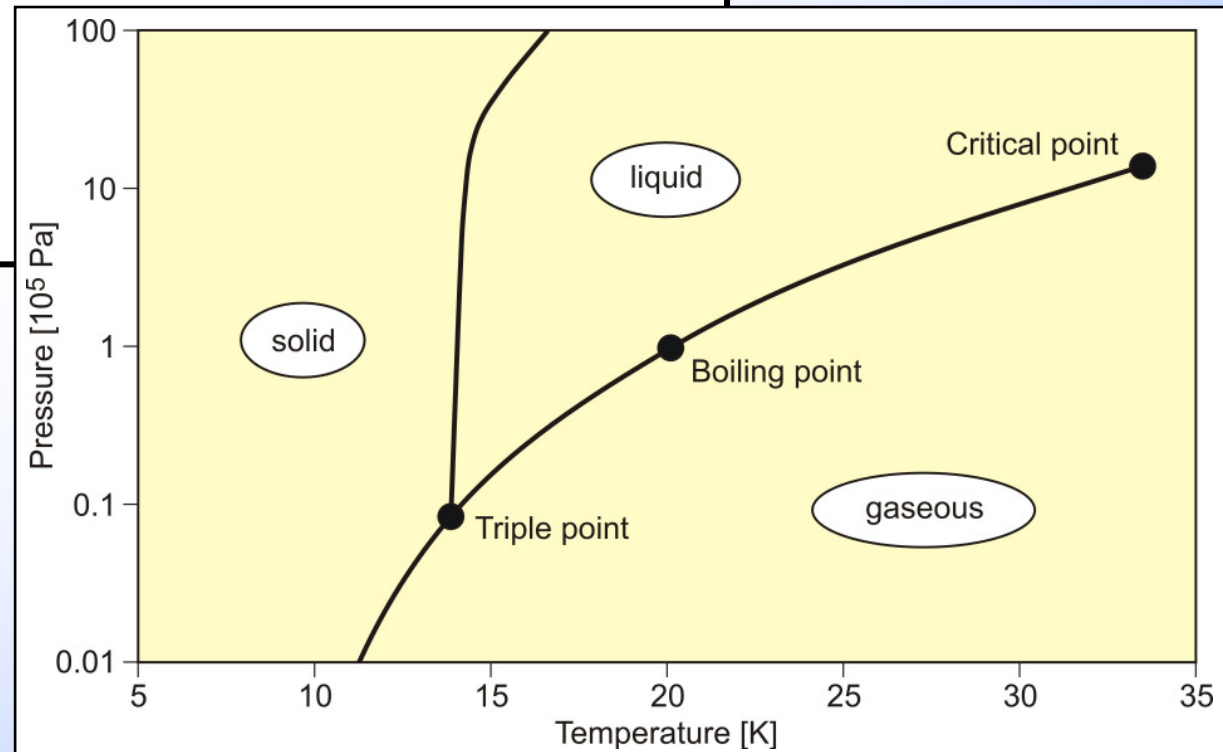
**Karl Verfondern**

**Research Center Jülich, Germany**

**2<sup>nd</sup> European Summer School on Hydrogen Safety  
Belfast, July 30 – August 8, 2007**

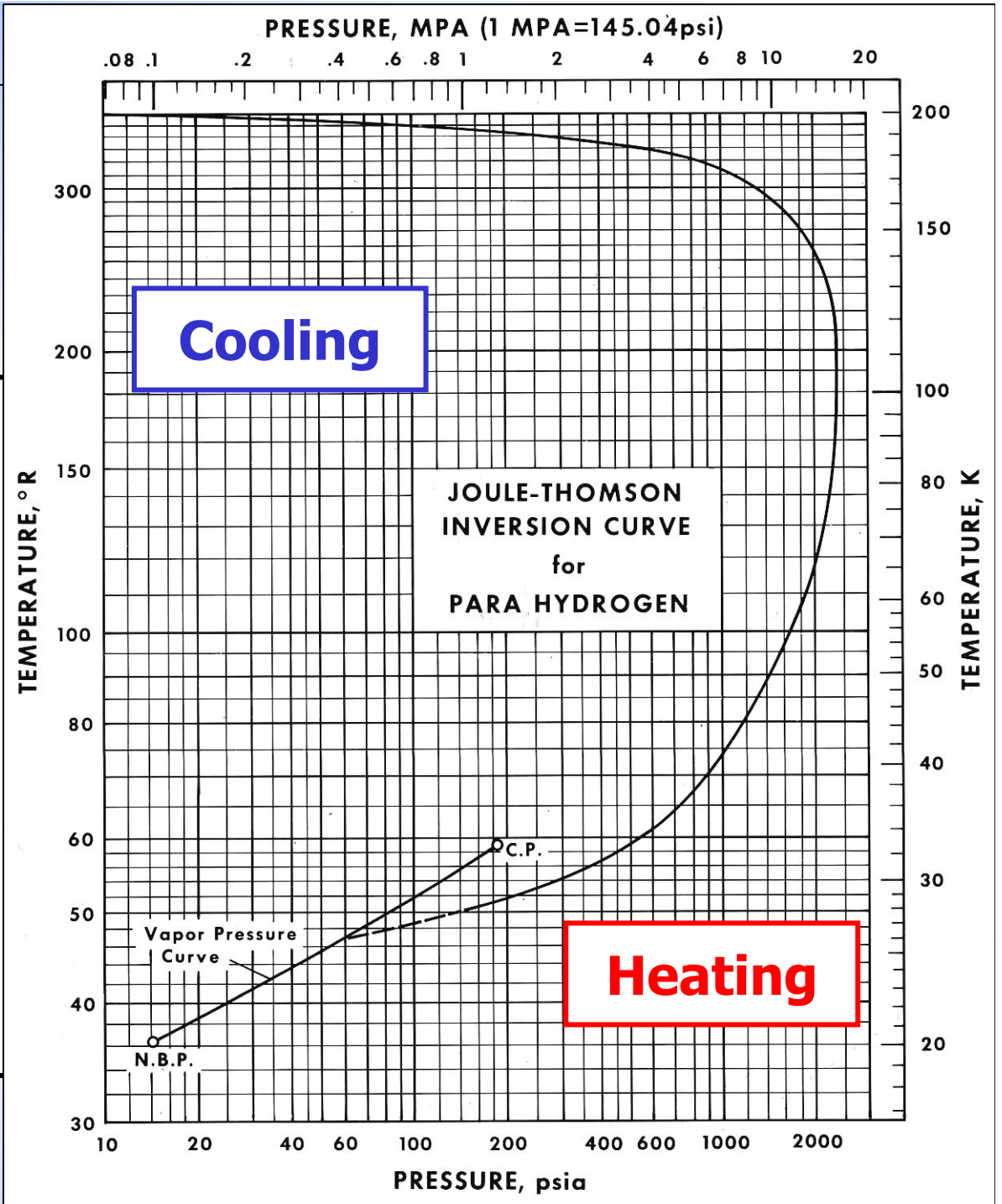
## Properties of Liquid Hydrogen (1)

- cold (14-20 K)  
max. BP = 33 K @ 1.3 MPa [critical point]
- light (71 grams per liter)
- high expansion ratio  
(~ 845)



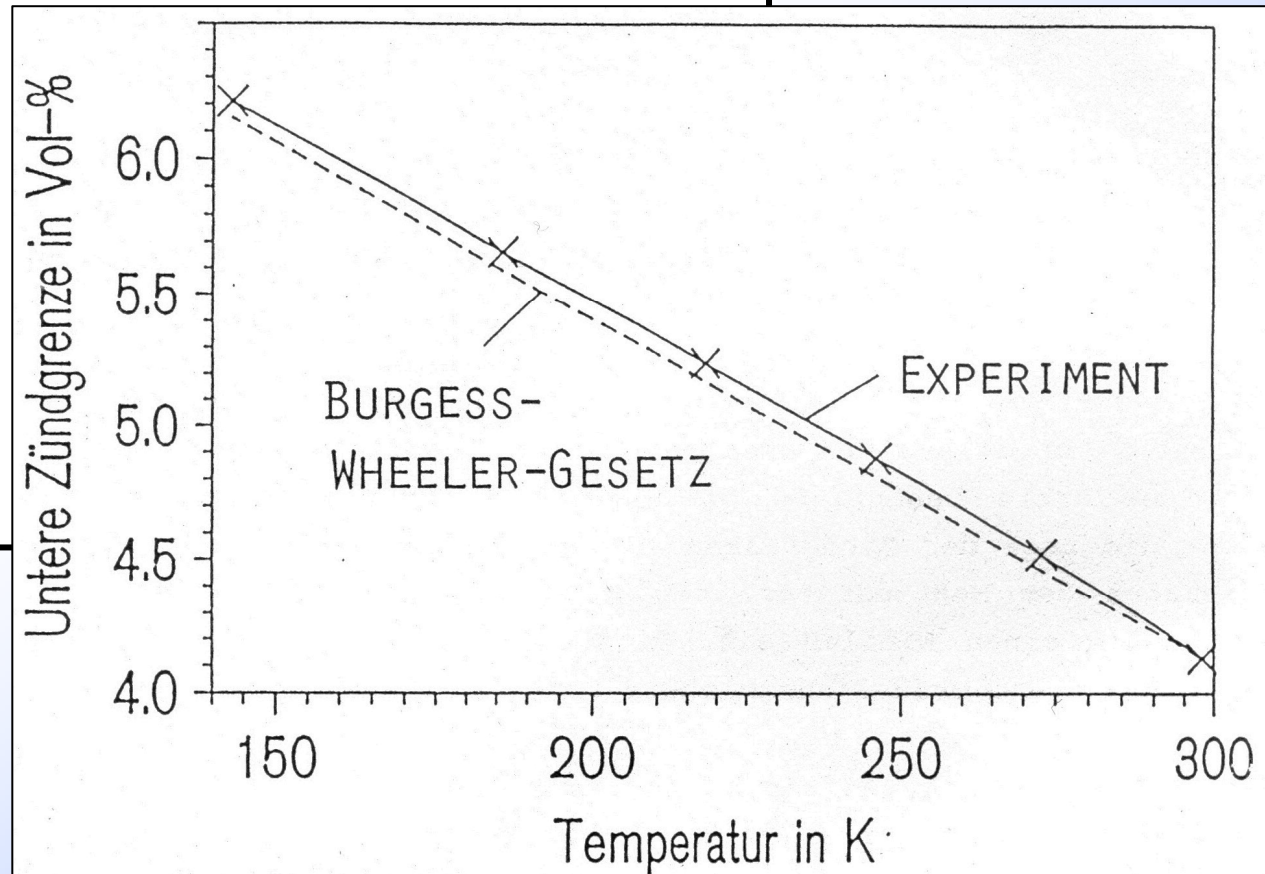
## Properties of Liquid Hydrogen (2)

- co-existing in ortho and para form, ( $\Delta H_c > \Delta H_v$ )
- Thomson-Joule effect negative for  $T_1=193$  K
- thermal contraction, cold embrittlement



## Properties of Liquid Hydrogen (3)

- smaller flammability range  
LFL = 7.7 vol% @ BP
- more difficult to ignite
- in open pool, air solidification  
→ O<sub>2</sub> enrichment

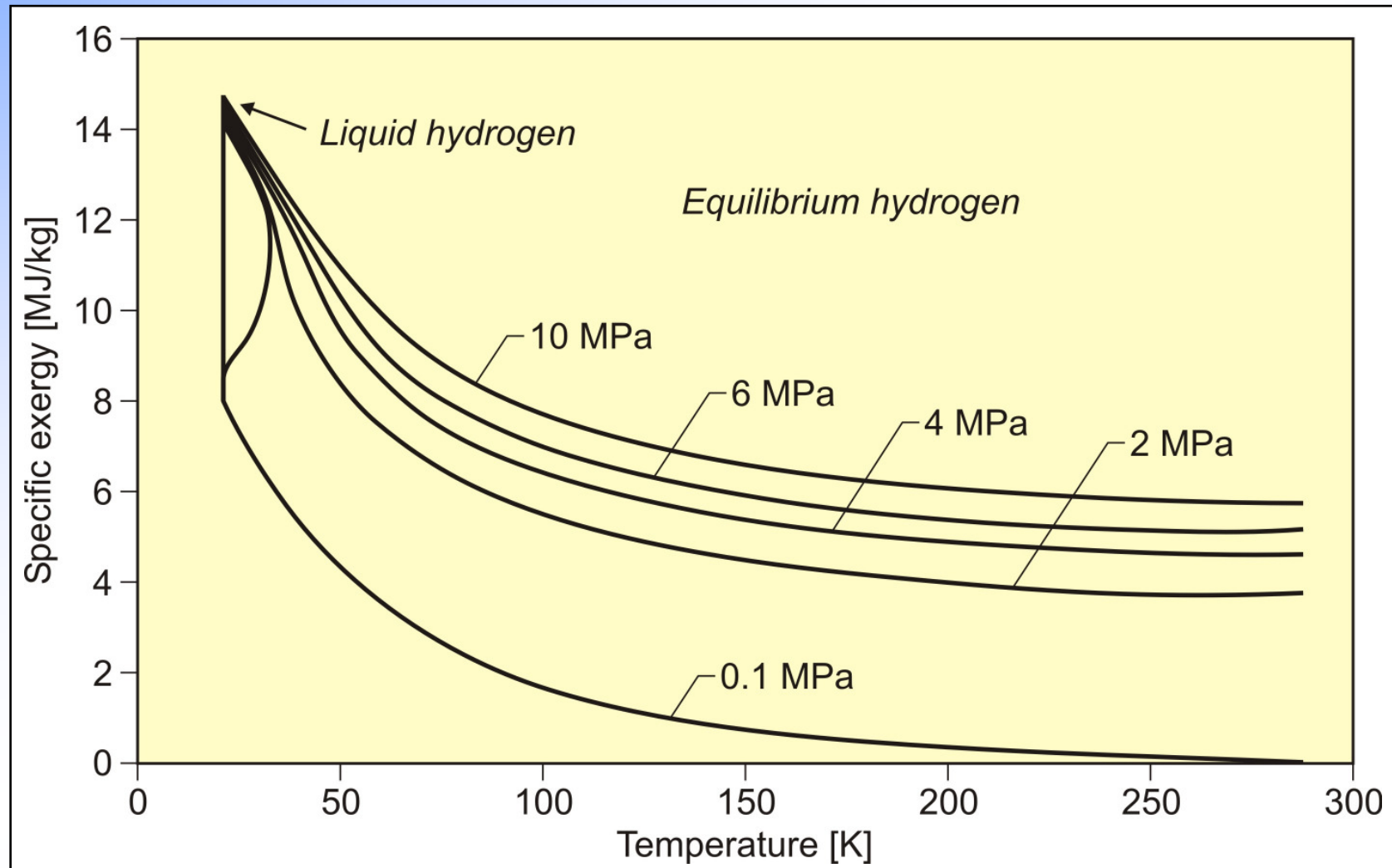


# Liquefaction of Hydrogen

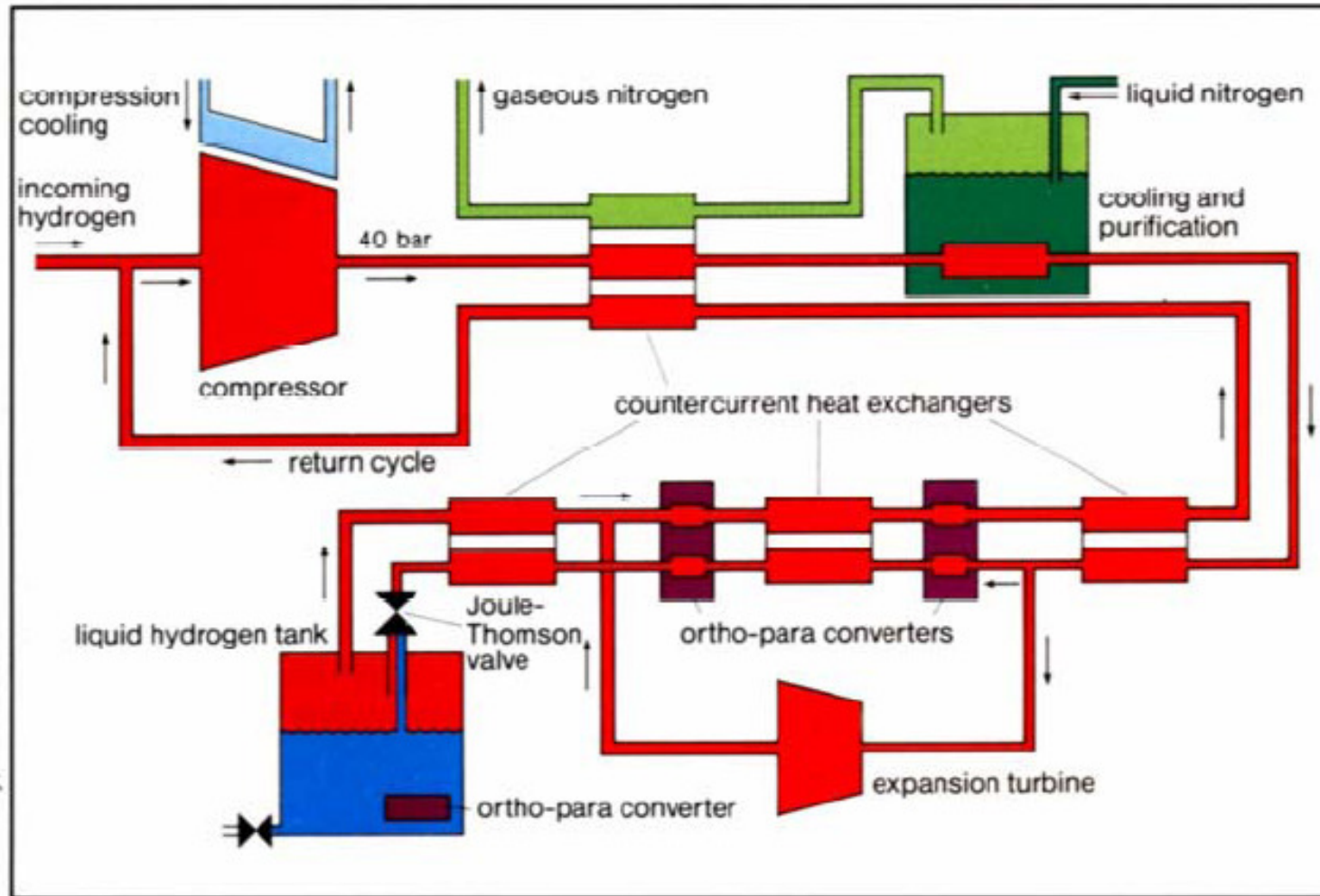
Gas	Boiling Point [K]	Heat of vaporization [kJ/kg]	Minimum Work [kWh/kg]		
			Cooling NTP → BP	Condensation	Total
Hydrogen	20.268	445.59	2.242*	1.666	3.91
Methane	111.632	509.88	0.077	0.230	0.31
Nitrogen	77.34	201.	0.055	0.156	0.21
Helium	4.216	20.9	1.917	0.398	2.32

