INCREASE YOUR H_2IQ

The #H2IQ Hour

Today's Topic:

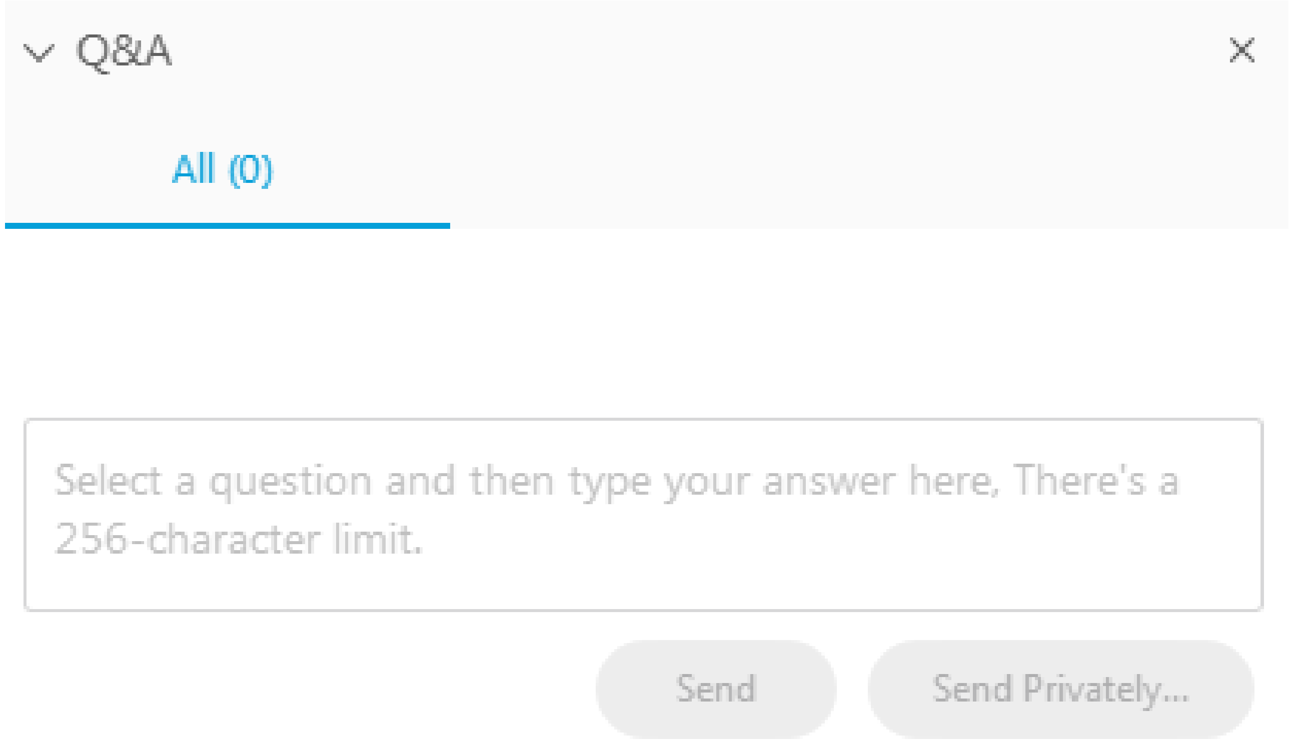
Ammonia: From Fertilizer to Energy Carrier

This presentation is part of the monthly H2IQ hour to highlight research and development activities funded by U.S. Department of Energy's Hydrogen and Fuel Cell Technologies Office (HFTO) within the Office of Energy Efficiency and Renewable Energy (EERE).

INCREASE YOUR H2IQ

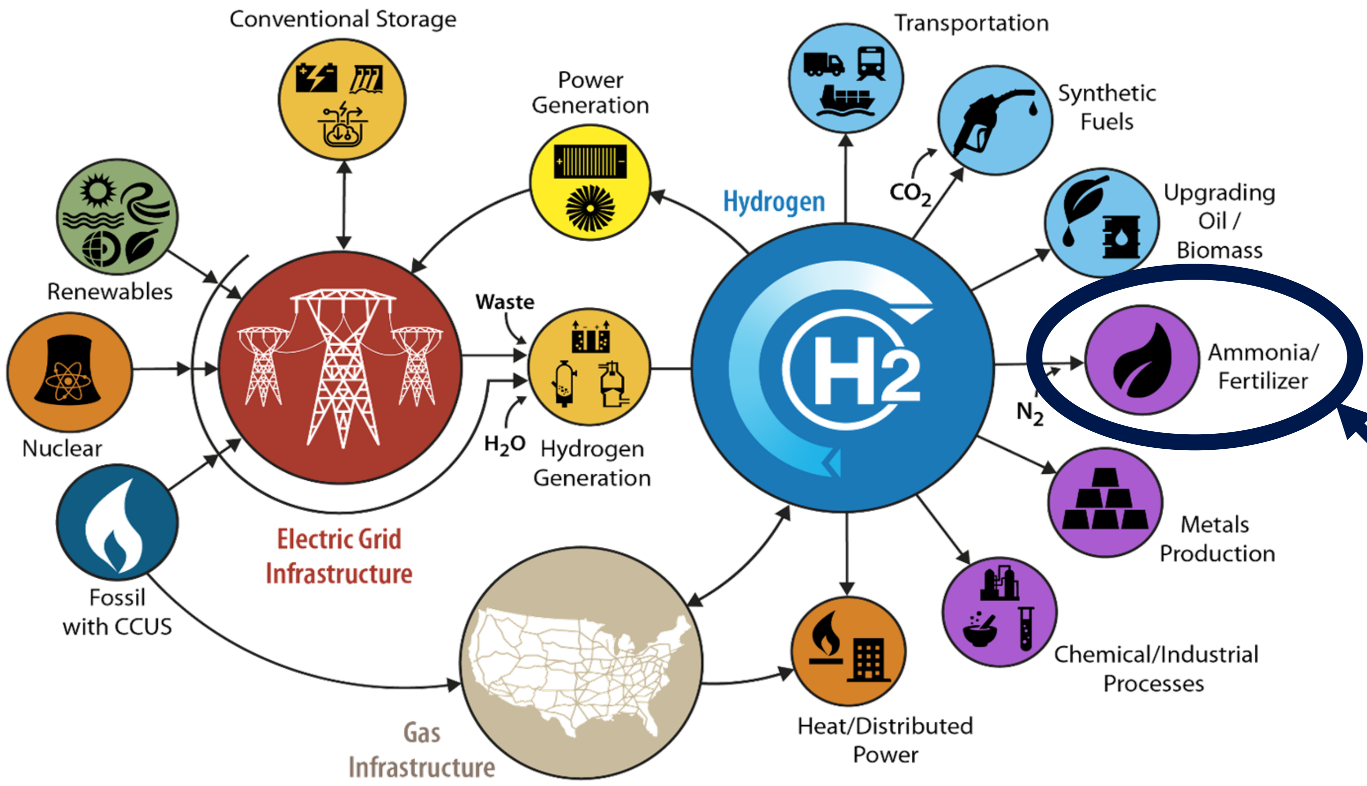
The #H2IQ Hour Q&A

Please type your questions into the **Q&A Box**



Hydrogen at Scale

DOE's H2@Scale initiative provides an overarching vision for how hydrogen can enable energy pathways across applications and sectors in an increasingly interconnected energy system.



Global potential estimated by H_2 Council: $2.5 trillion, 30 million jobs, 6 GT CO_2 reduction.

Priorities

1. **Low cost, zero carbon hydrogen generation: $1 - $2/kg**
2. **Low cost, efficient, safe hydrogen delivery and storage**
3. **End use applications to achieve scale and sustainability, enable emissions reduction and address EJ40 priorities**

Enablers: Workforce development, safety, codes, standards

U.S. DEPARTMENT OF ENERGY
Office of ENERGY EFFICIENCY & RENEWABLE ENERGY

arpa·e

Ammonia: From Fertilizer to Energy Carrier

Grigorii Soloveichik
Program Director/ARPA-E
Senior Advisor/HFTO

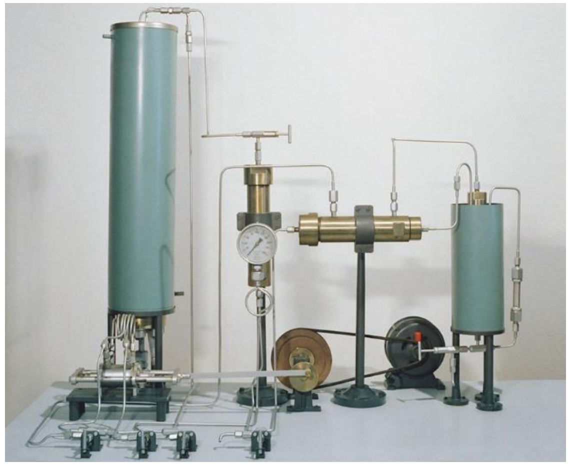
Ammonia synthesis

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

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

Air (78% N_2) separation as nitrogen source

H_2 from methane (SMR) or water (electrolysis)

