CHANGING WHAT'S POSSIBLE

Ammonia as Virtual Hydrogen Carrier

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U.S. DEPARTMENT OF ENERGY

Who am I?

- **Moscow State University** – MS (1972), PhD in Inorganic Chemistry (1976), Doctor of Sciences in Chemistry (1992)
- **Institute of Chemical Problems of Chemical Physics RAS** (Chernogolovka, (1975 – 1993)

  - metal hydrides, Ziegler-Natta catalysis, metallocene chemistry, electrochemistry, organometallic hydrogenation catalysis, bimetallic complexes, C-H bond activation
- Visiting scholar at **Indiana University**, Bloomington (1991), **Boston College** (1993 – 1995)
- **Moltech Corp.** (now Sion Power) (Tucson, AZ) (1996 – 1998)

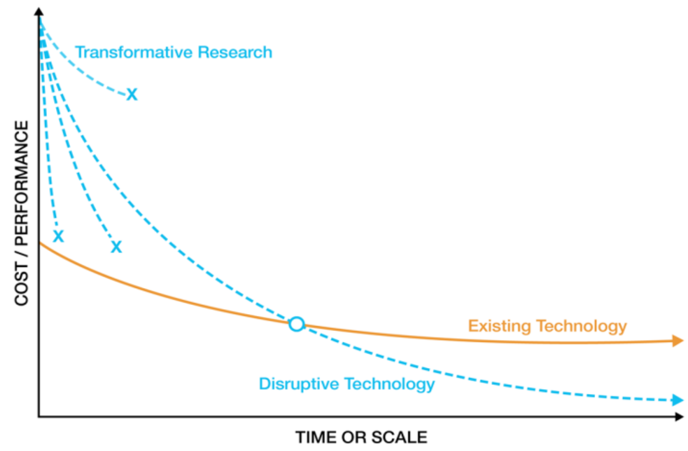
  - anode protection and electrolyte development for lithium metal/sulfur battery
- **GE Global Research** (Niskayuna, NY) (1998 – 2014)

  - created and shaped internal and external projects
  - direct synthesis of diphenylcarbonate
  - homogeneous and heterogeneous catalysis projects
  - electrosynthesis of small organic molecules
  - hydrogen storage and production (water electrolysis)
  - CO_2 capture
  - sodium/metal chloride battery, flow batteries (ARPA-E performer)
  - **Director of Energy Frontier Research Center for Innovative Energy Storage**
- **ARPA-E** (2015 –

  - Program Director focusing on electrochemical energy storage (secondary and flow batteries), generation (fuel cells), chemical processes (catalysis, separation)

Why I work at ARPA-E?

ARPA-E is a unique agency



- **Creating new learning curves**
  - failure acceptance
- **Program driven**
  - no roadmaps
- **Innovative start-up culture**
  - combination of fresh blood and corporate memory
- **Close involvement in project planning and execution**
  - cooperative agreement
- **Technology to market focus**
  - techno-economical analysis
  - minimum value prototype deliverable
  - technology transfer

Ammonia as energy vector and hydrogen carrier

- Direct agricultural application
- Production of nitrogen-based fertilizers
- Feedstock for chemical processes
- **Energy storage**
- **Energy transportation**
- **Direct fuel for**
  - fuel cells
  - ICEs
  - turbines
- **Hydrogen carrier**

Ammonia NH_3 facts

- Properties: b.p. -33 C, density 0.73 g/cm^3,
  stored as liquid at 150 psi
  - 17,75% H, 121 kg H/m^3
- Synthesis: reaction of N_2 and H_2 under high pressure and temperature (Haber-Bosch process)
- World production 150MM tons
  - current cost about \$0.5/L
- Octane number 120
- Blends with gasoline and biofuels (up to 70%)
  - mixtures preserve performance in ICE (torque)
  - proportional drop in CO_2 emission
- Partial cracking improves combustion
- **Proven, acceptable safety history for over 75 years**
  - inhalation hazard, must be handled professionally
- **Energy density 4.3 kWh/L**