\* includes ortho-para conversion

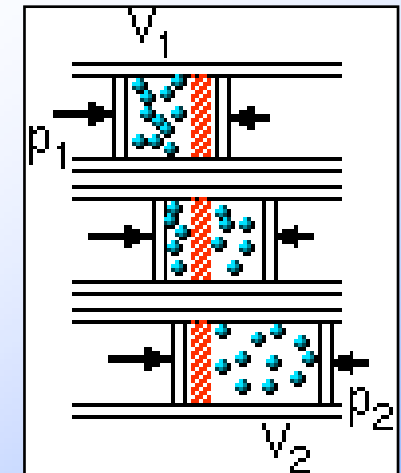
# Liquefaction of Hydrogen



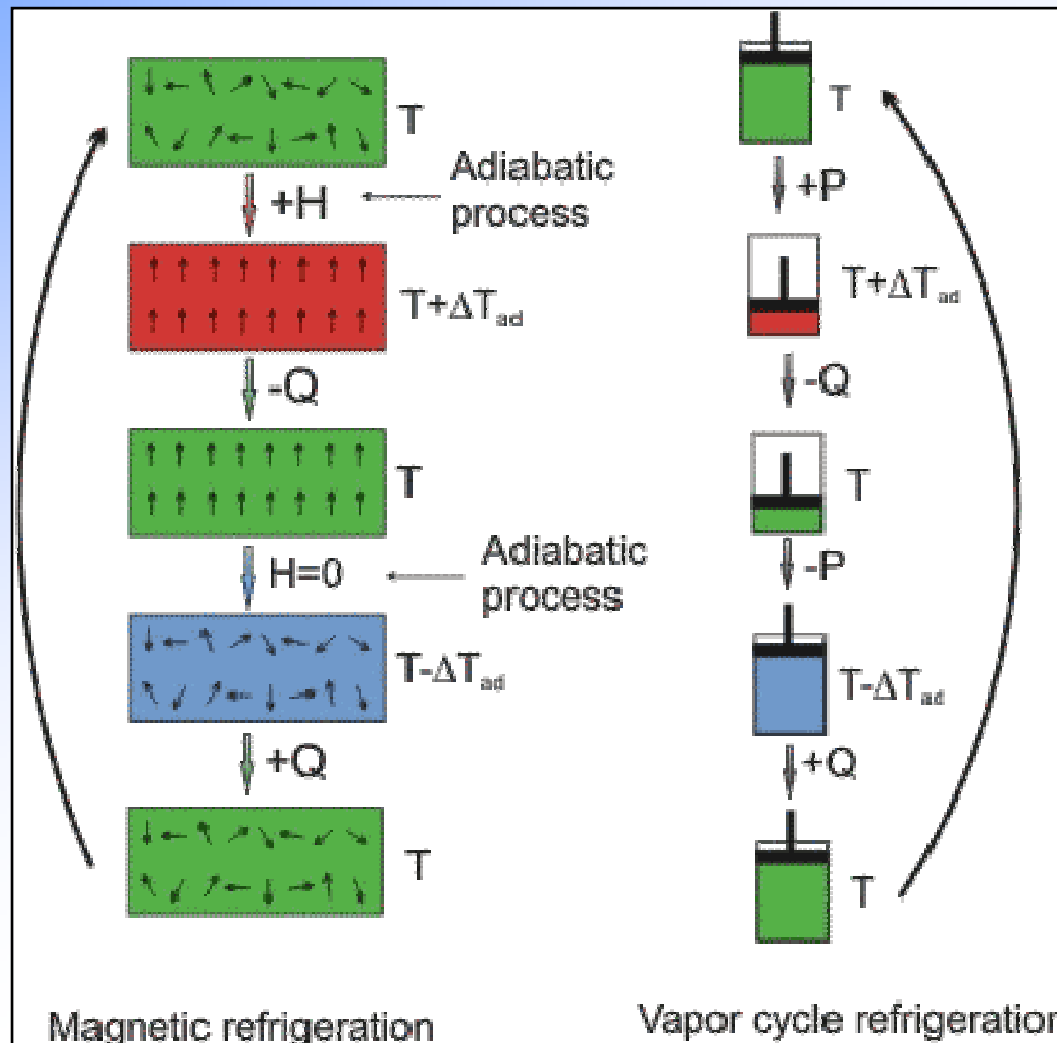
# Claude Process



## Thomson-Joule Expansion



# Magnetic Refrigeration Process



**Magnetization**

**Heat removal**

**De-magnetization**

**Heat transfer from  
gas to be cooled**

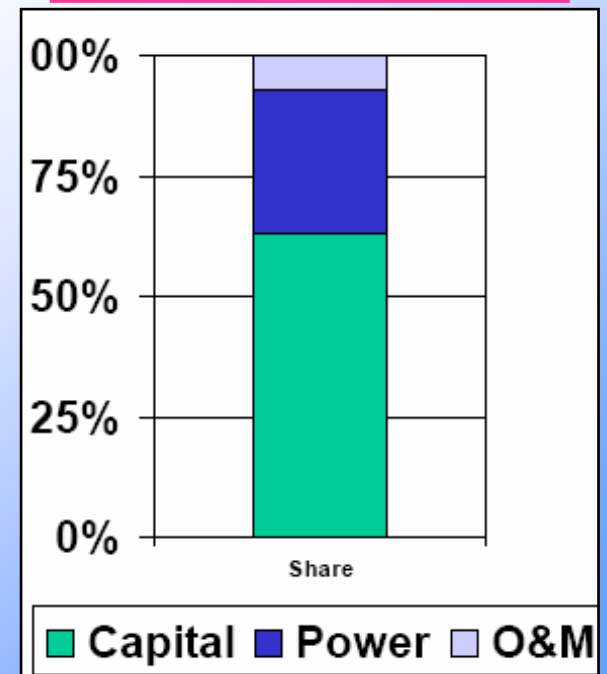
**Ideal: Gd materials**



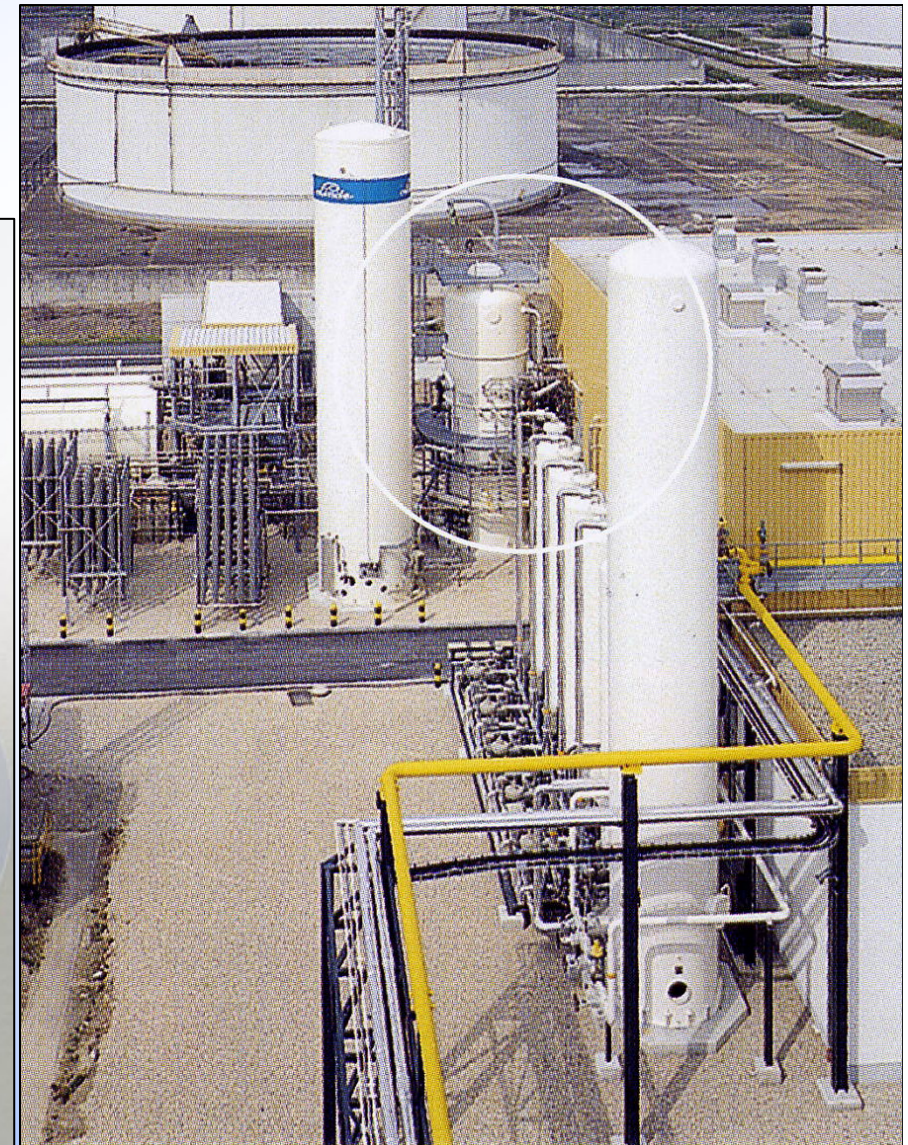
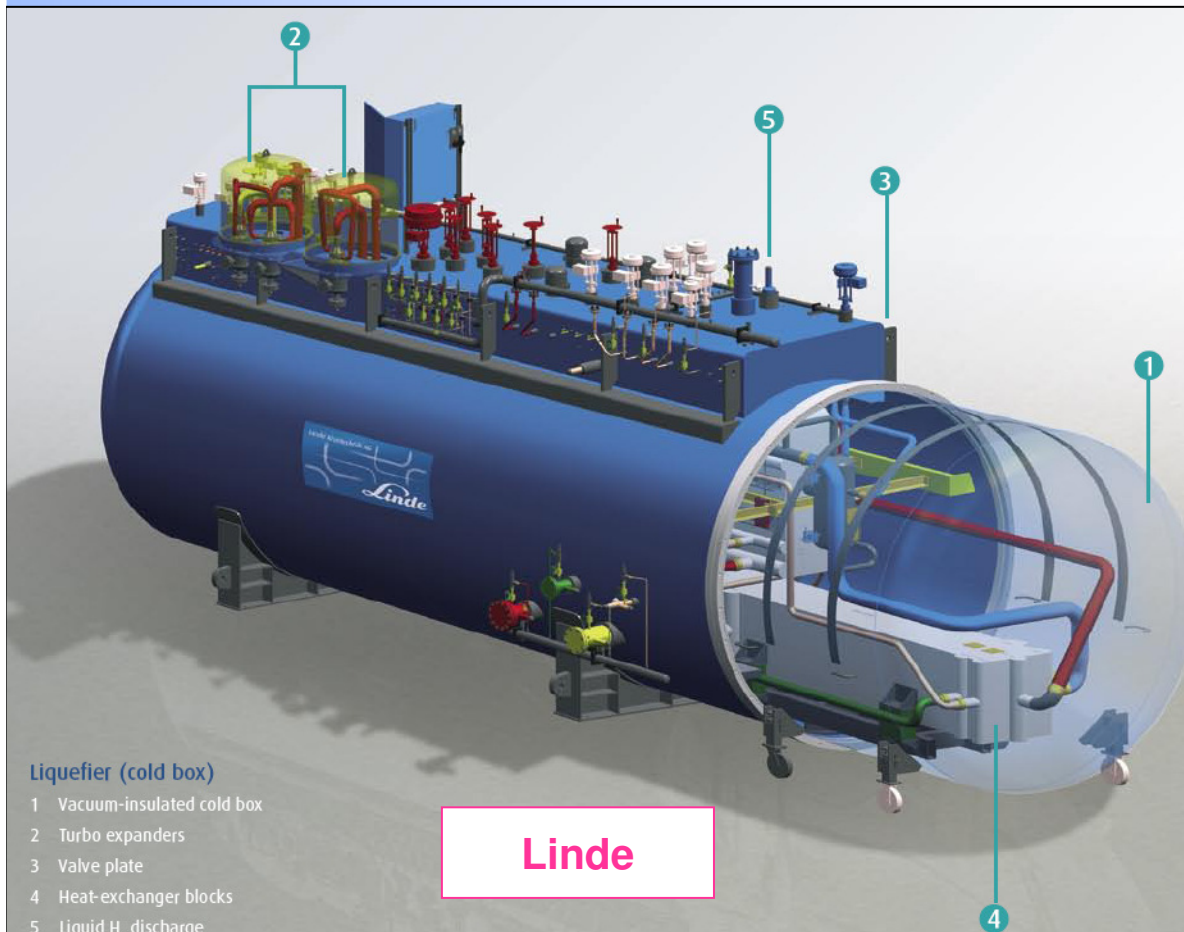
# H<sub>2</sub> Liquefaction Capacity in the World

Place	Operator	Capacity [t/d]	Operation since
<b>America</b>			
Sarnia, ON, Canada	Air Products, USA	29	1962
New Orleans, LA, USA	Air Products, USA	68	1977
Pace, USA	Air Products, USA	29	1994
Sacramento, CA, USA	Air Products, USA	6	1986
Magog, QU, Canada	BOC, USA	15	1990
Becancour, QU, Canada	HydrogenAI, Canada	11	1986
Kourou, French Guiana	L' Air Liquide, France	5	1990
East Chicago, IN, USA	Praxair	29	1999
McIntosh, AL, USA	Praxair	29	1995
Niagara Falls, NY, USA	Praxair	38	1981 /1989
Ontario, CA, USA	Praxair	22	1962
<b>Total America</b>		<b>281</b>	
<b>Europe</b>			
Rozenburg, Netherlands	Air Products, USA	5.0	1987
Lille, France	L' Air Liquide, France	10.5	1987
Ingolstadt, Germany	Linde, Germany	4.4	1991
Leuna, Germany*	Linde, Germany	5.0	2007
<b>Total Europe</b>		<b>24.9</b>	
<b>Asia</b>			
Amagasaki, Japan	Iwatani Gas, Japan	1.2	1978
Ooita, Japan	Pacific Hydrogen Co., Japan	1.4	1986
Kimitsu, Japan	Nippon Steel Corp., Japan	0.2	2004
Sakai, Japan	Iwatani Gas, Japan	1.1	2006
<b>Total Asia</b>		<b>3.9</b>	
<b>Total World</b>		<b>316.8</b>	

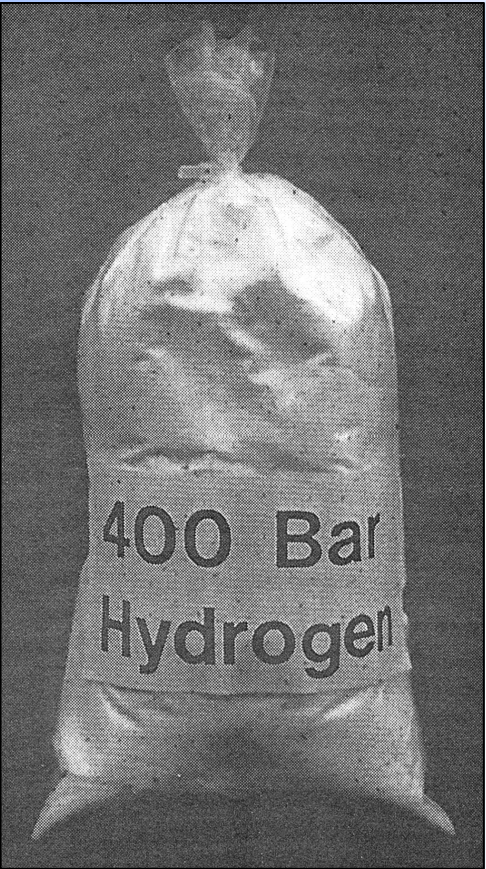
## Cost Stack



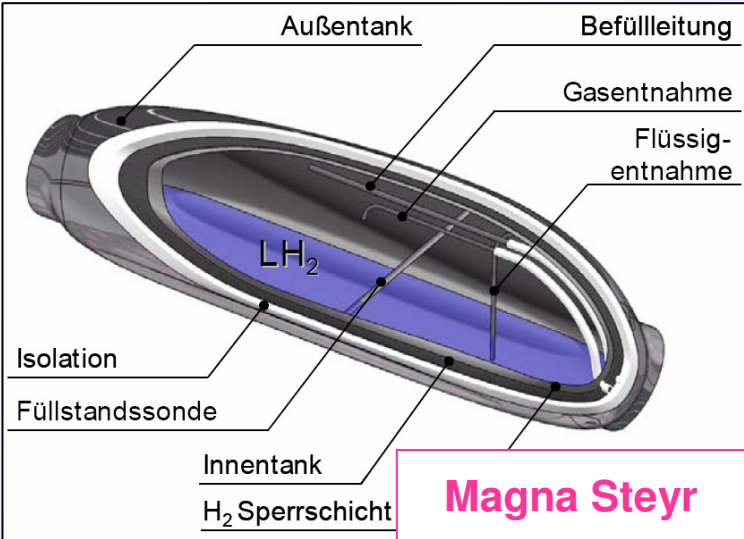
# 4.5 t/d LH<sub>2</sub> Liquefaction Plant in Ingolstadt