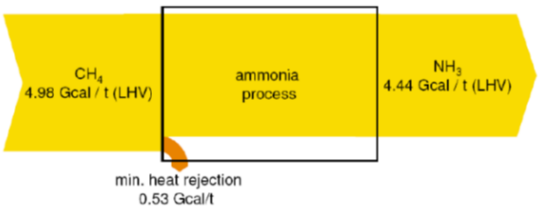


1909

2013

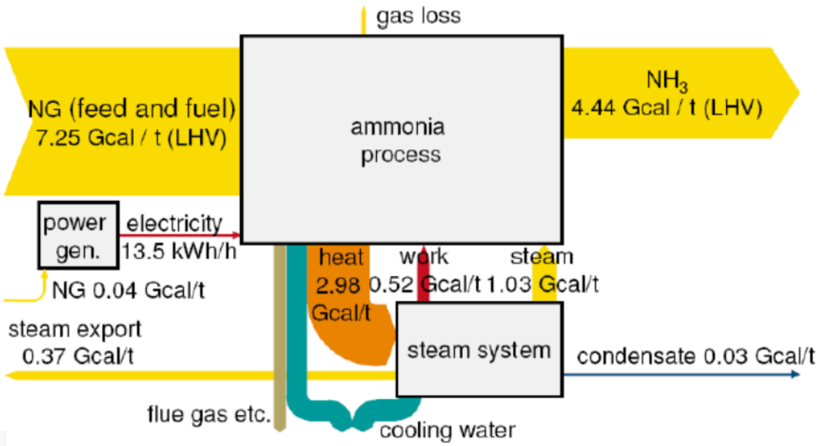
Today’s Haber-Bosch process

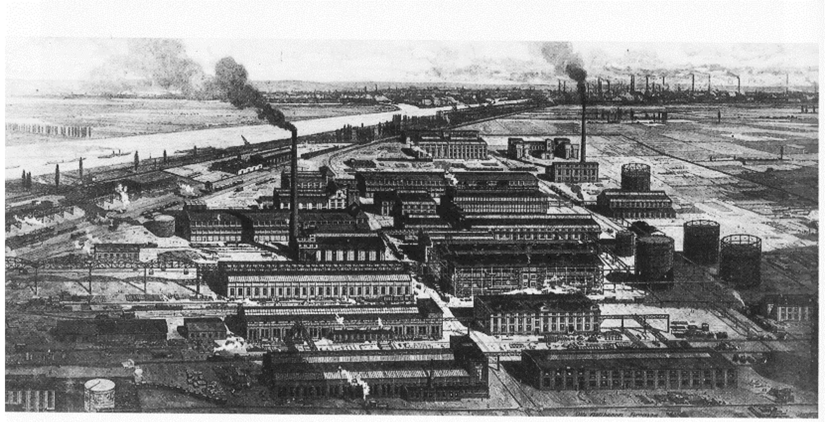
Theory



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

Practice




Die Ammoniakfabrik der BASF in Oppau. Gemälde von Otto Bollhagen, 1914. Ludwigshafen, Unternehmensarchiv BASF

First NH_3 plant in Oppau, 9,000 tons/year

BASF plant in Ludwigshafen, 875,000 tons/year

- **Efficiency still needs improvement**
- **Gigantic plant size to be economical**

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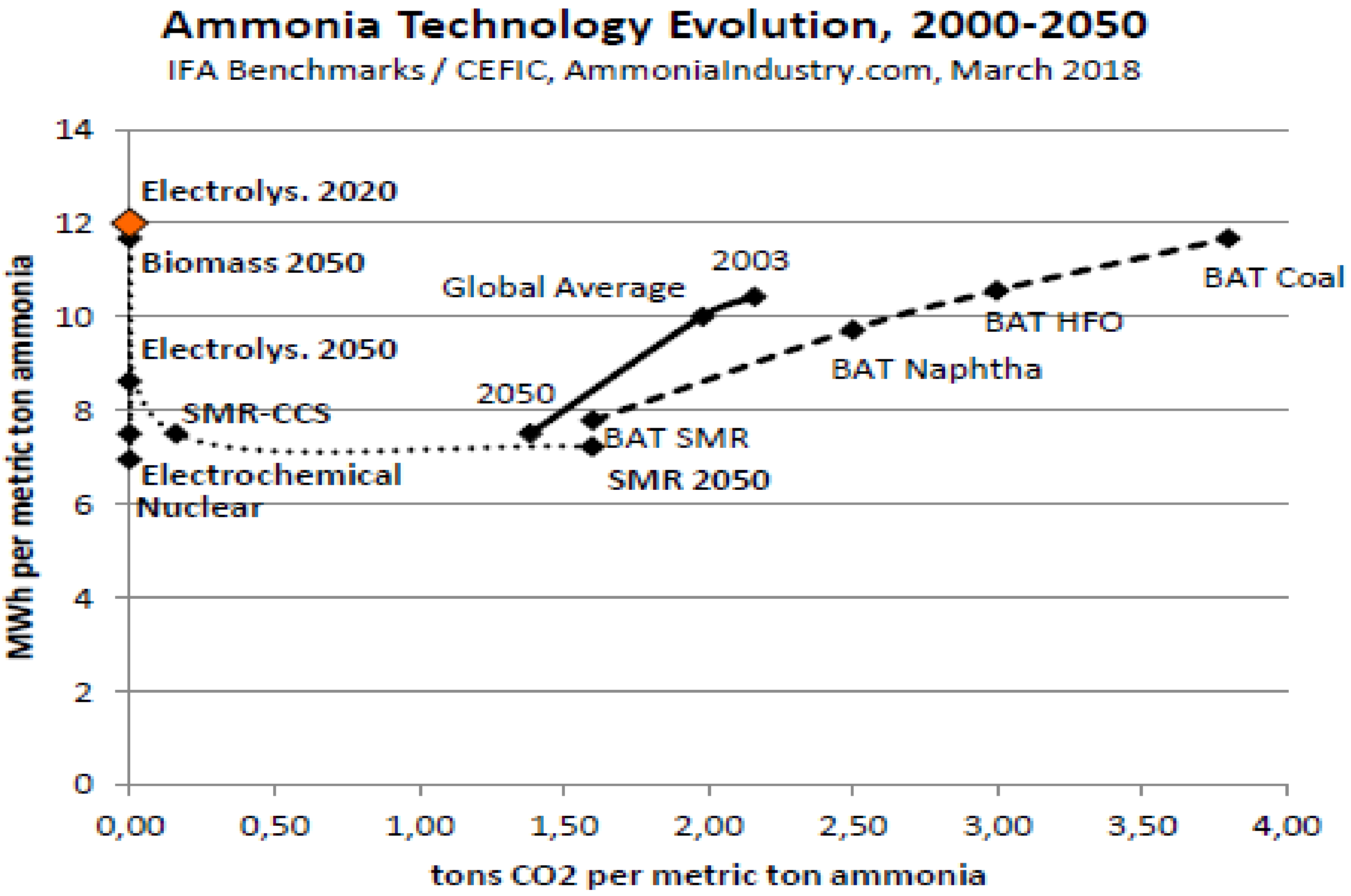
Ammonia production emissions



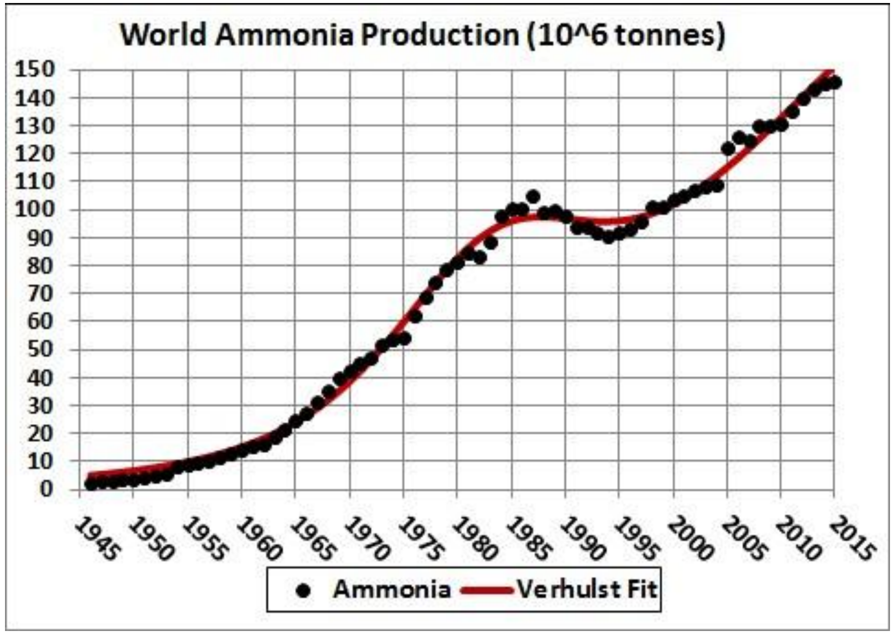
- Ammonia synthesis constitute 1.44% of global CO_2 emissions
- The global average is 2.86 ton CO_2/ton NH_3 (1.6 for the most efficient plants)

Current ammonia production

Ammonia Plant (1850 metric tons per day)

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



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

Disconnect between ammonia production scale and scale of renewables generation

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

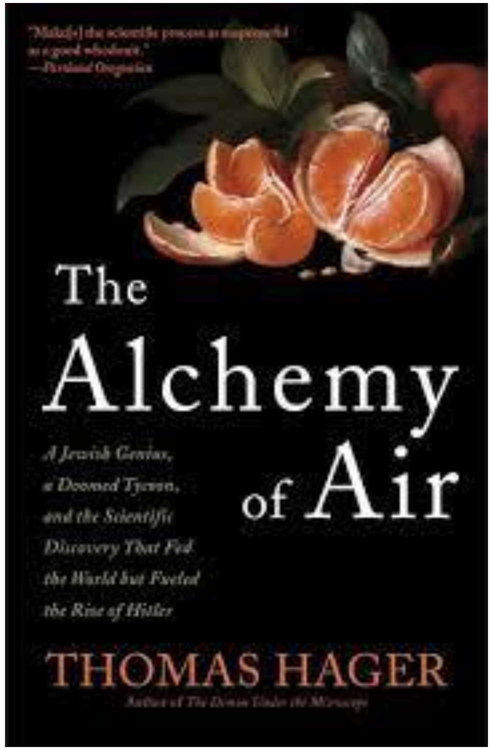
Ammonia as fertilizer

85% of ammonia used as fertilizer and fertilizer feedstock

- other applications: chemical feedstock, refrigeration, explosives

Only because of synthetic ammonia availability humankind is growing

- 80% of the nitrogen in human body has been through the Haber process!
- ammonia used as anhydrous or converted to urea and nitrates



Energy vectors for zero-carbon economy

Requirements

- Zero or low carbon emissions in life cycle
- Production scale of millions tons a year
- Availability of feedstock
- International commodity
- Easy storage
- Developed infrastructure
- Wide variety of utilizations
  - Transportation fuel
  - Electricity generation
  - Heating
- Energy cost competitive with fossil fuels

