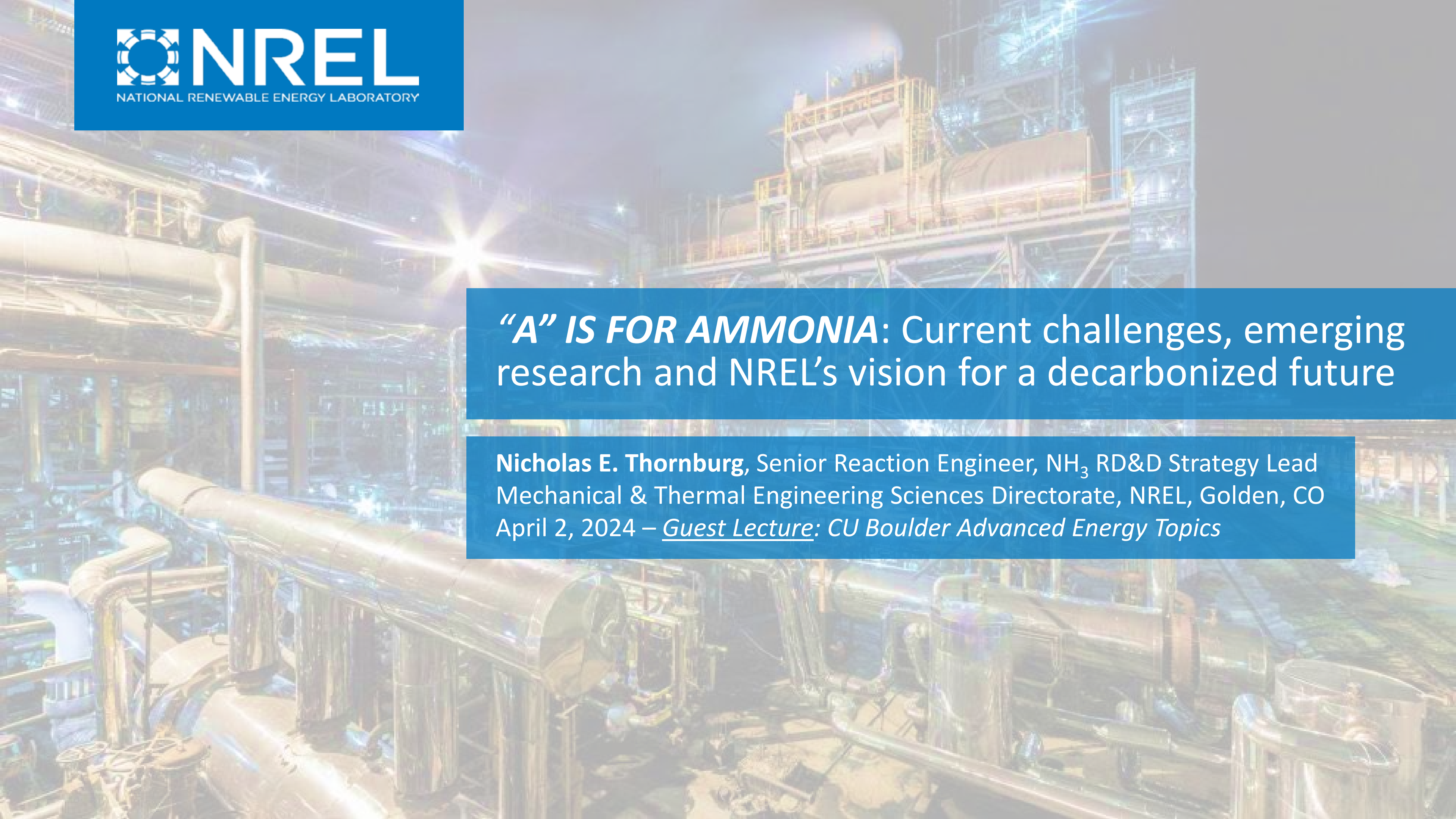


NATIONAL RENEWABLE ENERGY LABORATORY

“A” IS FOR AMMONIA: Current challenges, emerging research and NREL’s vision for a decarbonized future

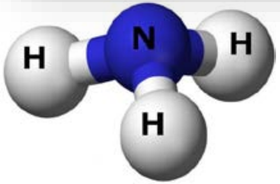
Nicholas E. Thornburg, Senior Reaction Engineer, NH_3 RD&D Strategy Lead
Mechanical & Thermal Engineering Sciences Directorate, NREL, Golden, CO

April 2, 2024 – *Guest Lecture: CU Boulder Advanced Energy Topics*

The (infamous) Haber-Bosch process

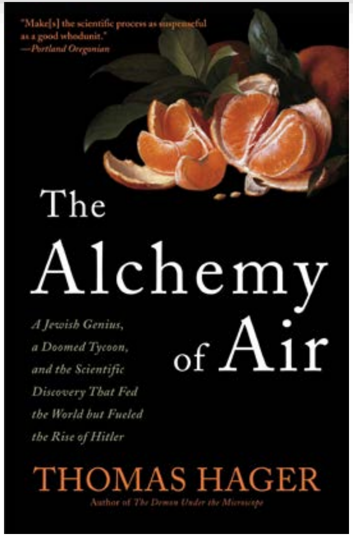
Global NH_3 production, by the numbers

- Direct synthesis from **N_2** (from distillation of air) and **H_2** (from steam reforming of methane (SRM))
- ~180 million t produced annually, with >80% relegated solely to nitrogenous fertilizers
- ***Consumes 1–2% of the global energy supply!*** *(and nearly ~5% of all natural gas produced)*
- Accounts for ≤3% of the world's carbon emissions → ~340 million t CO_2-e yr^{-1} (#1 of chemicals)



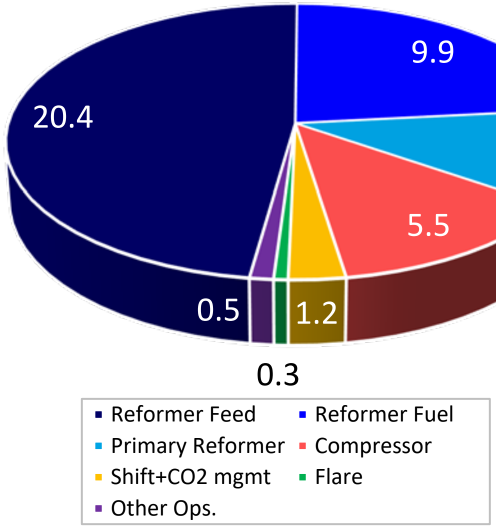
Haber-Bosch facts to impress (or scare) your friends at happy hour