# Storage



NASA

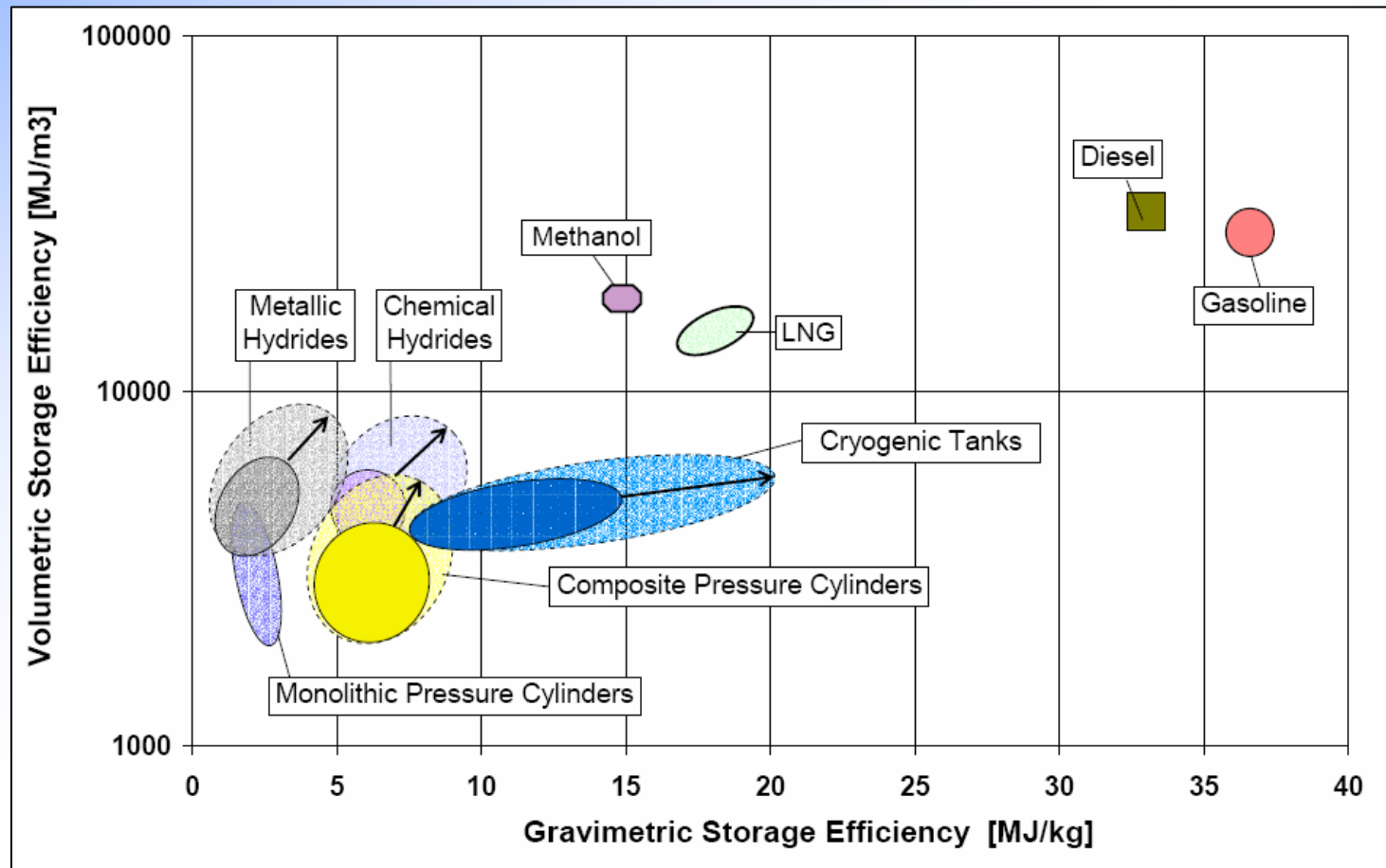


Magna Steyr



Messer Griesheim

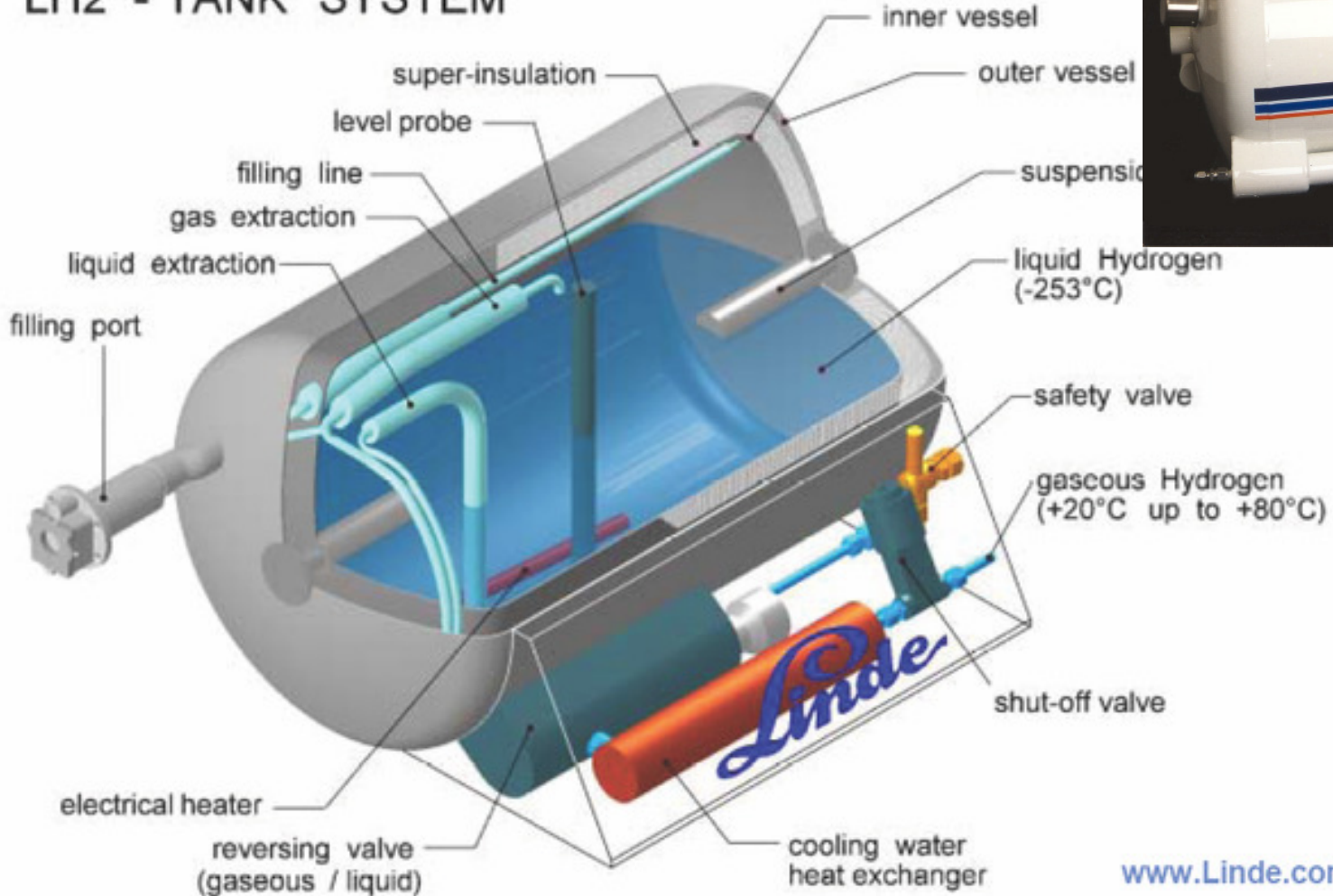
# Storage of Liquid Hydrogen



**Volumetric-Gravimetric Tank Characteristics**

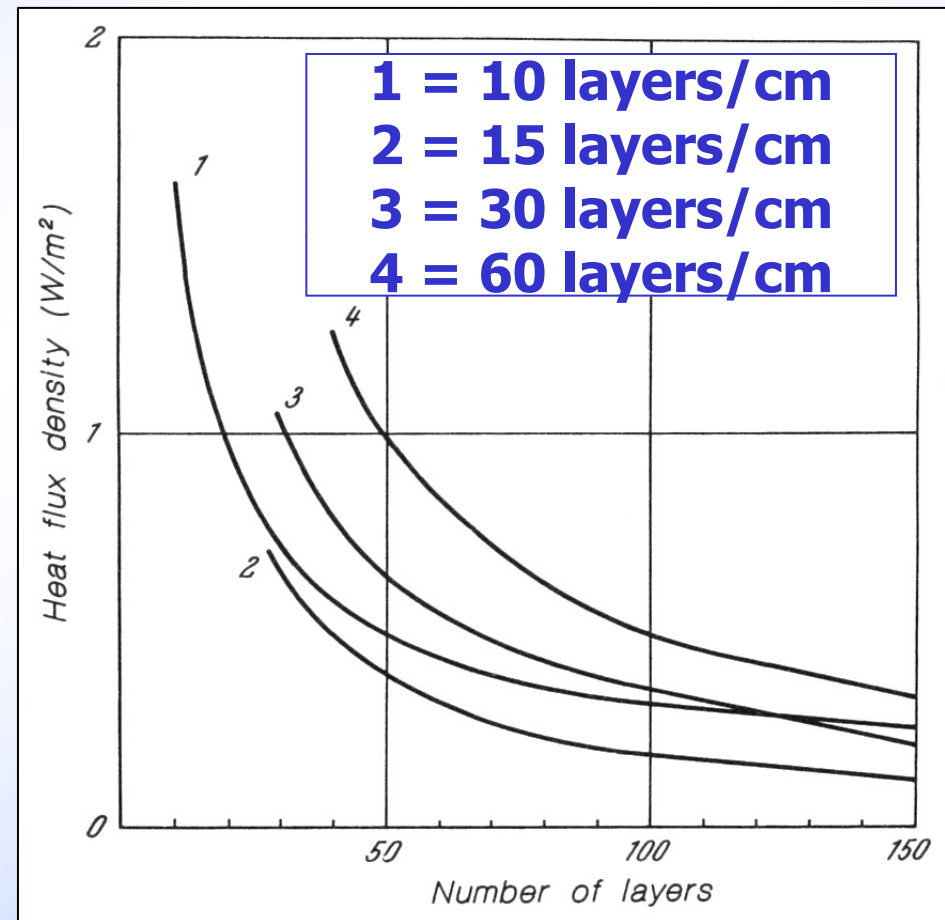
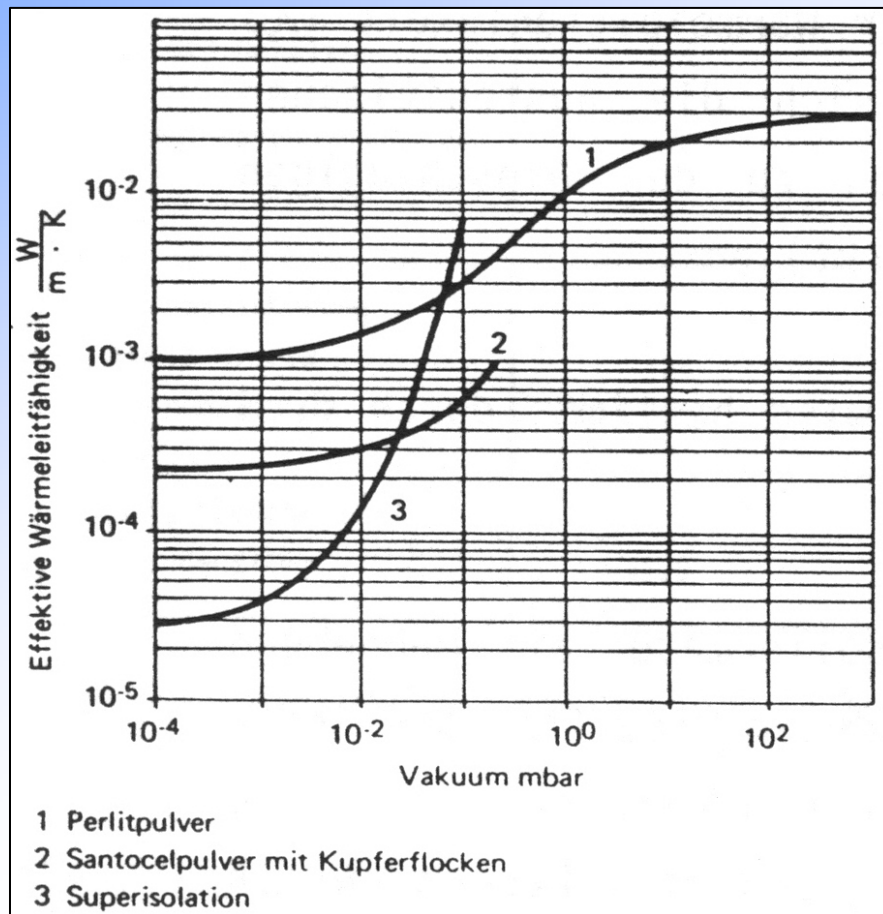
# LH<sub>2</sub> Tank for Passenger Car

## LH<sub>2</sub> - TANK SYSTEM



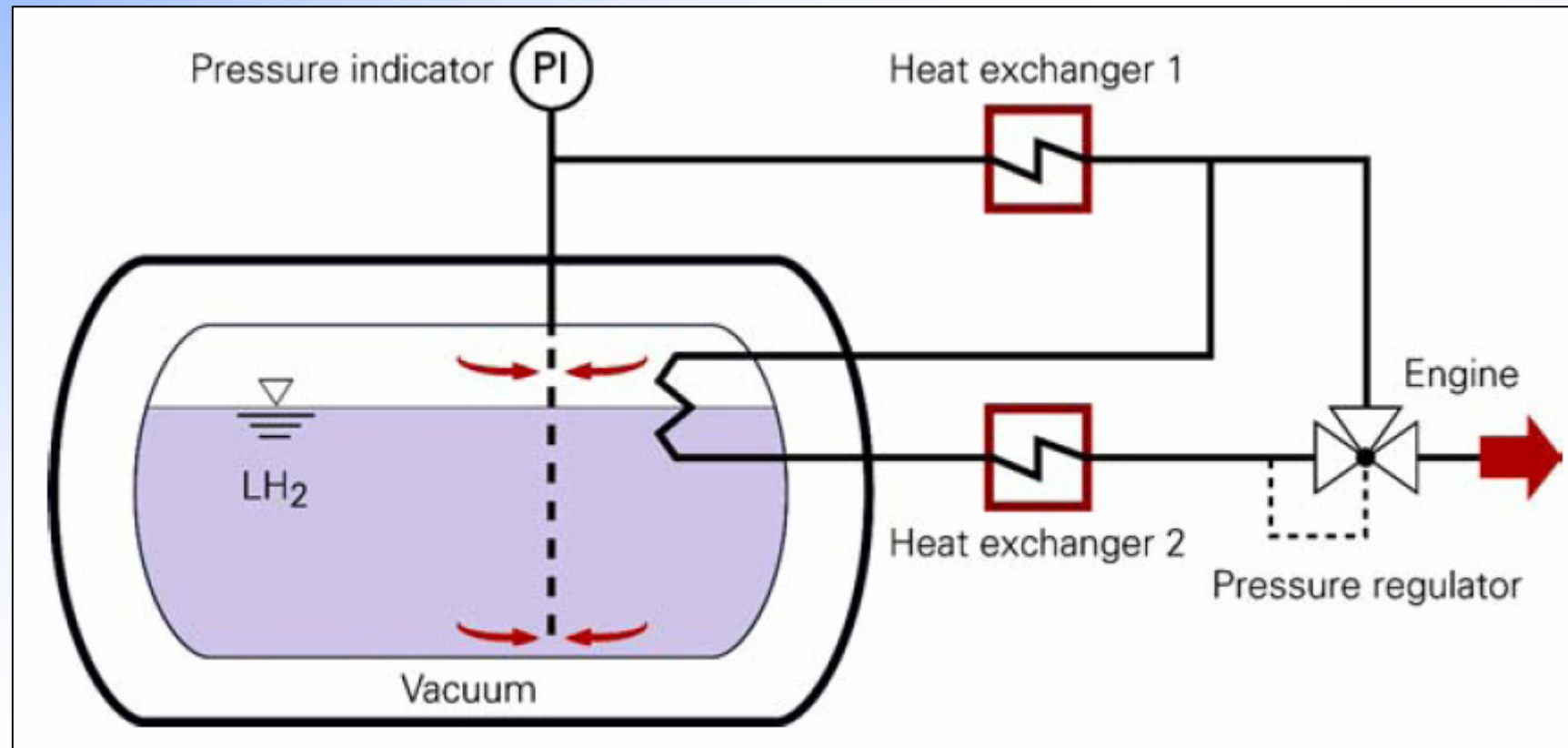
Messer Griesheim

# Superinsulation



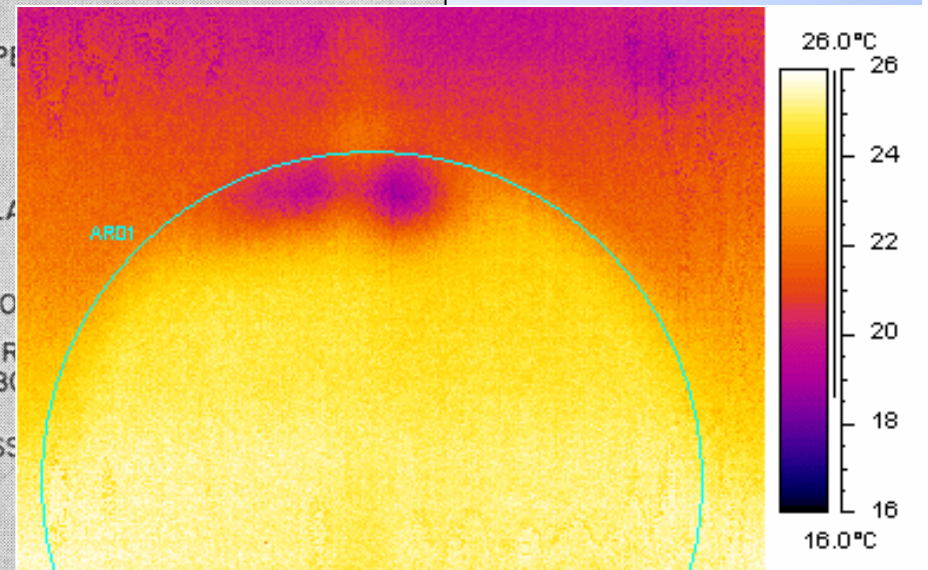
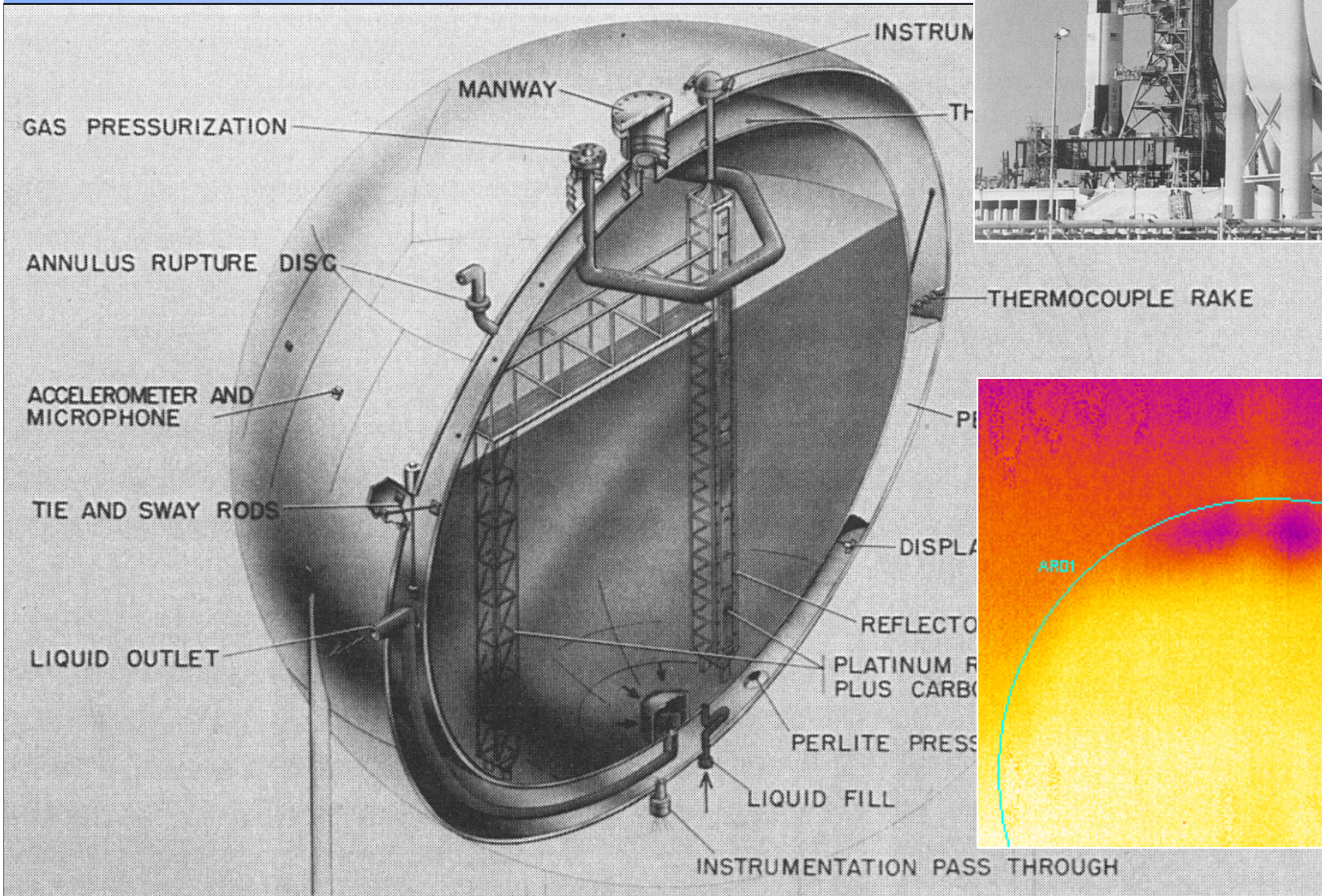
Peschka 1992

# New Pressure Management System



Air Liquide 2006

# Stationary LH<sub>2</sub> Tank at KSC



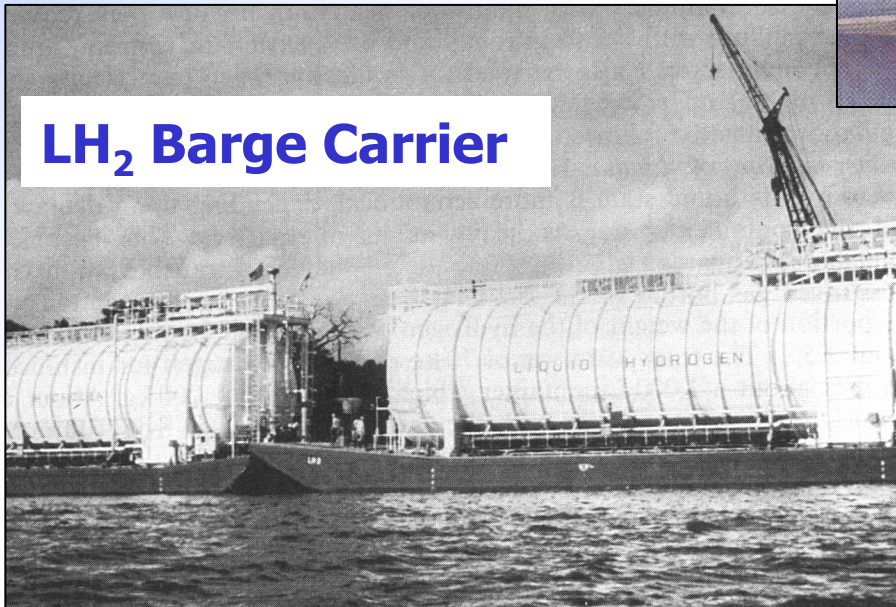


# Transportation

Natural Gas, low pressure, 2005



LH<sub>2</sub> Barge Carrier

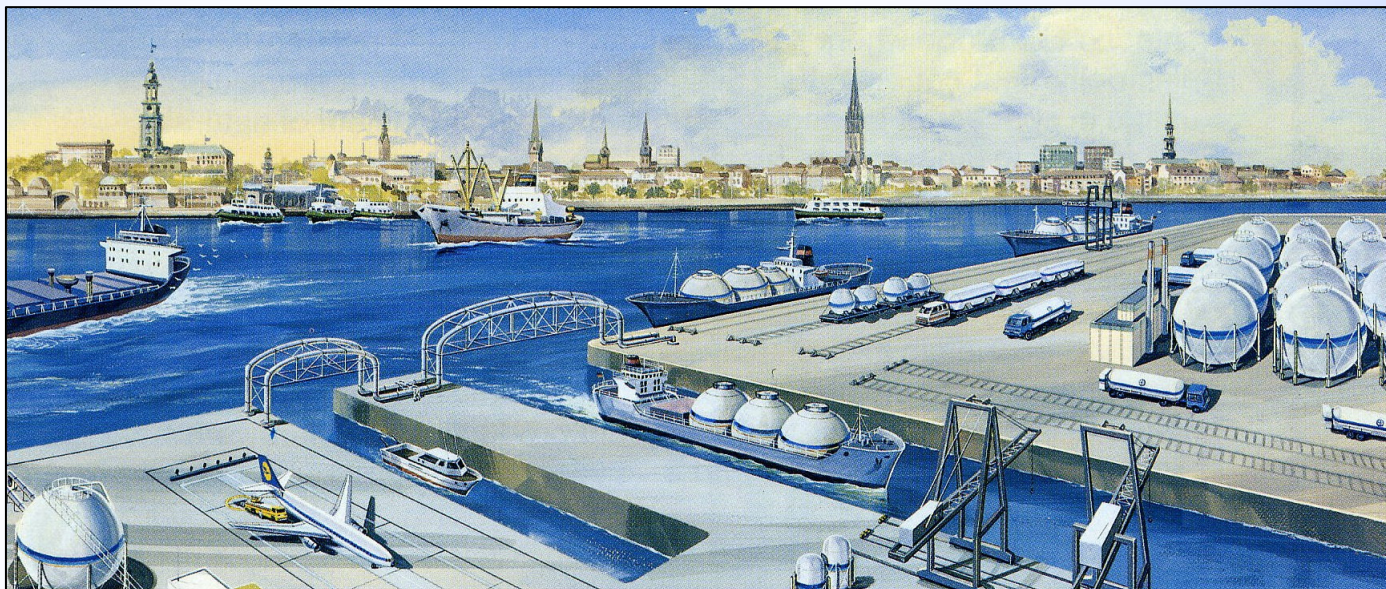
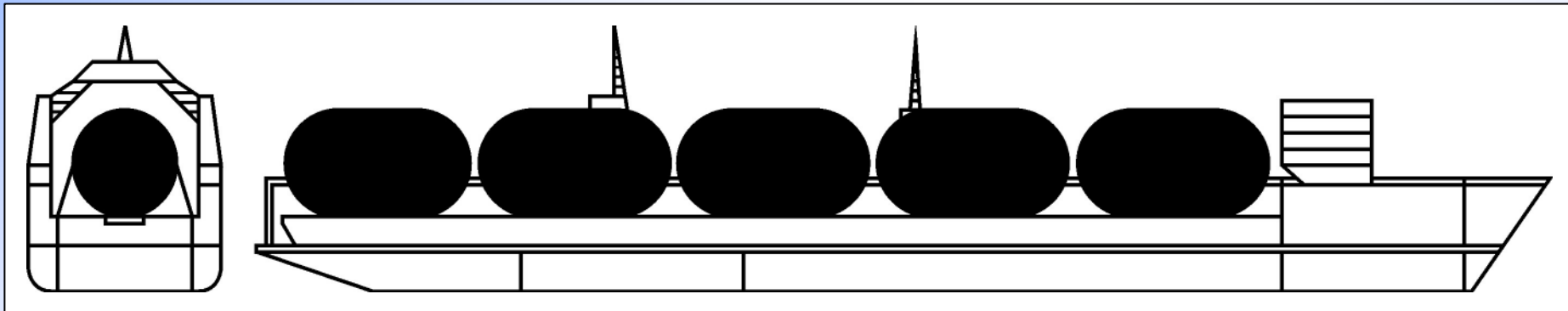


LOX, medium pressure, 1960s



# Euro-Quebec Barge Carrier

**Dock ship**  
**Length: 180 m, Width: 29 m**  
**5 barges with 3000 m<sup>3</sup> of LH<sub>2</sub> each**

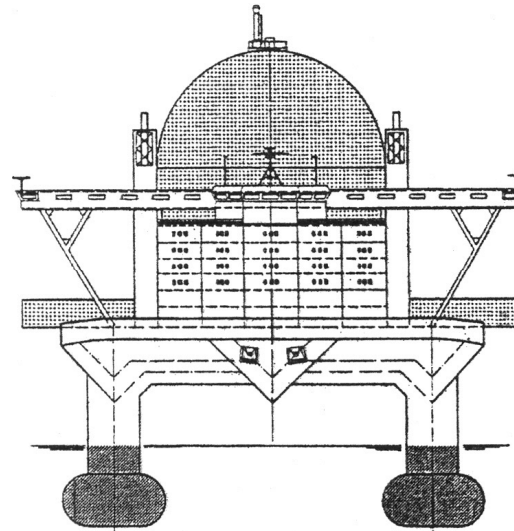
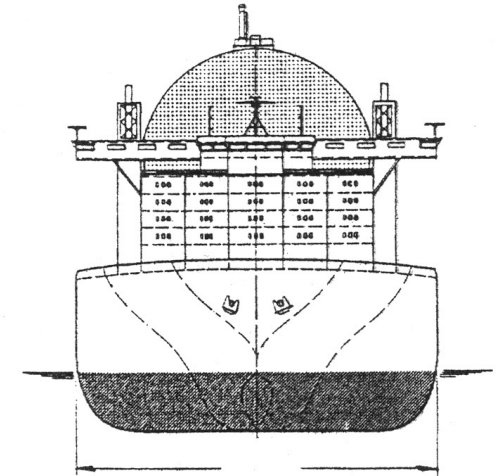