Ammonia as energy vector

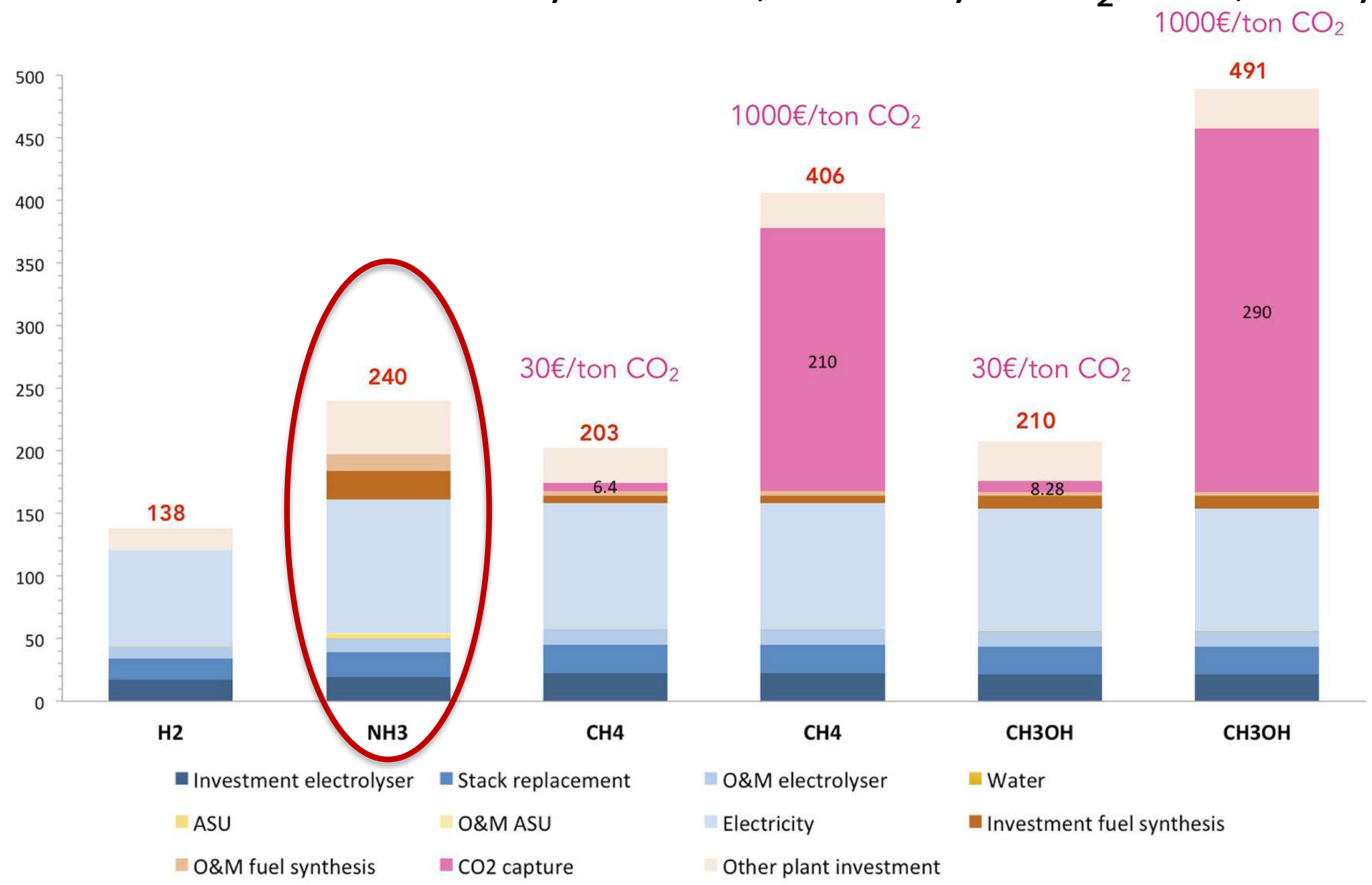
- Truly zero-carbon fuel
- Energy dense (liquid):
  - 4.3 kWh/L, 5.25 kWh/kg
  - 17,75% hydrogen, 121 kg H/m^3
- World production 180MM tons per year (~1,000,000 GWh)
- Can be stored indefinitely as liquid at 10 bar or -33^{o}C
- Well developed infrastructure
- Can be utilized by multiple ways (electricity, motive power, H_2 carrier)
- Excellent safety record

Low-carbon fuels comparison

Fuel	Energy density, kWh/L	B.p., deg C	Feedstock availability	Production efficiency, %	Storage cost	Transportation	Use
Compressed H_2	1.5	gas	High	65	high	Pipeline, tube trailer	Fuel cells
Liquid H_2	2.5	-253	High	39	high	Tanker	Fuel cells
Ethanol	6.3	78	Medium	50	low	Tanker, rail, truck	Fuel cells, ICEs
Synfuel	9.7	69-200	Low	31	low	Tanker, truck, rail, pipeline	Turbines, ICEs
Renewable methane (liq)	6.2	-162	Low	61	high	Pipeline, tanker	Turbines, ICEs, burners
	4.3	-33	High	55	**medium**	All the above	All the above

Production cost of renewable fuels

Production costs for each fuel in €/MWh fuel, with 30 €/tonCO_2 and 1,000 €/tonCO_2.



V. Diaz, et al. *Front. Mech. Eng.*, 2020, https://doi.org/10.3389/fmech.2020.00021

Drivers for zero-carbon ammonia

- **Decarbonization of fertilizers production – decrease carbon intensity of food and biofuels - ammonia synthesis constitute 1.44% of global CO_2 emissions**
- **Decarbonization of transportation fuels**
  - maritime shipping presents the greatest opportunity
  - hydrogen generation from ammonia enables remote FCEV fueling stations
- **Energy delivery**
  - the least expensive way for long distance energy delivery
- **Need in long duration energy storage**
  - offsetting intermittency of renewable energy sources
  - utilize unused generating capacity and waste heat of nuclear plants
- **Decarbonization of industrial processes**
  - replace fossil fuels in heat intense processes (steel/cement/grain drying)
- **Falling renewable electricity price makes zero-carbon ammonia cost competitive**

Benefits

Benefits of using low carbon ammonia

- **Lower carbon footprint for agriculture, transportation and industrial sectors**

  - Use of renewable hydrogen enables over 80% reduction in life cycle emissions of ammonia production, relative to conventional Haber-Bosch using SMR

  Source: https://pubs.rsc.org/en/content/articlelanding/2020/gc/d0gc02301a#!divAbstract

- **Effectively utilize surplus of renewable energy sources**

  - From 3 to 30% of wind and solar generation curtailed in California

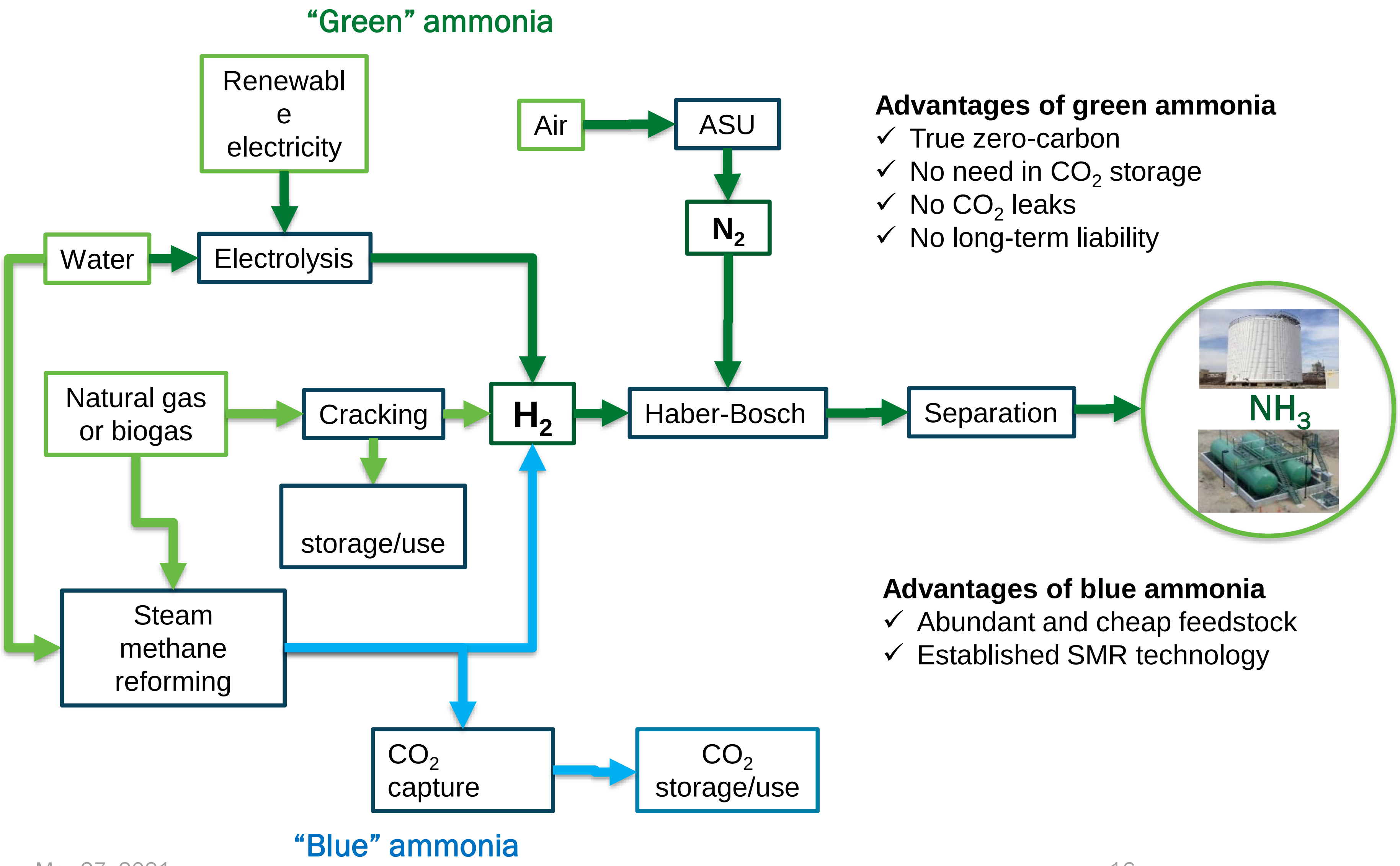
  Source: https://www.caiso.com/documents/curtailmentfastfacts.pdf