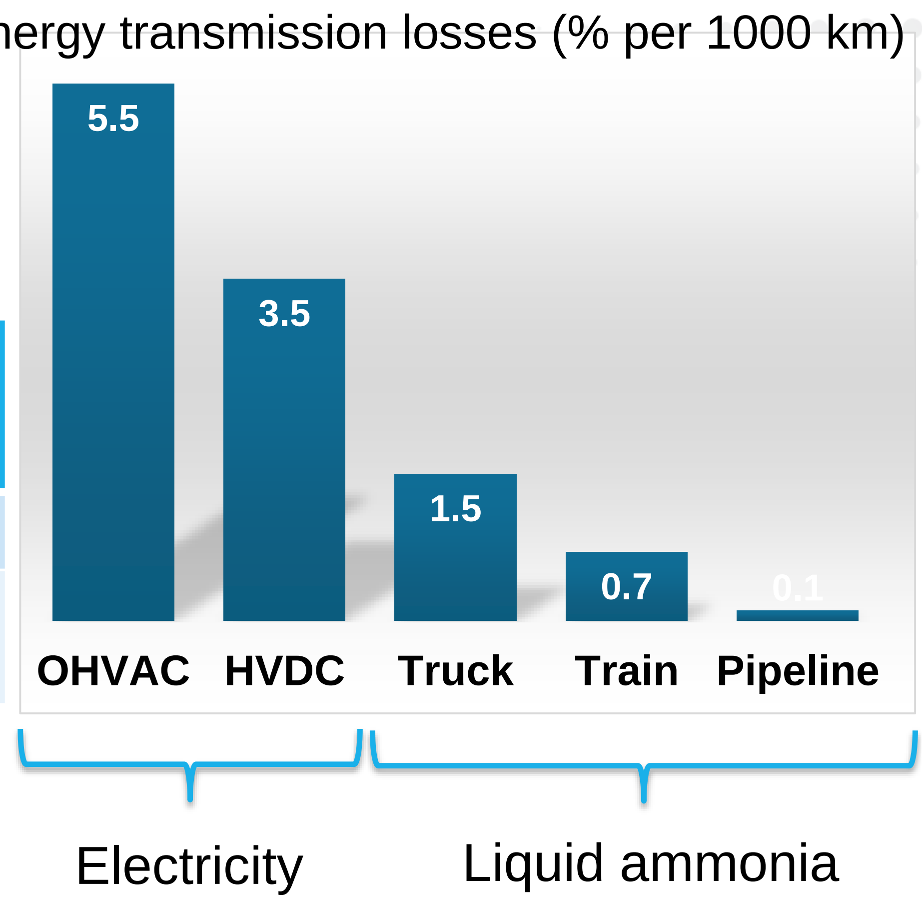
Comparing ammonia with carbon-neutral liquid fuels

LOHC couple	B.p., deg C	Wt. % H	Energy density, kWh/L	E^0, V	η, %
Synthetic gasoline	69-200	16.0	**9.7**	-	-
Biodiesel	340-375	14.0	**9.2**	-	-
Methanol	64.7	12.6	4.67	1.18	96.6
Ethanol	78.4	12.0	**6.30**	1.15	97.0
Formic acid (88%)	100	3.4	2.10	1.45	105.6
Ammonia	-33.3	**17.8**	**4.32**	1.17	88.7
Hydrazine hydrate	114	8.1	**5.40**	**1.61**	**100.2**
Liquid hydrogen	-252.9	100	2.54	1.23	83.0

G.Soloveichik, *Beilstein J. Nanotechnol.* **2014,** *5,* 1399

Ammonia is promising media for energy storage and delivery

Energy transportation capacity and losses



Energy transmission capacity
(at the same capital cost)

	Power line	CH_2 (350 bar)	Liquid NH_3
Capacity	1.2 GW	6.5GW	41GW
Protective zone	50-70 m	10 m	10 m