**Germanischer Lloyd  
Howaldtswerke Deutsche Werft AG**

### Dockship

Capacity	8 150 t
	115 000 m <sup>3</sup>
Length (l <sub>pp</sub> )	318 m
Breadth (WL)	62 m
Draught (CWL)	10 m
Displacement	134 400 t
Power (mcr)	36 000 kW
trial speed	16 kn

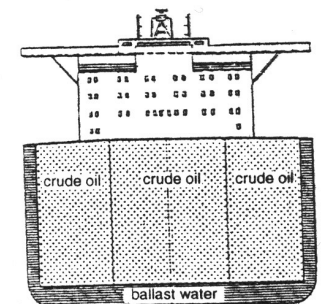


### SWATH carrier

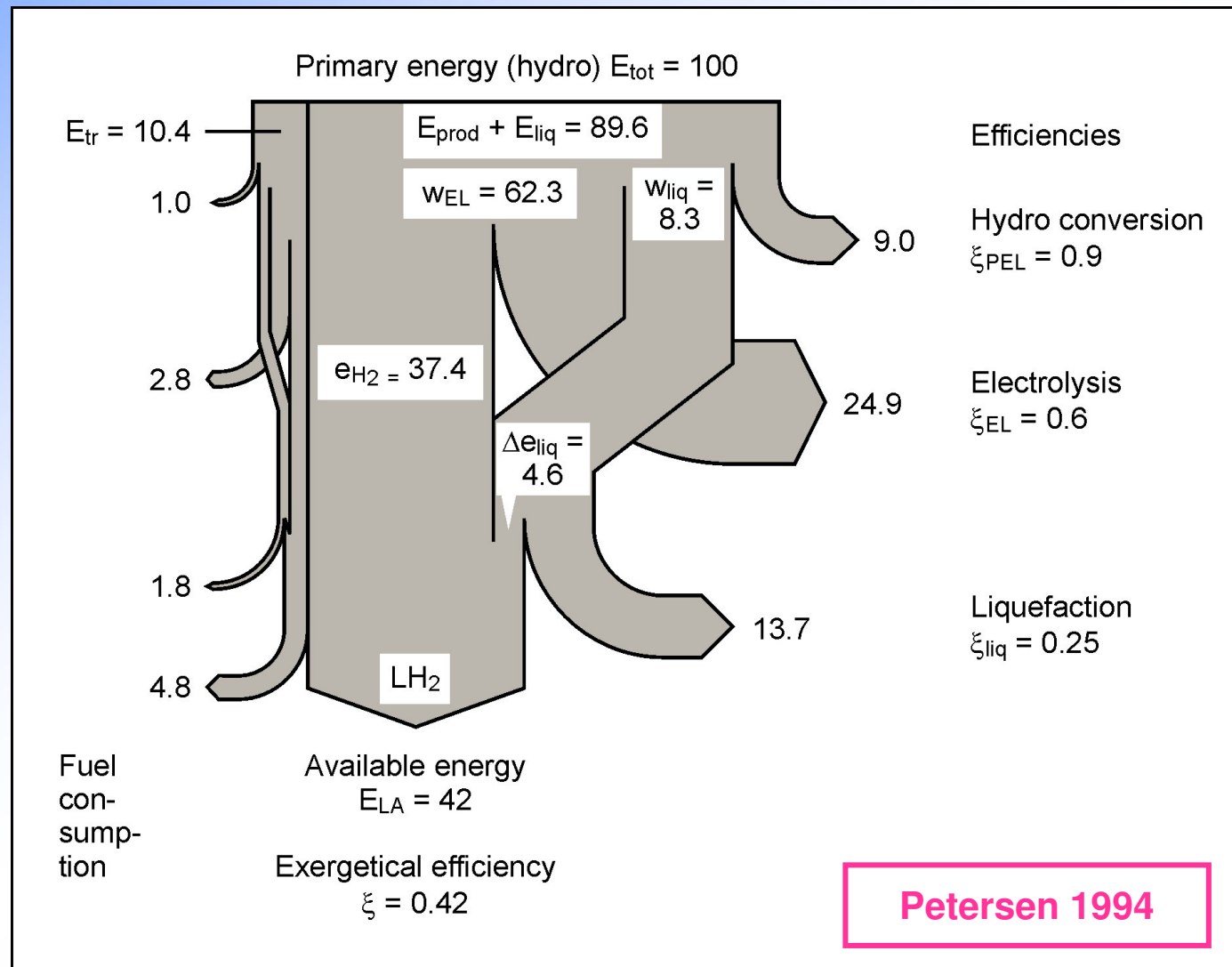
Capacity	8 150 t
	115 000 m <sup>3</sup>
Length (l <sub>pp</sub> )	322 m
Breadth (WL)	65 m
Draught (CWL)	14 m
Displacement	104 000 t
Power (mcr)	36 000 kW
trial speed	17,5 kn

### Double hull tanker

Capacity	273 000 t
	300000 m <sup>3</sup>
Length (l <sub>pp</sub> )	330 m
Breadth (WL)	58 m
Draught (CWL)	20,6 m
Power (mcr)	22 450 kW
trial speed	14,5 kn



# Exergy Analysis for Sea-Borne LH<sub>2</sub>-Transport



**SWATH ship**

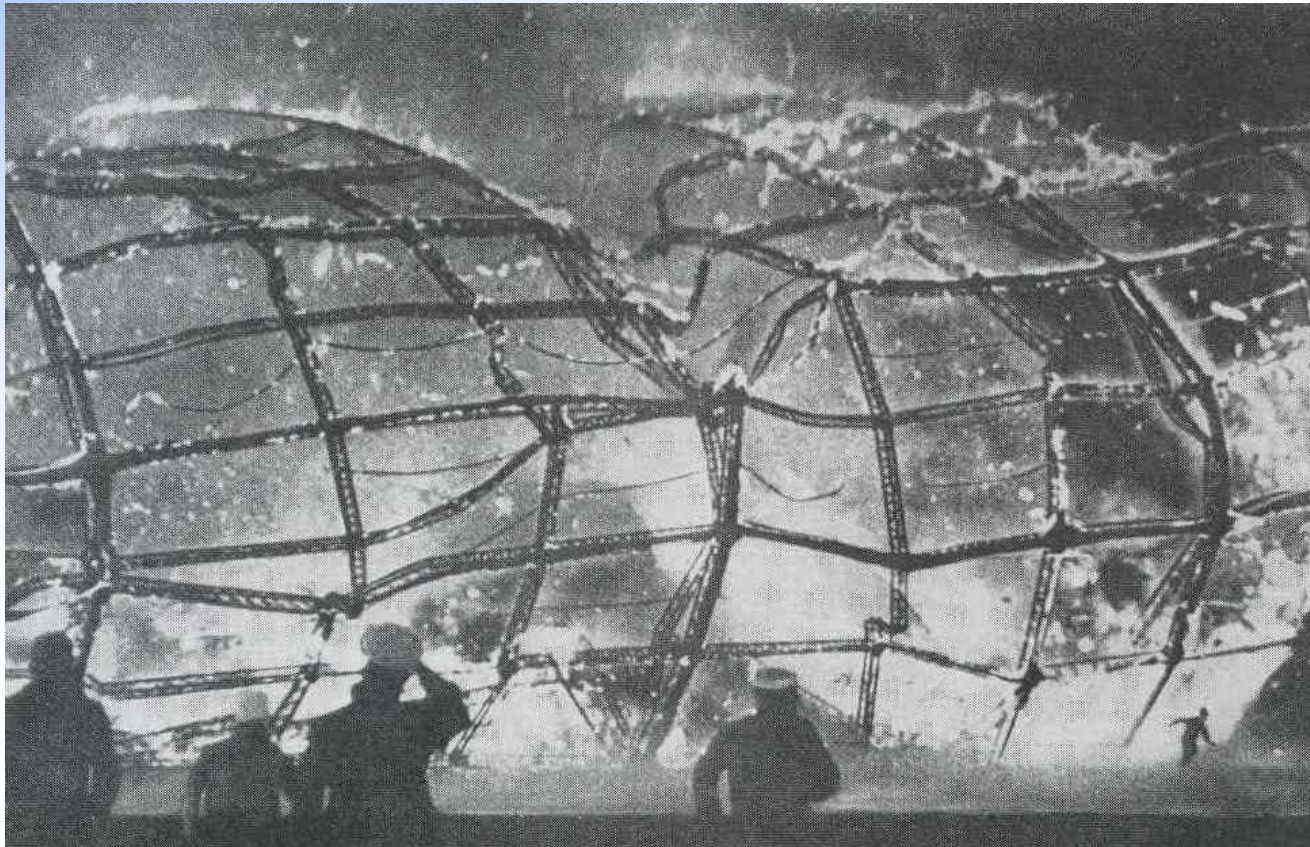
# WE-NET Design of Maritime LH<sub>2</sub>-Transport



Length: 345m  
Capacity: 200,000 m<sup>3</sup>  
Boil-off rate: 0.2-0.4 %/d

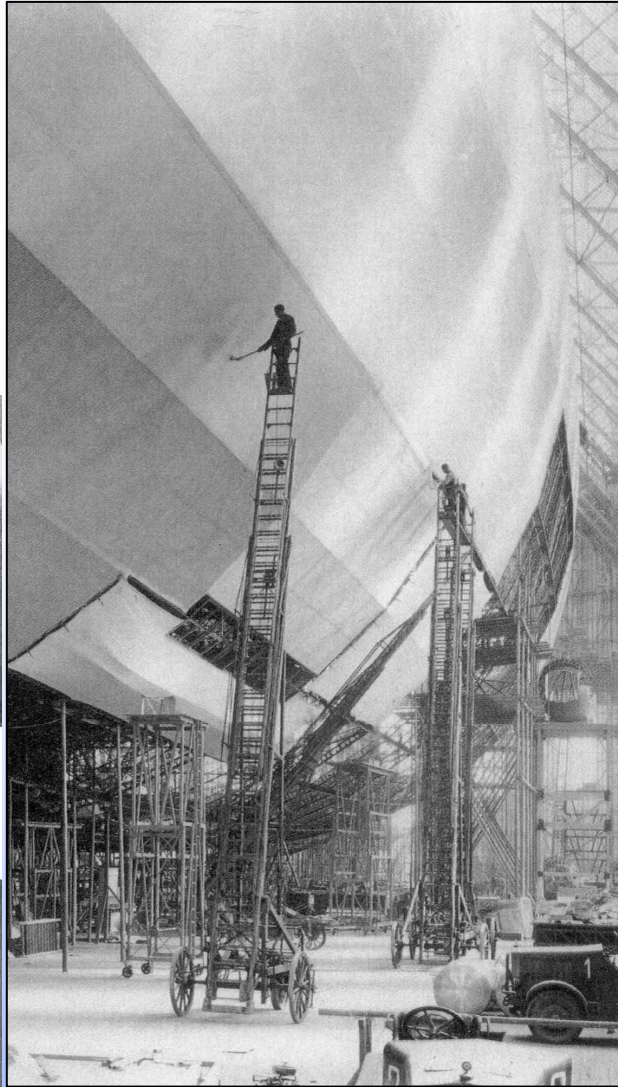
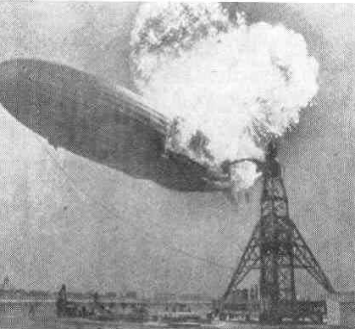
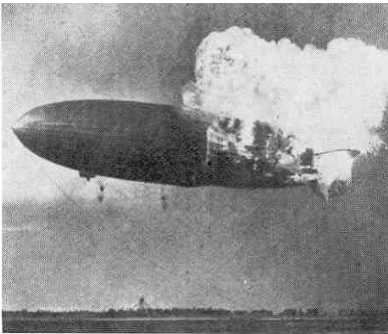
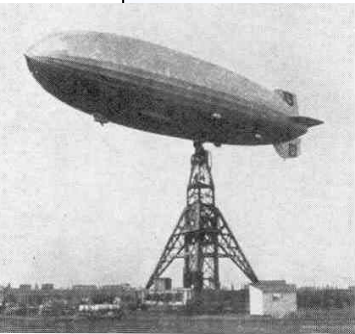
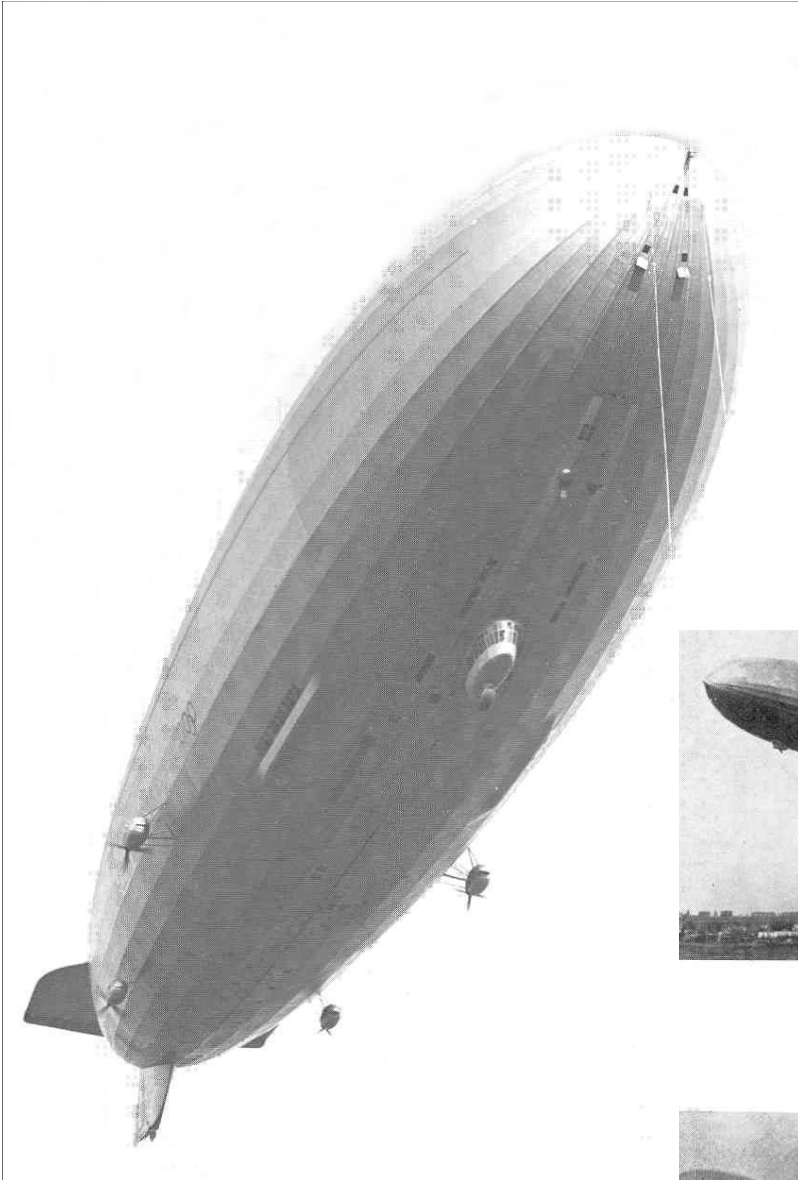
Hijikata 2002

# Accidents



German Newspaper, 1937

# Hindenburg 1937



# Car Accidents



**Truck after LOX tank explosion**



**UCLA car overturn, rapid LH<sub>2</sub> boil-off**





# Accident with H<sub>2</sub> Truck



June 2006, H<sub>2</sub> Tube Trailer Accident, Germany

# Accident Simulation Test

Comparison  
of fuel  
behavior  
after  
leakage and  
ignition



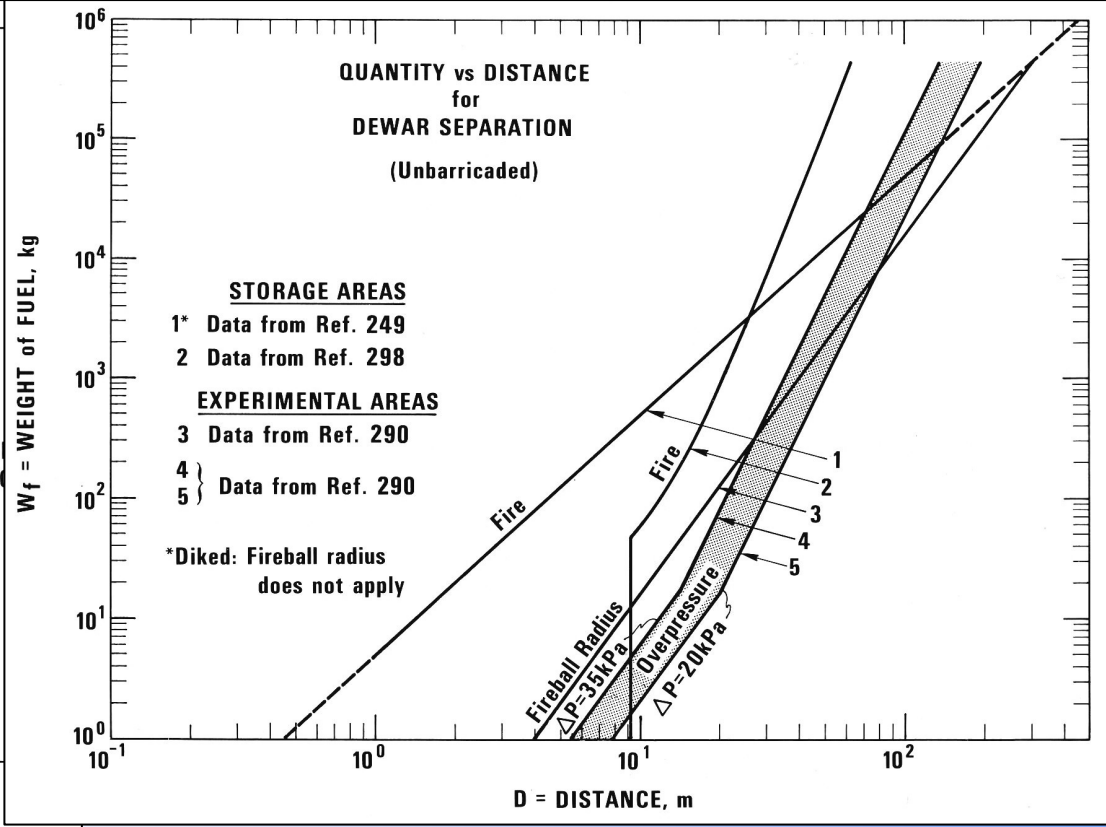
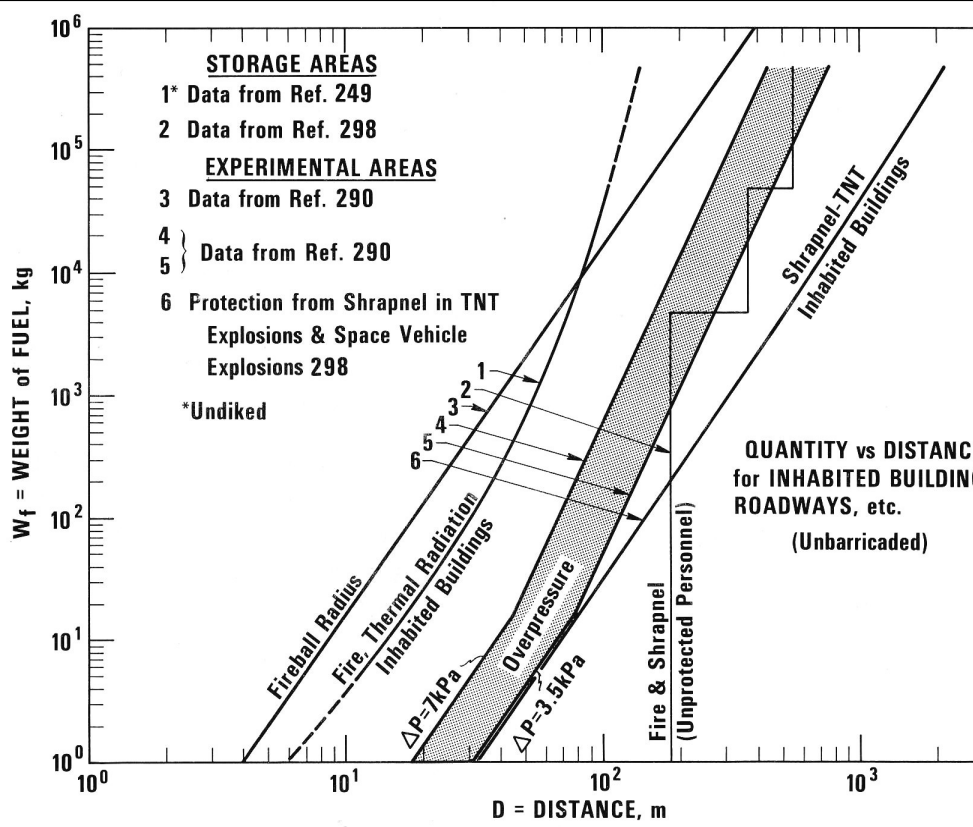
hydrogen

vs.

