Ammonia

Key to Expanding Deployment & Utilization of Green Hydrogen

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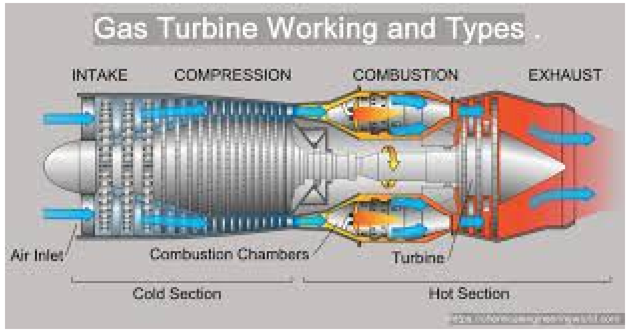
Acknowledgements

Heavy Industry and Commercial Transport

Accounts for ~35% of CO_2 emissions

High power and/or temperature precludes batteries, electrification





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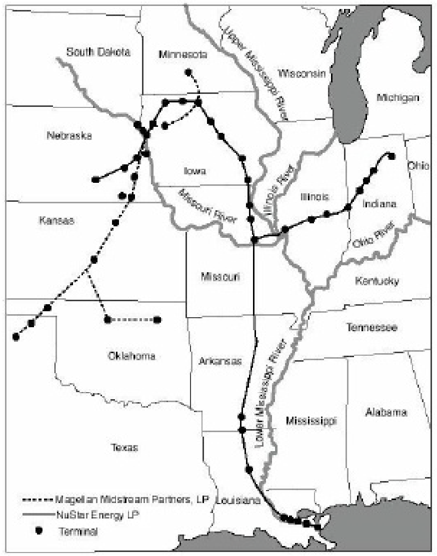
Ammonia: The Ideal Vector for H_2@Scale

Solves the storage & distribution problem

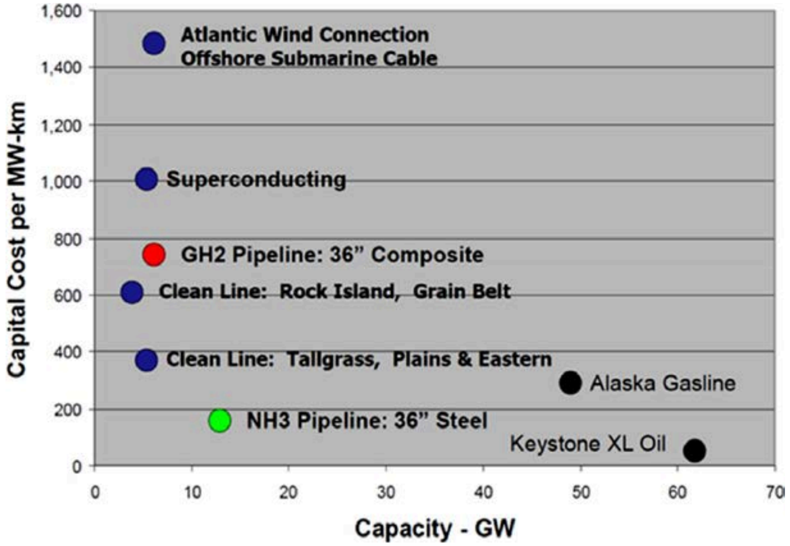
- T = 25 °C >> -253 °C
- P = 10 bar << 700 bar
- Liquid NH_3: 40% more H by volume than liquid H_2
- Liquid NH_3: 60% more energy by volume than liquid H_2
- Existing production/distribution/storage infrastructure