D. Stolten (Institute of Electrochemical Process Engineering), BASF Science Symposium, 2015

Liquid pipelines have highest capacity and efficiency

Energy storage comparison

30,000 gallon underground tank contains 200 MWh (plus 600 MMBTU CHP heat

Capital cost ~$100K

=

6 x

1,000kg H_2 Linde storage in Germany

or

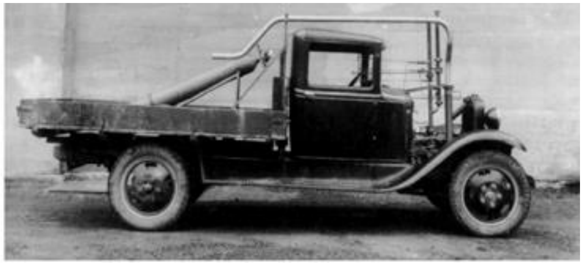
40 x

5 MWh A123 battery in Chile

Capital cost $50,000 - 100,000K

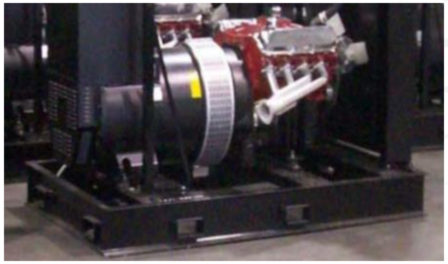
Ammonia provides smallest footprint and CAPEX

Ammonia as internal combustion fuel



Norsk Hydro, Norway, 1933

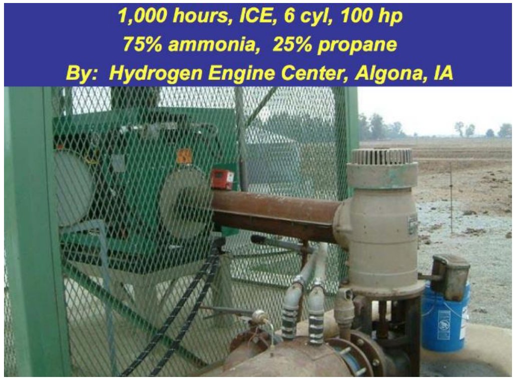
Belgium, 1943



HEC-TINA 75 kVA
NH_3 Generator Set

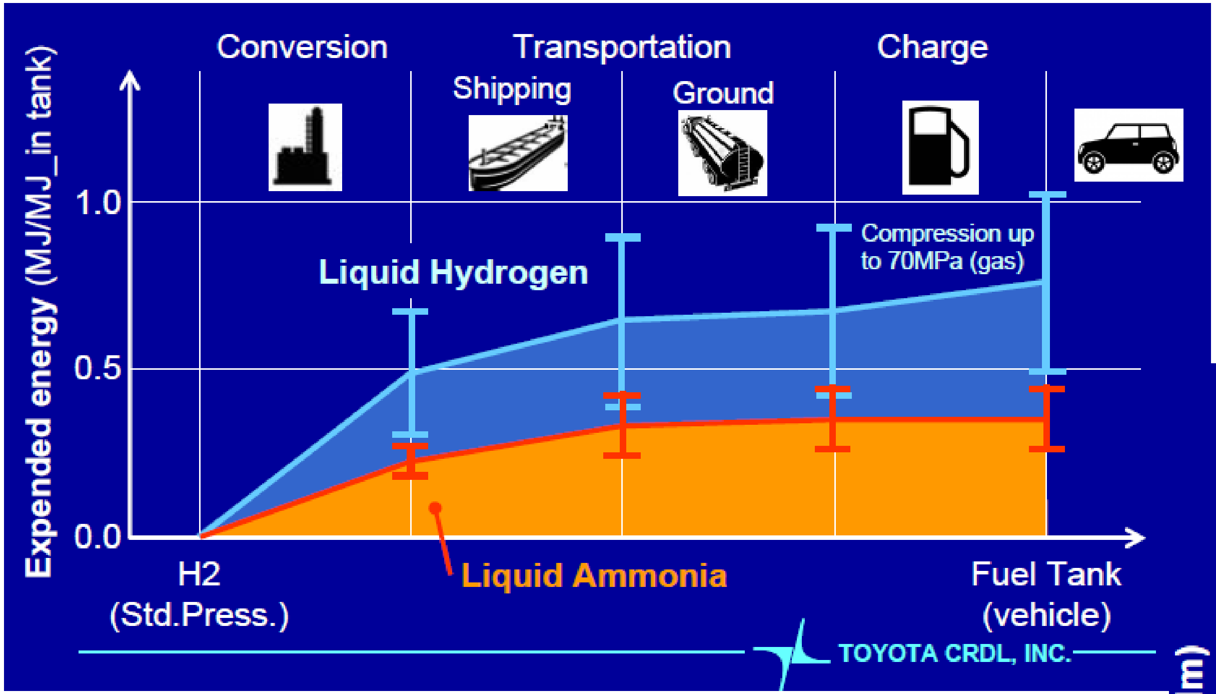
2013 Marangoni Toyota GT86 Eco Explorer, 111 mile zero emission per tank (7.9 gal NH_3)