gasoline

# Quantity-Distance Relationships

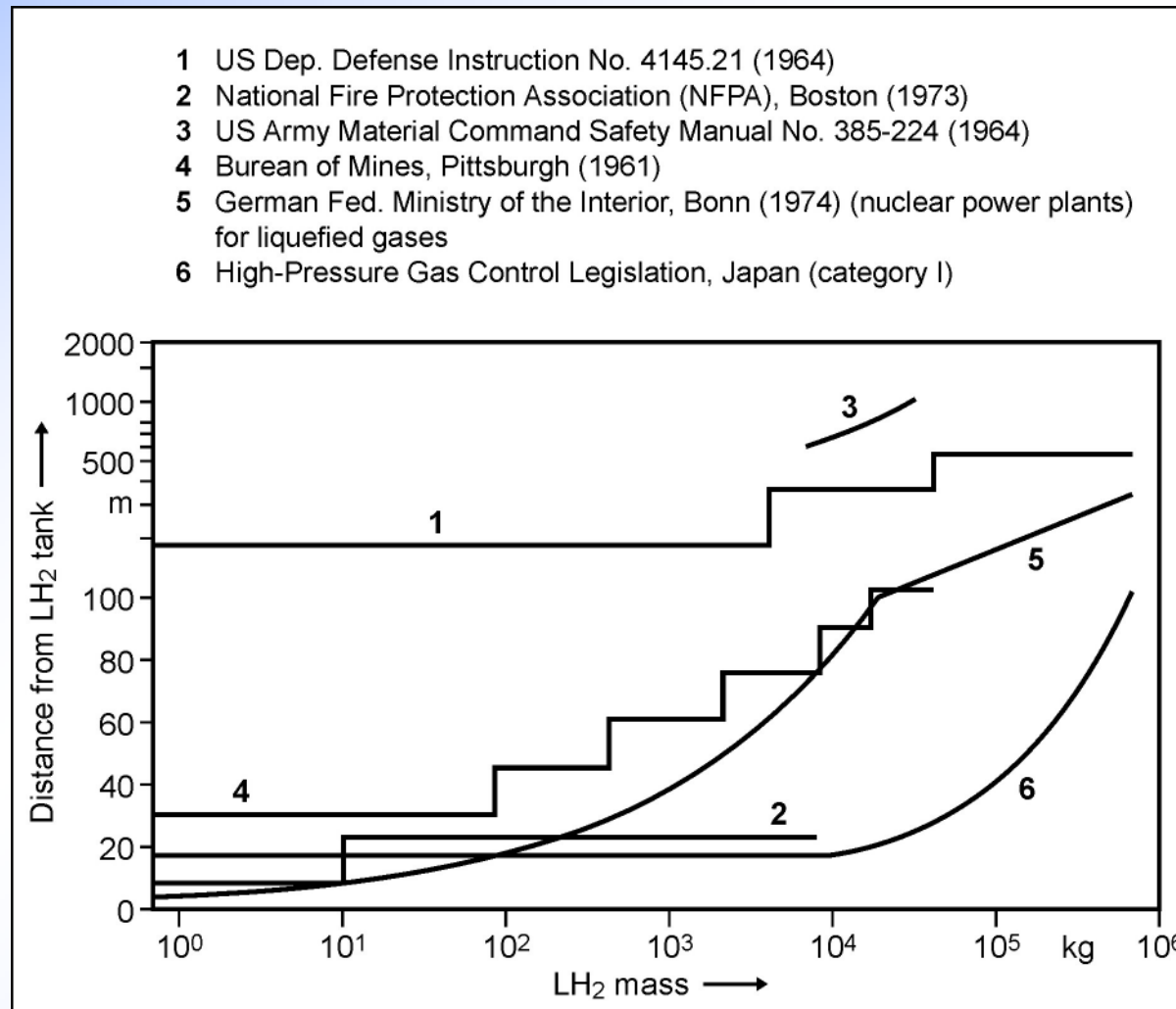
Hord 1978



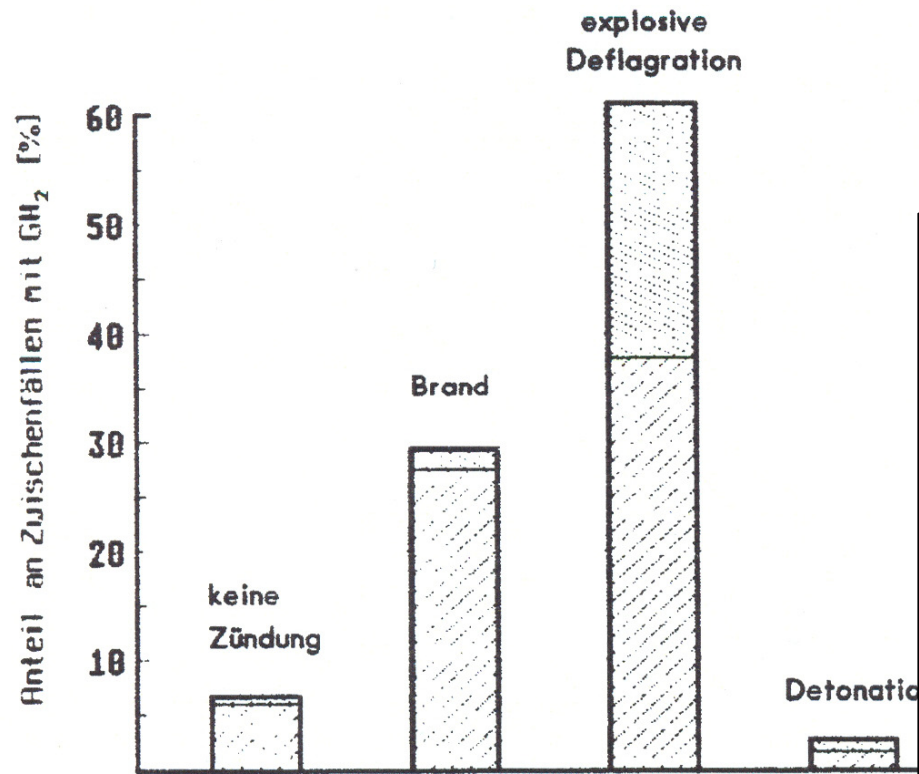
Protection of adjacent LH<sub>2</sub> tanks

Protection of personnel and residential area near LH<sub>2</sub> tanks

# Safety Distances in Different Countries

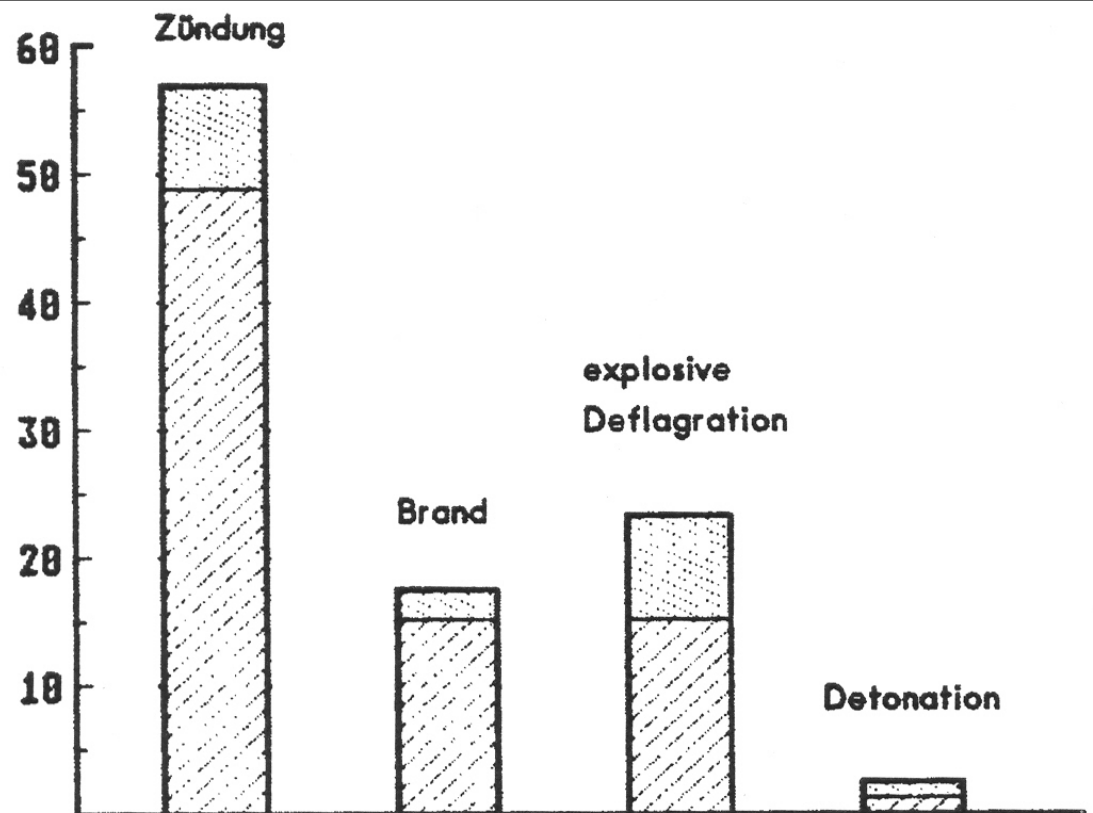


# Accident Statistics (Kreiser)



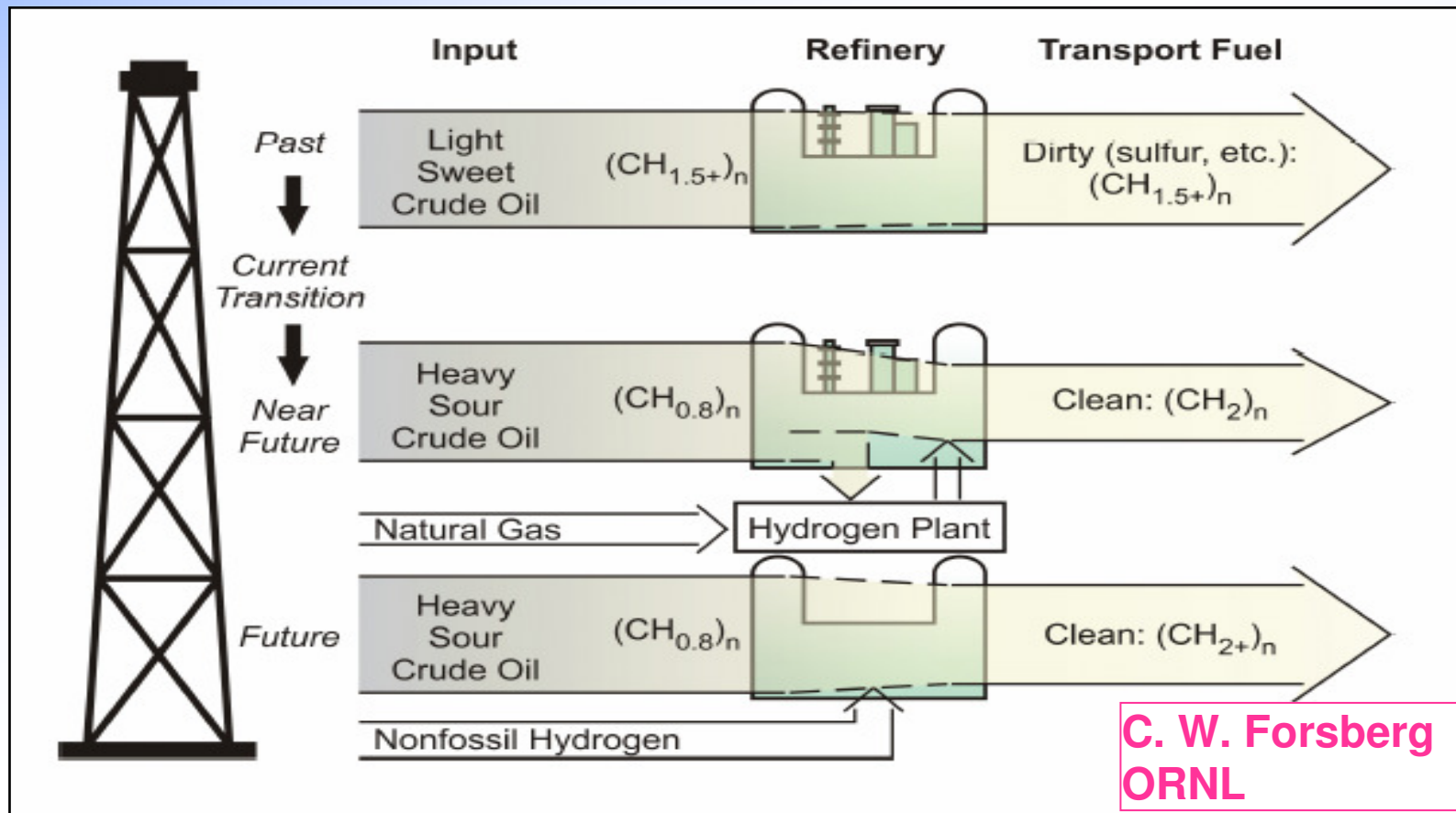
Gaseous Hydrogen

## Liquid Hydrogen



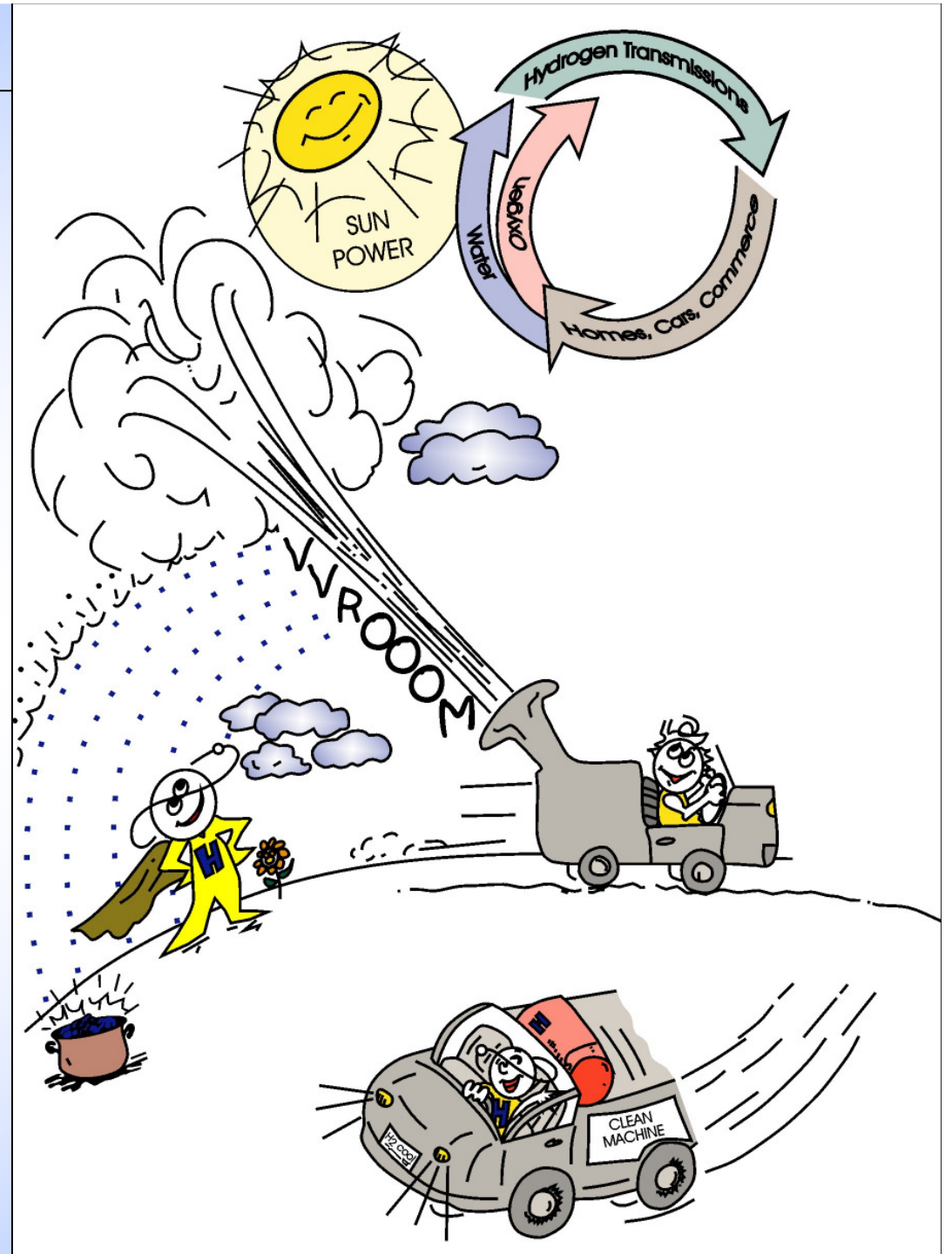
# Applications of Liquid Hydrogen

## Crude Oil Quality Change



„Dirty fuels“ requiring even more  $H_2$  and process steam

# Hydrogen-Driven Vehicles



# First Hydrogen Vehicles





# NASA Space Program



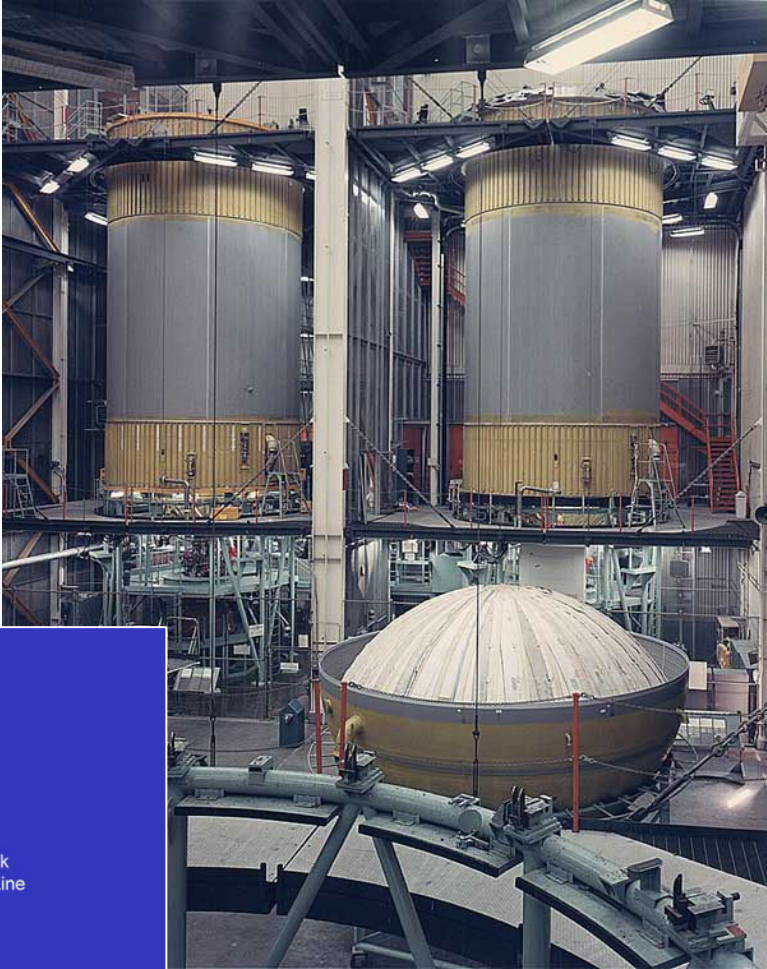
Space  
Shuttle

Saturn /  
Apollo

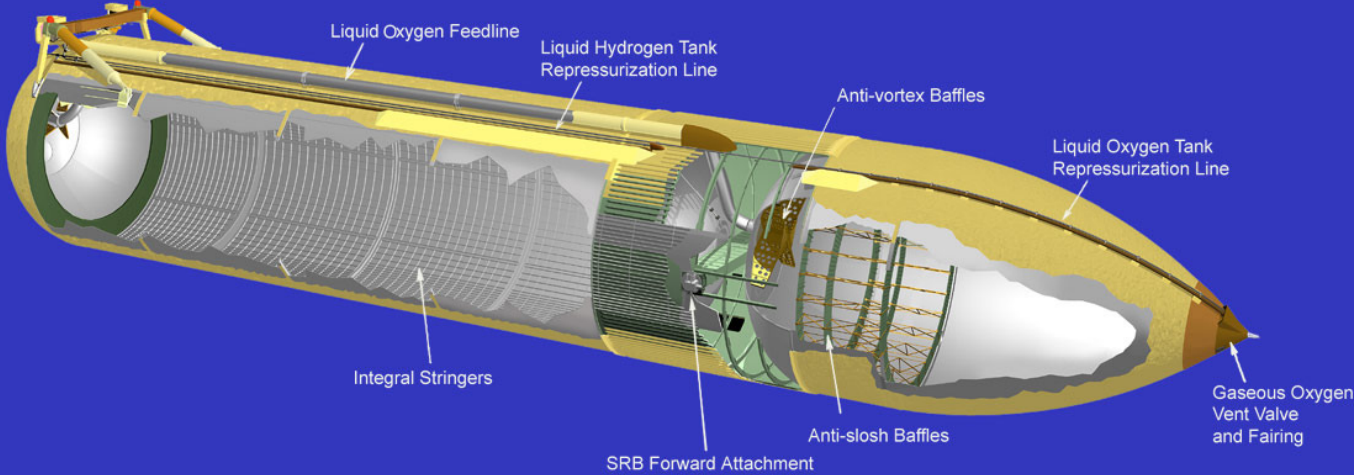


# Space Shuttle External Tank

**Length: 46.9 m**  
**Diameter: 8.4 m**  
**Gross weight: 762.1 t**  
**LOX: 629.3 t**  
**LH<sub>2</sub>: 106.3 t**



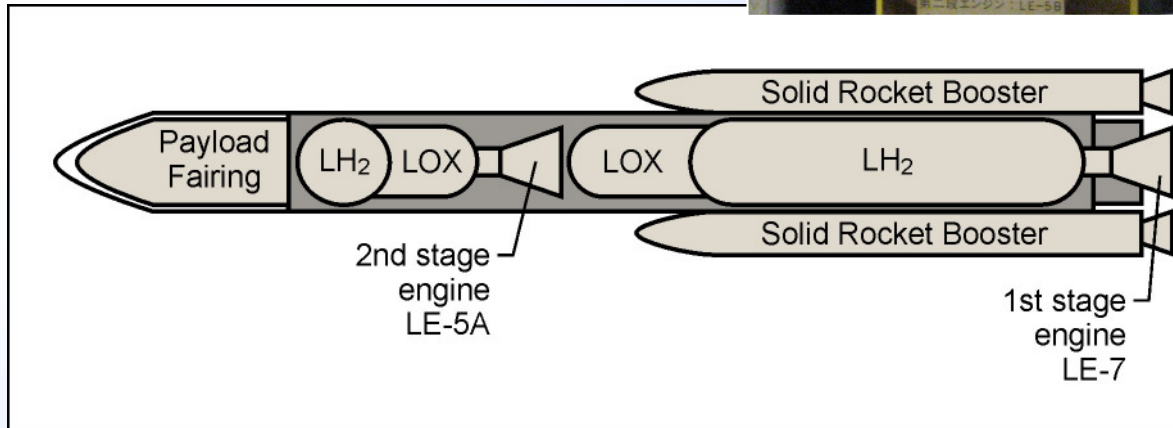
Orbiter Aft Attachment  
Propellant Feed, Pressurization Lines  
and Electrical Umbilicals