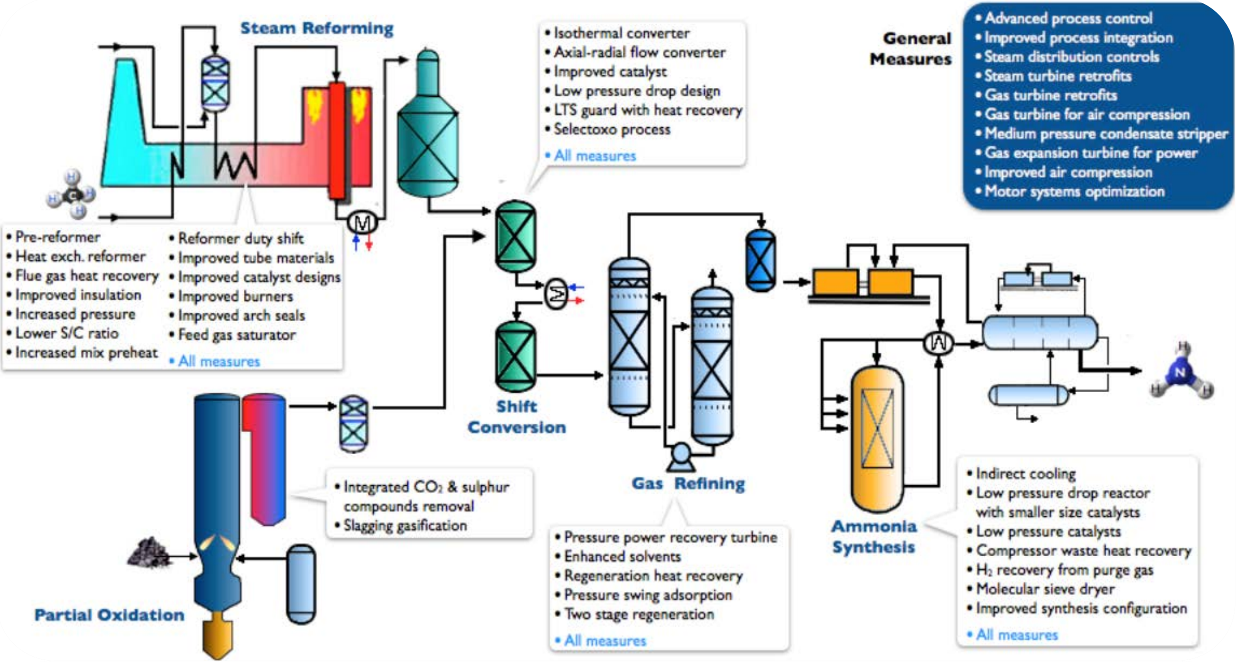
- ➢ Saved Germany's population in WWI (and, sadly, later enabled the evil of WWII and beyond…)
- ➢ Today… feeds >50% of the world's population
- ➢ Accounts for ~50% of N atoms in our bodies(!!)



Production statistics from *IHS Markit*. Happy hour statistics adapted from The Alchemy of Air (2008). Images from Google Images. Accessed 2020 September 8.

Estimated Energy Inputs in GJ (LHV) t^{-1} NH_3 for U.S. Ammonia Plants (*1996*)





Steam Reforming

- Pre-reformer
- Heat exch. reformer
- Flue gas heat recovery
- Improved insulation
- Increased pressure
- Lower S/C ratio
- Increased mix preheat

- Reformer duty shift
- Improved tube materials
- Improved catalyst designs
- Improved burners
- Improved arch seals
- Feed gas saturator
- All measures

Shift Conversion

- Isothermal converter
- Axial-radial flow converter
- Improved catalyst
- Low pressure drop design
- LTS guard with heat recovery
- Selectoxo process
- All measures

General Measures

- Advanced process control
- Improved process integration
- Steam distribution controls
- Steam turbine retrofits
- Gas turbine retrofits
- Gas turbine for air compression
- Medium pressure condensate stripper
- Gas expansion turbine for power
- Improved air compression
- Motor systems optimization

Partial Oxidation

- Integrated CO_2 & sulphur compounds removal
- Slagging gasification

Gas Refining

- Pressure power recovery turbine
- Enhanced solvents
- Regeneration heat recovery
- Pressure swing adsorption
- Two stage regeneration
- All measures

Ammonia Synthesis

- Indirect cooling
- Low pressure drop reactor with smaller size catalysts
- Low pressure catalysts
- Compressor waste heat recovery
- H_2 recovery from purge gas
- Molecular sieve dryer
- Improved synthesis configuration
- All measures

Opportunities to improve Haber-Bosch

- Numerous strategies proposed by academia and industry to lower the massive energy intensity of Haber-Bosch process
- Synthesis reactors operate at up to 300 atm and 550°C
- Catalysts are thermodynamically limited to low conversions *(and no, “new” thermochemical catalysts won’t change that)*

Pie chart values rendered from: I. Rafiqul, A. Voss et al., *Energy* 30 2487–2504 (2005). (*link*)
Process schematic adapted from: Industrial Efficiency Technology Database, “Ammonia.” Accessed 2020 September 8. (*link*)

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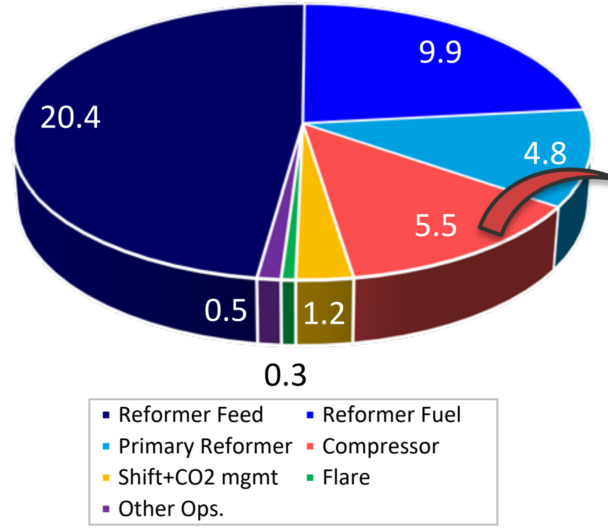

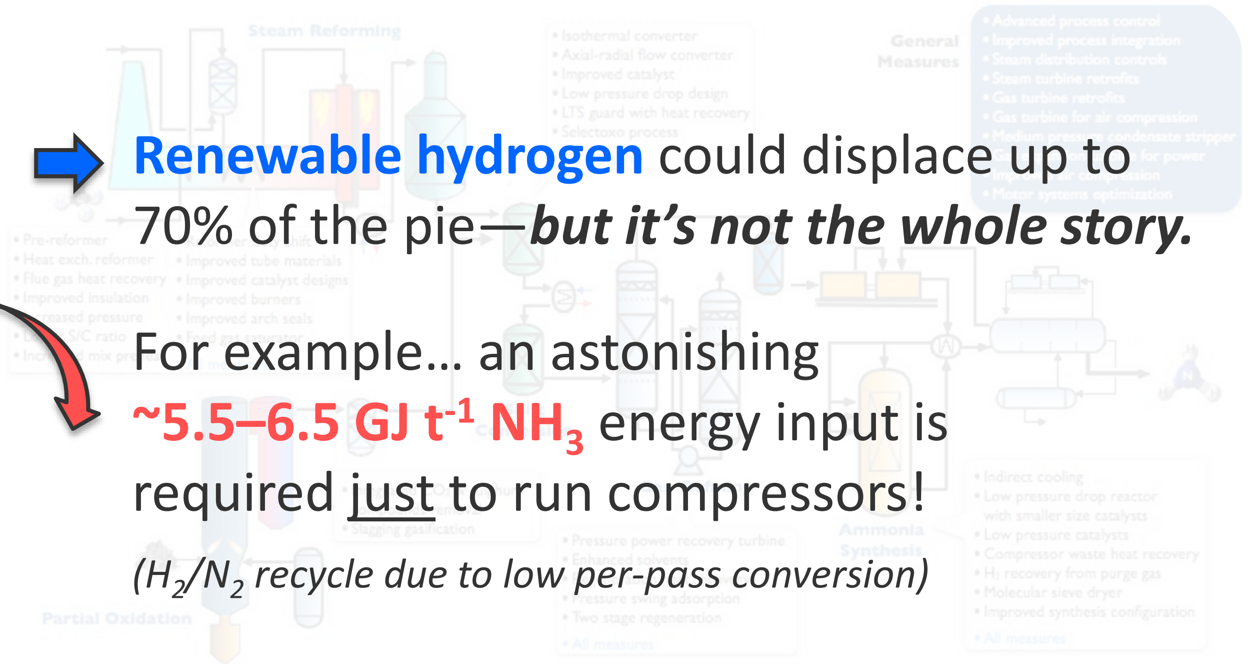

➡ **Renewable hydrogen** could displace up to 70% of the pie—***but it's not the whole story.***

For example… an astonishing **~5.5–6.5 GJ t^{-1} NH_3** energy input is required just to run compressors!