2013 AmVeh x250, South Korea runs on 70%NH_3 +30% gasoline

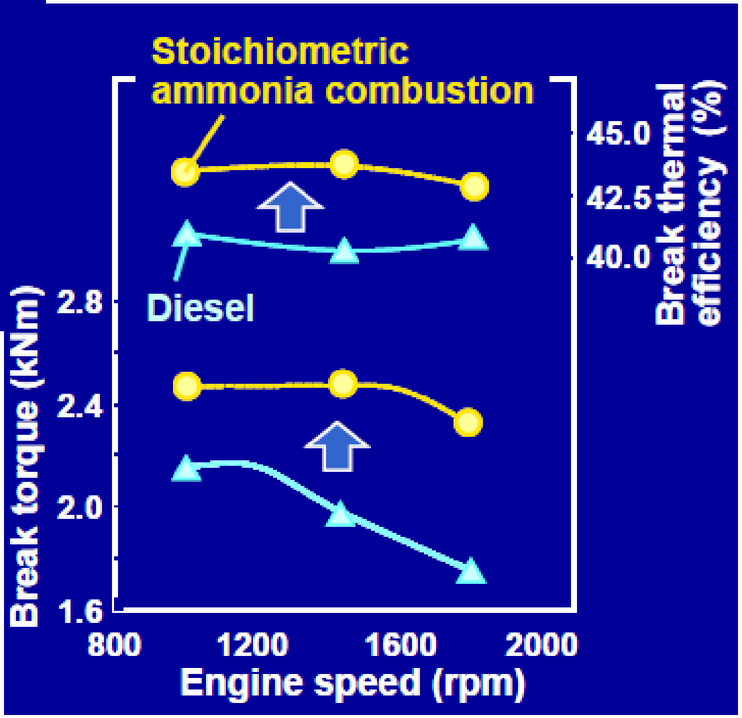


NH_3-fueled ICE operating an irrigation pump in Central Valley, CA; ~ 50% total efficiency

Use of ammonia fuel in ICEs



Toyota Central R&D Labs. Inc.



