Opportunities for Green Ammonia Combustion in Internal Combustion Engines

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ASME Future of Internal Combustion Engine Webinar Series

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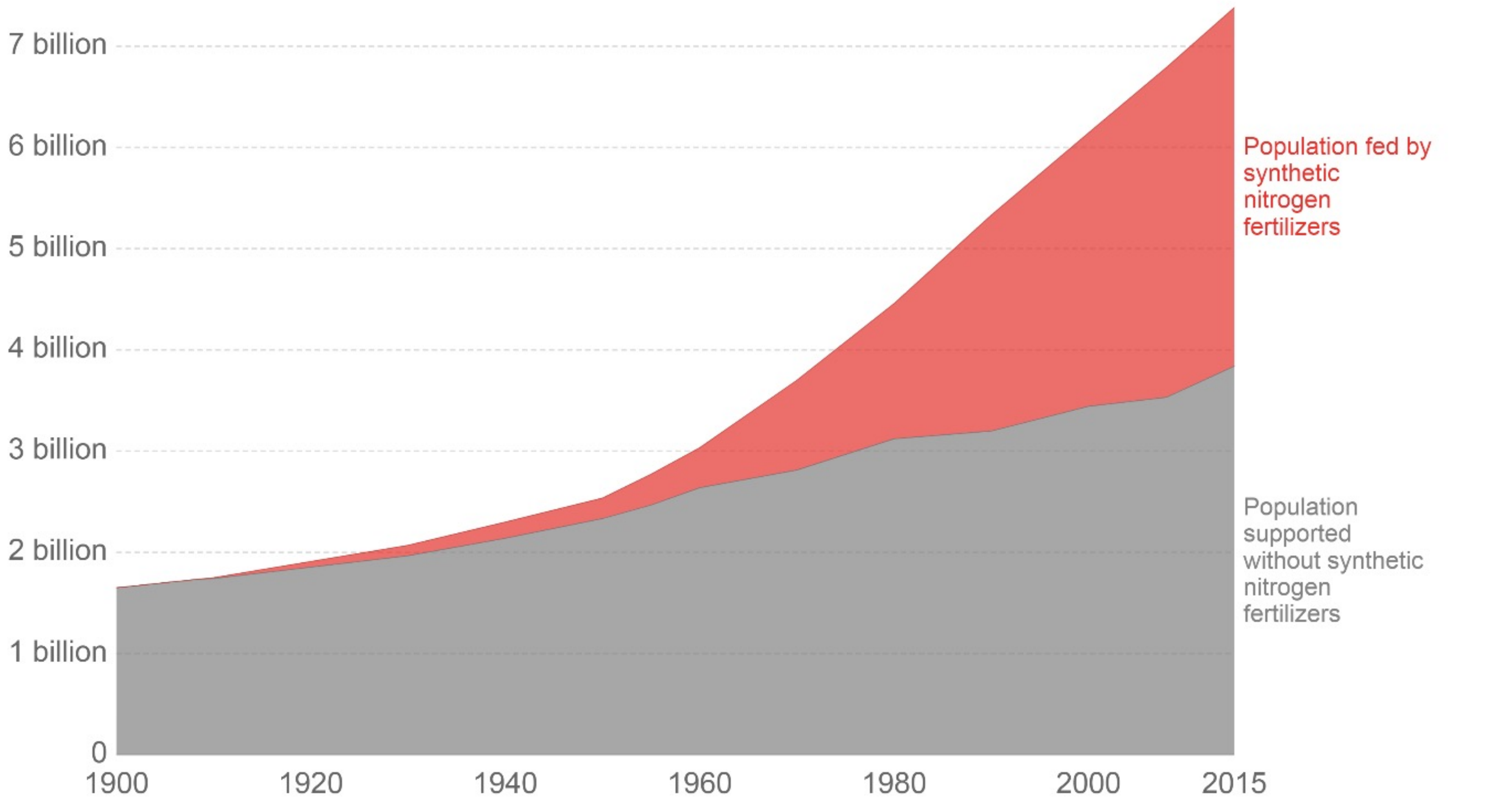
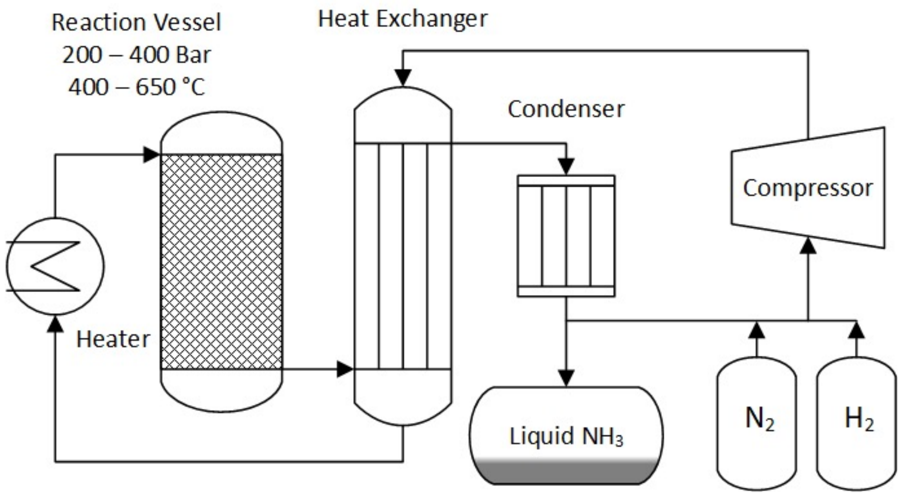
Anhydrous ammonia enables the feeding of over half of the global population and is the 5th highest volume chemical produced