(H_2/N_2 recycle due to low per-pass conversion)

Opportunities to improve Haber-Bosch

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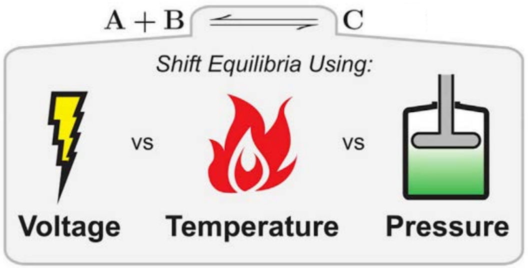
Process schematic adapted from: Industrial Efficiency Technology Database, "Ammonia." Accessed 2020 September 8. (*link*)

Could renewable e^- be used to make NH_3?

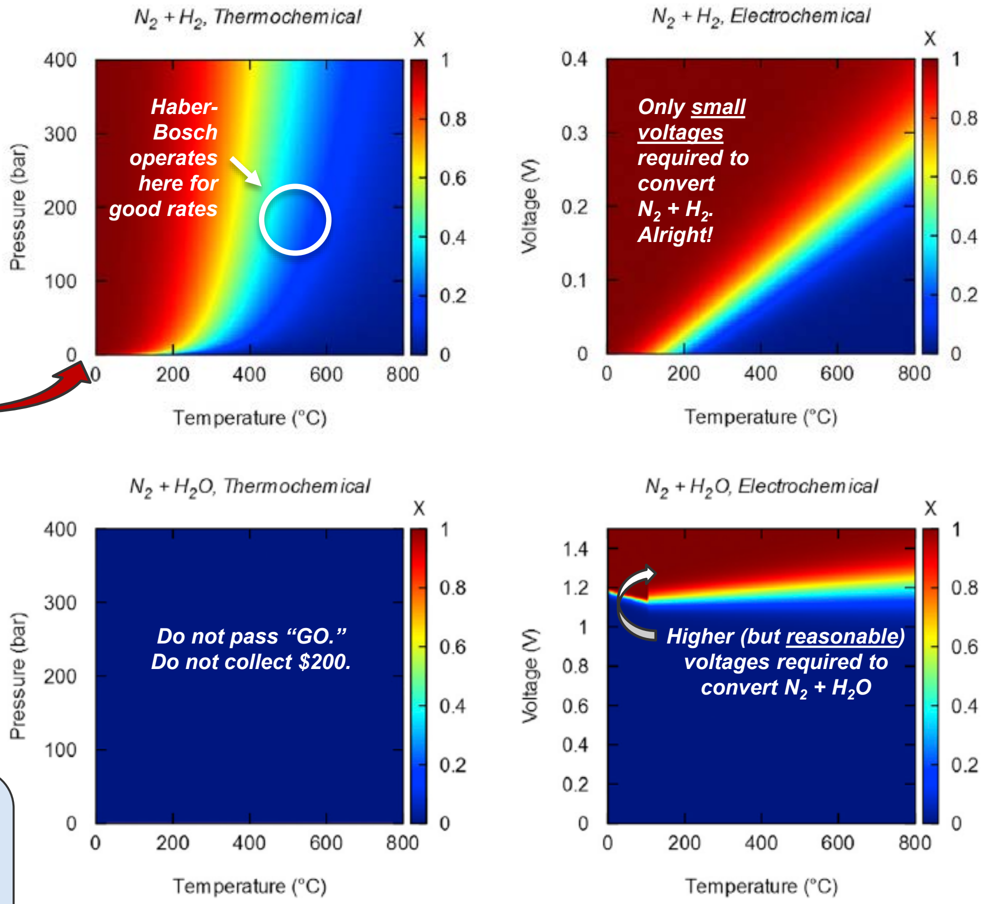
$$N_{2\,(g)} + 3\,H_{2\,(g)} \rightleftharpoons 2\,\mathbf{NH_3}\,_{(g)}$$

$$\Delta H_{rxn} = \mathbf{-45.9}\ \text{kJ mol}^{-1}$$

Red regions favor NH_3 formation



High T & P often mean giant capital investments!



Haber-Bosch operates here for good rates

Only small voltages required to convert $N_2 + H_2$. Alright!

Do not pass "GO." Do not collect $200.

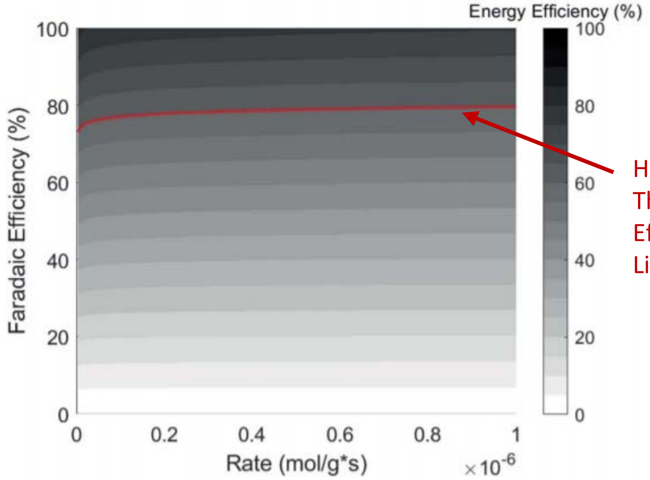
Higher (but reasonable) voltages required to convert $N_2 + H_2O$

Beware of low Faradaic efficiencies. New electrocatalysts must achieve intrinsically higher selectivity to N_2 reduction. (*Most would much rather make hydrogen!*)

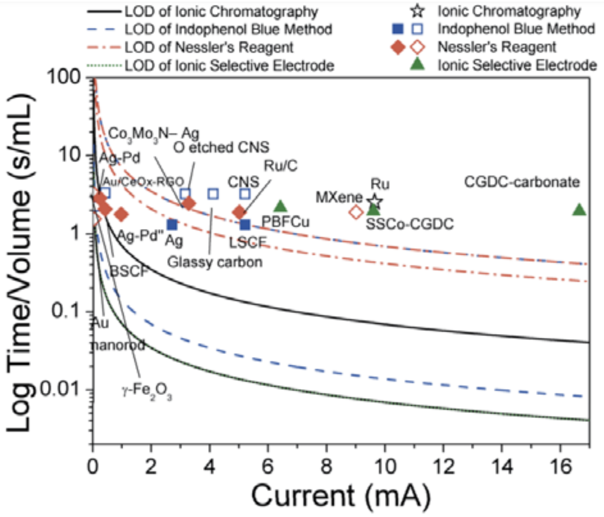
Figures adapted from: Z. J. Schiffer, K. Manthiram, *Joule* 1 10–14 (2017). (*link*)

Electrochemical routes and their challenges

- Electrochemical reactions scale areally, while thermochemical reactions scale volumetrically
- Energy efficiencies (~1%) are largely governed by the overall system faradaic efficiencies (FEs), which are a long way from Haber-Bosch (~60%)
  - However, optimizing solely FEs is often at the expense of the rate of ammonia production
- ➢ ***Increasing FE requires design of electrocatalysts with high selectivity for nitrogen reduction***
  - Unfortunately, the redox potential for nitrogen reduction is very close to the hydrogen evolution reaction (HER), and most electrocatalyst surfaces will preferentially bind H* and not N*
- Further, critical NH_3 measurement issues from ***false positives and/or easily reducible laboratory contaminants*** (e.g., NO_3^{2-}, NO_x), while isotopic $^{15}N_2$ gas is prohibitively expensive