- **Enable long term energy storage**

  - Global energy storage capacity to grow at CAGR of 31% to 2030 to reach 740 GWh

  Source: https://www.woodmac.com/press-releases/global-energy-storage-capacity-to-grow-at-cagr-of-31-to-2030/

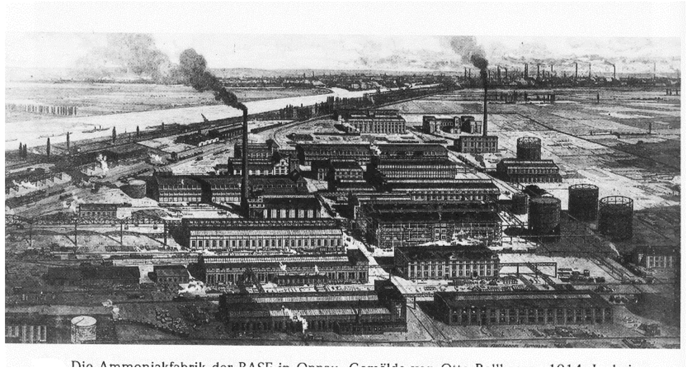
Zero-carbon ammonia synthesis

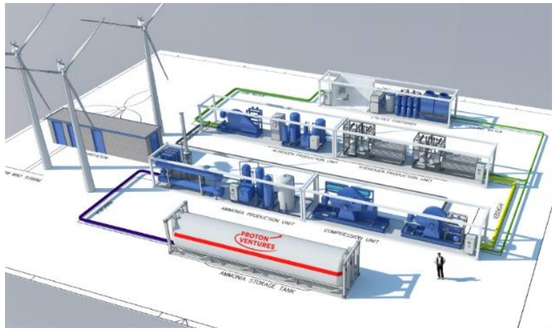


Advantages of green ammonia
- ✓ True zero-carbon
- ✓ No need in CO_2 storage
- ✓ No CO_2 leaks
- ✓ No long-term liability

Advantages of blue ammonia
- ✓ Abundant and cheap feedstock
- ✓ Established SMR technology

Up and down in scale of ammonia production





Proton Ventures, 1000 – 20,000 tons/year
http://www.protonventures.com/projects/

Yara BASF Ammonia Plant, Freeport Verbund, TX

750,000 metric tons per year

Siemens Green Ammonia Demonstrator at the Rutherford Appleton Laboratory (UK)

10 metric tons per year

Liquid ammonia transportation

US Ammonia pipeline network

- Multiple means…
- Pipeline transportation is the most cost effective

Use of ammonia for energy storage

Storage options for 200 MWh electric (plus 600 MMBtu CHP heat)

30,000 gallon underground tank

Capital cost ~$100K

= 6 x

or

1,000kg H_2 Linde storage in Germany

Capital cost ~$1,500K

100,000 MWh

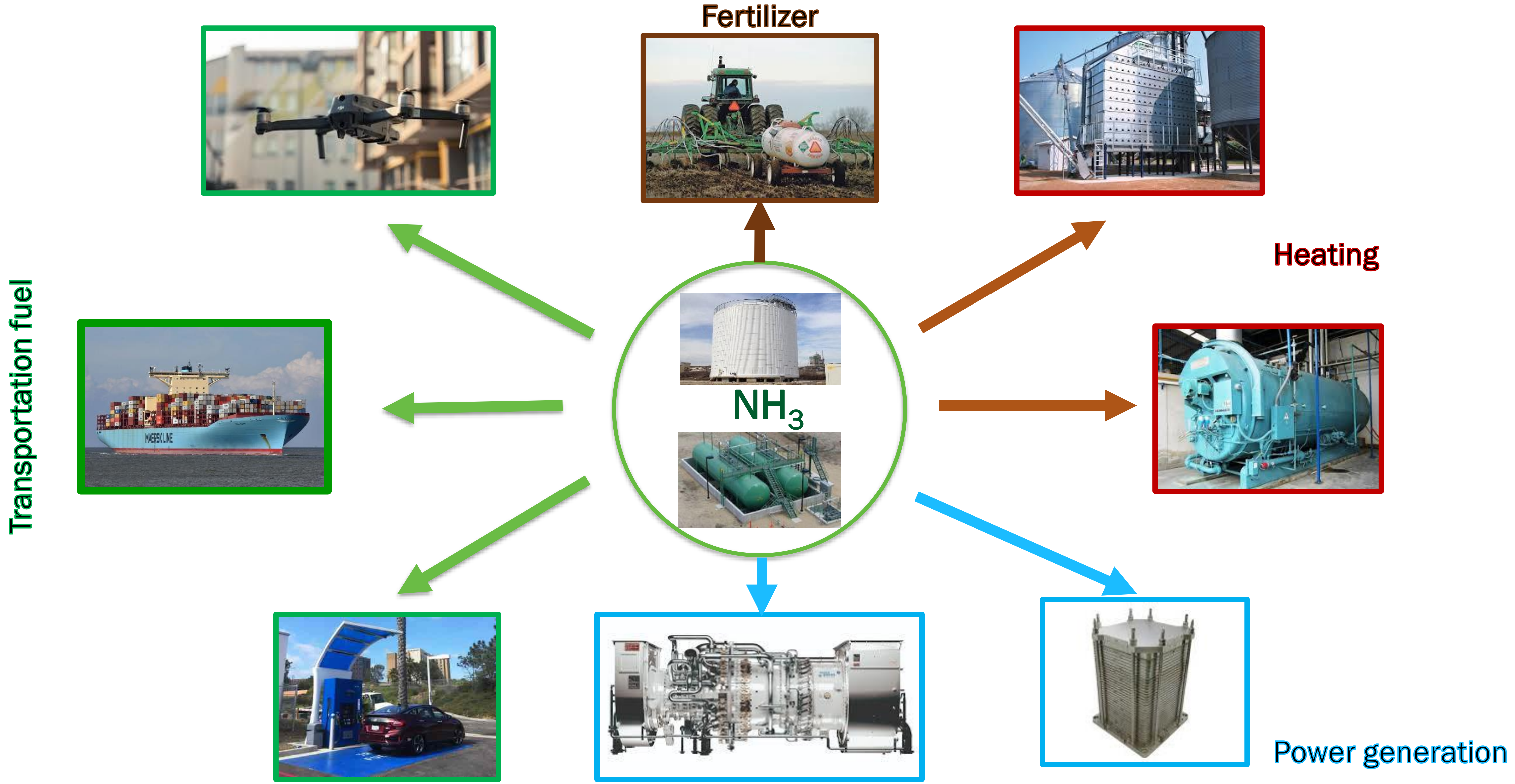
or 40 x

5 MWh A123 battery in Chile

Capital cost $50,000 - 100,000K

Liquid ammonia provides smallest footprint and CAPEX

Zero-carbon ammonia use



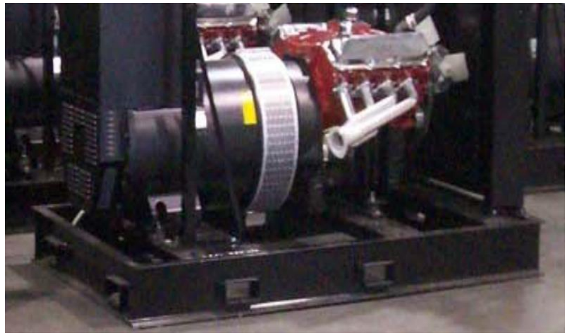
Ammonia as fuel: first attempts

Norsk Hydro, Norway, 1933

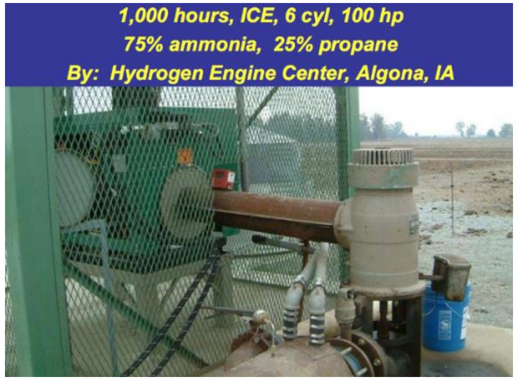
Belgium, 1943

Ammonia powered X-15 rocket plane (1955 – 1969)