SIEMENS

Ammonia pipelines in the US



CapEx Competitive



A. Valera-Medina et al., "Ammonia for power," *Progress in Energy and Combustion Science* **69,** 63-102 (2018)

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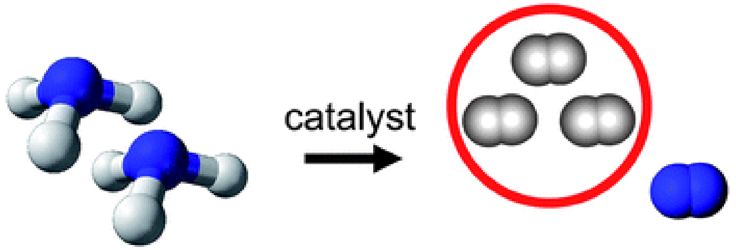
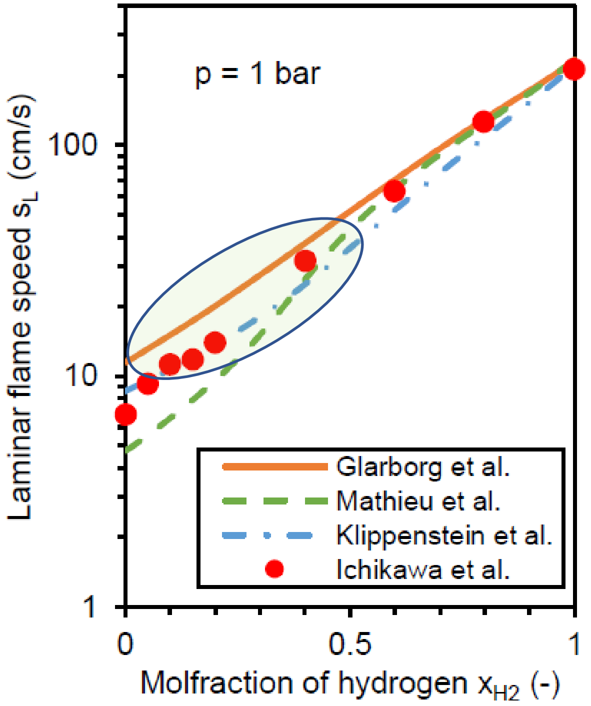
Ammonia: Clean Combustion

Single, dense liquid fuel source

- Difficult to burn ammonia directly
- Partial decomposition into H_2/NH_3 mixtures
- Flame speed scales monotonically with H_2 fraction
- Drop-in replacement for hydrocarbons
- Ignites, burns nominally identically (except it's orange)



$$2NH_3 \rightarrow 3H_2 + N_2$$
$$2NH_3 + 1.5O_2 \rightarrow 3H_2O + N_2$$
$$H_2 + 0.5O_2 \rightarrow H_2O$$



Target Market

Hydrocarbons

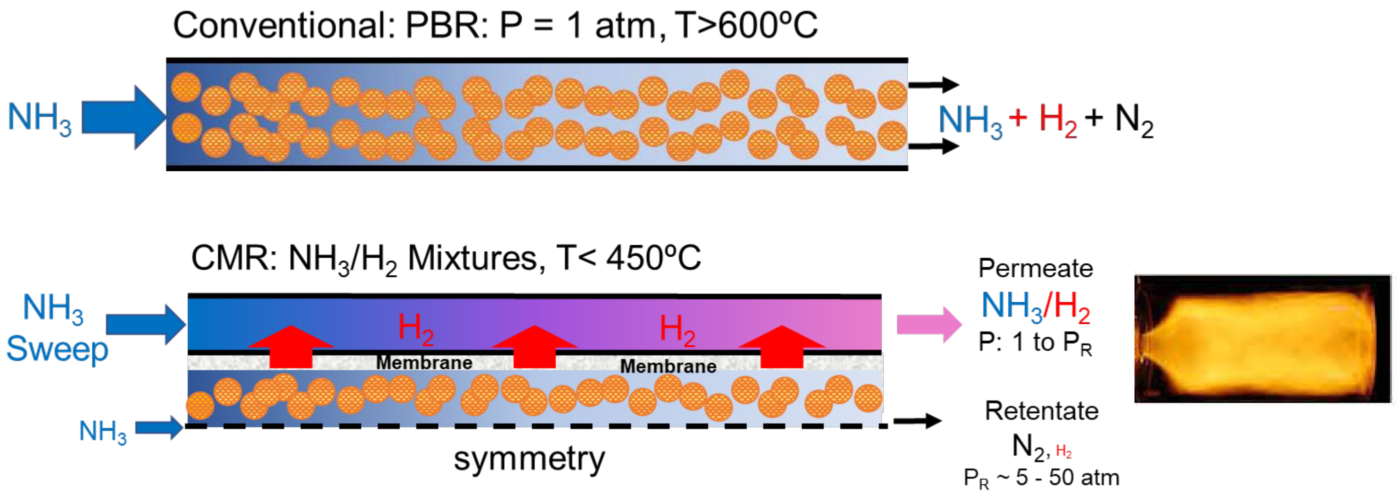
- Fuel oil
- Natural gas
- Gasoline
- Jet Fuel