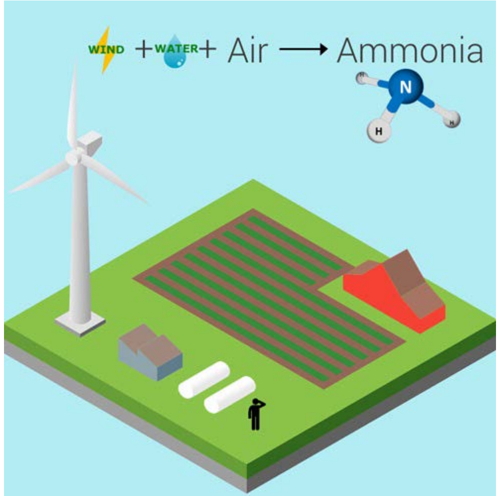


Haber-Bosch Theoretical Efficiency Limit

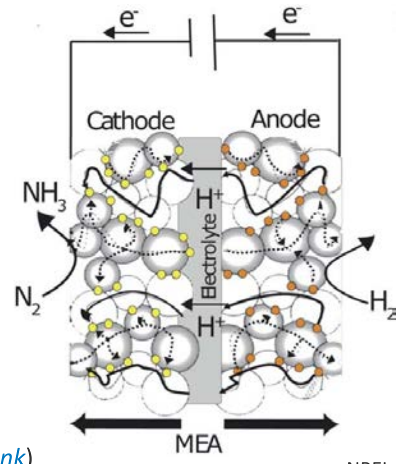


Figures and data adapted from: C. A. Fernandez, M. C. Hatzell et al., *J. Mater. Chem. A* 8 15591–15606 (2020). (*link*)

Emergent R&D trends in ammonia synthesis

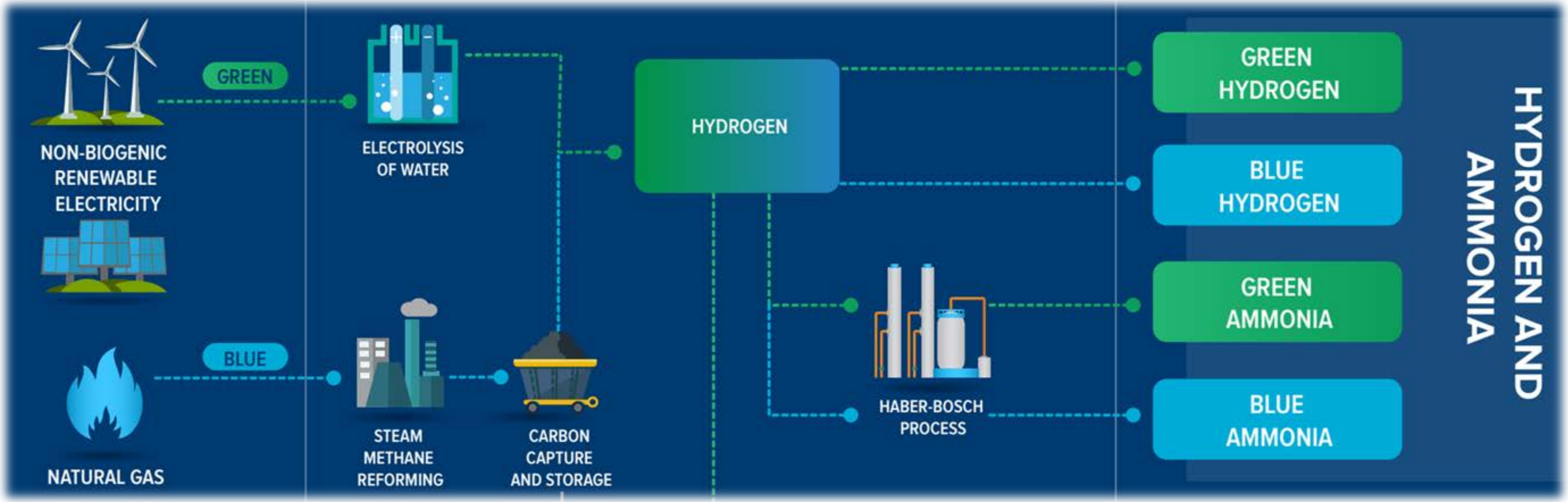


1. **Less-energy-intensive feeds and unit operations for Haber-Bosch**
   - Renewable hydrogen (e.g., from electrolysis)
   - Renewable electrification in lieu of steam/nat. gas
   - Energy efficient ammonia separations
     - ➢ Reactive swing sorption/desorption for ammonia recovery
2. **Distributed NH_3 synthesis: miniaturized, electrified Haber-Bosch**
   - Modularized synthesis for synergistic agriculture, energy and chemicals sectors, with immediate opportunities for H_2@Scale integration
   - Different design problem: *scaling <u>down</u>* & *numbering <u>up</u>* (vs. scaling up)
   - Greatest challenges are in addressing operational intermittencies
3. **Direct, low-temperature electrochemical NH_3 synthesis**
   - Electrosynthesis via N_2 reduction and H_2O splitting
   - Despite popularity, low rates/e^- efficiencies & major throughput hurdles to match Haber-Bosch scales (recall, electrochemistry scales <u>areally</u>)



Wind farm graphic adapted from: M. Reese, E. Cussler et al., *Ind. Eng. Chem. Res.* <u>55</u> 3742–3750 (2016). (*link*)
Electrochemistry graphic adapted from: C. A. Fernandez, M. C. Hatzell et al., *J. Mater. Chem. A* <u>8</u> 15591–15606 (2020). (*link*)

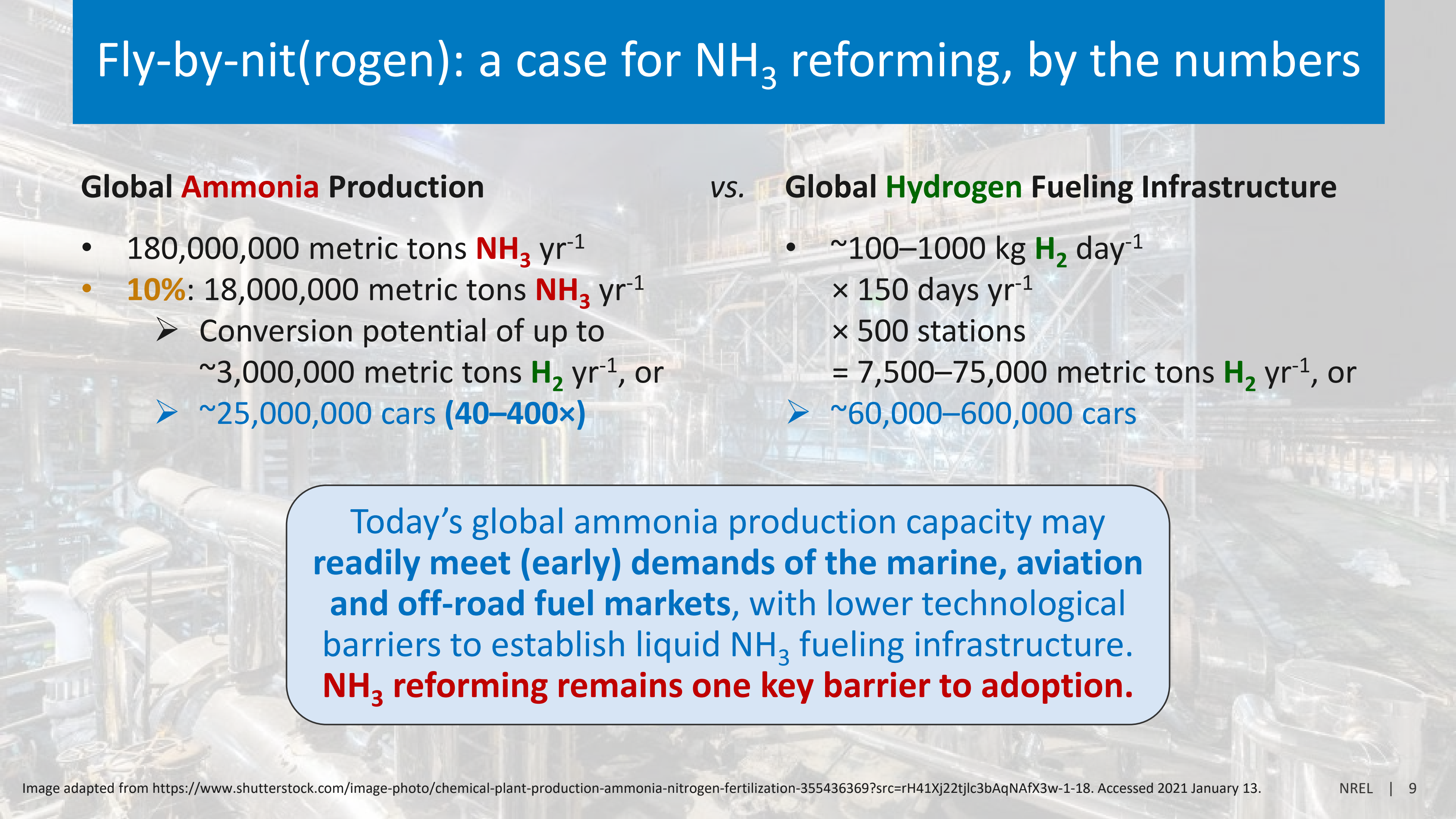
Taste the rainbow: colors of ammonia and hydrogen



