

Ammonia, Fuel for Future

3rd International Seminar of Torres Vedras

April 29th and 30th, 2010

Portugal

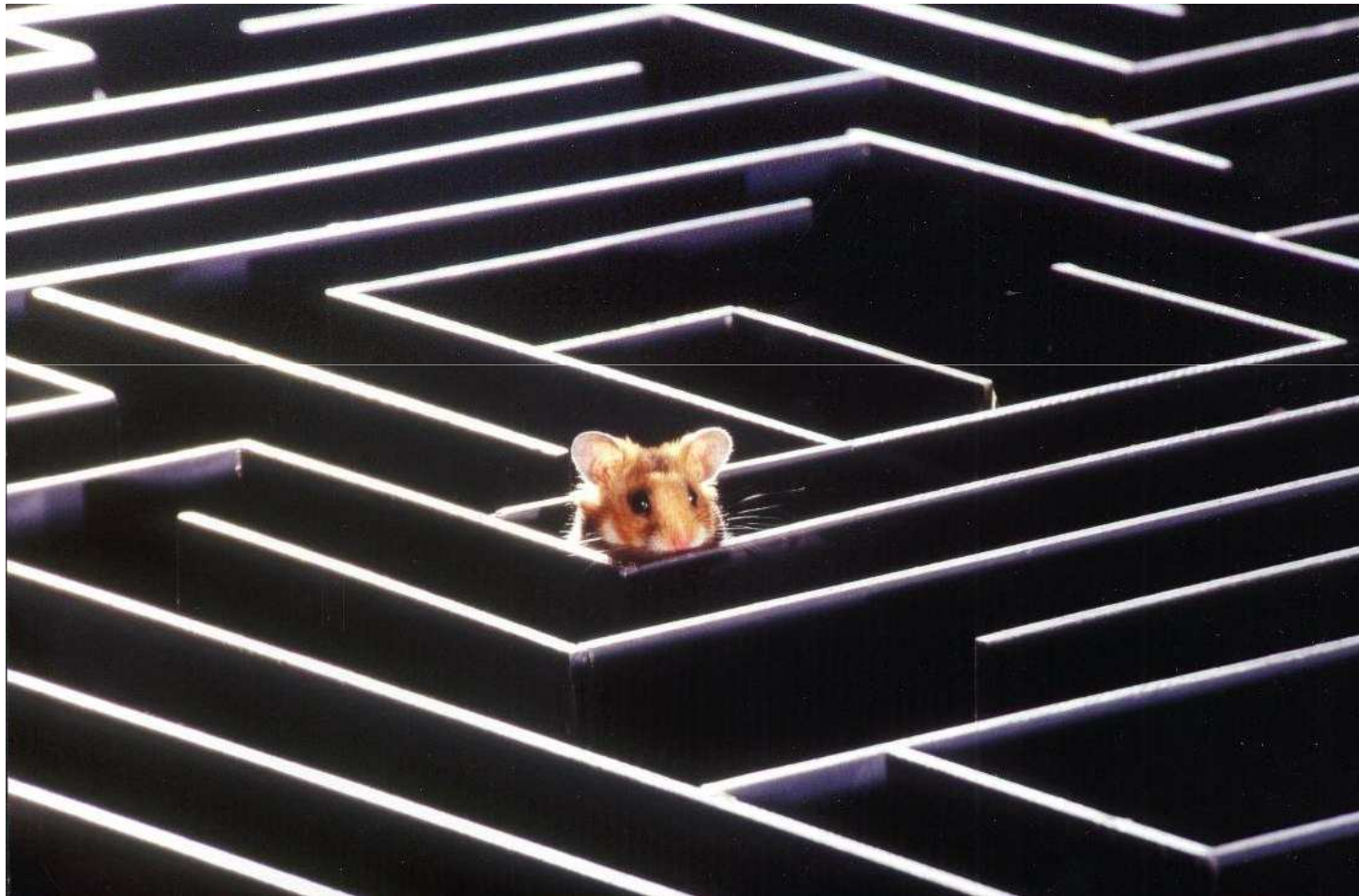
Hans Vrijenhoef,

Proton Ventures BV, The Netherlands

Member of the Ammonia Fuel Network

www.ammoniafuelnetwork.org

Escaping the Energy Maze

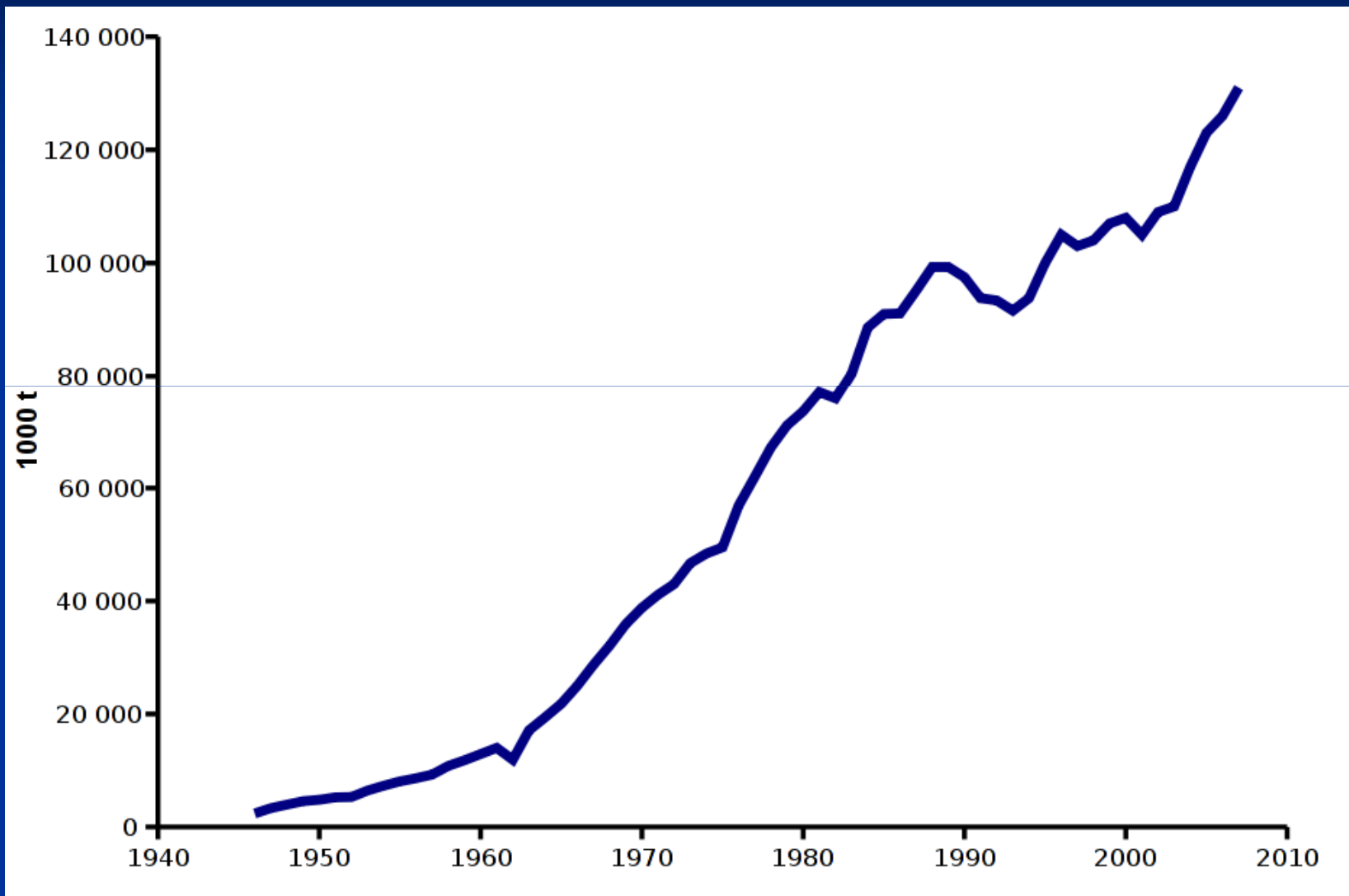


Ammonia Fuel



- Anhydrous ammonia
- Top 3 world chemicals by tonnage
- 99%+ produced with natural gas or coal
- Prevents millions of deaths from hunger
- U.S. uses 15-20 million tons per year
- Needed for corn, wheat, potatoes...
- Many non-agricultural uses
- One of top GHG producers in world (each ton of natgas NH₃ produces 1.8 tons of CO₂)

NH₃ Consumption by Year



Why Ammonia?