Directly from CSM Reformer

Generation of NH_3/H_2 Mixtures

Conventional Technology

- Packed bed reactor (PBR)
- Atmospheric pressure, high T (>600°C)
- Inflexible, large pressure drop

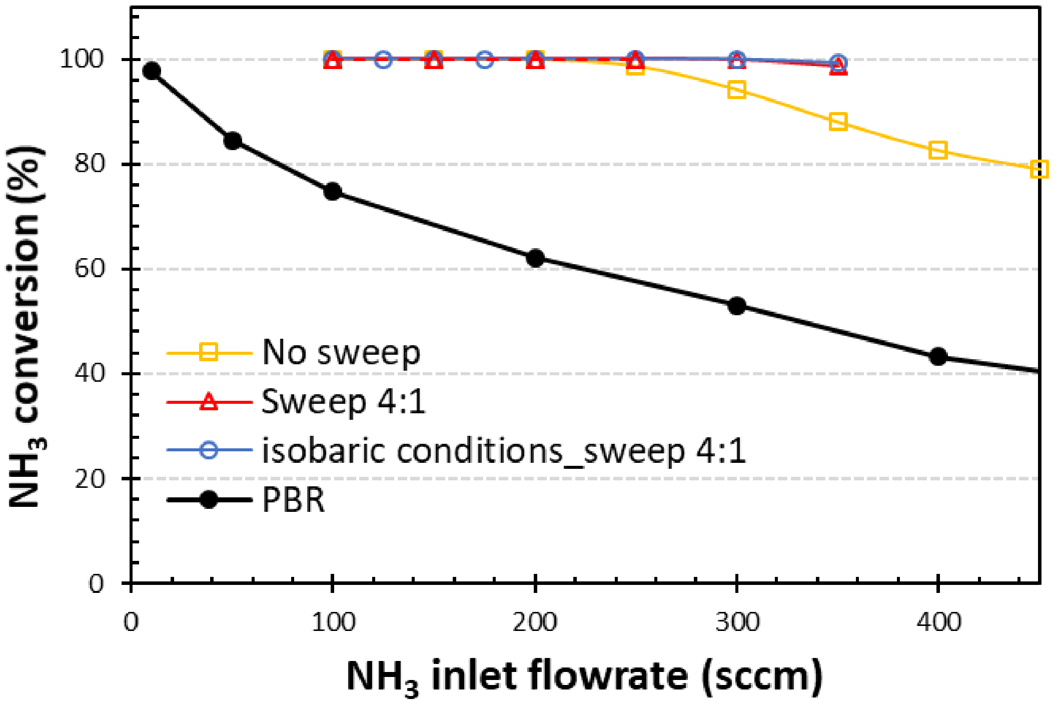


Catalytic Membrane Reactor (CMR)

- Fully decompose fraction / recover H_2
- Remove H_2 inhibition, much higher throughput

$$r = \frac{k(K_A P_A)^2}{(K_A P_A + P_H^{1.5})^2}$$

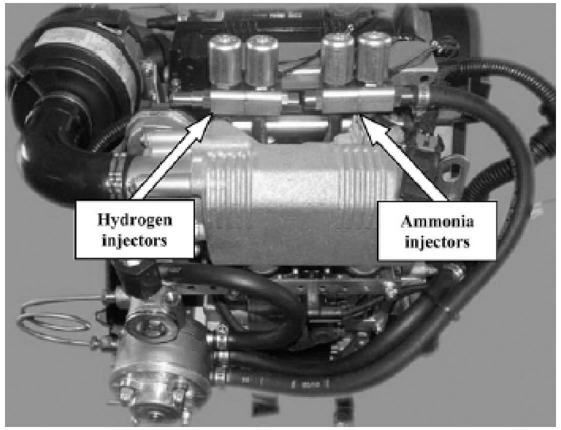
- Mix with NH_3 sweep: tune composition
- Sweep enables isobaric operation
- Robust: >1000 hrs online and performance improves
- No Nitrogen! Benefits for performance