Color matters! Carbon emissions must be negated across the broader supply chain to allow for truly renewable NH_3.

"The Potential of Zero-Carbon Bunker Fuels in Developing Countries," World Bank Group, 15 Apr 2021. (*link*)

Fly-by-nit(rogen): a case for NH_3 reforming, by the numbers



Global Ammonia Production *vs.* **Global Hydrogen Fueling Infrastructure**

Global Ammonia Production

- 180,000,000 metric tons NH_3 yr^{-1}
- **10%**: 18,000,000 metric tons NH_3 yr^{-1}
  - ➢ Conversion potential of up to ~3,000,000 metric tons H_2 yr^{-1}, or
  - ➢ ~25,000,000 cars **(40–400×)**

Global Hydrogen Fueling Infrastructure

- ~100–1000 kg H_2 day^{-1}
  × 150 days yr^{-1}
  × 500 stations
  = 7,500–75,000 metric tons H_2 yr^{-1}, or
  - ➢ ~60,000–600,000 cars

Today's global ammonia production capacity may **readily meet (early) demands of the marine, aviation and off-road fuel markets**, with lower technological barriers to establish liquid NH_3 fueling infrastructure. **NH_3 reforming remains one key barrier to adoption.**

Image adapted from https://www.shutterstock.com/image-photo/chemical-plant-production-ammonia-nitrogen-fertilization-355436369?src=rH41Xj22tjlc3bAqNAfX3w-1-18. Accessed 2021 January 13.

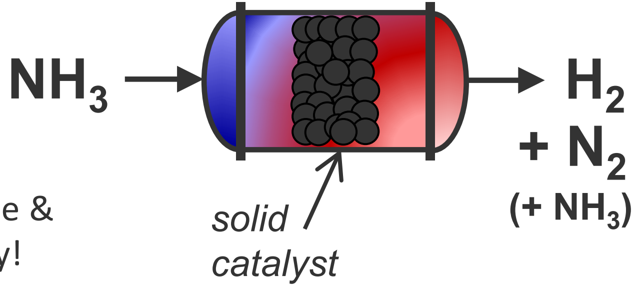
Ammonia planes, trains & automobiles

Ammonia is a promising net-zero-carbon liquid H_2 carrier and transportation fuel.

internal combustion (IC) engine & fuel cell (FC) designs underway!

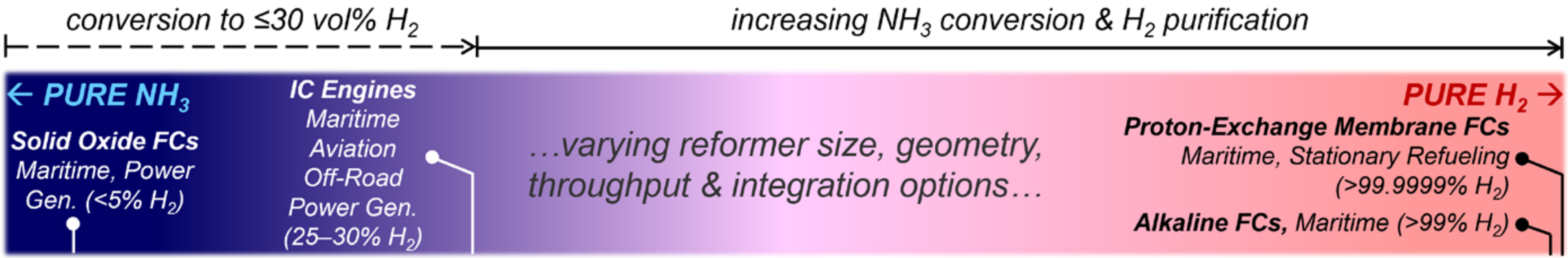
AMMONIA REFORMING

(reverse of Haber-Bosch)



NH_3 → → H_2 + N_2 (+ NH_3)

solid catalyst



conversion to ≤30 vol% H_2

increasing NH_3 conversion & H_2 purification

← PURE NH_3

Solid Oxide FCs

Maritime, Power Gen. (<5% H_2)

IC Engines

Maritime
Aviation
Off-Road
Power Gen.
(25–30% H_2)

…varying reformer size, geometry, throughput & integration options…

PURE H_2 →

Proton-Exchange Membrane FCs

Maritime, Stationary Refueling (>99.9999% H_2)

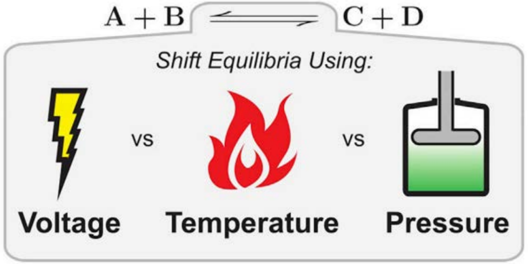
Alkaline FCs, *Maritime (>99% H_2)*

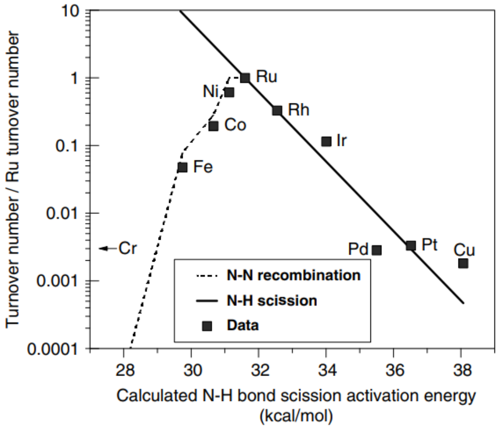
"Energy Storage Grand Challenge Roadmap," U.S. Department of Energy DOE/PA–0022, December 2020. Images adapted from Google Images. Accessed 2021 April 21.