- Transmission and firming storage for renewables
- Large existing market and delivery infrastructure
- Energy dense
- Clean burning direct fuel: no carbon
- Excellent hydrogen carrier
- Exists as liquid at moderate pressure/temperature
- Widespread use/experience (#2 chemical)
 - 130 million tons produced annually worldwide
 - US consumes 20 million tons per year
- Can be made from water + air + renewable energy

Relevant Ammonia Properties

- Fuel is same as fertilizer, NH_3 , anhydrous ammonia
- 18% hydrogen by weight
- Liquid at >125 psi at room temperature
- About half energy density of gasoline, by volume (HHV)
- About 50% more energy dense than LH_2 *
- At point of use can be used as direct fuel or cracked to provide GH_2 **

* LH_2 : Liquid Hydrogen

** GH_2 : Gaseous Hydrogen

Ammonia Fuel History

- 1930s Norsk Hydro and Fiat
- 1940s Belgium—Ammonia Buses
- 1960s U.S. Military “Energy Depot” Study
- 1960s X-15 Rocket Plane
- 1974 Univ Tennessee Ammonia AMC Gremlin
- 1981 “Hydrofuel” Chevy Impala
- 1994 & 1996 Avery and Steele “Ammonia Economy” papers
- 2004 1st AFN Conf
- 2007 Matt Simmons receives NH₃ fuel vision
- 2009 NH₃ Hot Rod 9.3L V8
- 2010 First commercial NH₃ engine sold
- ?? DOE officially recognizes NH₃ as a fuel

Zero-Emission Combustion

- Only hydrogen and ammonia burn without emitting greenhouse gases (contain no carbon)
- Also, no CO, SO_x, or NO_x
- Hydrogen combustion--



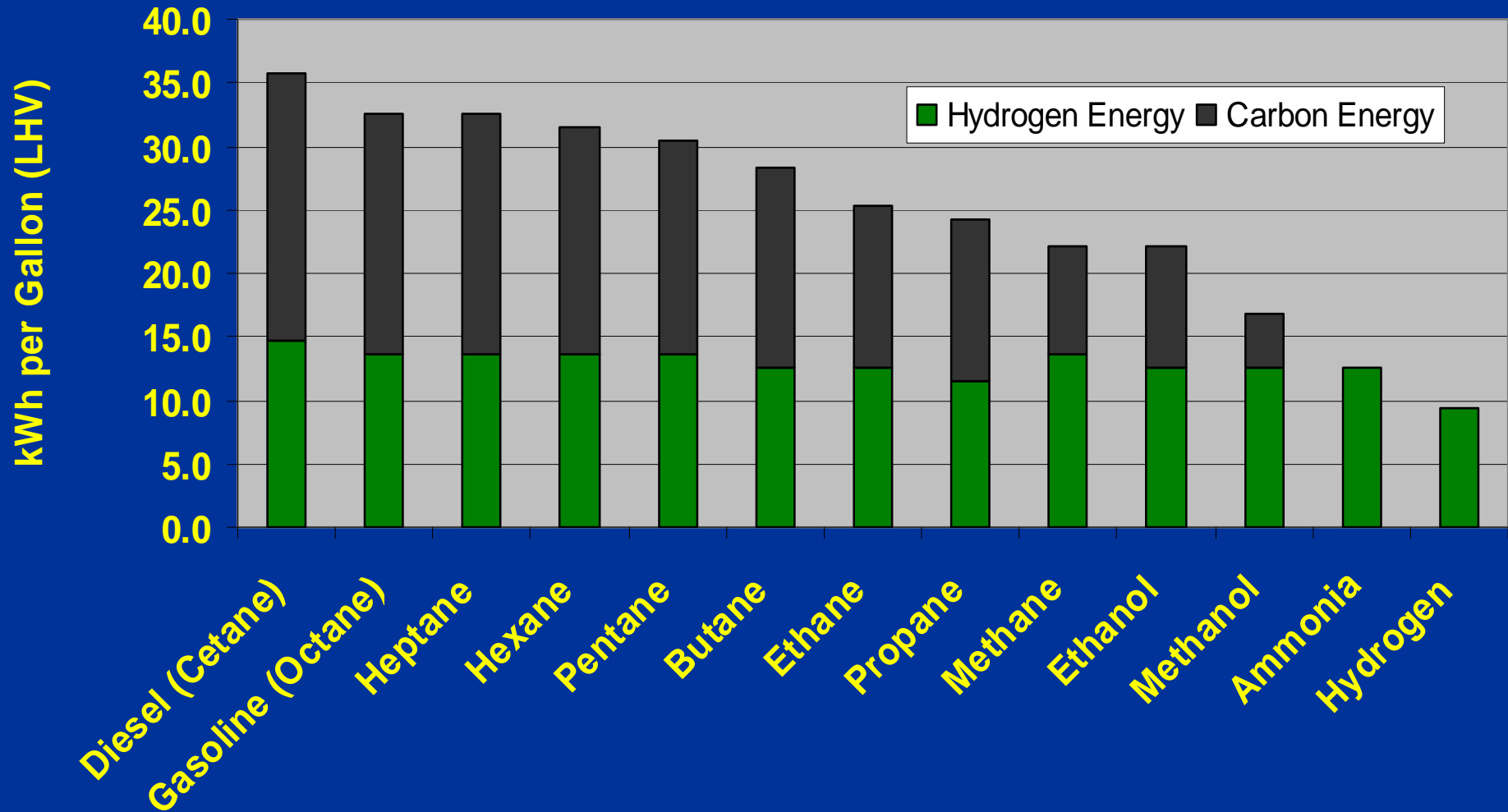
(water only combustion product)

- Ammonia combustion--

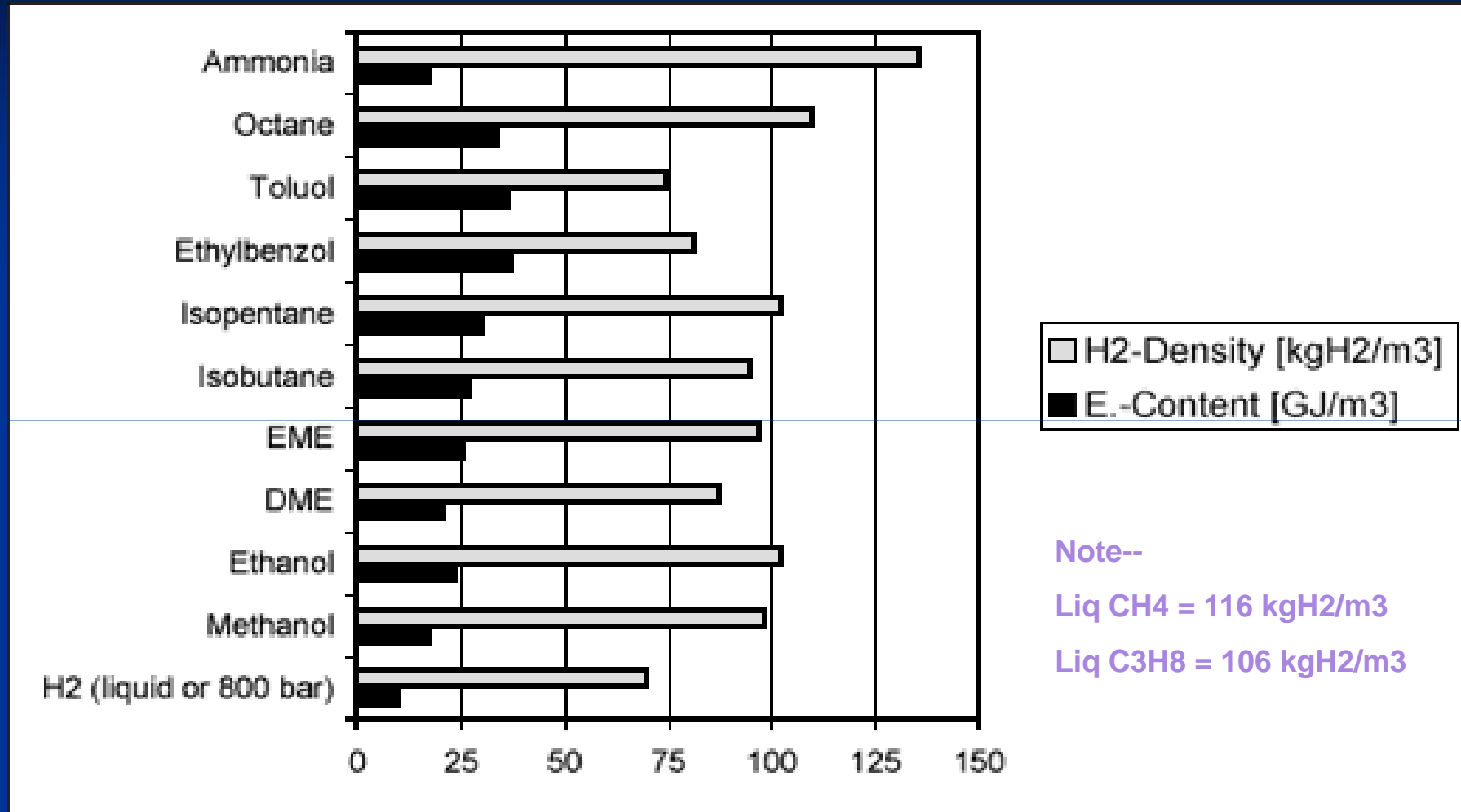


(nitrogen and water only combustion products)