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



HEC-TINA 75 kVA NH_3 Generator Set



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

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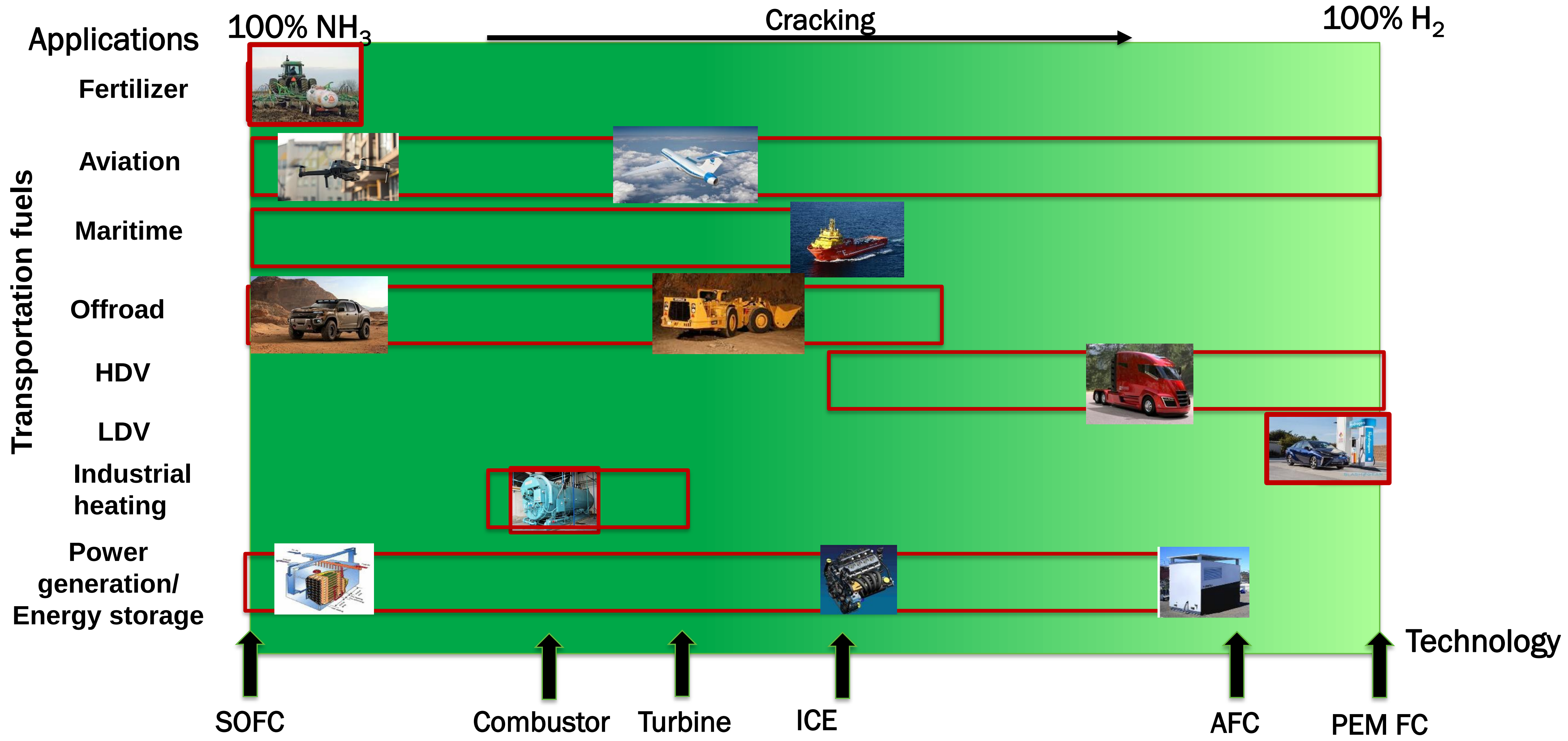
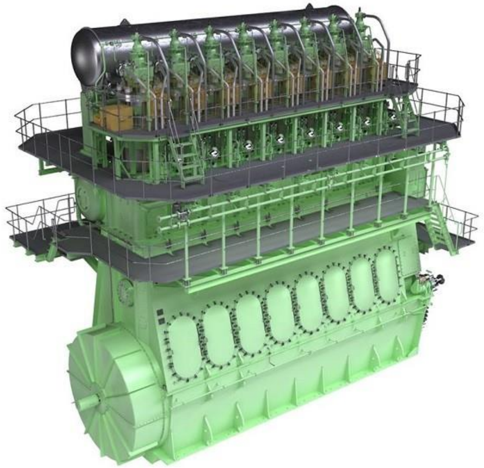
Zero-carbon ammonia application space



Ammonia as fuel: current status

Wartsila 4 stroke engine fueled by NH3, 2020

https://www.swzmaritime.nl/news/2020/06/30/marine-engine-to-be-tested-running-on-ammonia/?gdpr=deny



MAN 2 stroke engine fueled by NH3, 2020

https://man-es.com/marine/products/

John Deere 6400 tractor fueled by NH_3, Morris, MN, 2019

https://www.mprnews.org/story/2019/06/19/can-fertilizer-fuel-greener-tractors

Mitsubishi Power 40-MW class ammonia gas turbine, 2021

https://www.powermag.com/mitsubishi-power-developing-100-ammonia-capable-gas-turbine/

IHI 70% liquid NH_3 cofiring 2MW-class gas turbine, 2020

https://www.ihi.co.jp/

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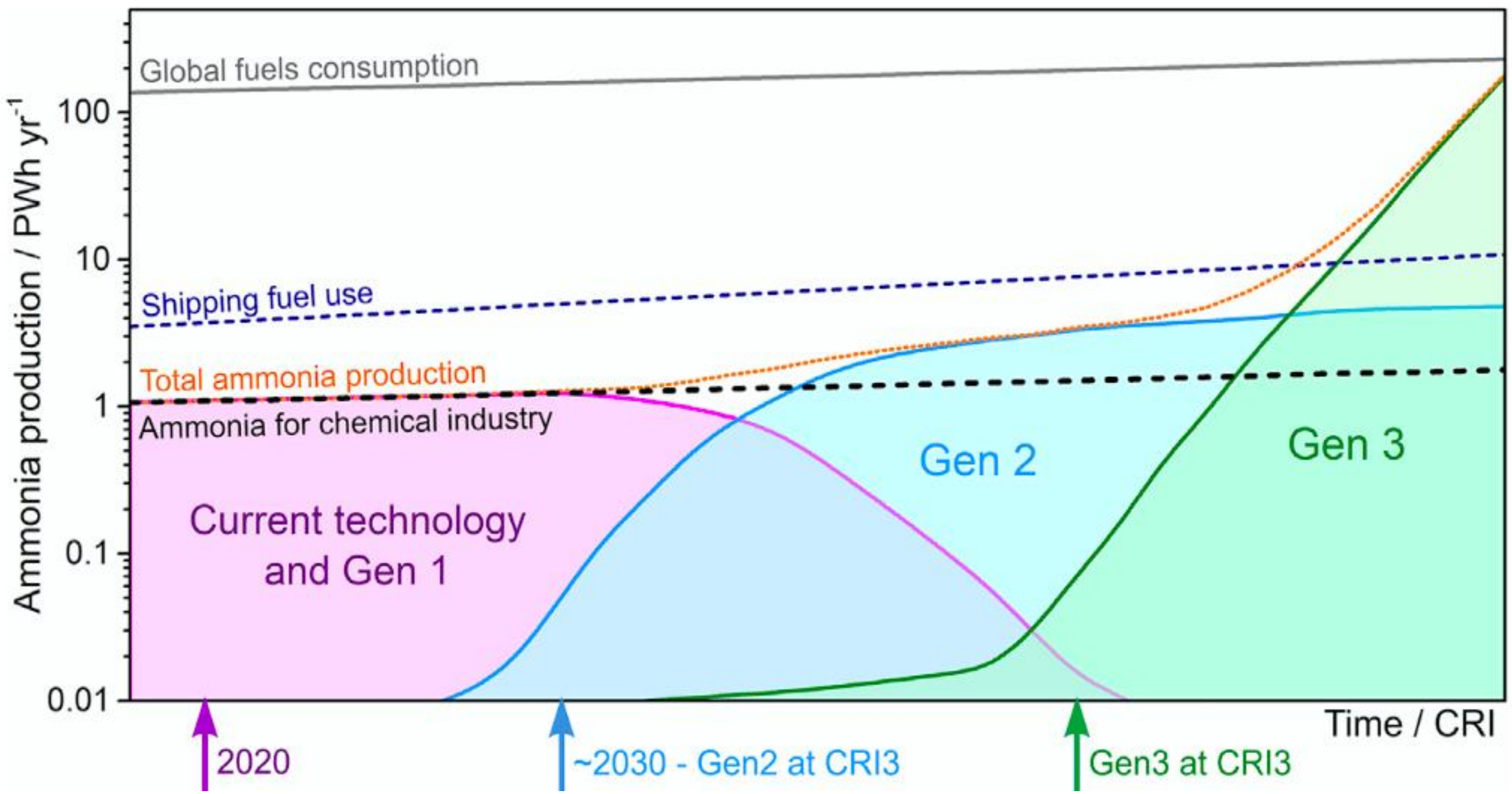
Zero-carbon ammonia market potential

- **Currently ammonia is used mostly for fertilizers and chemicals production**
- **Market size is $71.2B in 2019 and expected to grow to $81.4B by 2025 at a CAGR of 5.59%**
- **Green and blue ammonia predicted CAGR is 54.9%**
- **Green and blue ammonia will dominate by 2050**
- **The use as maritime fuel will triple current ammonia production by 2050**
- **The use for energy storage and hydrogen delivery will multiply this number even further**



MacFarlane et al., A Roadmap to the Ammonia Economy, *Joule*, 2020

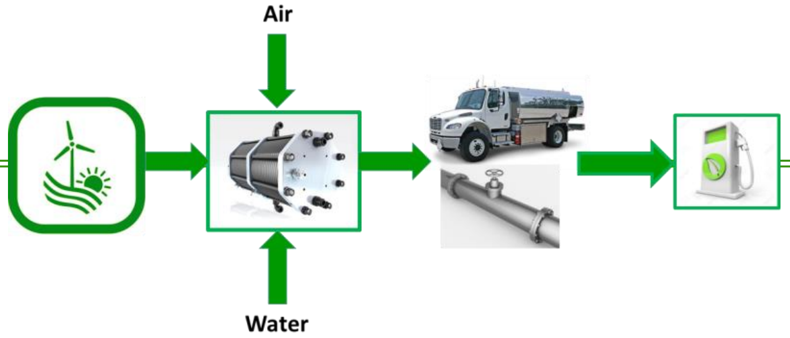
Research needs

Major goal to decrease CAPEX and increase energy efficiency

- **Research focus:**
  - synthesis: catalysts, direct synthetic methods, ammonia separation
  - utilization: fuel cells, cracking, low NOx
- **Development focus:**
  - heat integration of all process steps
  - algorithms for transient operations
- **Deployment focus:**
  - demonstration of whole system in the field
  - scaling up

REFUEL

Renewable Energy to Fuels through Utilization of Energy-dense Liquids



Mission

Reduce transportation and storage costs of energy from remote renewable intermittent sources to consumers and enable the use of existing infrastructure to deliver electricity or hydrogen at the end point

Program Director	Dr. Grigorii Soloveichik
Year	2017
Projects	16
Total Investment	$36 Million

Investment areas and impacts

1. **Area:** Small- to medium-scale synthesis of energy-dense carbon-neutral liquid fuels using water, air, and renewable energy source.
   Impact: Develop technologies to produce fuels at cost <$0.13/kWh to enable long term energy storage.