Example: Internal Combustion Engines

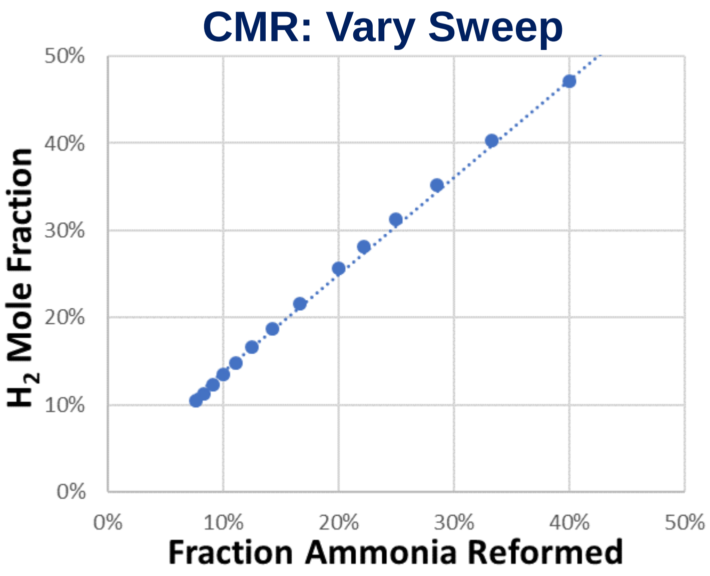
Modified standard SI engine (Frigo lab)

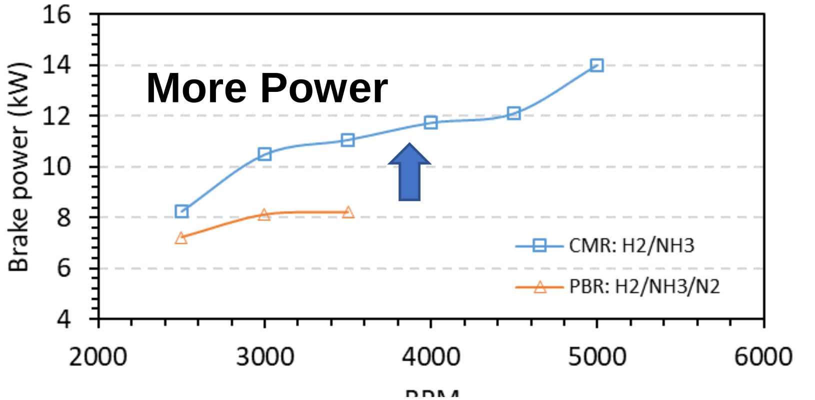
- Compared NH_3/H_2 (CMR) vs. $NH_3/H_2/N_2$ (PBR)
- Benefits of N_2 removal:
  - Achieved ~35% more power, greater range of stable operation
  - Produced >65% less NO_x (even less than gasoline)

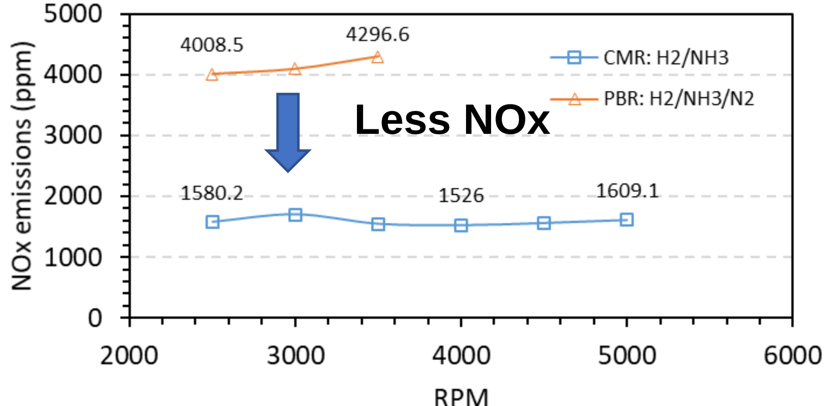


Requires Dynamic Composition Control

- ~50% H_2 at ignition
- ~10% H_2 under full load
- Easily achieved in CMR







M. Comotti and S. Frigo, "Hydrogen generation system for ammonia–hydrogen fuelled internal combustion engines," *International Journal of Hydrogen Energy* **40,** 10673 (2015).