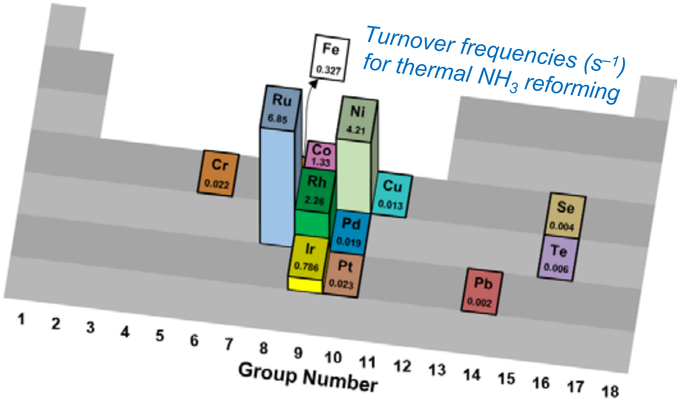
NH_3 reforming requires (electro-/photo-)catalyst discovery, reactor design

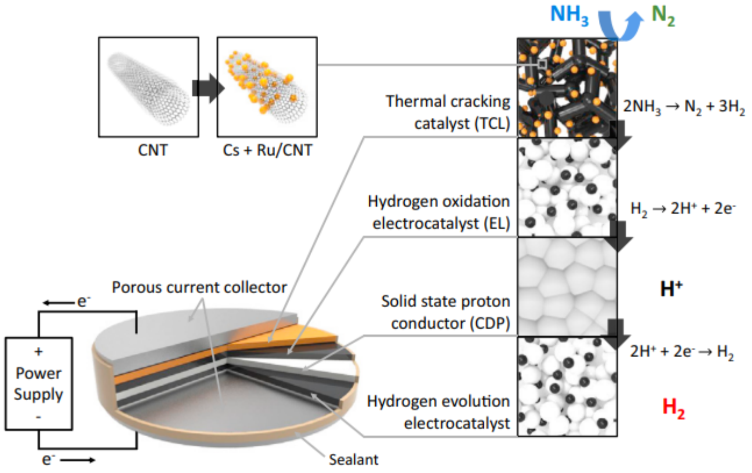
$$2\ NH_{3\,(g)} \rightleftharpoons N_{2\,(g)} + 3\ H_{2\,(g)}$$

$$\Delta H_{rxn} = \mathbf{+45.9}\ \text{kJ mol}^{-1}$$









CATALYST & REACTOR DESIGN CONSIDERATIONS

- Laboratory catalyst selectivity, activity and stability (“The Big Three”)
- Technical catalyst formulation, metal identity/loading ($$), tolerance to dynamic conditions*, mech. stability* (*esp. for mobile settings)
- Reforming reactor must feature light weight*, compact size*, high surface area, low pressure drop, low thermal latency, ability to reach required H_2 purity (perhaps requiring separation/purification steps)

Thermodynamic graphic adapted from: Z. J. Schiffer, A. M. Limaye, K. Manthiram, *Joule* 5 135–148 (2021). (*link*)
Volcano plot adapted from: J. C. Ganley, R. I. Masel et al., *Catal. Lett.* 96 117–122 (2004). (*link*)
Periodic TOF graphic adapted from: L. C. Caballero, N. E. Thornburg, M. M. Nigra, *Chem. Sci.* 13 12945–12956 (2022). (*link*)
Electrochemical cell graphic adapted from: D.-K. Lim, S. M. Haile et al., *Joule* 4 2338–2347 (2020). (*link*)

A ship-load of CO_2: decarbonizing maritime transportation

THINK FAST.

New maritime engines built in this decade will still be in use in 2050.

80% of global trade by volume and over 70% by value

6.1% of world oil demand (2012)

2.5% of global GHG emissions (940 million tons CO_2/yr)

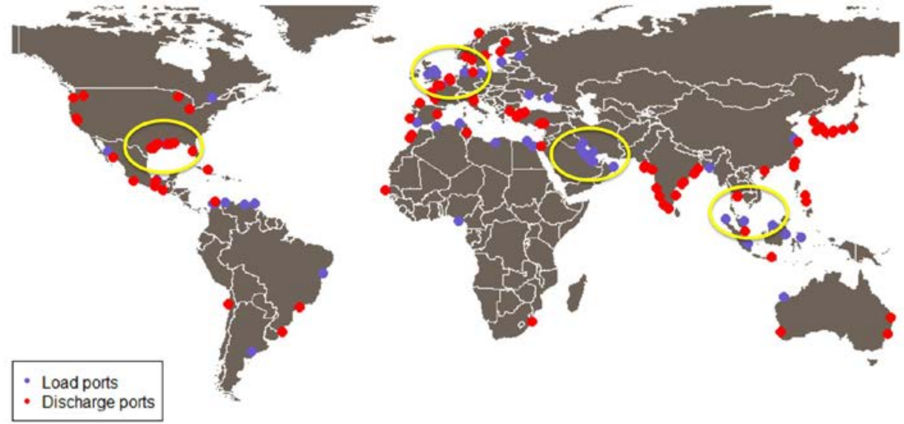
https://www.concawe.eu/wp-content/uploads/2017/01/marine_factsheet_web.pdf
http://www.imo.org/en/OurWork/Environment/PollutionPrevention/AirPollution/Pages/GHG-Emissions.aspx

Unique opportunities in the maritime sector

Wärtsilä is already testing an ammonia engine. (Credit: Wärtsilä)

- ➢ However, combustion/ignition methods and fuel cells are not well understood for ammonia blended with other fuels