Volumetric Energy Density of Fuels (Fuels in their Liquid State)



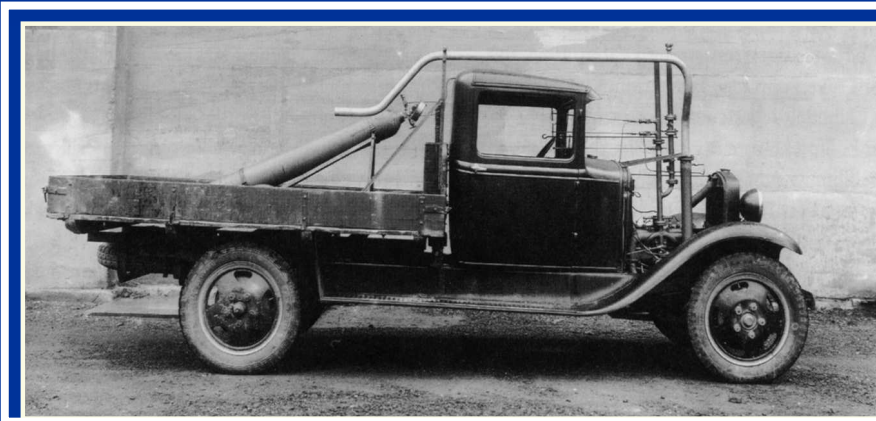
H₂ and Energy Density for Various Fuels



Hydrogen density and HHV energy content of ammonia and selected synthetic liquid hydrocarbon fuels

Ammonia Fueled Vehicles

Rjukan 1933



Ann Arbor 2007



Another Ammonia-Powered Vehicle

X-15 Rocket Plane

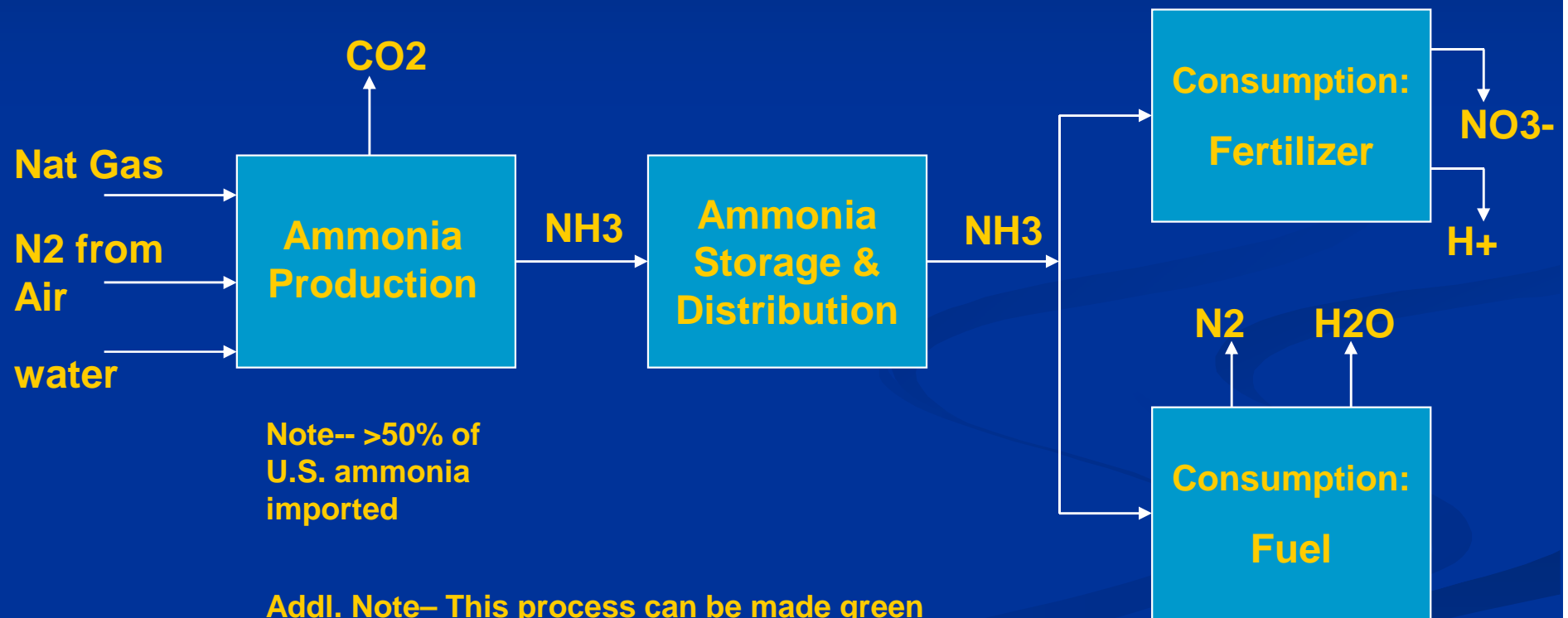


Getting Power Out Of Ammonia

- Spark-Ignited Internal Combustion Engines
- Diesel ICEs with H₂ or diesel “spike”
- Combustion turbines
- Gasoline or ethanol blend ICEs
- Converted Biogas Generators
- Direct Ammonia Fuel Cells

- Reform to liberate H₂ $[2\text{NH}_3 \rightarrow 3\text{H}_2 + \text{N}_2]$

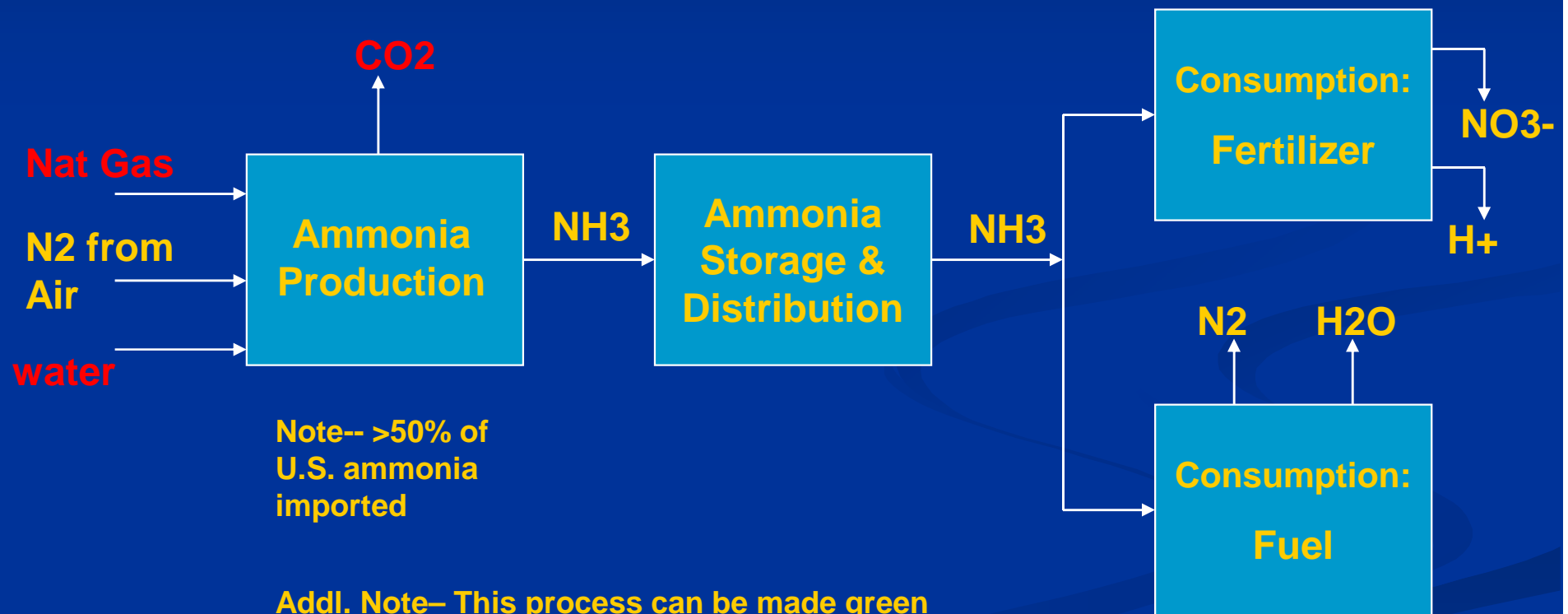
Ammonia Cycle Brown— Natural Gas SMR



Note-- >50% of U.S. ammonia imported

Addl. Note— This process can be made green with CO₂ sequestration, at additional expense