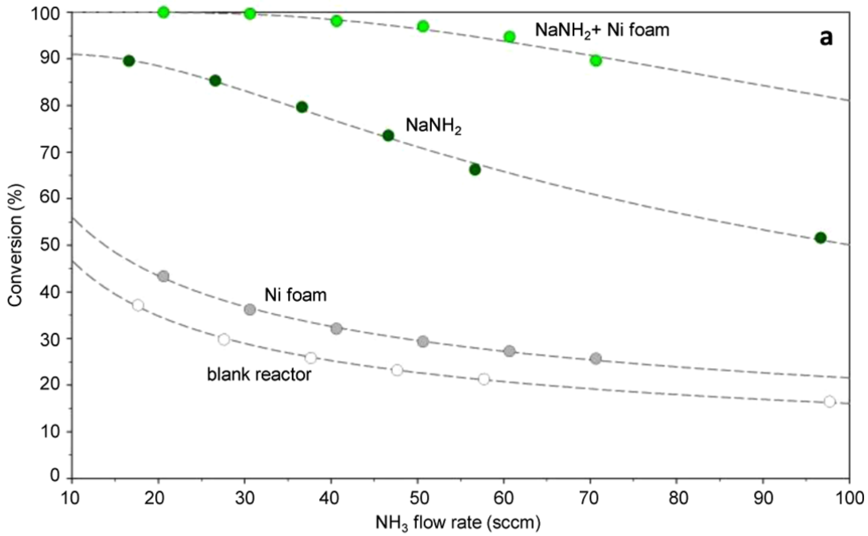
13L 6 cylinder engine test

CHANGING WHAT'S POSSIBLE

Ammonia as a hydrogen carrier

Ammonia cracking

Breakthrough in catalyst design



W. David et al., *J. Am. Chem. Soc.*, **136** (2014) 13082
J. Guo et al., *ACS Catal*., **5** (2015) 2708

Ammonia cracking unit

200 nm^3/h, 900 C, Ni catalyst

Ammonia electrolysis

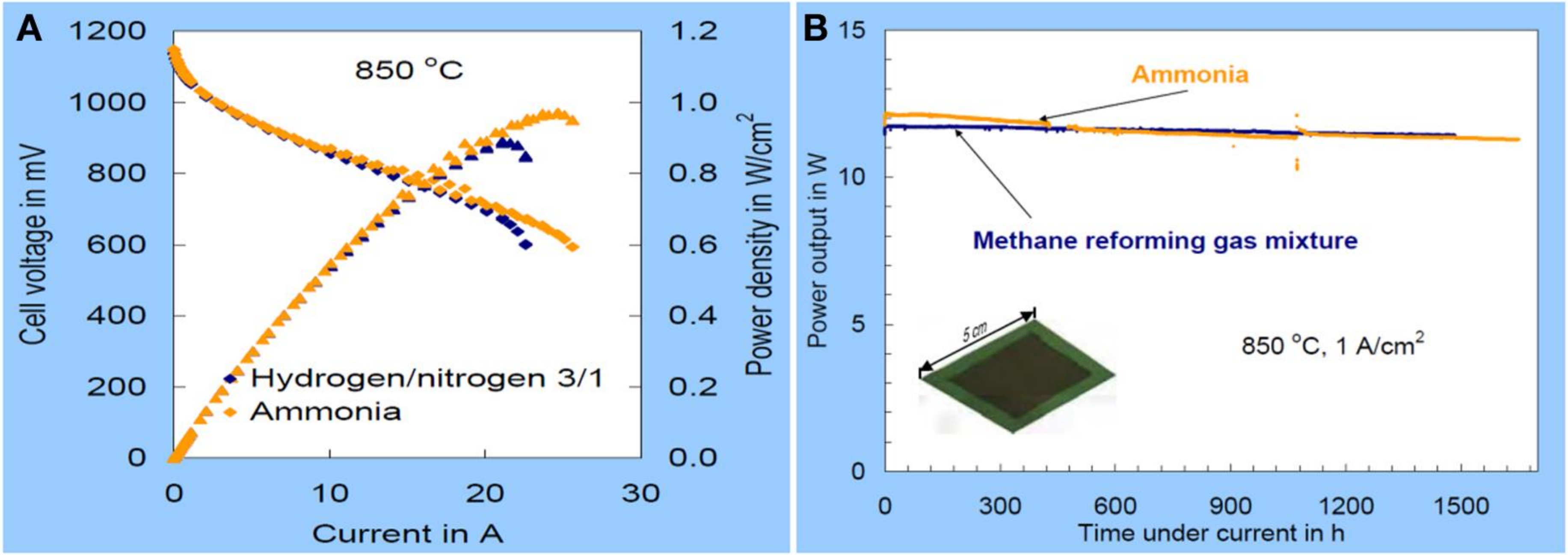
(Ohio University)

Low cell potential (E^0 = 0.077V)
Theoretical efficiency 95%

B. Boggs et al., *J. Power Sources* **192** (2009) 573

Ammonia as a fuel for fuel cells

- Alkaline fuel cells
- Molten carbonate fuel cells
- Protonic conductor fuel cells
- Solid oxide fuel cells



A. Hagen, Use of alternative fuels in solid oxide fuel cells, 2007

Ammonia synthesis

Fritz Haber & Carl Bosch
(Nobel Peace Prize 1918 & 1931)

$N_2 + 3H_2 \leftrightarrow 2NH_3$ $\Delta H = -92.4$ kJ/mol

Air (78% N_2) separation as nitrogen source

H_2 from methane (SMR) or water (electrolysis)