2. **Area:** Electrochemical processes for generation of hydrogen (2a) or electricity (2b) from energy-dense carbon-neutral liquid fuels.
   Impact:
   a) Develop catalytic or electrochemical fuel cracking to deliver hydrogen at 30 bar at the cost < $4.5/kg enabling hydrogen fueling stations;
   b) Develop fuel cell technologies for conversion of fuels to electricity with source-to-use cost <$0.30/kWh .

Portfolio – technology matrix for Category 1

Thermal (catalytic) processes (1a)

	Equilibrium shift	Catalyst/Reactor design
Hydrogenation catalyst (e.g. Haber-Bosch)	M; gti; School of Mines 1874 Colorado	RTI International; Starfire Energy Making Sustainable Energy A Reality
Physical effects (e.g. plasma)	Johns Hopkins University	WV

Electrochemical processes (1b)

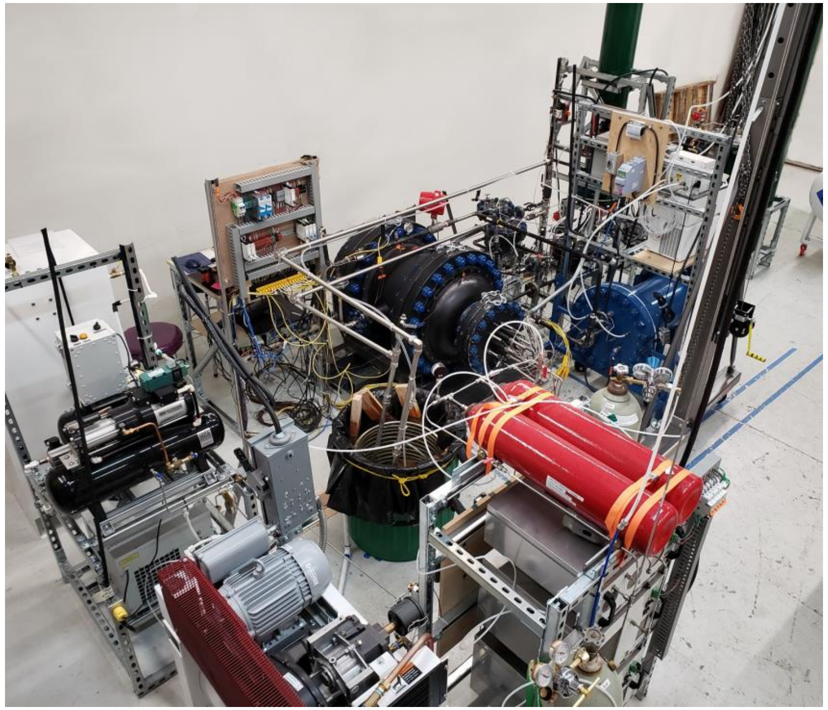
	PEM	AEM
Low temperature (<120 C)	Sustainable Innovations; parc A Xerox Company; OPUS 12	wsu; storaGENergy technologies; GINER
	FuelCell Energy; The University of New Mexico	MoleculeWorks Efficiency for a Sustainable World

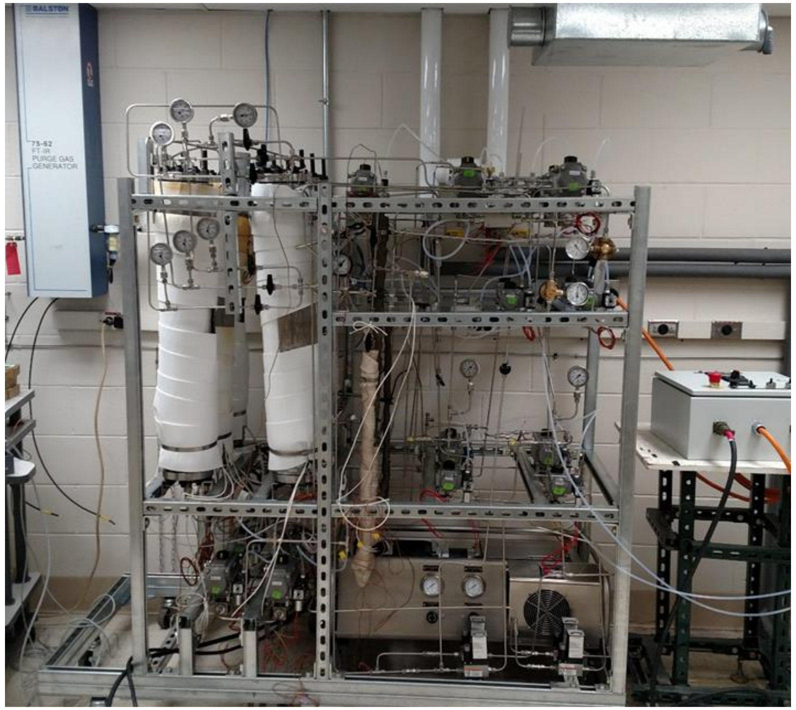
Ammonia

Carbon based

Seedling

REFUEL bench-scale process demonstration





- Integrated 10 kg/day system
- Capable of operation up to 500°C/100 bar
- Unattended operation, remote monitoring
- Can simulate intermittency, ~1400h on stream

- Integrated >10 kg/day unit
- Complete system with AEM electrolyzer and ASU
- High activity monolith catalyst
- Capable of operation at 30 bar

- Integrated 1 kg/day system
- Capable of operation at 30 bar
- Adsorbent capacity stable for 100 cycles
- Operation time over 500 hours

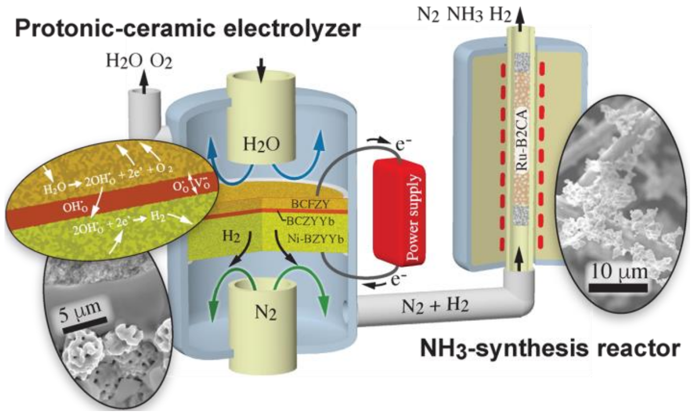
RTI INTERNATIONAL

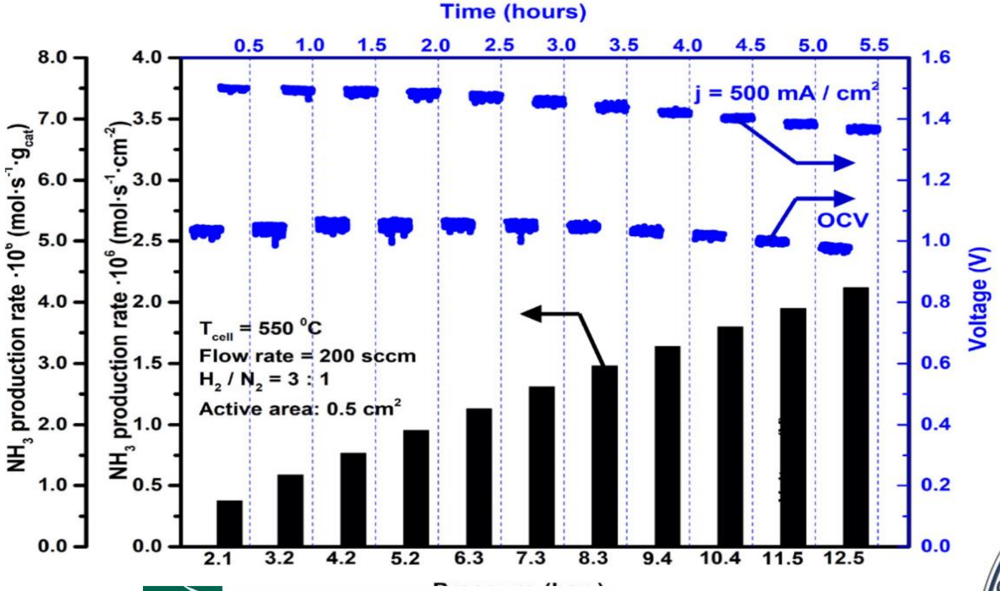
Starfire Energy
MAKING SUSTAINABLE ENERGY A REALITY

UNIVERSITY OF MINNESOTA

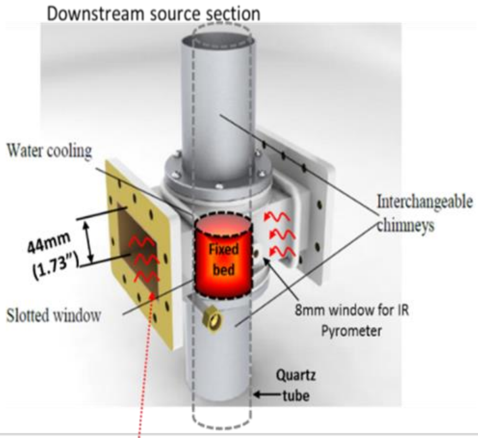
REFUEL: load following ammonia synthesis

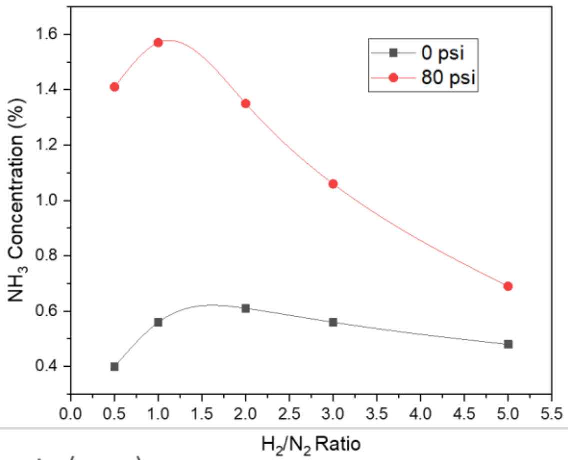
Chemical/electrochemical synthesis of ammonia