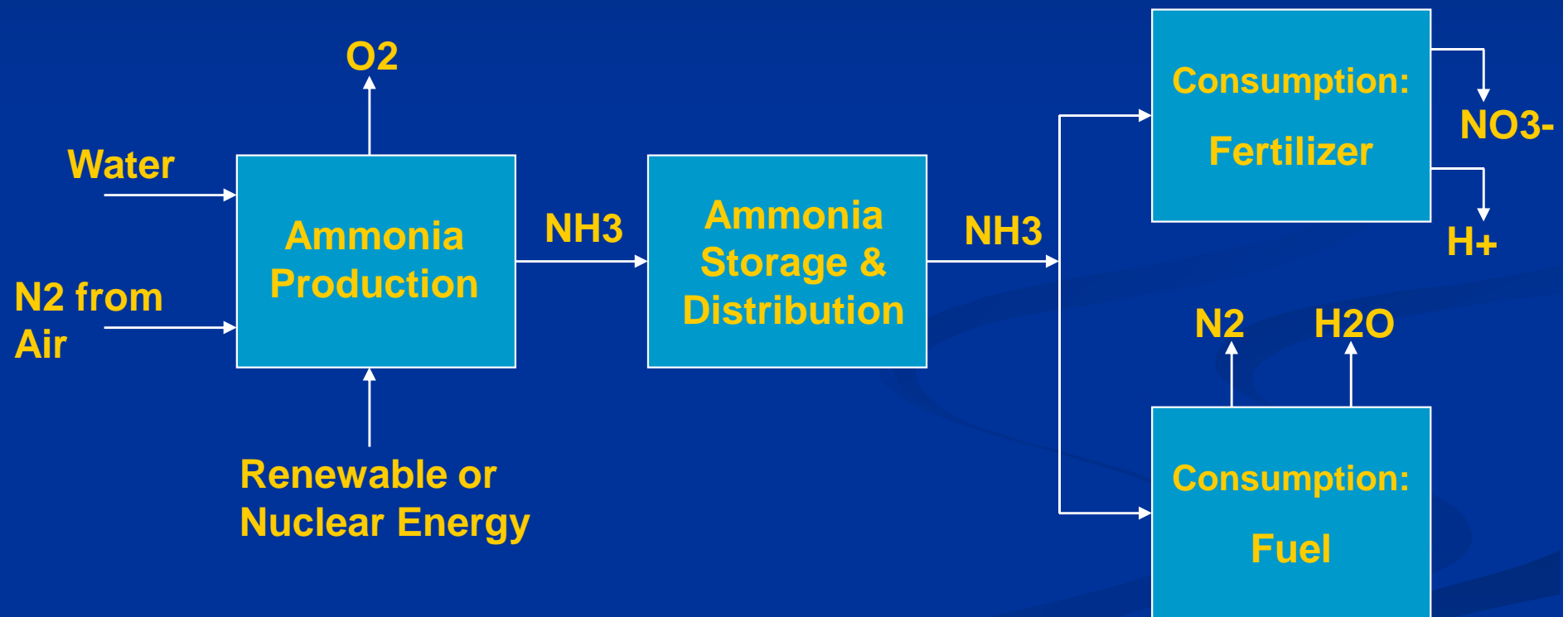
Ammonia Cycle Brown— Natural Gas SMR



Note-- >50% of U.S. ammonia imported

Addl. Note— This process can be made green with CO₂ sequestration, at additional expense

Ammonia Cycle Green— Dissociation of Water

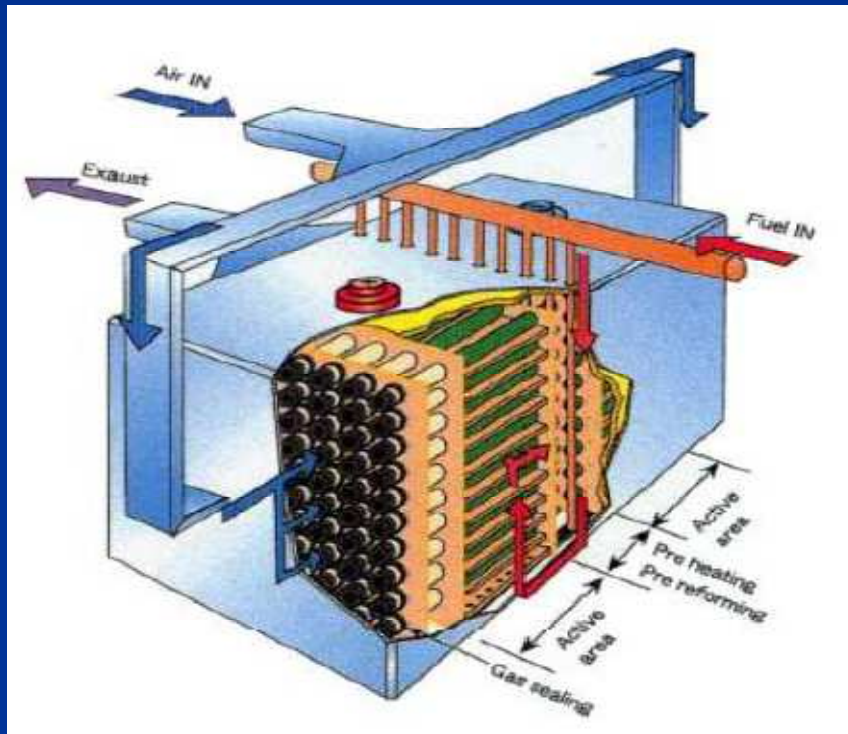


Old Style Electrolysis Ammonia Synthesis



- Electrolyzer used to crack water and provide H₂ for NH₃ synthesis
- Required ~12 MWh per ton of NH₃ (only about 50% overall efficiency)
- Intensely capital costly
- NH₃ production by this method largely abandoned by end of 1900s in favor of H₂ from natural gas

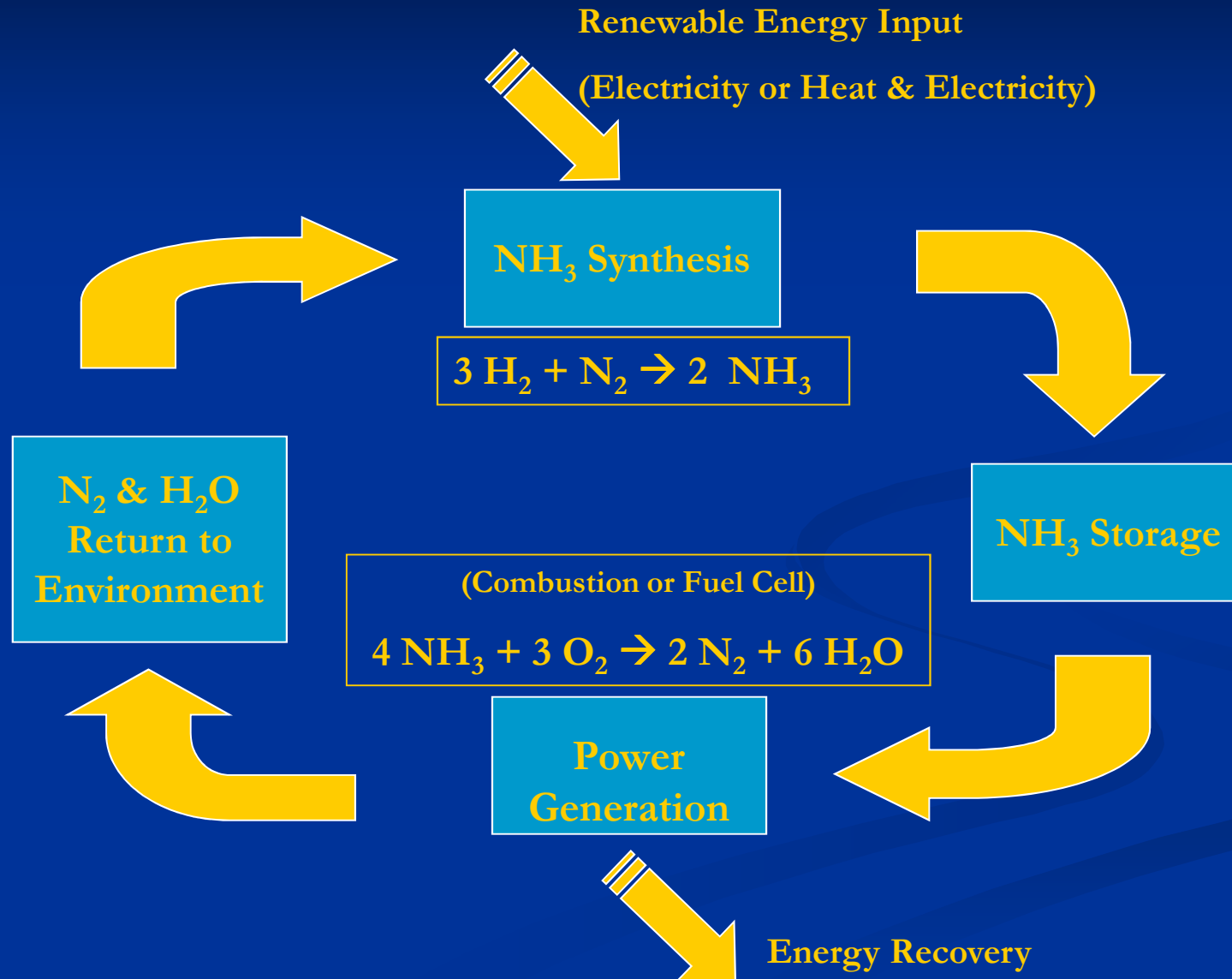
High-Efficiency Solid State Ammonia Synthesis (SSAS)