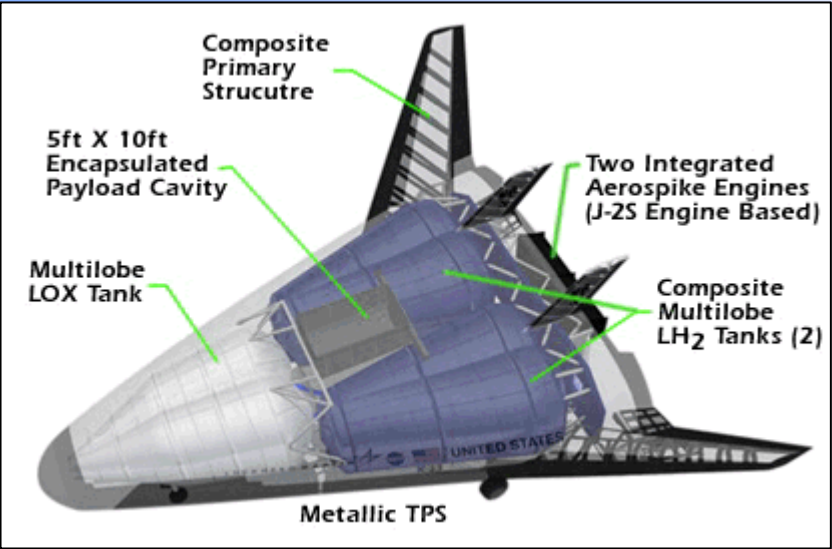


# Rockets with LH<sub>2</sub>/LOX Fueling System

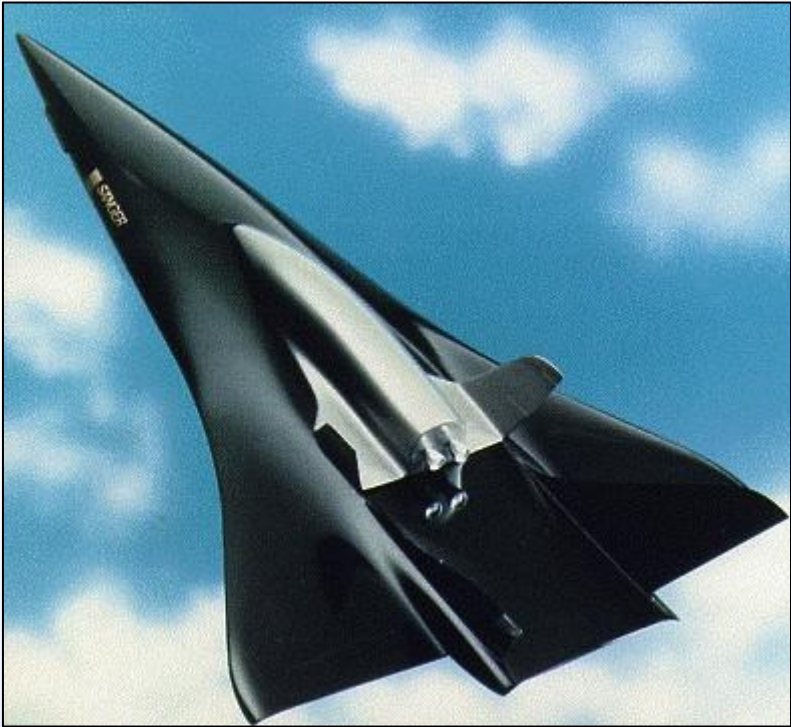
Fo



# Future Space Planes

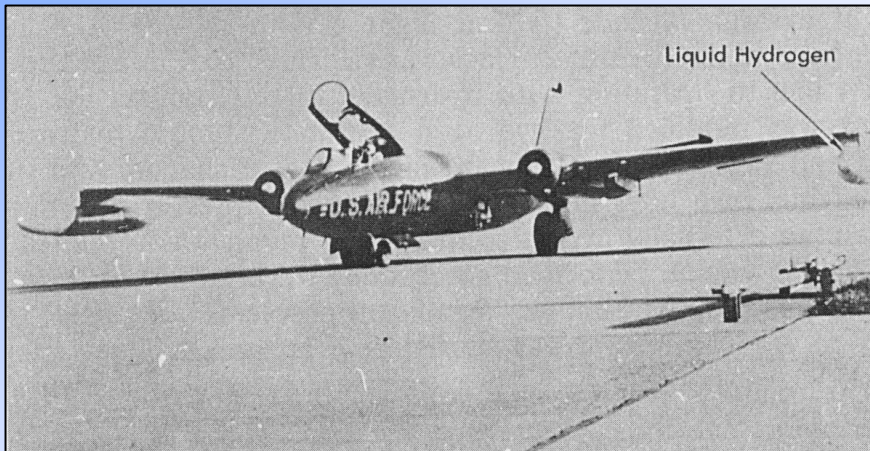


X-33

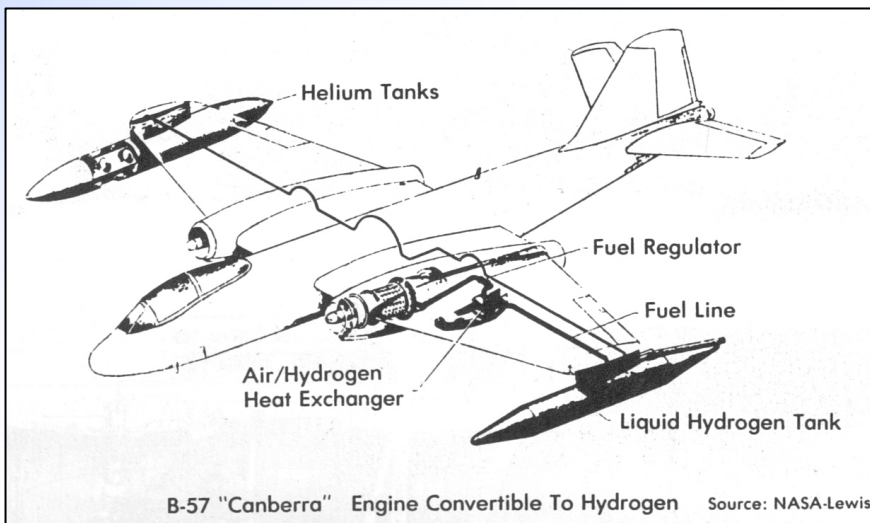


Saenger

# Airplanes to Fly with LH<sub>2</sub>



**1956**  
**Twin-jet B-57 Canberra**  
**with one H<sub>2</sub> engine**



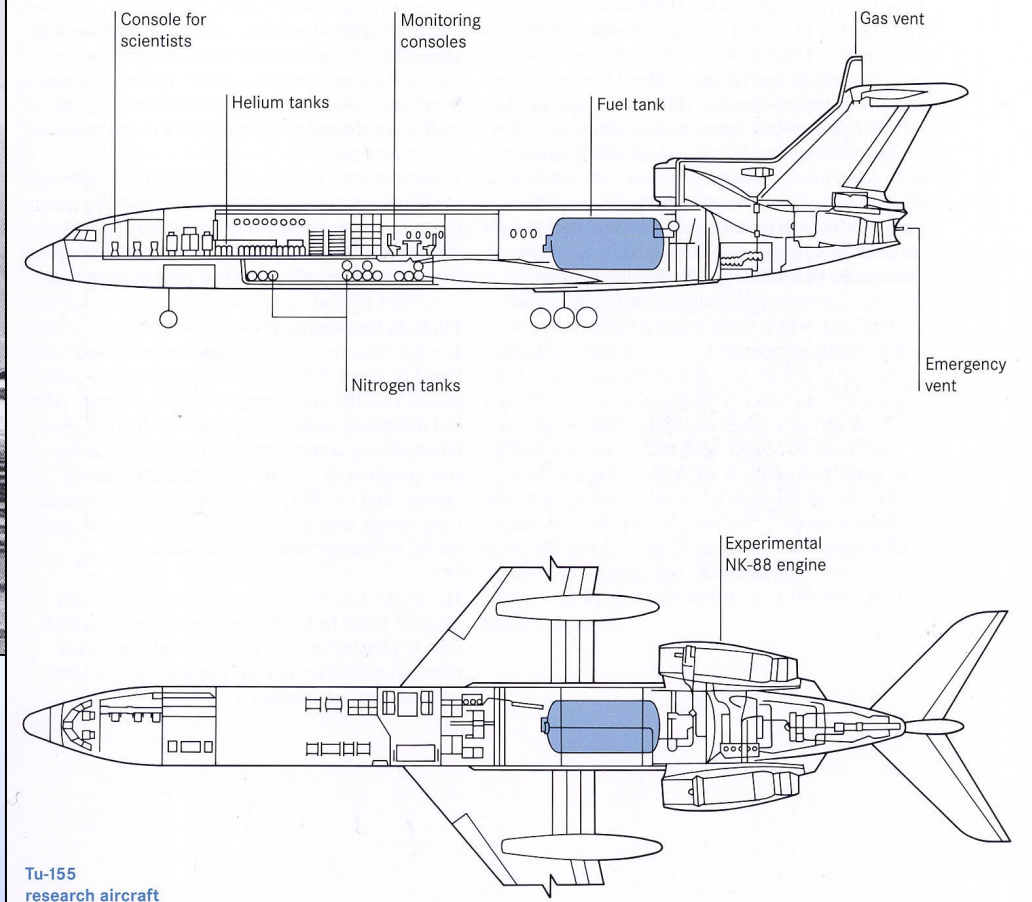
**1988**  
**Grumman Cheetah**



# Russian Tupulev 155 „Flying Laboratory“



**1988**  
**Central engine**  
**converted to H<sub>2</sub>/CH<sub>4</sub>**



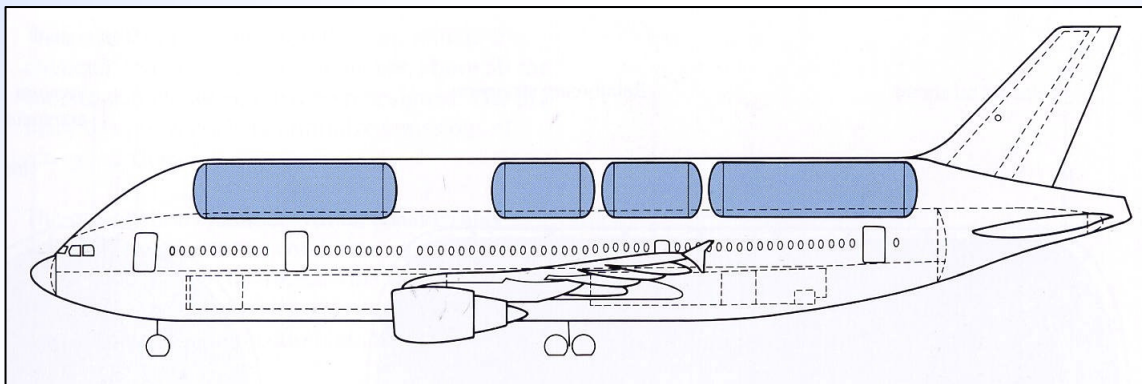
# Project CRYOPLANE



**Airbus A310-300**



**Fairchild Dornier 328**



**2 x 40 m<sup>3</sup> LH<sub>2</sub> tanks  
2 x 80 m<sup>3</sup> LH<sub>2</sub> tanks**

# LH<sub>2</sub> Cars

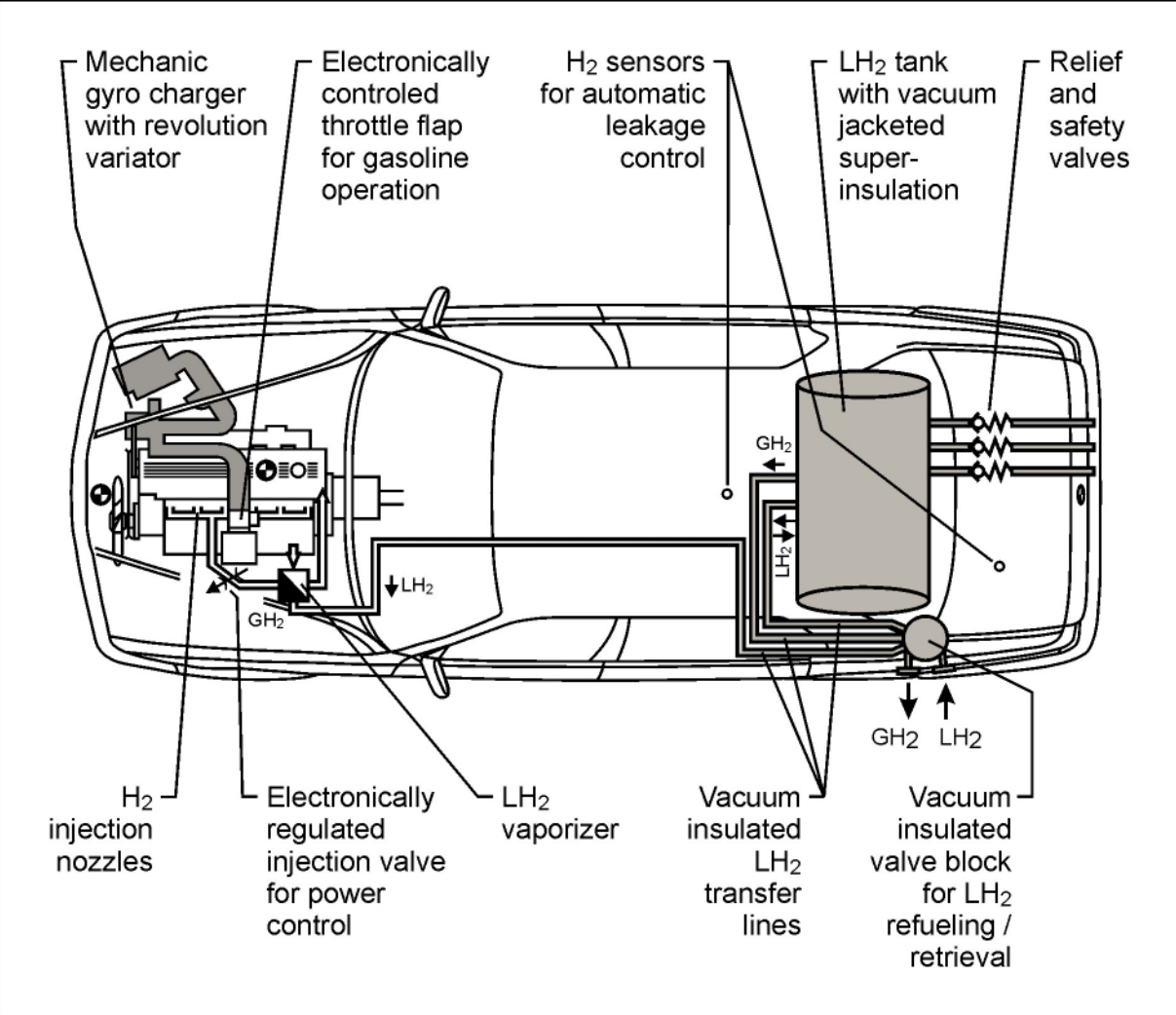
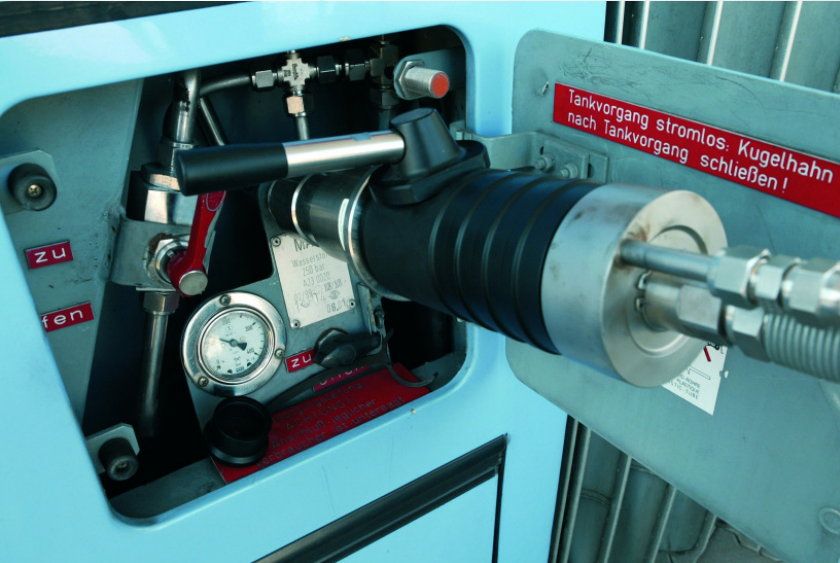
1973

One of the First!  
(LANL-DFVLR)

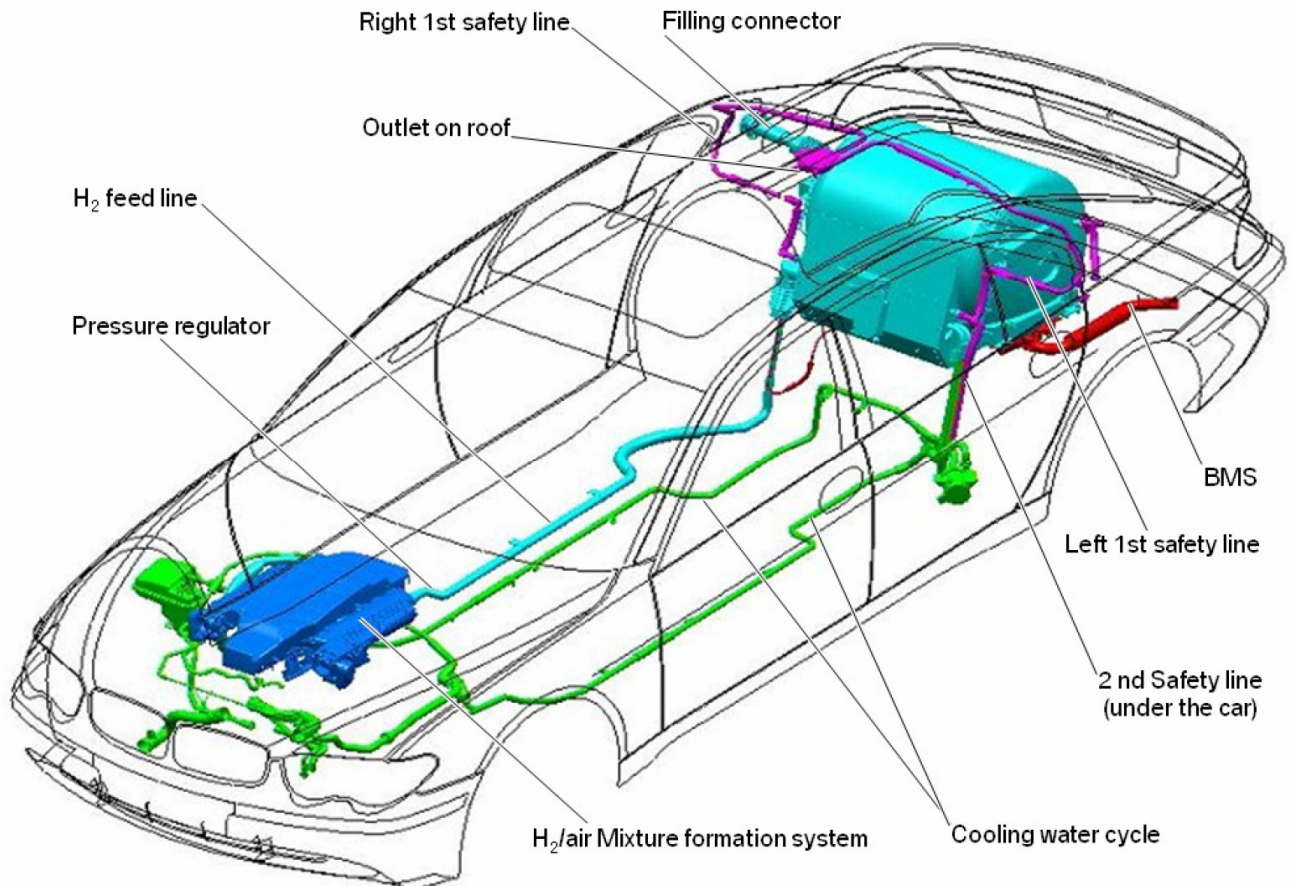




# 7 Generations of BMW



# BMW Hydrogen 7





## Buses using LH<sub>2</sub>

2001  
MAN Hydrogen FC Bus  
2 x 350 l LH<sub>2</sub> tanks

1995 (Euro-Quebec)  
Van Hool ICE Bus  
125 l LH<sub>2</sub> tank  
experimental demonstrator