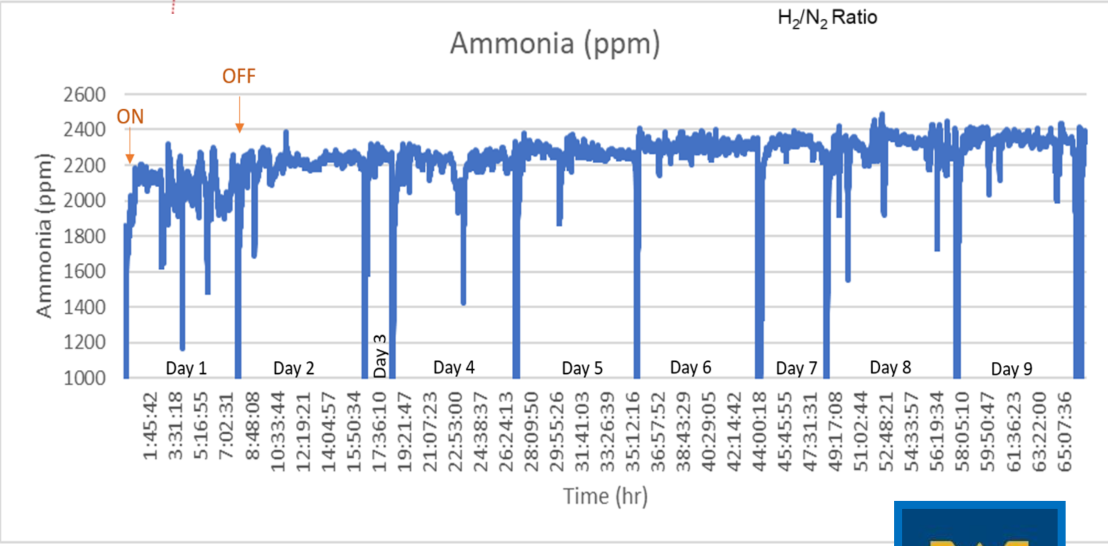




Microwave catalytic synthesis of ammonia







FuelCell Energy
Ultra-Clean, Efficient, Reliable Power

REFUEL

16 Project Teams • 3 Technology Areas

Portfolio – technology matrix for Category 2

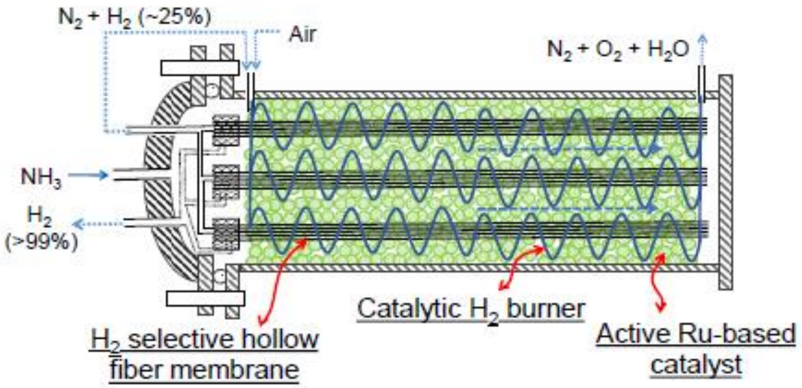
Hydrogen generation (2a)		
	Cracking reactor	Photo/electrochemical cell

Conversion to electricity in fuel cell (2b)			
	PEM	AEM	SOFC
Low temperature (<120 C)			
High temperature (>250 C)			

REFUEL: hydrogen generation from ammonia

Solid Acid NH_3 Stack

- 10 cell @ 400 mA/cm^2
- ~0.4 kg H_2/day @ 30 bar
- 750 hours stable run
- 3-6 kWh/kg H_2
- 100% pure hydrogen



Parameter	Achieved
Energy efficiency	87%
H_2 purity	>99.9%
Deliver volumetric rate	0.47 g H_2/h/cm^3
NH_3 conversion	>99.5%
NH_3 concentration in H_2	<10 ppb

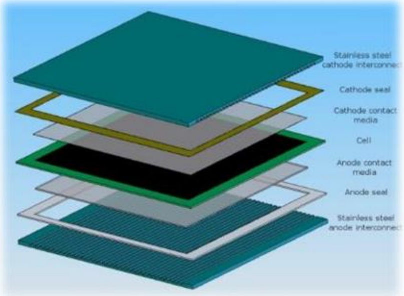
Rensselaer

Robust metal doped zeolite membrane

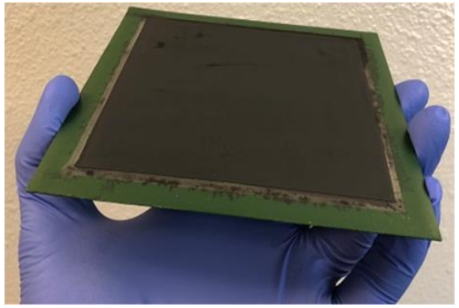
Parameter	Achieved
Temperature, oC	450-550
Pressure, bar	10
Membrane, cm^2	>100
Selectivity, %	>75
Membrane life, h	5,000
Catalyst life, h	>500
Conversion, %	>99

BETTERGY Clean Energy for Better Life™

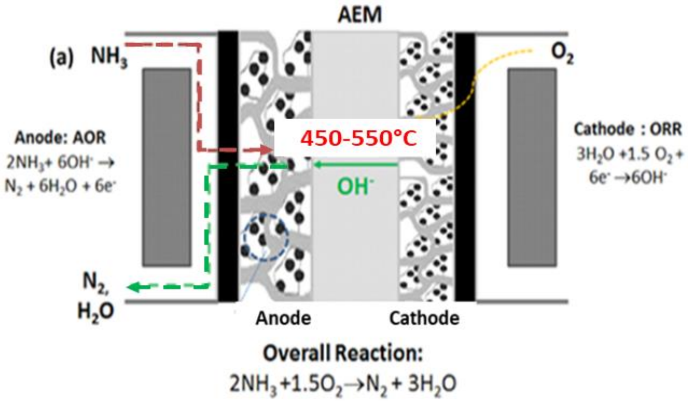
REFUEL fuel cell projects

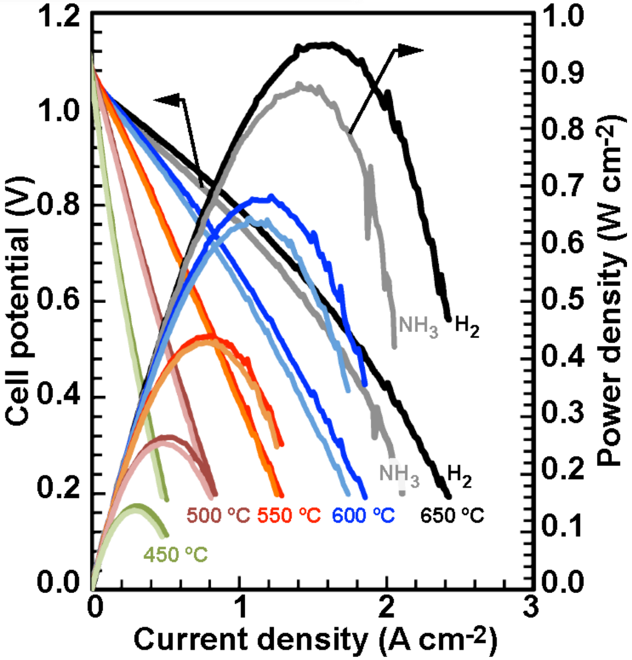


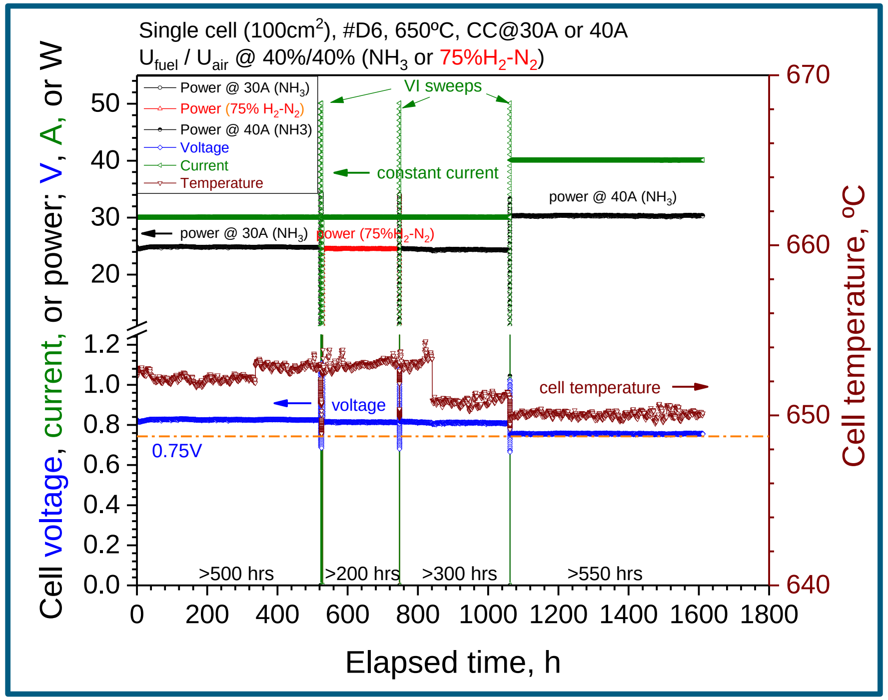
Fuel-cell performance under NH_3 reaches 90% of performance under H_2