S. Frigo and R. Gentili, "Analysis of the behaviour of a 4-stroke Si engine fuelled with ammonia and hydrogen," *International Journal of Hydrogen Energy* **38,** 1607 (2013).

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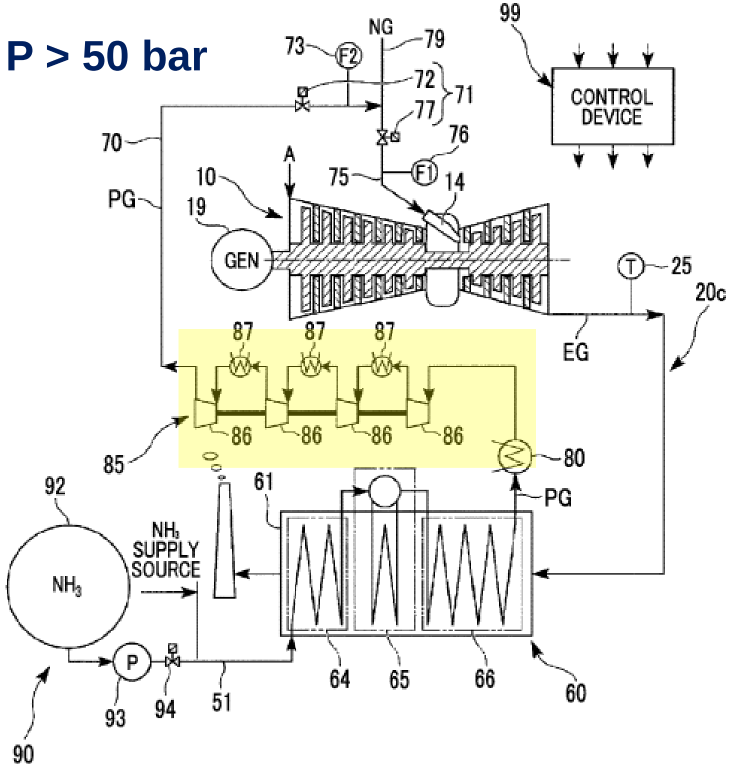
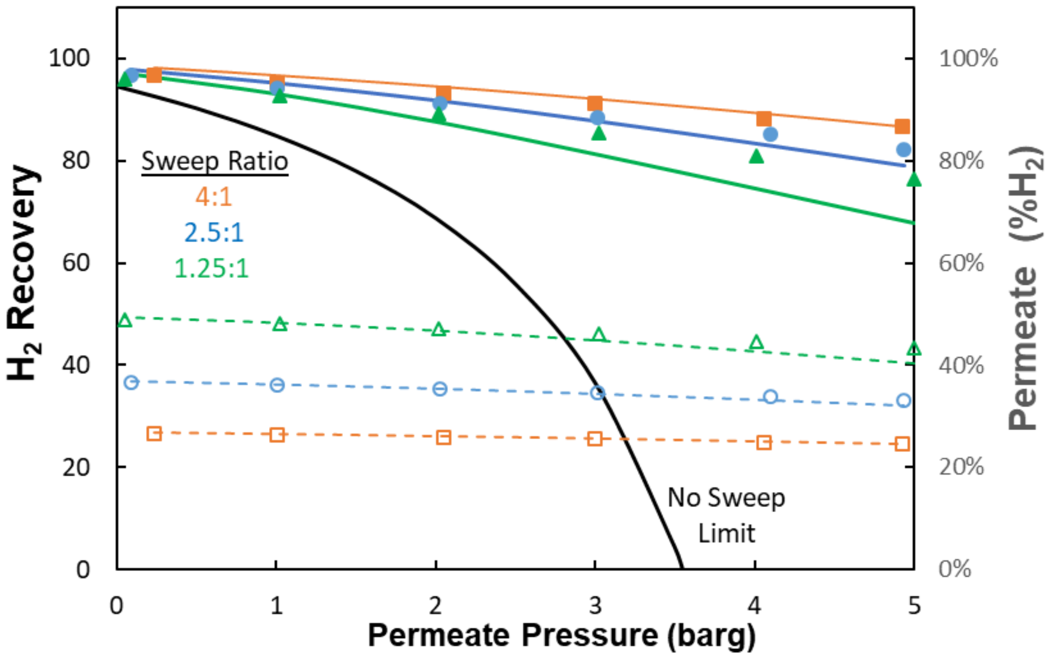
Example: Gas Turbines