Tubular Solid Oxide Fuel Cell (SOFC)

- SSAS reactor module will operate much like a tubular SOFC in reverse
- Overall efficiency improvement of 50% over electrolysis because H₂ is never made – direct water (steam) to NH₃
- Capital costs much less (~50%)
- NH₃ will be produced with SSAS at costs equal or lower than NH₃ from natural gas

Green Ammonia – a Renewable Cycle



Keys to the Ammonia Cycle

- Ammonia is the only practical (viable?) liquid fuel that can be made from water, air, and renewable energy
- The Ammonia Cycle can be totally carbon-free, starting with water and nitrogen and ending with water and nitrogen

Side Benefits

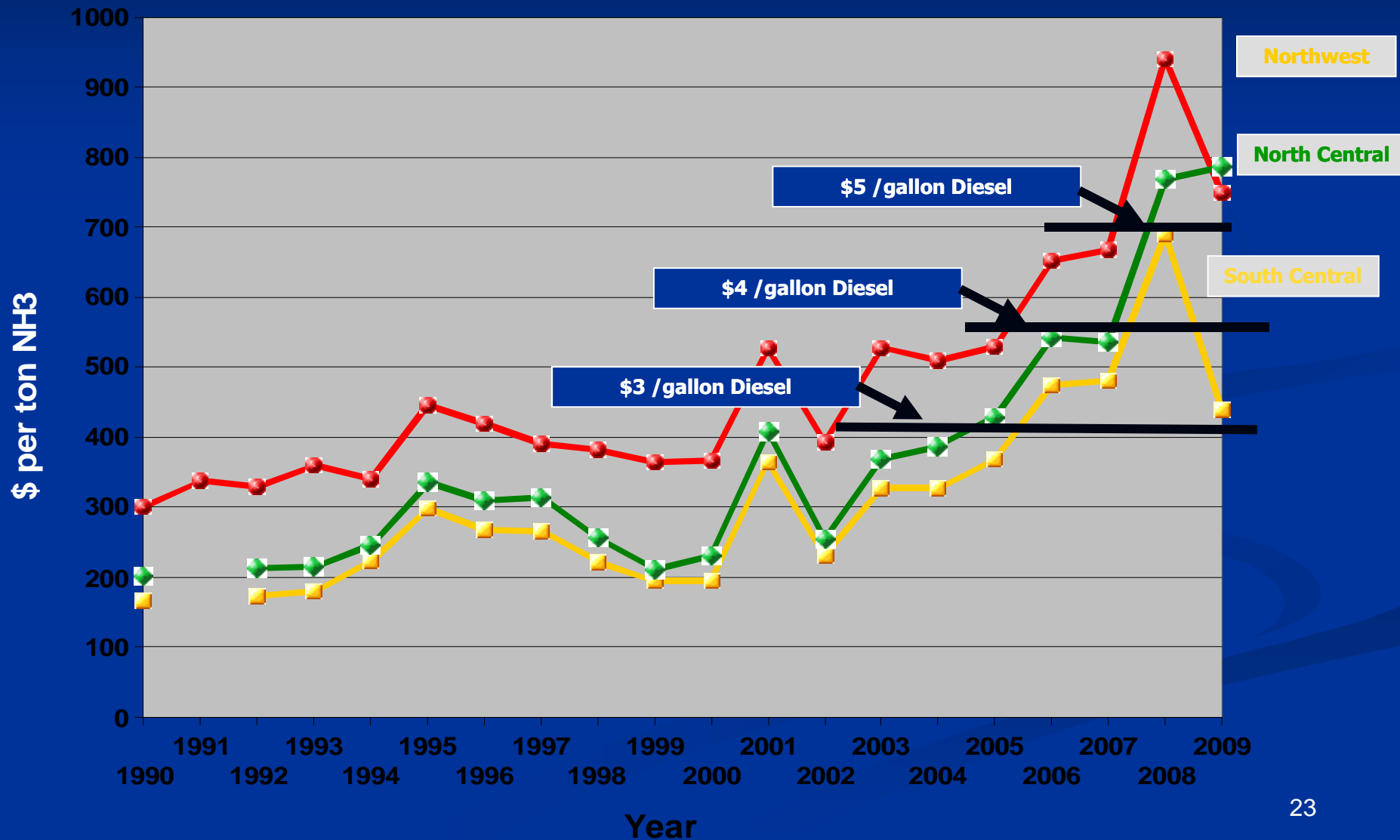
- Water recovery from NH_3 combustion
- Oxygen recovery from water “cracking” and air separations (+ some Argon and CO_2)
- Desalination opportunities

Price of NH₃ Fuel

- 1 metric ton of NH₃ has the energy content of ~150 gallons of gasoline or diesel
- U.S. price of NH₃ (merchant – made from natural gas) has varied from \$150 to \$1200 per ton over the last 5 years
- Price of “electrolytic” NH₃ will depend strongly on effective cost of electric power input

Ammonia Price History (USDA)

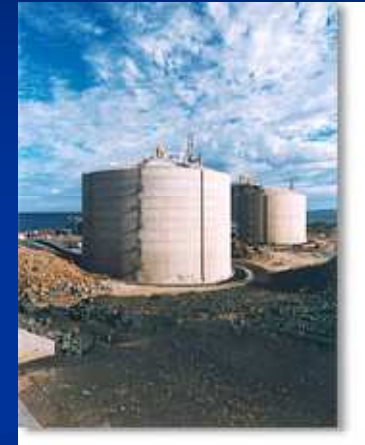
Price per ton of NH₃ at the end of April for each year