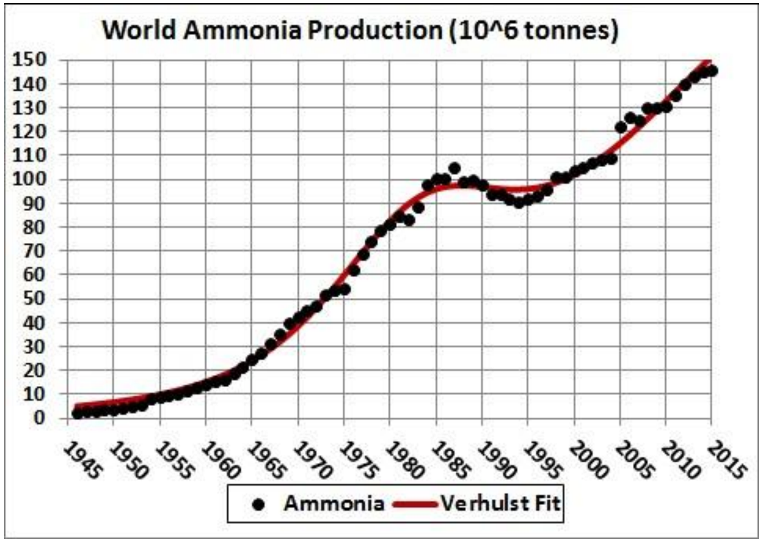
1913

2013

Ammonia production

https://chemengineering.wikispaces.com/Ammonia+production

Current ammonia production plant:
- H_2 via steam methane reforming
- N_2 via cryogenic air separation
- produces 2,000 to 3,000 tons per day
- equivalent 600 – 1,000 MW



Disconnect between ammonia production scale and scale of renewables generation

http://minerals.usgs.gov/minerals/pubs/commodity/nitrogen
P. Heffer, M. Prud'homme "Fertilizer Outlook 2016-2020" International Fertilizer Industry Association (2016)

Projected AGR 2.5 – 3.5% (230 Mt NH_3 in 2020)

Improving ammonia production

Advanced Haber-Bosch process

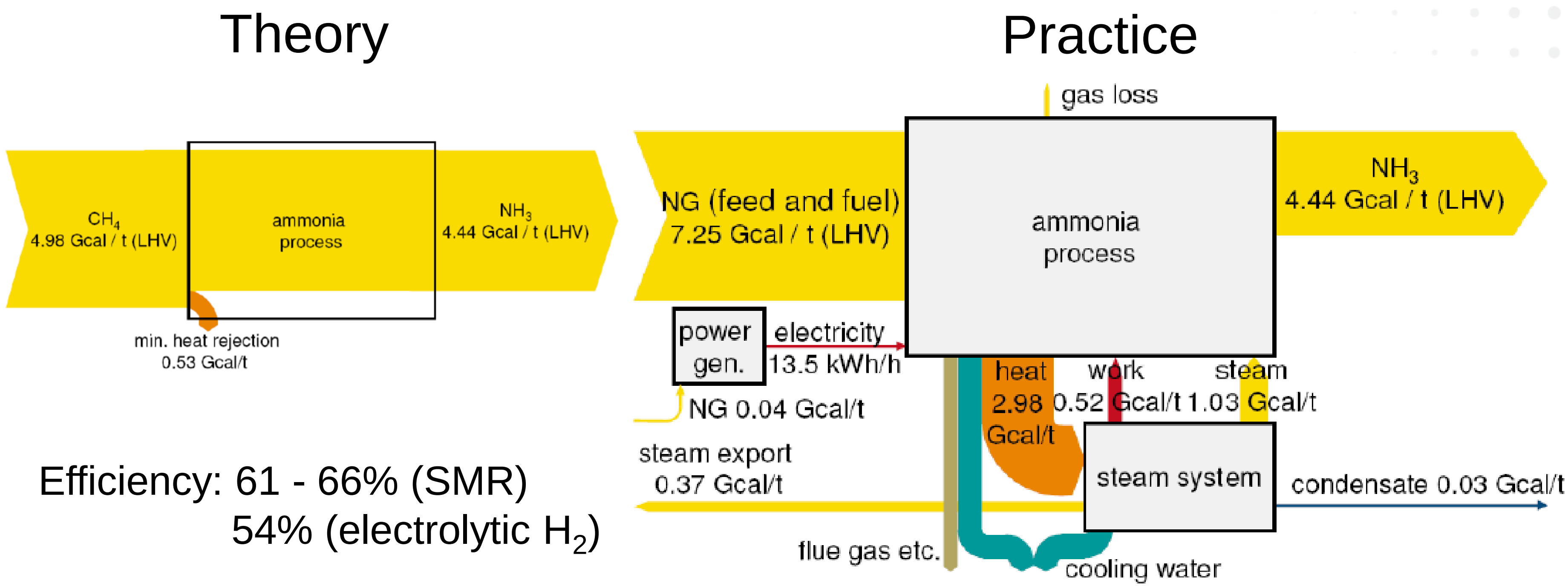
- Lower pressure synthesis (adsorptive enhancement)
- Low temperature synthesis (catalyst development)
- Ambient pressure synthesis (plasma enhancement)