Recent Mitsubishi Patent

- Need to increase volumetric energy density
- Achieved by increasing pressure (up to 50 bar)
- High temperature decomposition
- 4 compressors with inter-stage cooling (CapEx & OpEx)



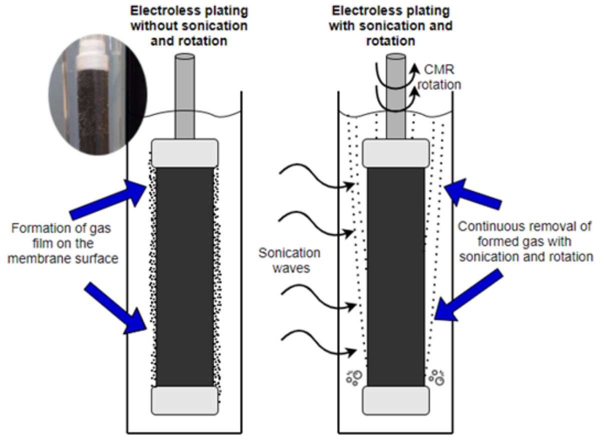
M. Nose, H. Uechi and S. Tanimura, "Gas turbine plant having thermal decomposition of ammonia and pressurization of the decomposed gas and method thereof," US Patent 11,156,168, (2021.



CMR: Sweep Enables Isobaric Operation

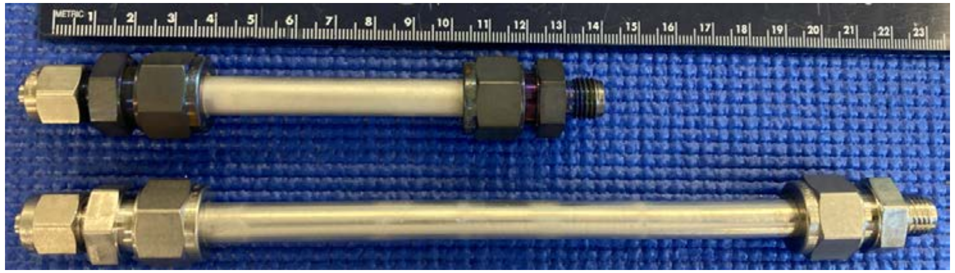
- CMR maintains hydrogen high recovery
- Pump liquid ammonia at high pressure
- Vaporize with low grade heat (T < 100 °C)
- Pressure for free

Ongoing Work: Scale-up & Validation



CMR Demonstration Module

- Capacity: 40 slm ammonia
- Ultrasonic membrane fabrication / improved catalyst
- Switch from gas to liquid delivery: Enable high pressure operation (to > 50 bar)
- Targeting 10X further improvement in performance