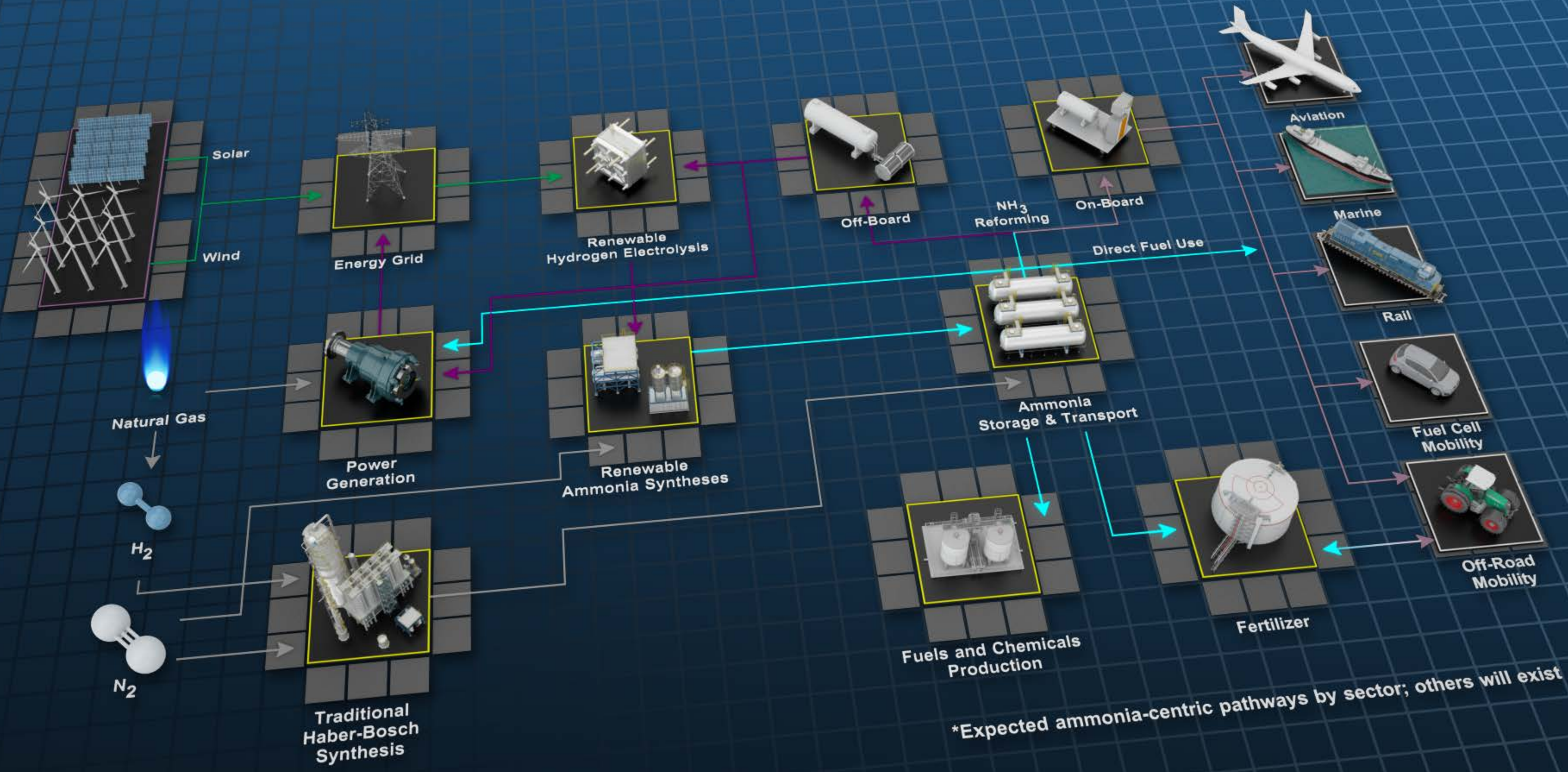
Worlwide ammonia ports



Visions for off-shore bunkering & synthesis

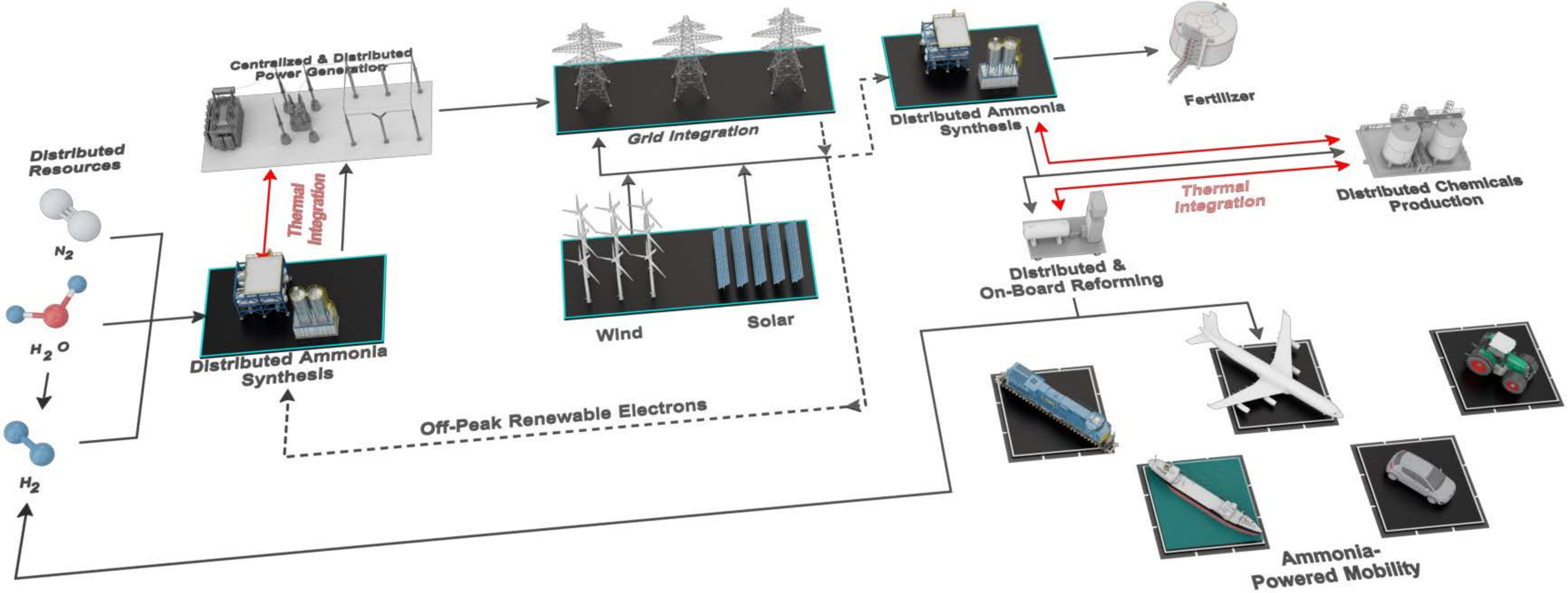
https://www.greentechmedia.com/articles/read/marine-sector-looks-to-ammonia-to-decarbonize-shipping, https://www.dnv.com/expert-story/maritime-impact/Harnessing-ammonia-as-ship-fuel.html, https://www.offshore-energy.biz/yara-pre-orders-worlds-1st-green-ammonia-floating-bunkering-terminals/. Accessed 11 April 2022.