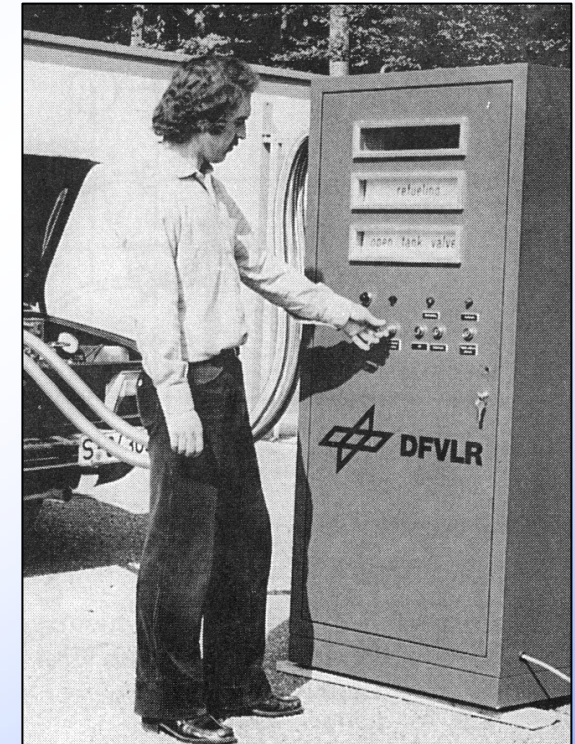


# LH<sub>2</sub> Refueling Station

Total 2006



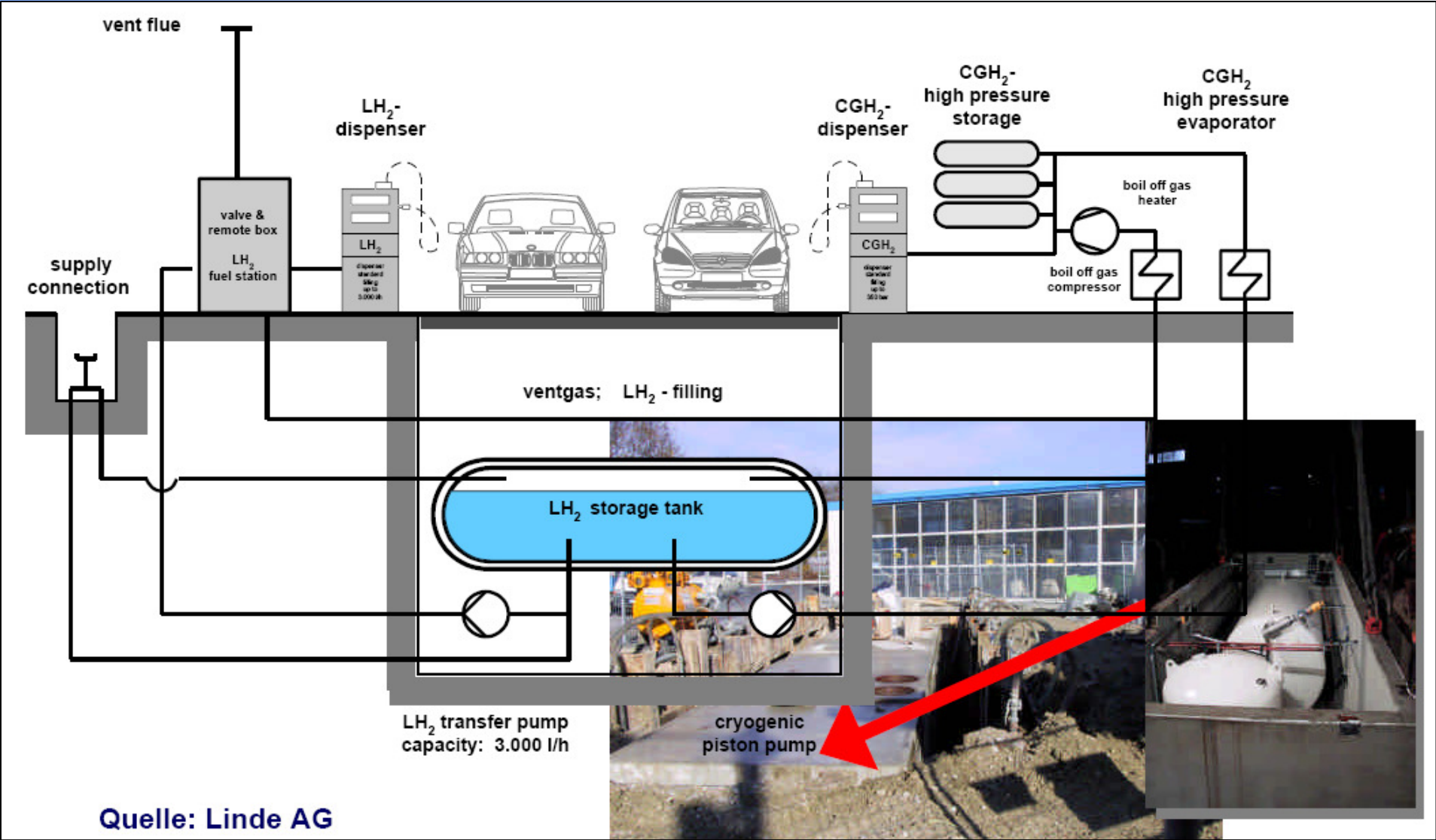
DFVLR/LANL 1979



ARGEMUC 1999-2006

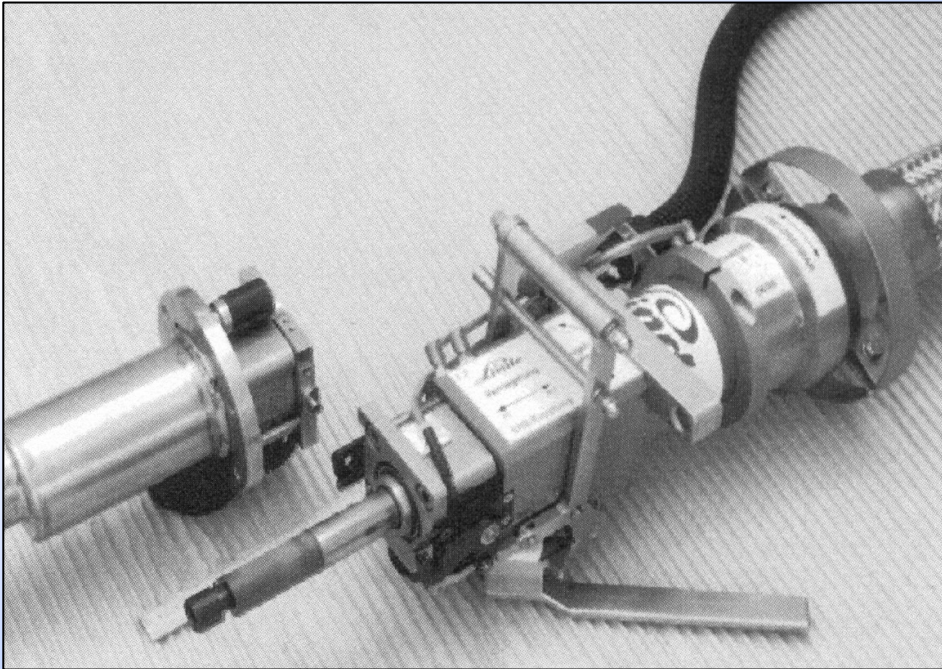
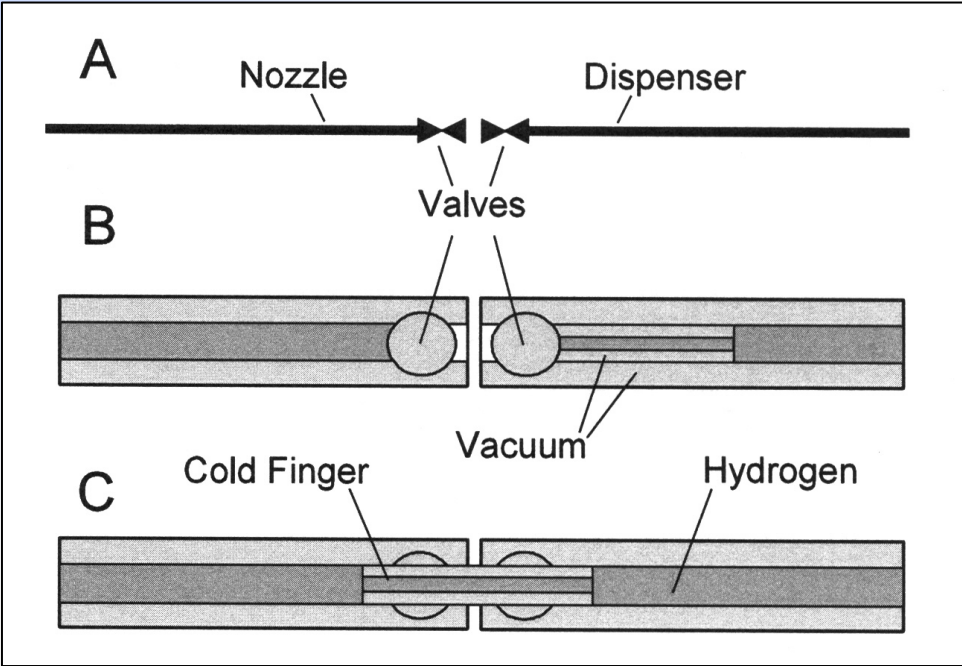
Betrag	00 12,48 €	Wasserstoff
Abgabe	000 1,58 kg	Hydrogen
Preis je kg	0800,0 ct	

# LH<sub>2</sub> Tank to supply both liquid as gas

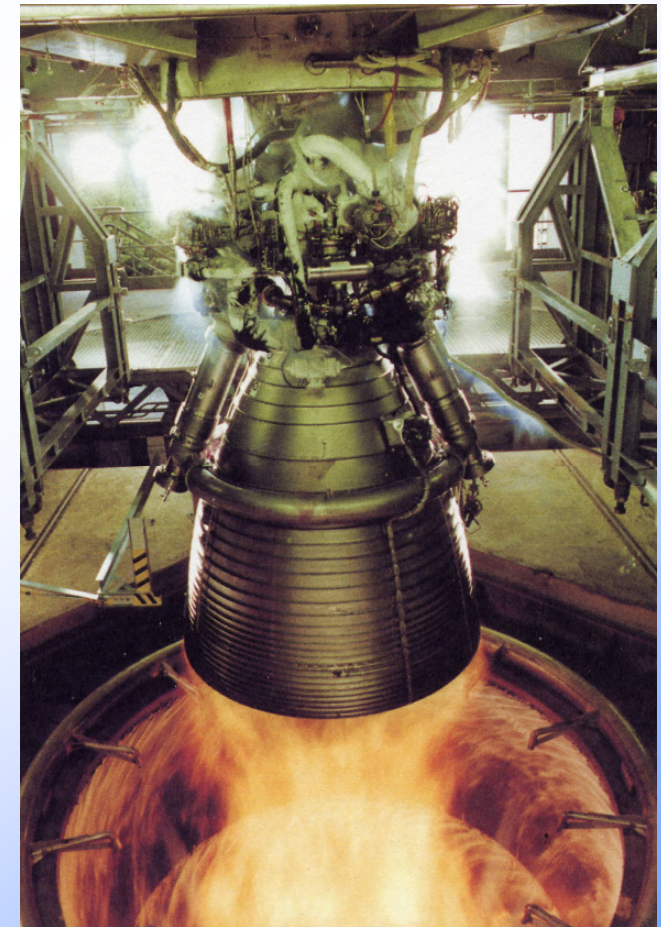
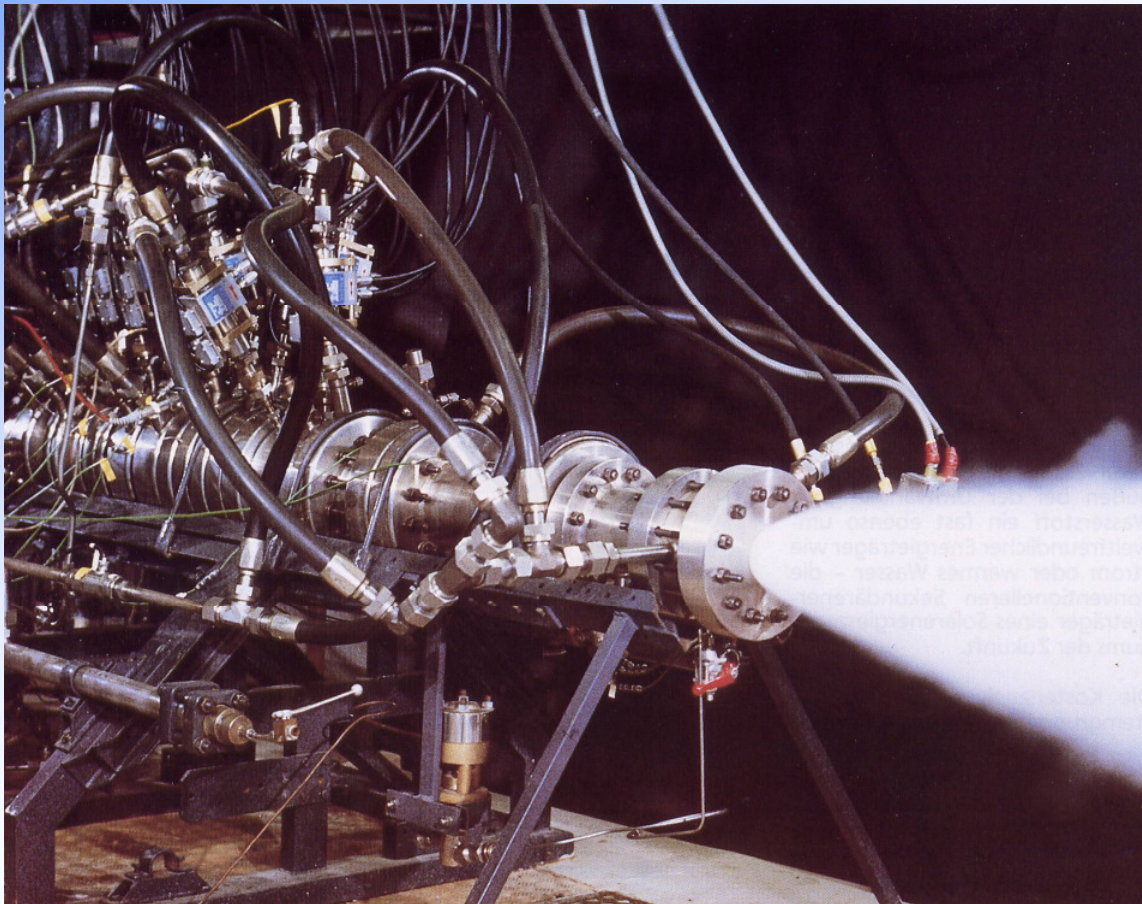


Quelle: Linde AG

# Refueling Process

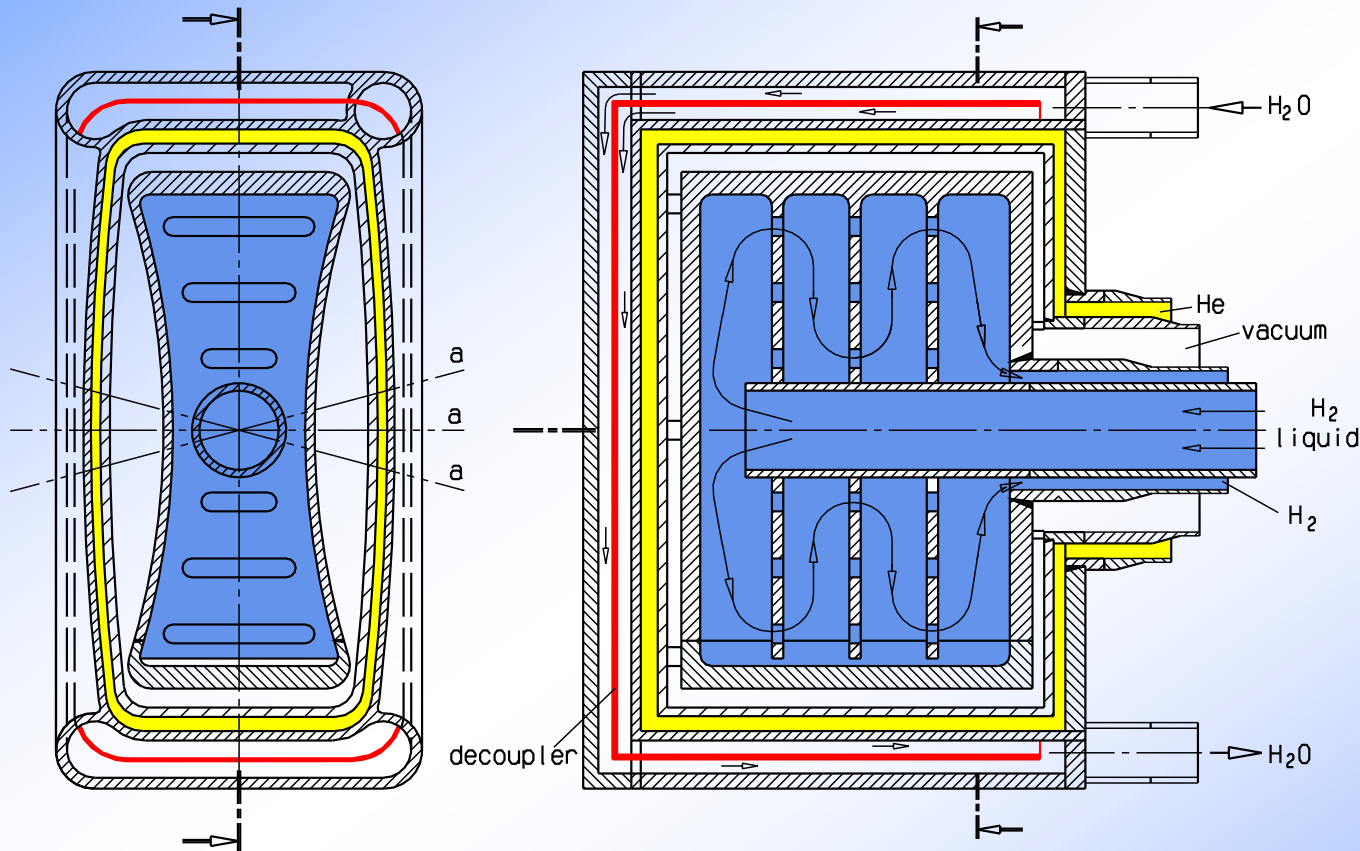


# DLR H<sub>2</sub>/O<sub>2</sub> Steam Generator

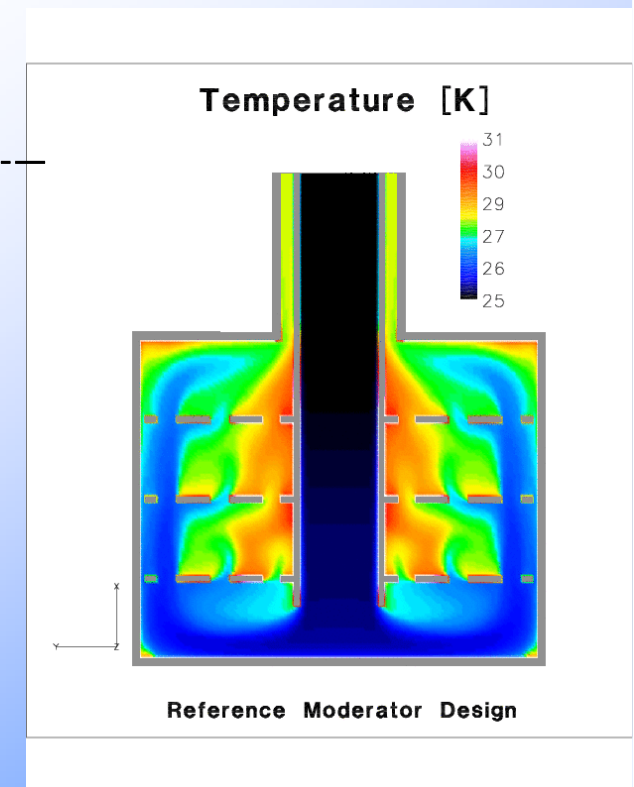


**DLR Testing of Vulcain Engine**

# Supercritical H<sub>2</sub> als Cold Neutron Moderator

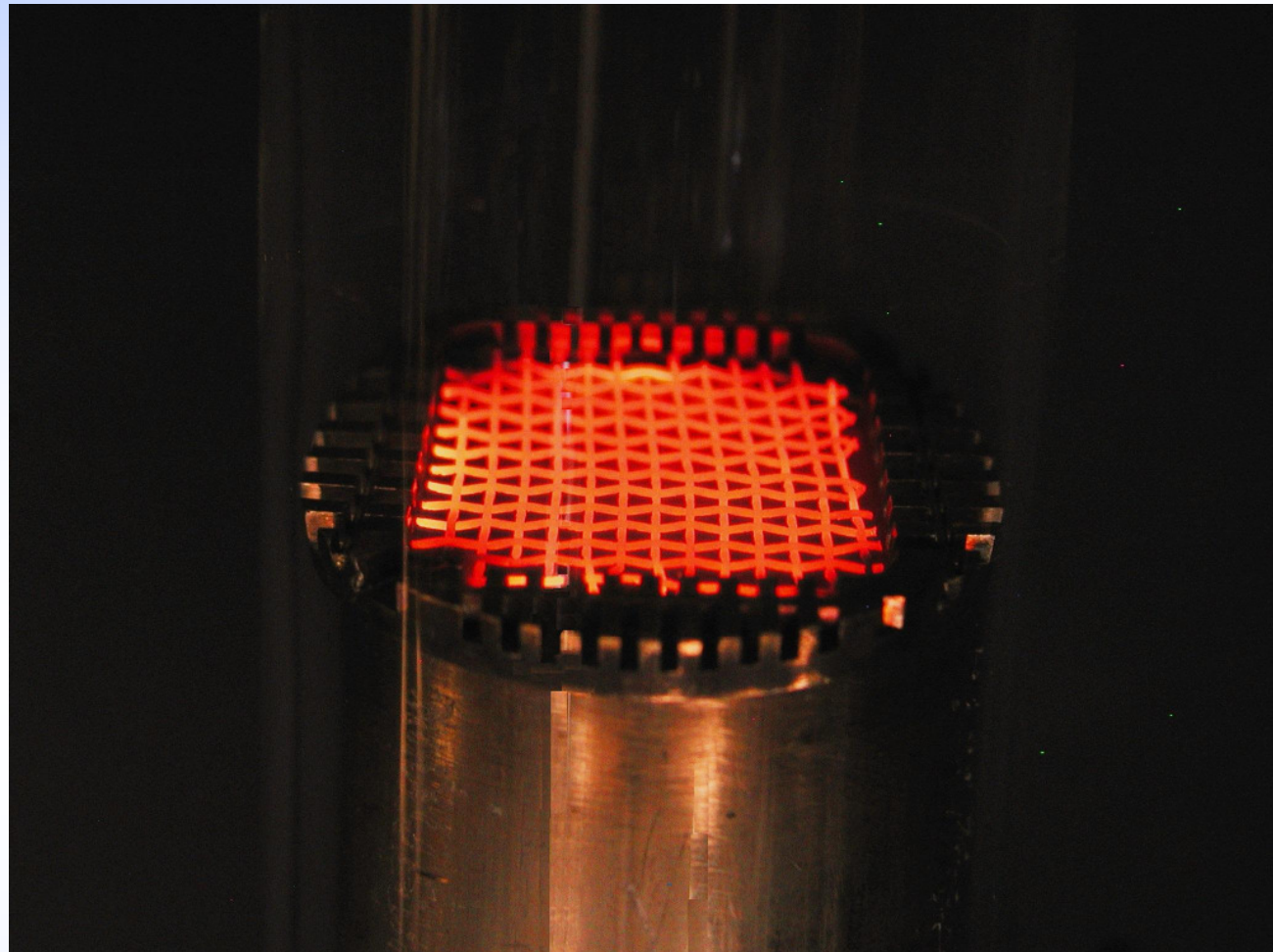


Horizontal (left) and vertical (right) cuts through the chamber for the supercritical H<sub>2</sub> moderator (gaps and walls enlarged), a: center line of beam tubes