Electrochemical synthesis

- Solid state medium temperature cells
- Low temperature PEM and AEM cells
- Molten salt electrolytes

Ammonia production: energy efficiency

Hydrogen from SMR process

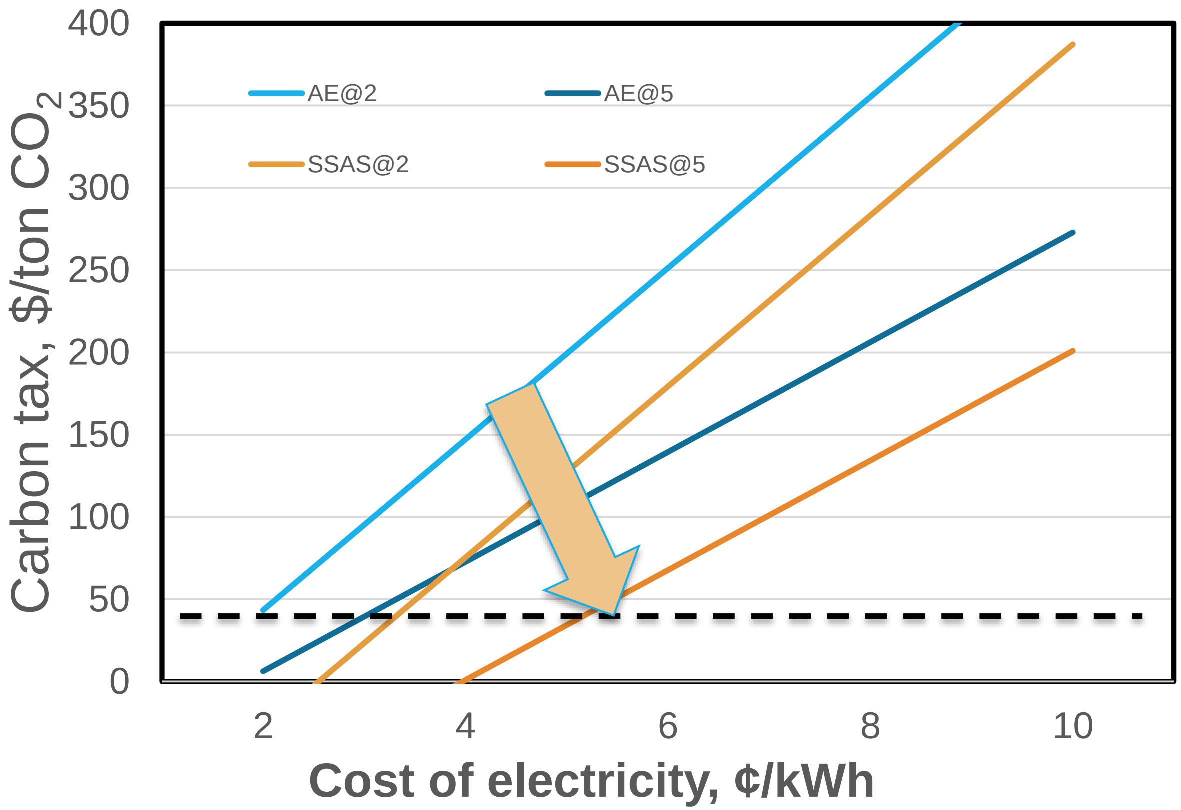


Efficiency: 61 - 66% (SMR)
54% (electrolytic H_2)

Energy consumption: 10000 - 12000 mWh/ton NH_3 (current SMR)
6500 - 7500 mWh/ton NH_3 (projected SSAS)