NREL’s vision for the future ammonia energy economy

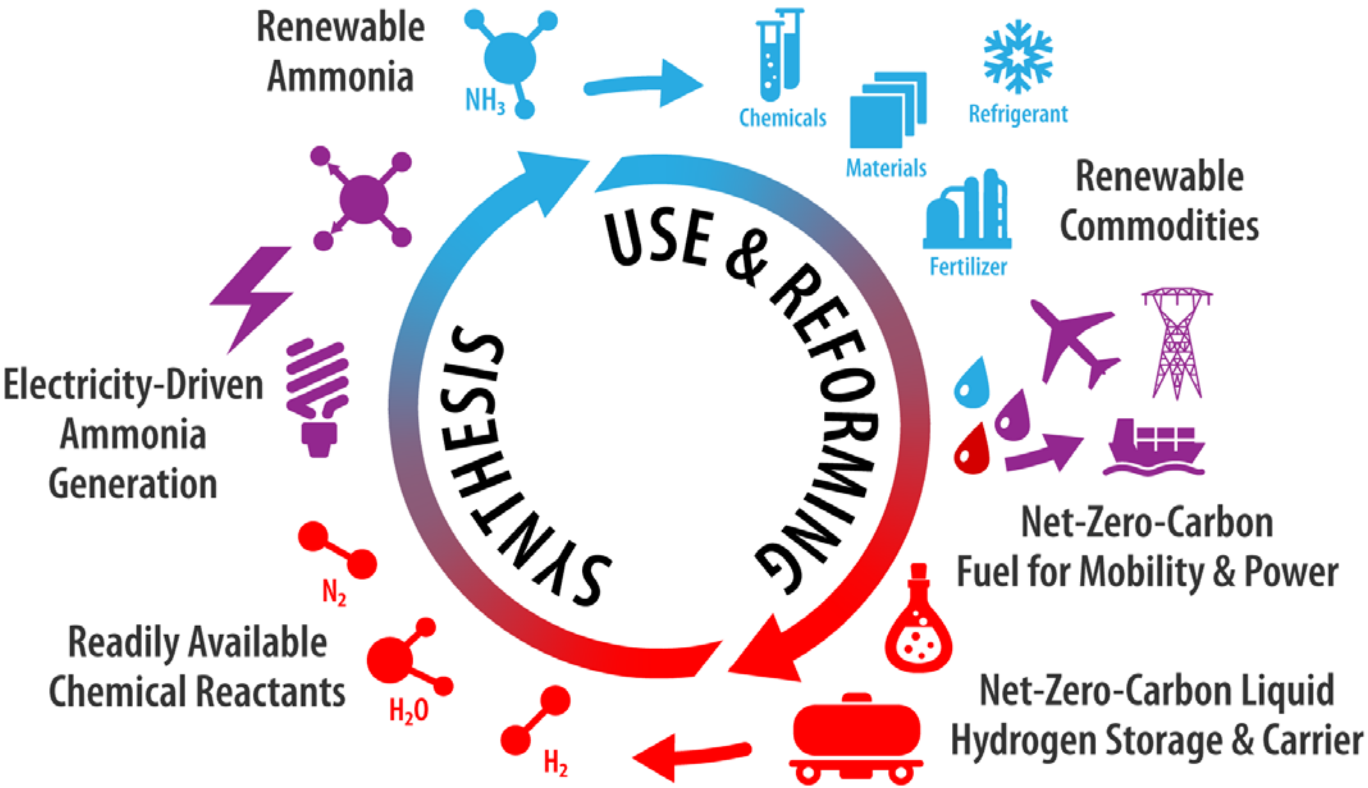


*Expected ammonia-centric pathways by sector; others will exist

Accessing ammonia and its energy—before *and* after the meter



Circularity (and abundancy) of the nitrogen and hydrogen atoms



Thank You

www.nrel.gov

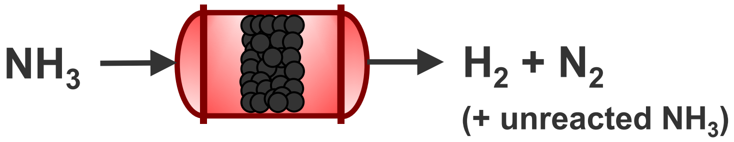
NREL/PR-5400-89437

NREL
NATIONAL RENEWABLE ENERGY LABORATORY

Ammonia vs. Hydrogen as Future Marine IC Fuels

Physicochemical Property	CNG	Ammonia	Hydrogen
Density [kg/m^3; 1 atm, 25°C]	0.65	**0.70**	0.090
Boiling Point [°C; 1 atm]	–162	**–33**	–253
Laminar Flame Speed [m/s; 1 atm, 25°C]	0.40	**0.12**	2.0
Lower Heating Value [MJ/kg]	50	19	120
Lower Heating Value [MJ/m^3; 1 atm, 25°C]	33	**13**	9.8
Stoichiometric AFR (mass basis)	17	6.1	34
Stoichiometric AFR (volume basis; 1 atm, 25°C)	9.5	**3.6**	2.4

- Ammonia exhibits **several physical advantages** over hydrogen as a fuel for IC engines



- However, ammonia's poor combustion properties will require blending with a pilot fuel—or **on-board reforming** to generate partial hydrogen fuel mixtures *in situ*

Technical Barriers to Ammonia as a Marine "Fuel"

Ammonia fuel cells (SOFCs) and advanced IC engines are already under development in Europe, Japan, and Australia, but several **key technical challenges** remain:

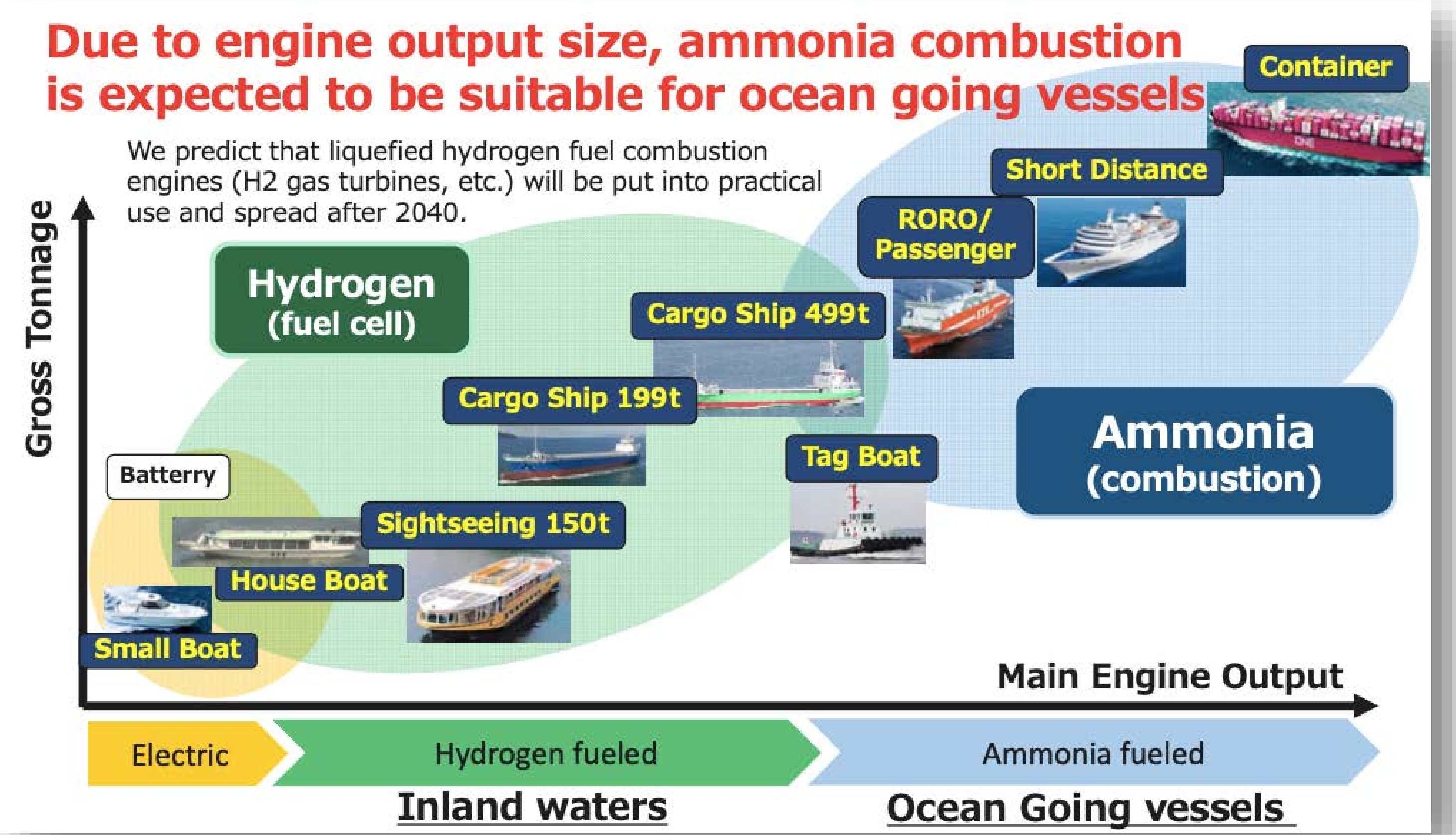
- Current ammonia SOFCs lack sufficient power density and load response capability for ocean-going trips
- Combustion and ignition methods are not yet well understood for ammonia blends
  - Pre-mixed vs. direct injection?
  - Spark (vs. pilot) vs. compression ignition?
  - Combustion promoter(s) required?
- Turbocharger, lubricating oil, and materials of construction requirements?
- Reformers and emissions management systems are also ill-defined and could be prohibitive (e.g., high NO_x emissions)

Wärtsilä is already testing an ammonia engine. (Credit: Wärtsilä)

…and it aaall hinges on NH_3 being made renewably….

https://www.greentechmedia.com/articles/read/marine-sector-looks-to-ammonia-to-decarbonize-shipping

Hydrogen and Ammonia May Play Different Roles



Graphic adapted from Kazumasa Taruishi, NYK Line, ICEPAG 2020. https://www.ammoniaenergy.org/articles/japans-nyk-and-partners-to-develop-ammonia-fueled-and-fueling-vessels/