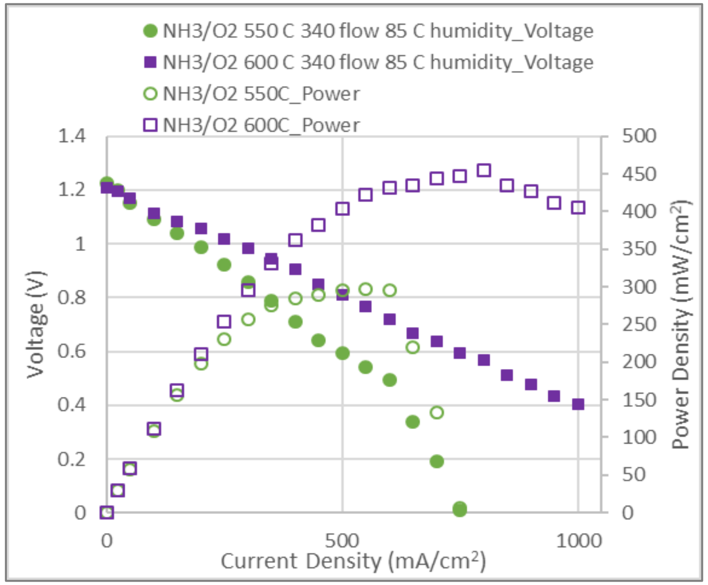


Cell temperature @ 650ºC
> 1600 hours of operation
> 550 hs with NH_3 @ 40A
Cell voltage ≥ 0.75V







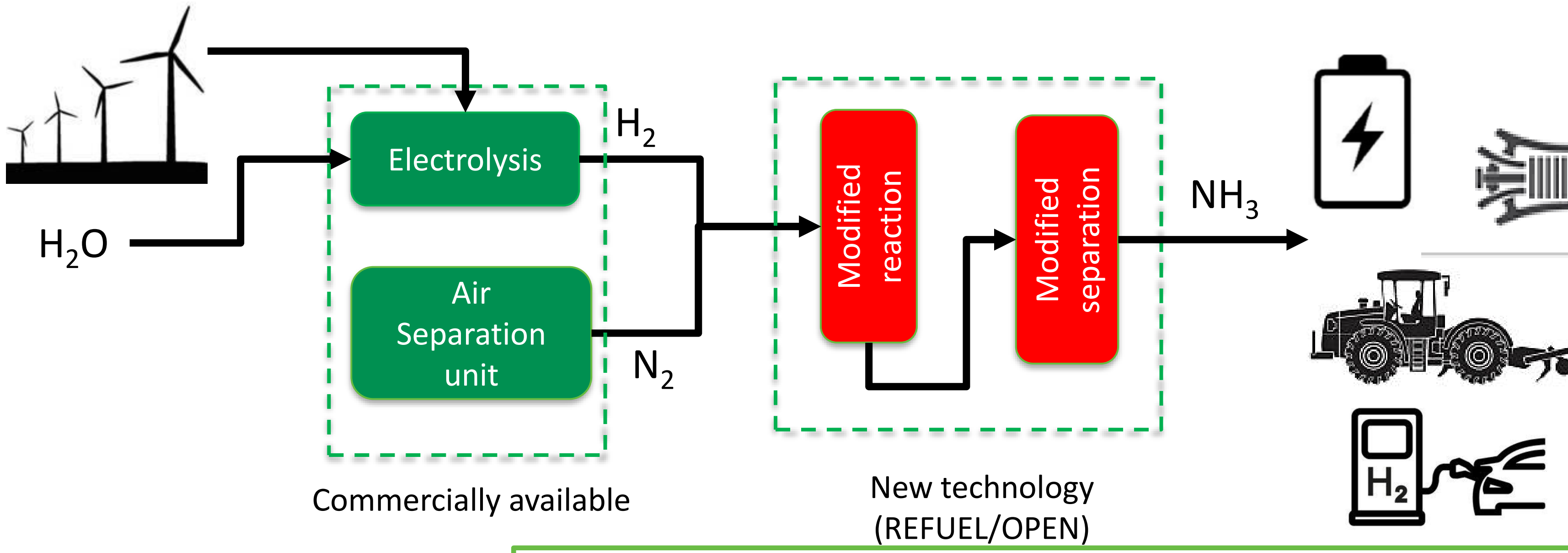


FuelCell Energy
Ultra-Clean, Efficient, Reliable Power

Chemtronergy

REFUEL+IT (Integration and Testing) Program

- Leverages success of several REFUEL projects in NH_3 synthesis and isolation
- Utilizes excess renewable power that would otherwise be curtailed ("load following")
- Low carbon ammonia can be used for agriculture, energy storage and transportation
- Target scale: ~1 ton/day, ~500kWh of renewables; estimated cost ~ $ 15MM
  - Test site location: wind and solar farm site(s)
  - Slipstream for demonstration of ammonia use (hydrogen production and ammonia fuel cells)



A modular, flexible plant to validate technologies in real life

RTI INTERNATIONAL
CASALE
UNIVERSITY OF MINNESOTA MORRIS
nel
GE Global Research
Chemtronergy

World attitude shifts to low carbon ammonia

Multiple feasibility studies

- Japan (Strategic Innovation Promotion Program): added ammonia to technology roadmap
- The Netherlands (ISPT): Power to Ammonia (2017)
- UK (Royal Society): Ammonia: zero-carbon fertilizer, fuel and energy store (2020)
- US (KBR, EPRI): Energy transitions and Renewable ammonia (2020)
- UK (BEIS): Ammonia to Green Hydrogen Project (2020)
- Australia (ARENA, SCIRO, Queensland Nitrates: Green Ammonia (2020)
- EU (ARENHA - Advanced materials and Reactors for ENergy storage tHrough Ammonia): consortium of 11 partners (2020)

Green/blue ammonia on the roadmap of major ammonia players

- Casale
- CF Industries
- Haldor Topsoe
- KBR
- Nutrien
- thyssenkrupp Industrial Solutions
- Yara

Green/blue ammonia demonstration projects

Fukushima Renewable Energy Institute – AIST (Japan)
- Runs 20 kg/day green ammonia demonstration

Haldor Topsoe's (the Netherlands)
- Plans to build 1-2 t/d all-electric SOEC ammonia plant in 2025

Yara and ENGIE (Australia)
- 10 MW solar-powered 7,000 t/y green ammonia plant funding approved

Yara and Ørsted (the Netherlands)
- Will jointly develop a 100 MW off-shore wind-powered 75,000 t/y green ammonia plant

CF Industries (US)
- Board-authorized green ammonia project ($450MM) to be built at the Donaldsonville Nitrogen Complex

KBR (US)
- Green ammonia process (K-GreeN™) under development

Monolith Materials (US)
- Announced plan to build 275,000 tons a year of carbon-free anhydrous ammonia using hydrogen from methane pyrolysis.

Ammonia as energy vector summary

- **Truly zero-carbon, energy dense (1.7x of liquid H_2) fuel**
- **Global commodity (180 MM t/year), established delivery infrastructure**
- **Excellent safety record**
- **Least expensive storage and transportation (0.5x of NG)**
- **Can be utilized by multiple ways in wide application**
- **Potential to reduce global CO_2 emissions by 1.4% (green fertilizer) and far beyond (as energy carrier)**
- **Anticipated to be cost competitive with fossil fuels by 2040s**
- **Demo projects for green/blue ammonia companies planned by largest producers and shipping companies**
- **Increased investment in R&DD and global collaboration will accelerate progress**

Thank you!

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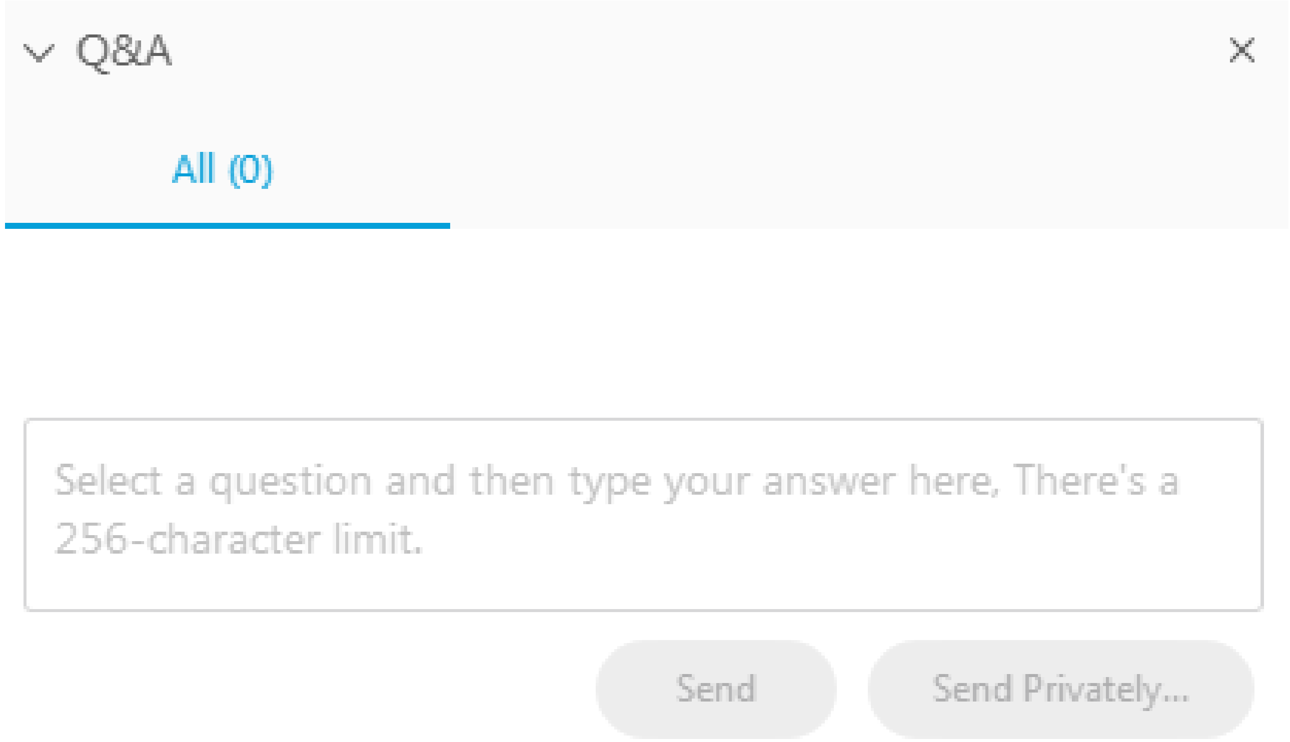
The #H2IQ Hour Q&A

Please type your questions into the **Q&A Box**



The #H2IQ Hour

Thank you for your participation!

Learn more:

energy.gov/fuelcells
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