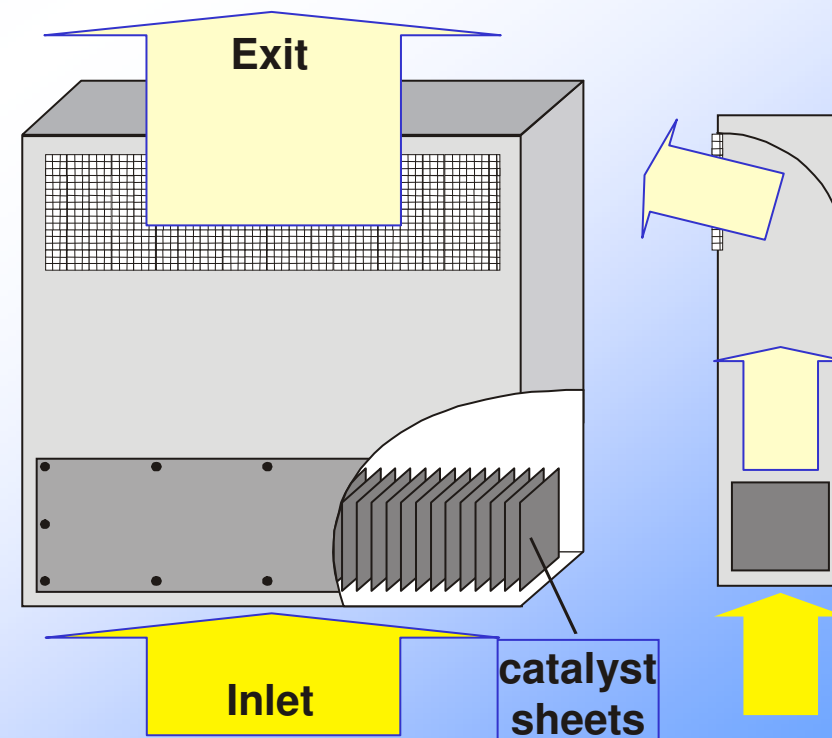
# Passive Auto-Catalytic Recombiners



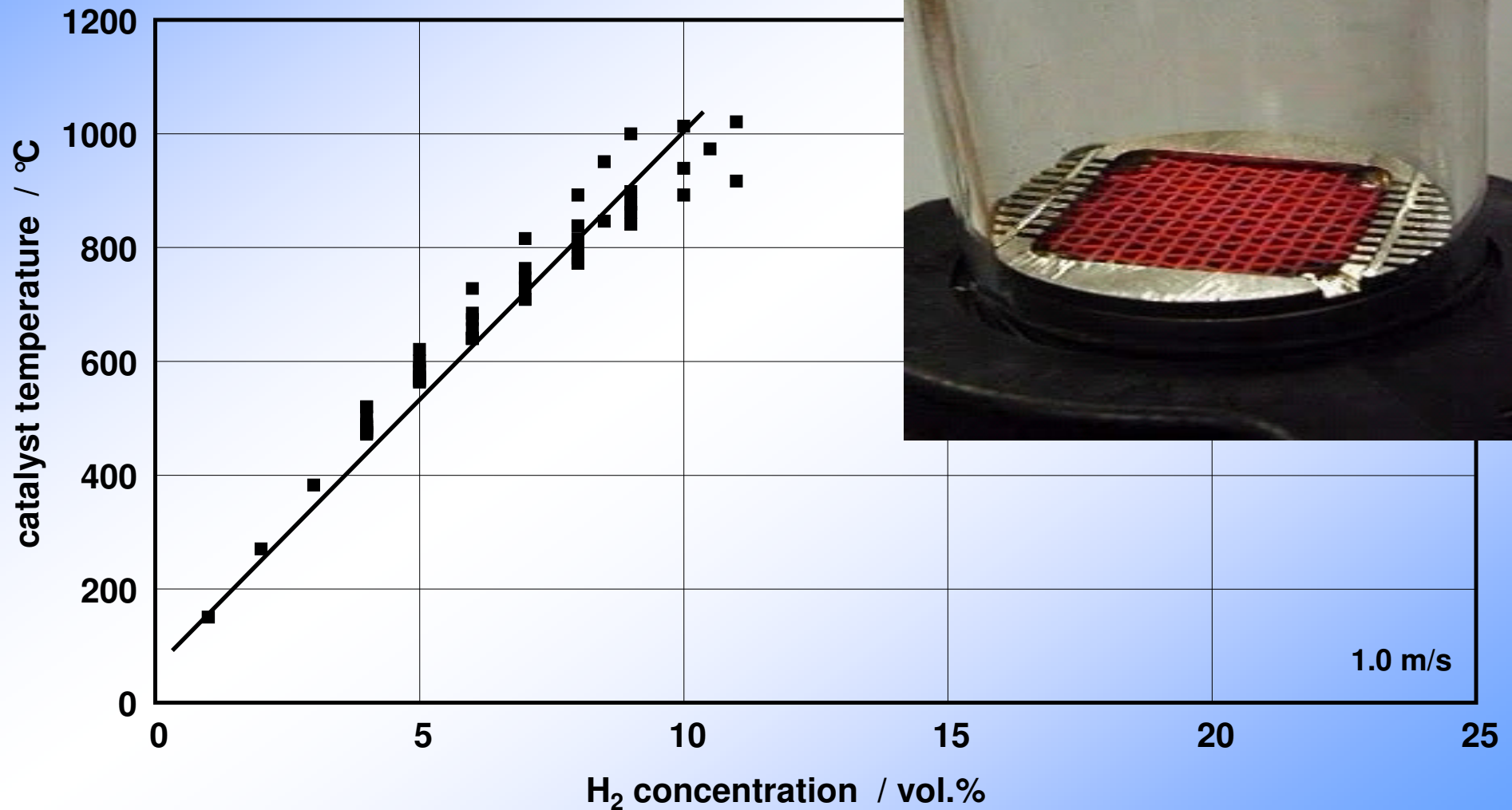
Reinecke et al.

# Passive Auto-Catalytic Recombiner (PAR)

- PAR: flameless conversion of  $H_2$  even at concentrations as low as 1-2 vol.% at ambient temperatures
- Installation in numerous European LWR since the 1990s

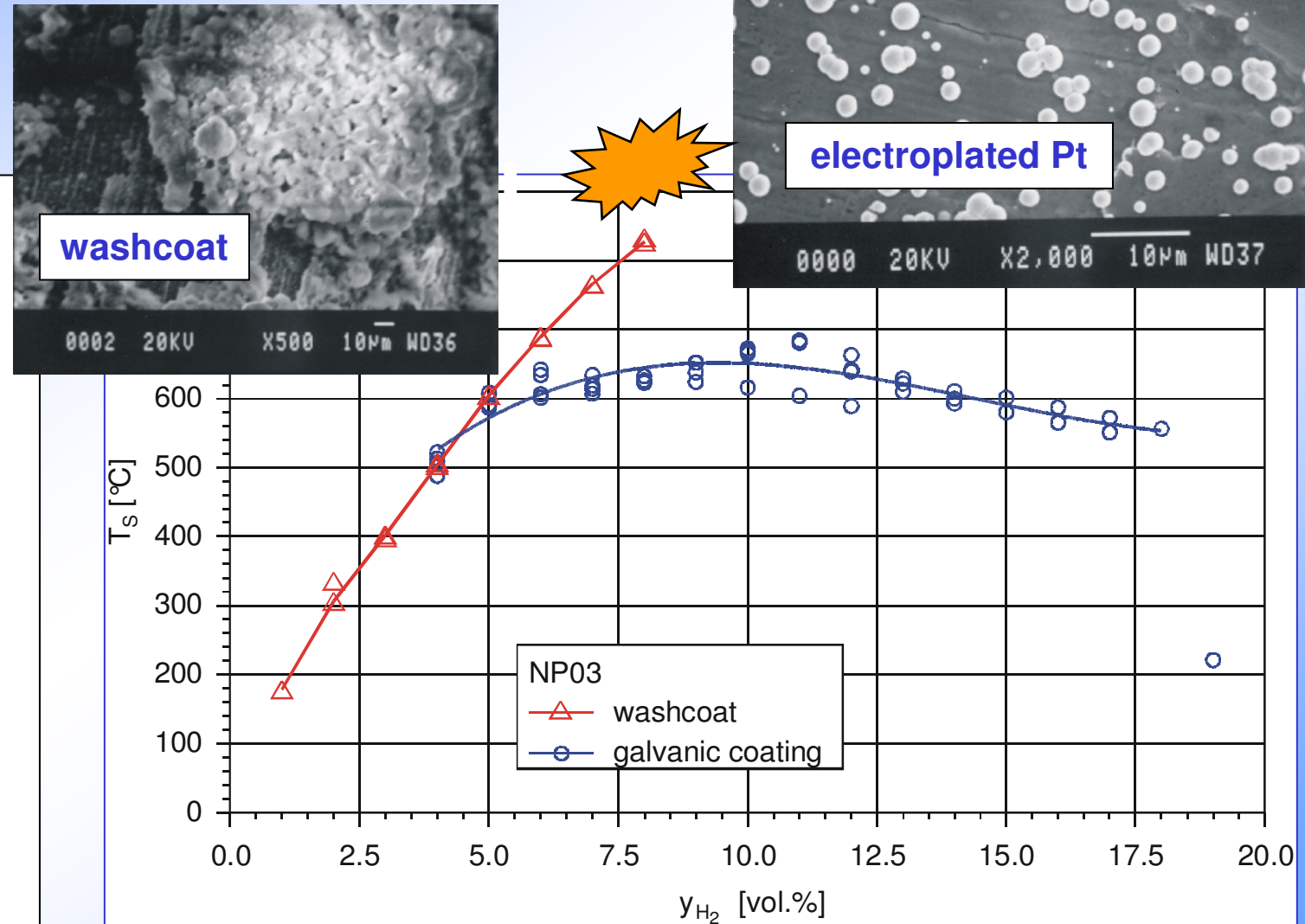


# Catalyst Temperature on Washcoat Meshes



# Adjustment of Activity

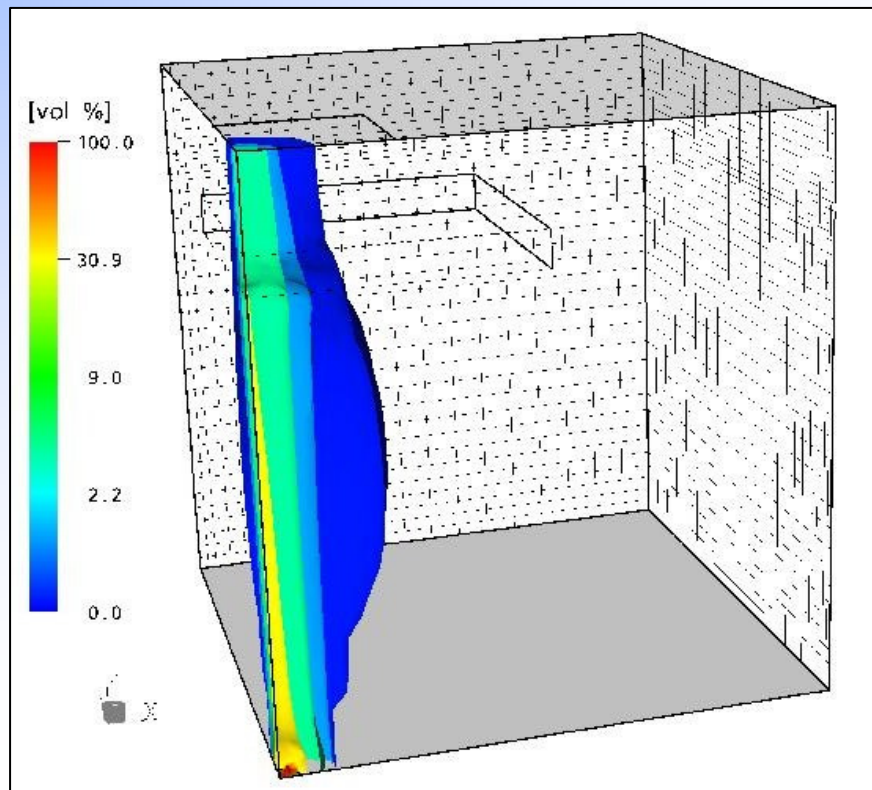
- Limitation of catalyst temperature
- Adjustment of catalytic activity
- Combination with passive cooling elements



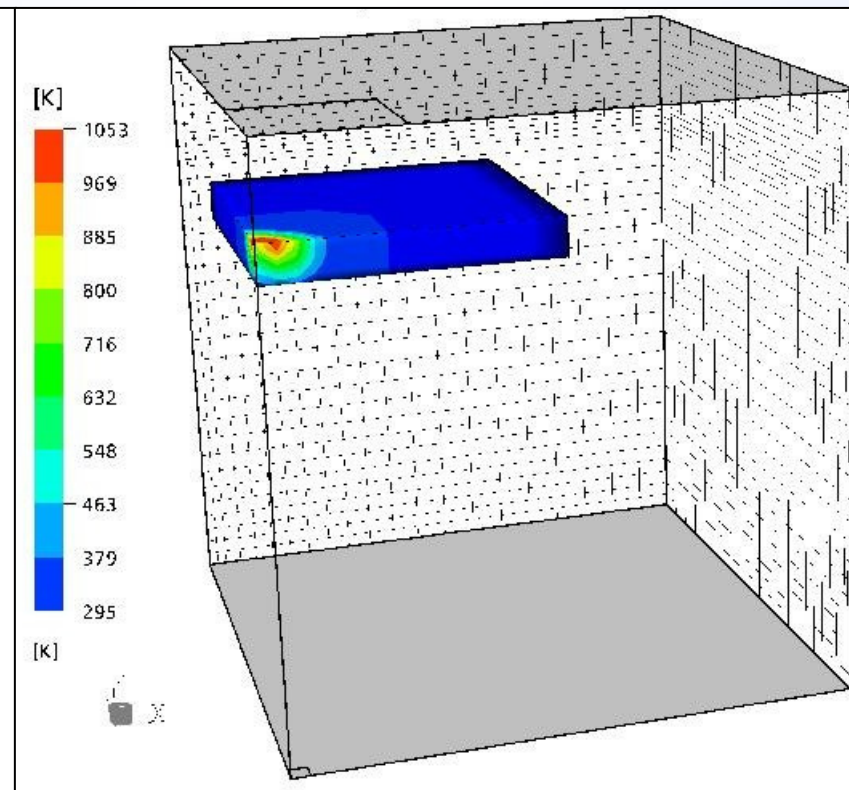
Catalyst Temperature vs.  $H_2$  Concentration

# CFX Application: Recombiner in a Garage

**H<sub>2</sub> concentration**



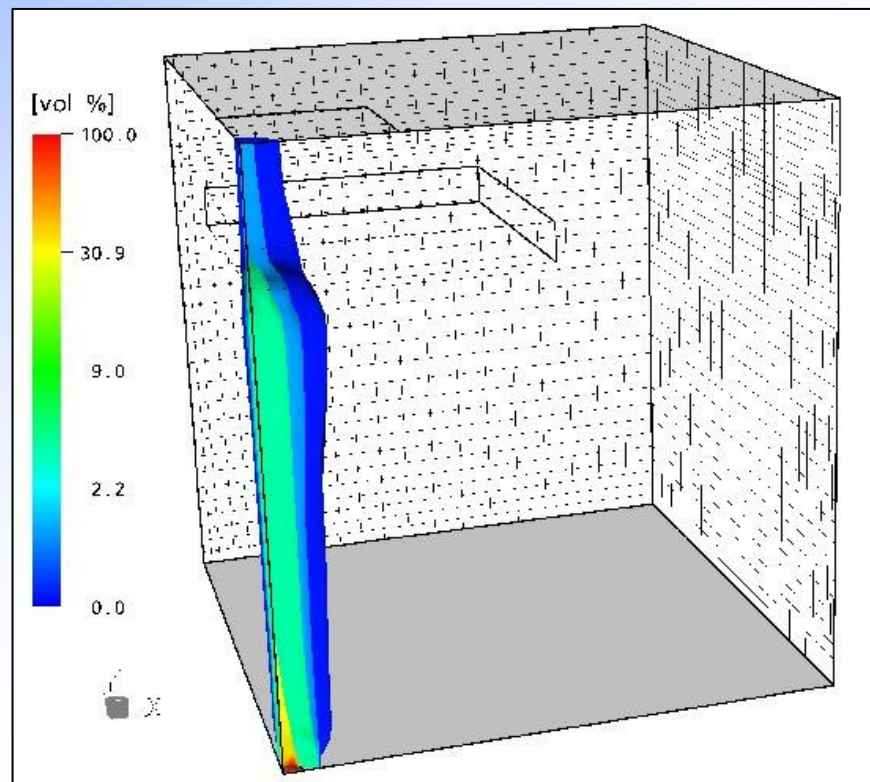
**Temperature distribution**



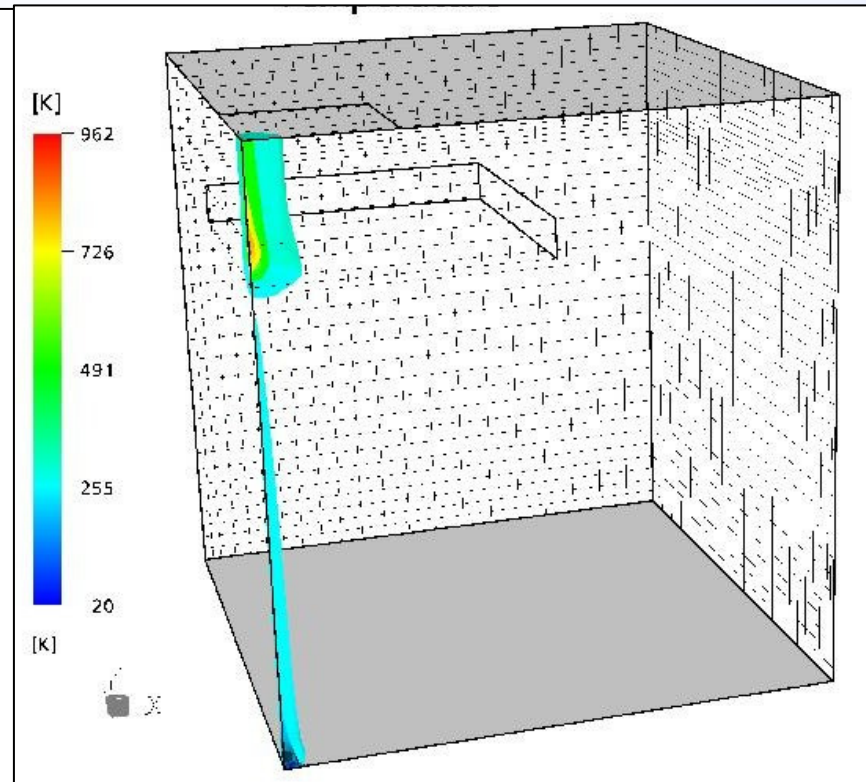
**Source: H<sub>2</sub> gas @ 300 K**

# CFX Application: Recombiner in a Garage

**H<sub>2</sub> concentration**



**Temperature distribution**



**Source: H<sub>2</sub> gas @ 20 K**

# End Part 1