Ammonia Is Easy To Store

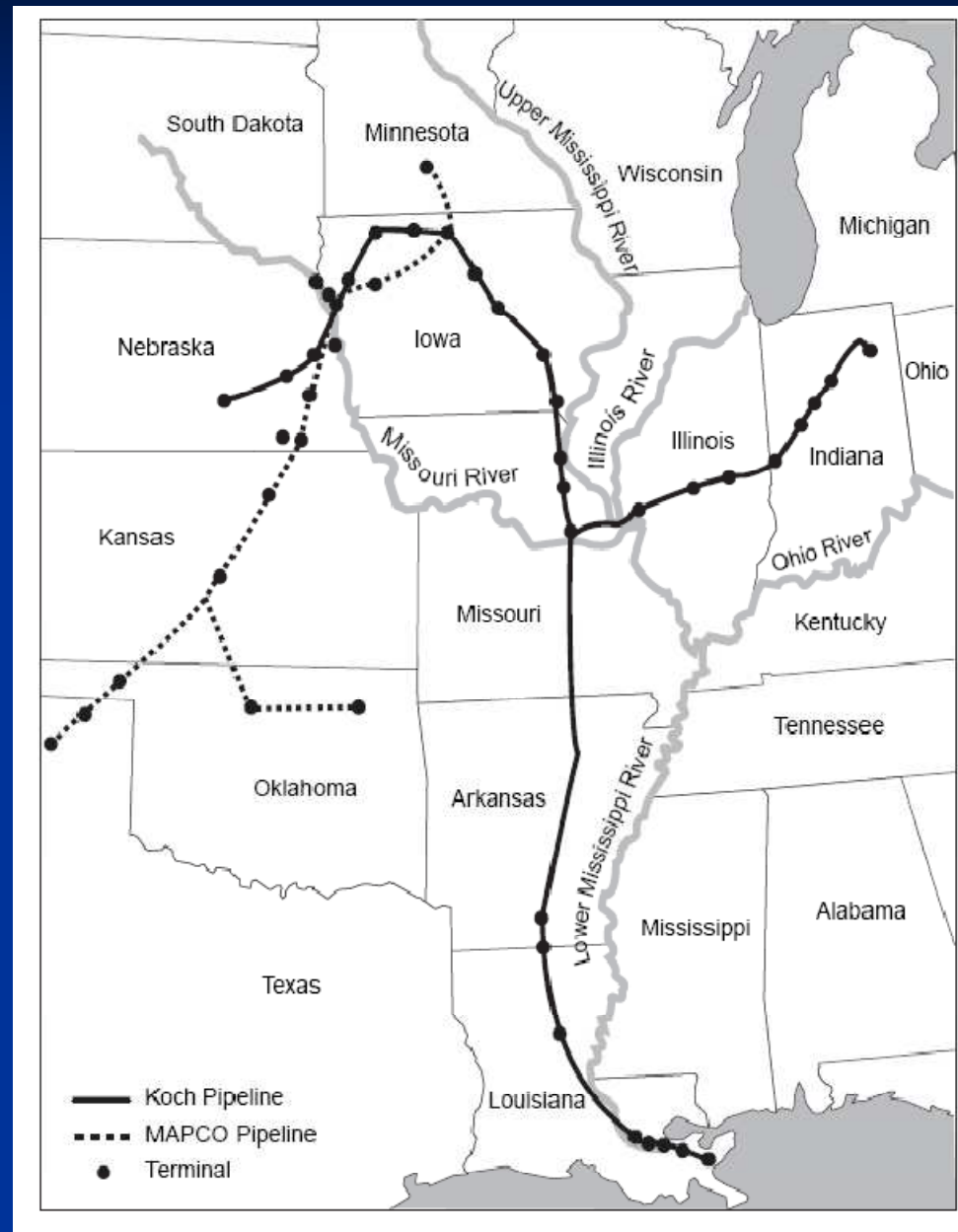


Ammonia Delivery Infrastructure



U.S. Ammonia Pipeline

3000 Miles
Total



Ammonia Pipelines

- ~3000 miles currently used
- Operate at 250 psi and above; Ammonia liquid
- Mild steel construction
- No corrosion or embrittlement problems
- Smaller diameter than NG or H₂
- Approximately 4.5 million tons of large-tank ammonia storage

Ammonia Safety

- Inhalation hazard, so must be handled with respect
- Millions of tons are stored, transported, and handled every year with an excellent safety record
- Not corrosive
- Not explosive nor highly flammable
- Can be stored at moderate pressures
- Safer than gasoline or propane
- Lighter than air
- Trapped by water
- Not a greenhouse gas

What About NO_x?

- Past R&D has shown that NO_x emissions from ammonia-fueled ICEs is about 1/4 of that from an equivalent gasoline engine
- Anhydrous ammonia (often delivered in the form of urea) is the chemical agent used for de-NO_x --
$$6\text{NO} + 4\text{NH}_3 > 5\text{N}_2 + 6\text{H}_2\text{O}$$
$$6\text{NO}_2 + 8\text{NH}_3 > 7\text{N}_2 + 12\text{H}_2\text{O}$$
$$4\text{NO} + 4\text{NH}_3 + \text{O}_2 > 4\text{N}_2 + 6\text{H}_2\text{O}$$
- Mercedes and Honda successful with de-NO_x approaches
- Direct ammonia fuel cells will generate virtually no NO_x



What about Proton Ventures ?

Proton has been established in 2001

Vision:

- New energy on basis of renewables
- Offering solutions for end users B2C

Main focus:

Production, storage of energy without CO₂ emission, NO_x emission, other non wanted emission

What about Proton Ventures ?



WWW.PROTONVENTURES.COM

Developments Proton:

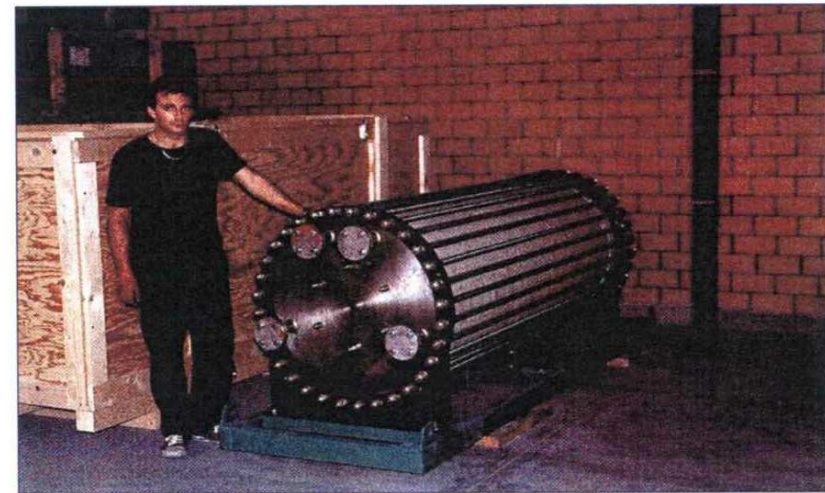
- H₂ production from electrolysis
- H₂ storage as such
- H₂ storage as NFUEL (NH₃)
- Production of NH₃ without Fossil Fuels
- Applications of Climate Neutral or Green NFUEL
 - NH₃ fuel cells
 - Automotive applications
 - Down stream production of chemicals
 - Storage concepts of large terminals
 - Solar Parks, buffering power

Proton Hydrogen production ?

- Supply of advanced Hydrogen stacks

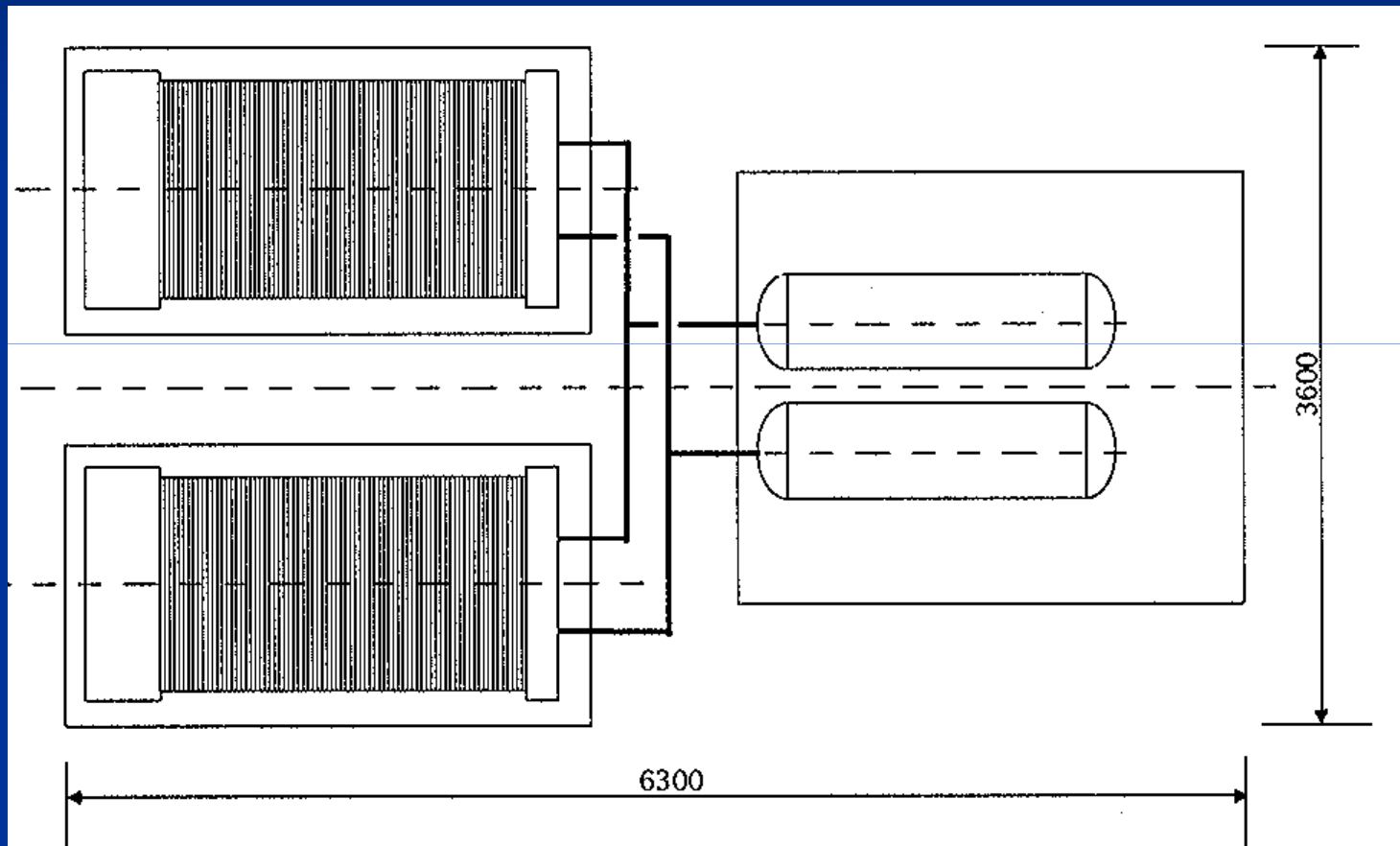
Sizes :