Validation of Combustion Performance

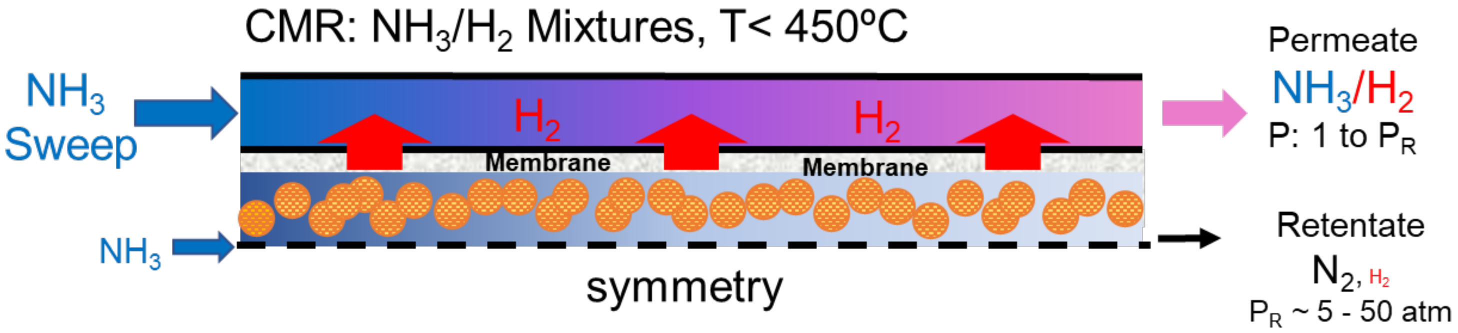
- Quantify benefits of NH_3/H_2 over $NH_3/H_2/N_2$
- Flame speed / temperature / emissions
- Potential Concerns: NO_x & NH_3 slip
- Characterize as a function of NH_3/H_2 and equivalence ratios, pressure

R. Sitar, J. Shah, Z. Zhang, H. Wikoff, J. D. Way, and C. A. Wolden, "Compact ammonia reforming at low temperature using catalytic membrane reactors," *Journal of Membrane Science* **644**, 120147, (2022).

Summary: NH_3 a Key to Industrial De-carbonization

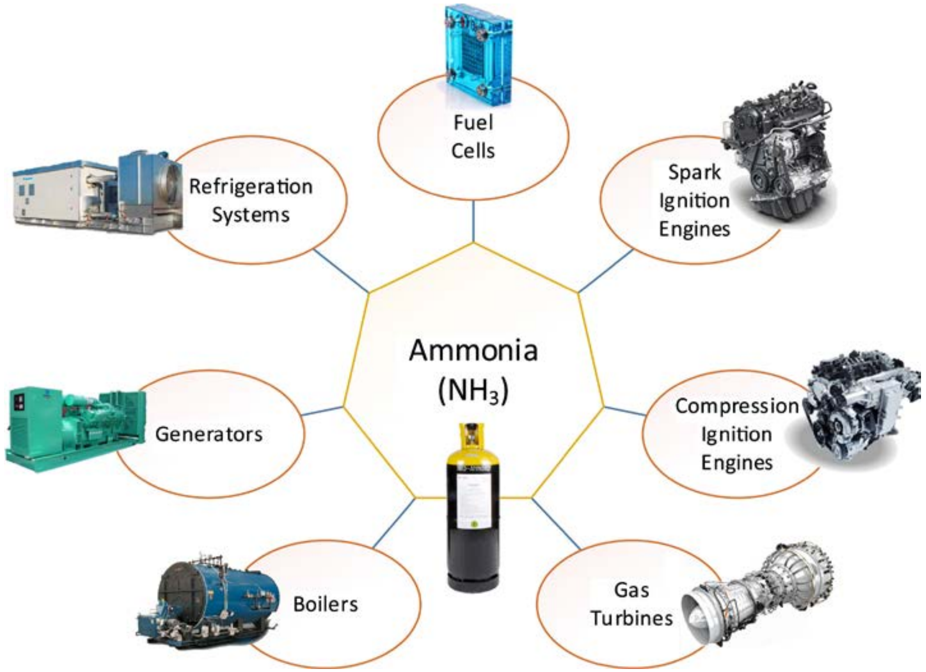
Attributes of Ammonia

- Single liquid fuel with high H_2 and energy density
- Leverage existing production / distribution / storage infrastructure
- Partially decomposed NH_3/H_2 is a tunable drop-in replacements for hydrocarbons



Efficient Reforming: Catalytic Membrane Reactors

- Compact / energy efficient / low temperature (down to 350 °C)
- Dynamic control over H_2/NH_3 composition
- No N_2 = More Power / less NO_x
- Enables high pressure / isobaric operation = Pressure for free
- Looking for OEM collaborators for integration / optimization



A. Yapicioglu and I. Dincer, "A review on clean ammonia as a potential fuel for power generators," *Renewable and Sustainable Energy Reviews* **103,** 96-108 (2019).

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