SMR vs. electrolytic hydrogen

Break even energy cost of ammonia synthesis



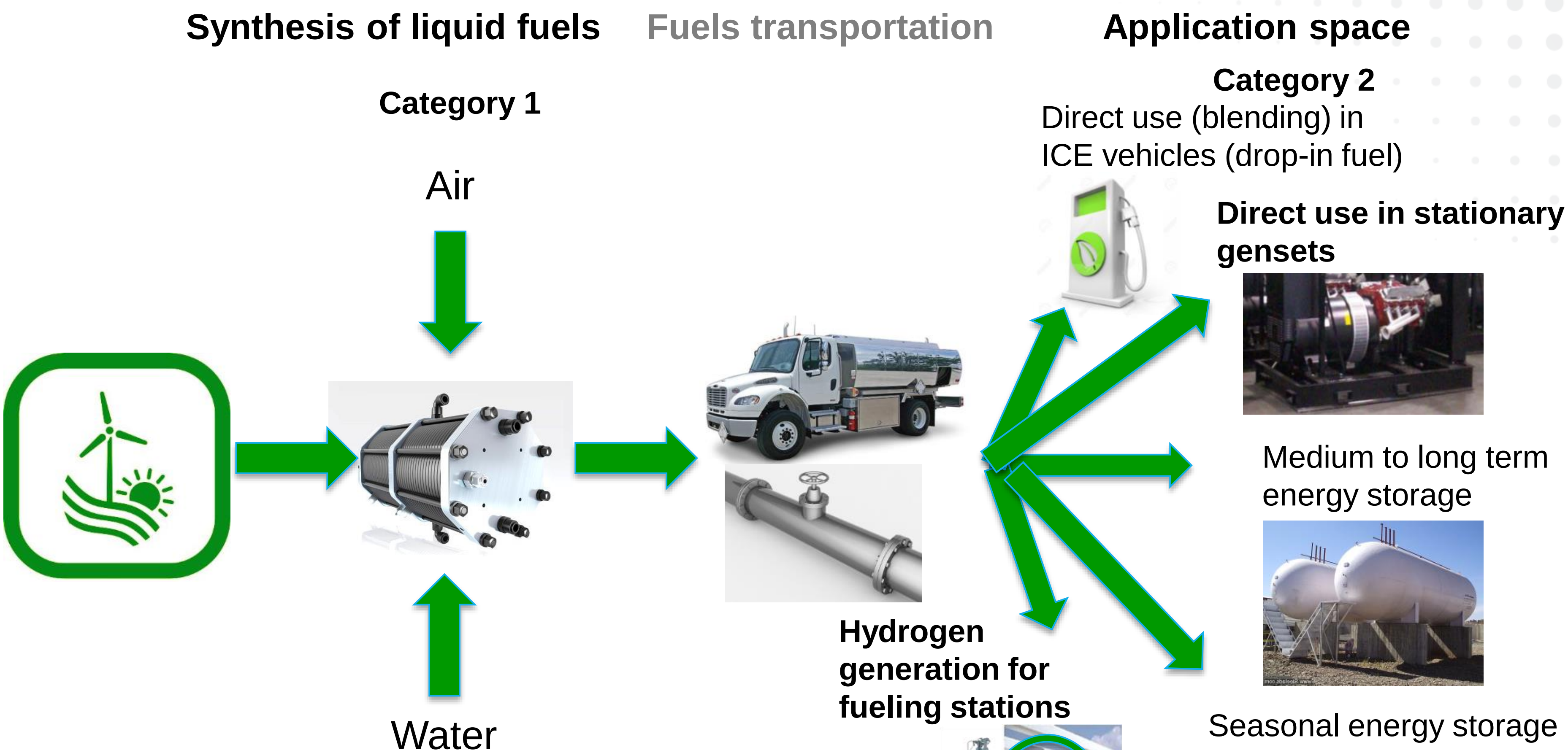
AE- advanced electrolysis, SSAS – solid state ammonia synthesis, NG prices from 2 to 5 $/MBtu

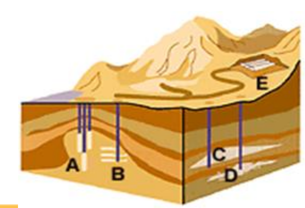
Hydrogen Cost ($/kg) = 0.286*NG price ($/MMBtu) + 0.15 (Penner)

Conclusions

- **Ammonia is an ideal candidate for long term energy storage and long distance energy delivery from renewable intermittent sources**
  - high energy density
  - feedstock widely available
  - production successfully scaled up (150MT annually)
  - zero-carbon fuel
  - infrastructure for storage and delivery technologies in place
  - can be used in fuel cells and thermal engines
- **Remaining challenges**
  - down scale of production economically (match renewables)
  - production tolerant to intermittent energy sources
  - improve conversion efficiency to electricity, power or hydrogen
  - improve safety
  - public acceptance/education

Renewable Energy to Fuels through Utilization of Energy-dense Liquids (REFUEL)





- Energy storage and delivery combined
- Small/medium scale to match renewables
- Cost effective methods for fuels conversion to electricity or H_2