1 Nm³/hr – 2500 Nm³/hr



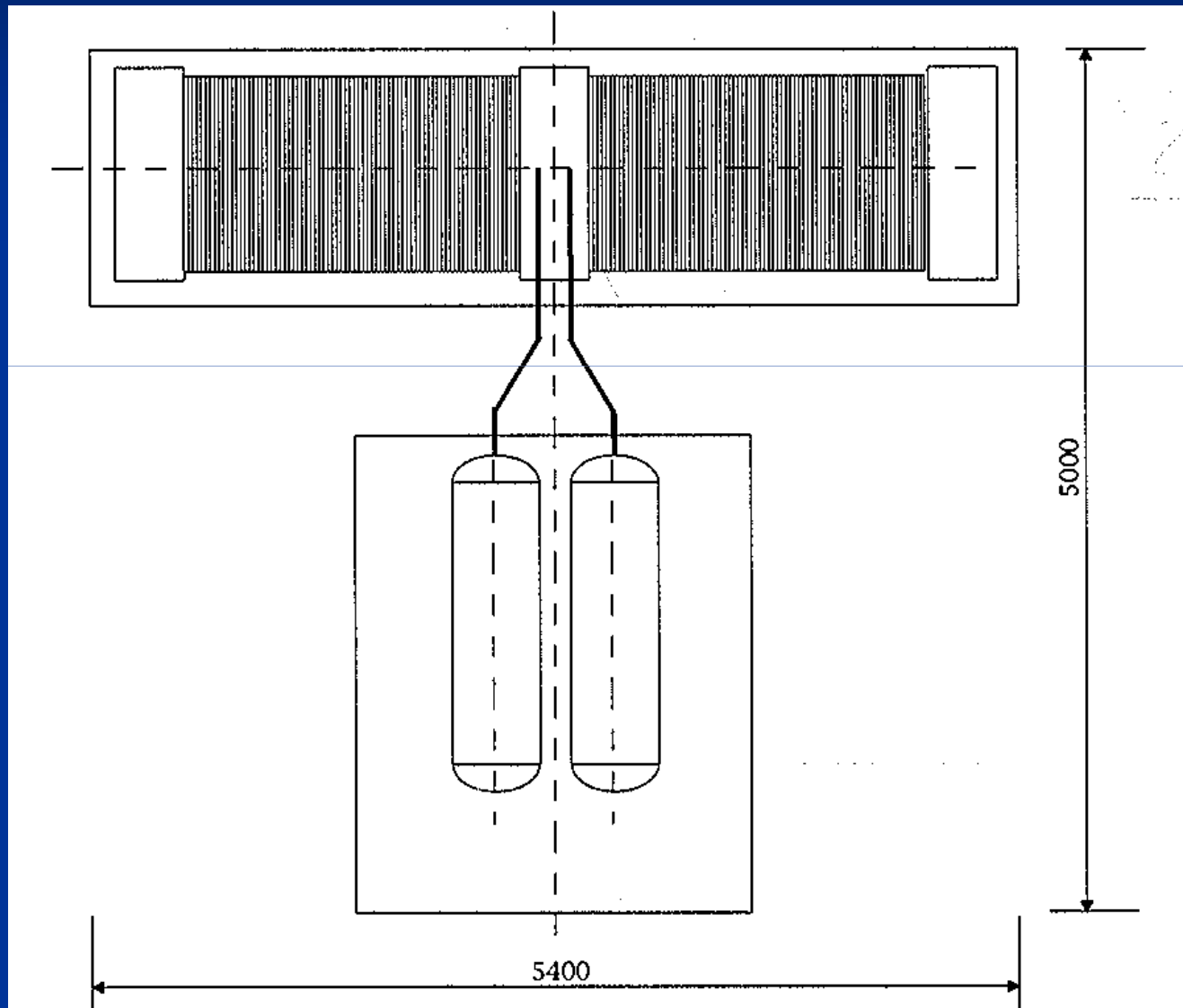
Proton Hydrogen production ?

- Lay-out of advanced Hydrogen stacks



Proton Hydrogen production ?

- Lay-out of advanced Hydrogen stacks



Proton Hydrogen production ?

Main Features of advanced Hydrogen stacks

Rated Capacity	as Hydrogen	NM3/hr	1	5	20	50	100	500
Turn down ratio			15%-100%	15%-100%	15%-100%	15%-100%	15%-100%	15%-100%
Energy consumption		kWh/Nm3	4,5	4,45	4,3	4,25	4,25	4,2
Required Power installed		kVA	10	40	150	350	700	3400
Standard Hydrogen pressure at outlet		Barg	10,00	10	10	25	25	25
Standard Hydrogen temperature at outlet		degree C	25-35	25-35	25-35	25-35	25-35	25-35
Hydrogen purity		% Vol	99,8	99,8	99,8	99,8	99,8	99,8
	incl deoxidiser	% Vol	99,999	99,999	99,999	99,999	99,999	99,999
Hydrogen moisture content			saturated	saturated	saturated	saturated	saturated	saturated
	incl drier	dew point C	-50	-50	-50	-50	-50	-50
Oxygen purity		% Vol	99,6	99,6	99,6	99,6	99,6	99,6
Oxygen moisture content			saturated	saturated	saturated	saturated	saturated	saturated
Electrolyte type			KOH	KOH	KOH	KOH	KOH	KOH
	concentration KOH		30%	30%	30%	30%	30%	30%
Electrolyte load		litres	12	60	240	500	1100	5000
skid dimensions								
	length	mm	600	1600	3000	5000	6000	12000
	width	mm	600	1000	1200	1800	2400	2400
	height	mm	1200	2250	2250	2250	2250	2250
Utilities								
Power		kW	6,5	29	105	260	500	2400
Cooling water		m3/hr	0,1	0,5	2	5	10	50
DM-water		l/hr	0,9	4,2	16,5	41	82	410

Proton Hydrogen production ?

Additional Features of advanced Hydrogen stacks

Available accessories:

PC-based data acquisition system, with graphical pages (flow sheet, actuators status, alarms list, historical data plots, etc.)

water demineralisation units

hydrogen deoxidation units

hydrogen drying units

closed-loop cooling systems

gas analysis systems (oxygen-in-hydrogen % or ppm, hydrogen-in-oxygen %, dew point)

gas compressors

gas storage vessels

Non-standard versions:

operating pressure up to 30 bar

intermediate sizes

DC direct feed (i.e. from solar-photovoltaic fields, wind turbines)

special electrodes for high energy efficiency (4.2 kWh/Nm³ hydrogen)

special electrodes for fluctuating input power

Proton NFUEL production ?

- Supply of advanced Mini-Ammonia units

Sizes :

3 kg/hr, (in development)

125 kg/hr (designing)

1000 kg/hr (ref in Argentina)



Typical idea of a 125 kg/hr unit
Dimensions within 40'' container
Ref Zeton Enschede

Proton NFUEL production ?

- Features of Mini-Ammonia units

Total package:

- DM-water unit for electrolyser (optional)
- Electrolyser (optional)
- N₂ unit (optional)
- Haber Bosch unit , based at app 500 barg
 - Fully automated, web enabled
 - Maintenance agreement included
 - Operations (optional) \
- No CO₂ emissions
- No NO_x emissions
- Ammonia releases (NON-Greenhouse Gas) , for emergency via scrubber

Proton Supplies?

Commercial possibilities:

- Proton allowed to sell the electrolysers worldwide
- Proton to sell mini-ammonia units worldwide
- Proton aims for 50 Nm³/hr electrolysers and larger as main markets

In relation with mini-ammonia/NFUEL units

• Possibilities:

- ❖ DB
- ❖ DBO
- ❖ DBMO
- ❖ Leasing option

- License agreements for use

Other developments

Start to change ADBLUE to NFUEL

Denmark:

Amminex:

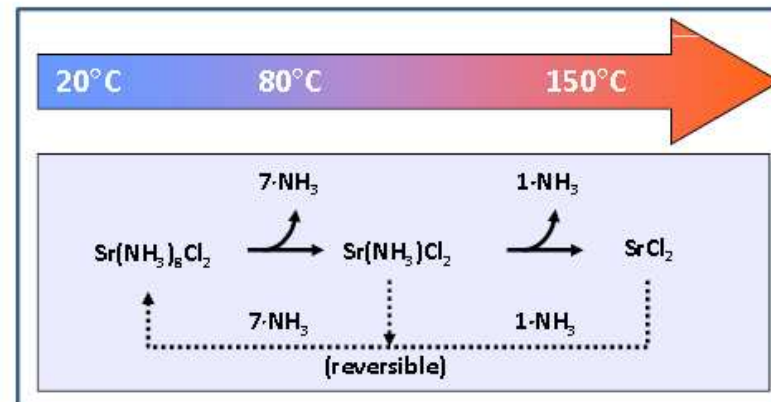


Solid-state ammonia based power generation



HydrAmmine™

75 liter NH₃-gas stored in a block



Other developments

AMMINEX DENMARK VISION:

Renewable ammonia – the big picture

Solar/wind energy capture



Nearby electricity-to-ammonia plant



Bulk shipment – long distance



Terminal →
Solid storage →
distribution to end-users



AMMINEX

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Other developments

AMMINEX DENMARK VISION:

Hydrogen production
from ammonia

Proven concept:

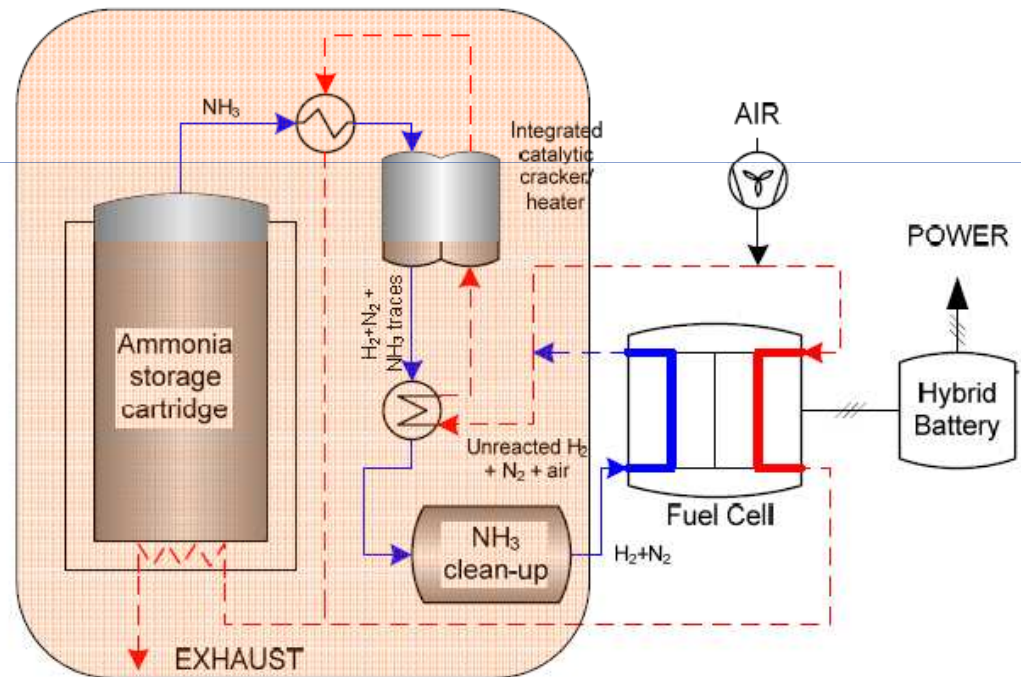
6,75 ltr H₂ /minute
For 1,1 KW

Cracking efficiency: over 80%



HydrAmmine™ with PEM-FC

•An ammonia cracker is needed to generate H₂ from ammonia



AMMINEX

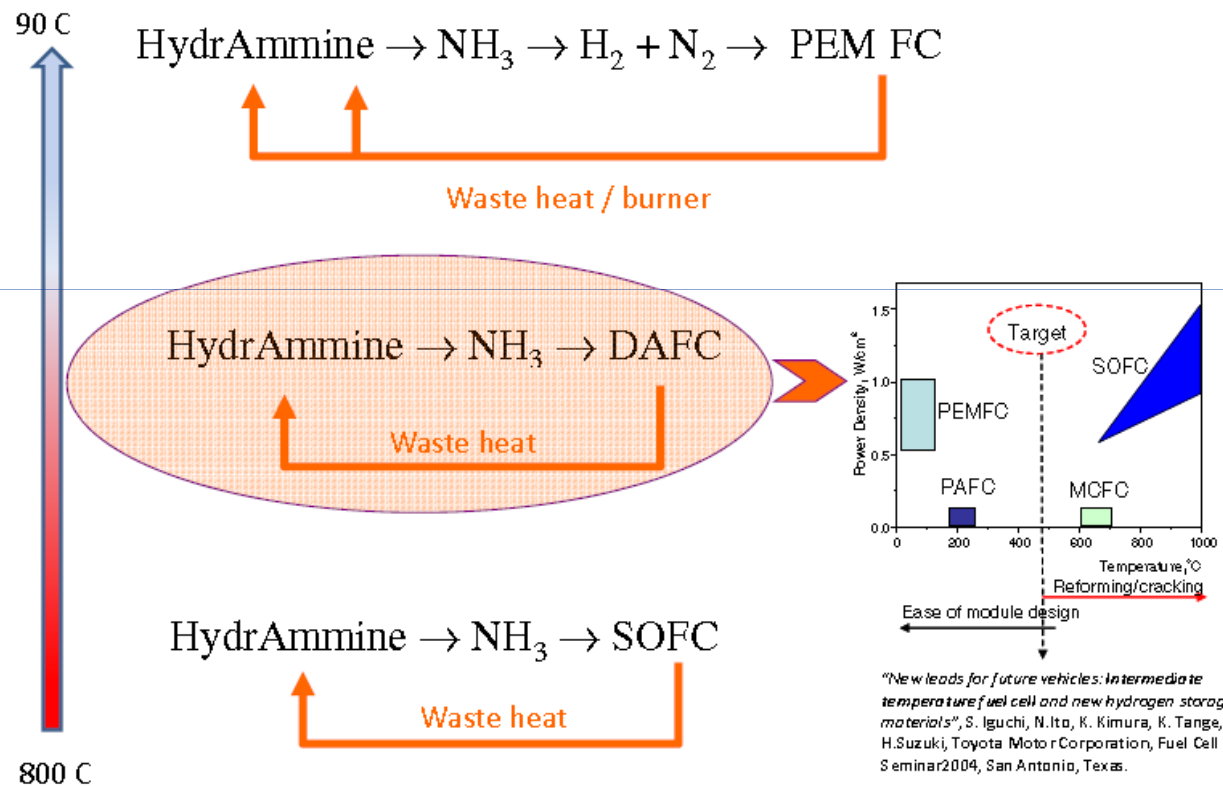
Other developments

AMMINEX DENMARK VISION:

AMMONIA FUEL CELL:

Optimal:
AT INTERMEDIATE
TEMPERATURE (400 C)

FC system overview: automotive perspective



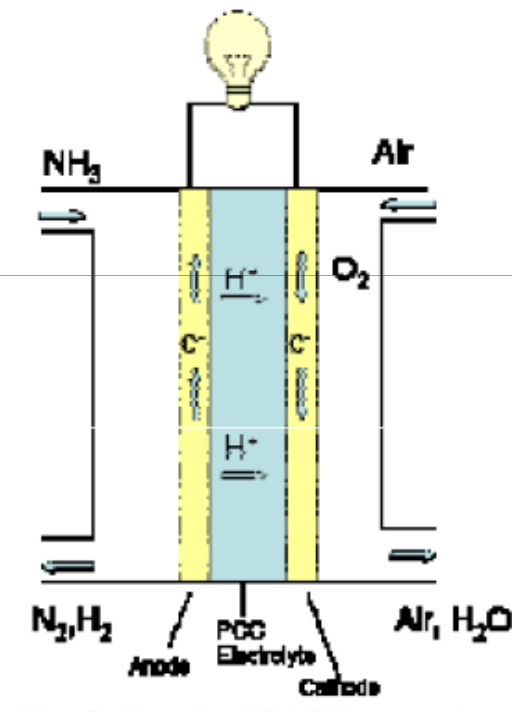
"New leads for future vehicles: intermediate temperature fuel cell and new hydrogen storage materials", S. Iguchi, N. Ito, K. Kimura, K. Tange, H. Suzuki, Toyota Motor Corporation, Fuel Cell Seminar 2004, San Antonio, Texas.

Other developments

AMMINEX DENMARK VISION:

Intermediate temperature direct ammonia fuel cell

- DAFC is fed directly with ammonia.
- The operating temperature is between 400-500°C
- The electrolyte consists of proton conducting ceramic (PCC)
- No noble metal as catalyst. Ni can be used instead of e.g. Pt for PEM.
- The operating temperature range of DAFC generates high quality waste heat to be used for degassing of ammonia from the storage unit. The system efficiency will be improved and heat exchange area is lowered.



Other developments

Truck Retrofit in NL

Co-operation Proton, Truck Company , Kennisalliantie, Honywell

Fuel/storage	Pressure (bar)	Energy density (GJ/m ³)
Diesel	1	38.6
Gasoline	1	34.4
CNG (CH ₄)	250	10.4
LPG (C ₃ H ₈)	14	19.0
Methanol	1	11.4
H ₂ /metal hydride	14	3.6
Ammonia	10	13.6

Re-Cap

- Ammonia offers the opportunity for a carbon-free energy cycle
- Ammonia has unique physical/ chemical properties, making it an attractive fuel option
- Ammonia is cost-competitive with fossil fuels
- Ammonia has a proven storage/delivery infrastructure and safety environment
- New applications under way: (learning curve will drive costs further down)

Ammonia Fuel Network

The international forum for Ammonia fuel business developments

- Proceedings of first six conferences at www.energy.iastate.edu/becon/ammonia.html
- Next Ammonia Fuel Conference: first or second Monday/Tuesday in Oct 2010, Detroit MI
- AFN web site and registration www.ammoniafuelnetwork.org