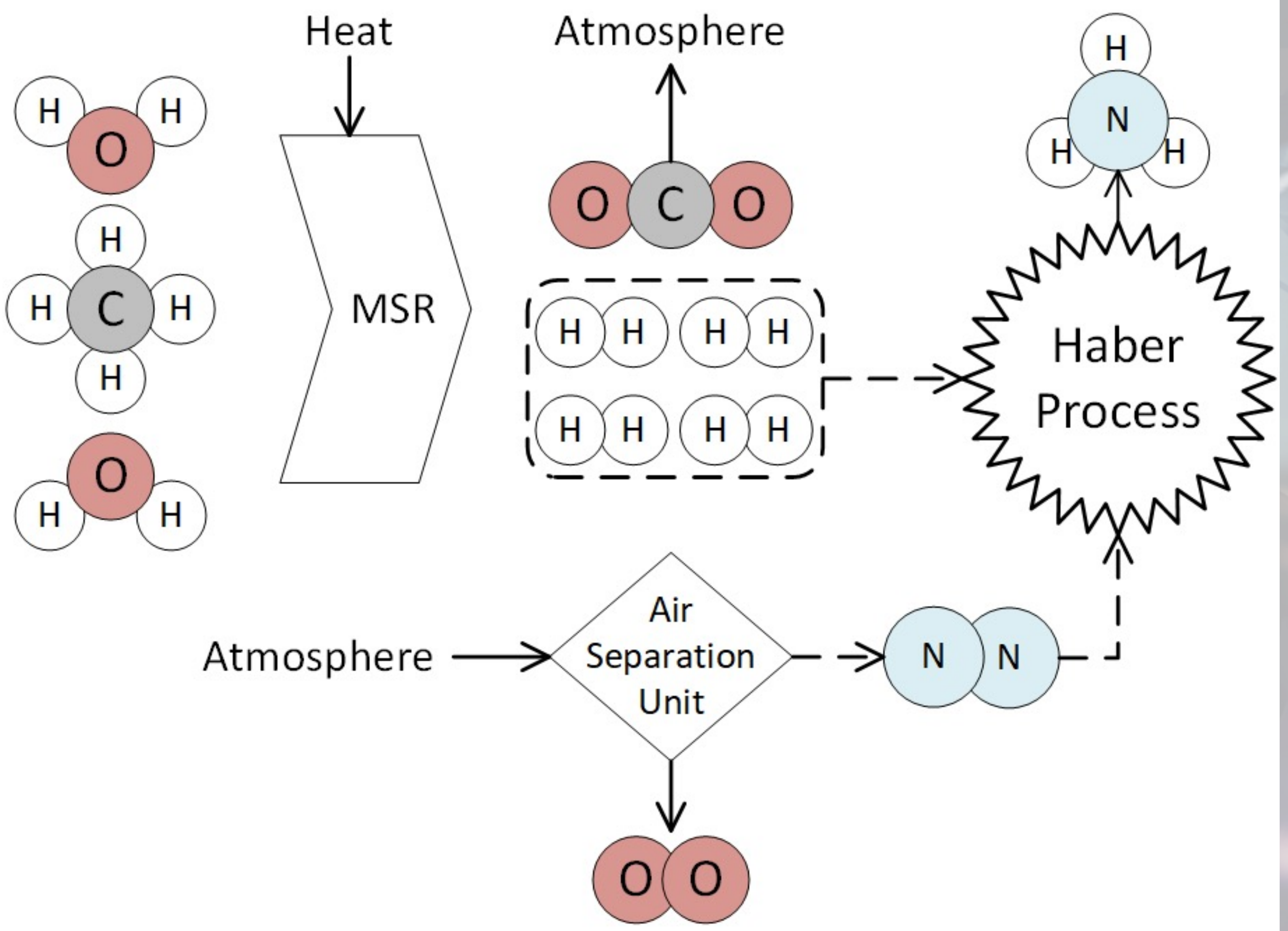


Ritchie, *Our World in Data*: https://ourworldindata.org/how-many-people-does-synthetic-fertilizer-feed#note-4; Erisman et al., 2008, Nat. Geoscience, 1 (10), 636-639.

It is produced conventionally through the Haber-Bosch Process using natural gas as the primary feedstock

- >180 millions tons produced annually
- 1.5-2.0% of **all** CO_2 emissions





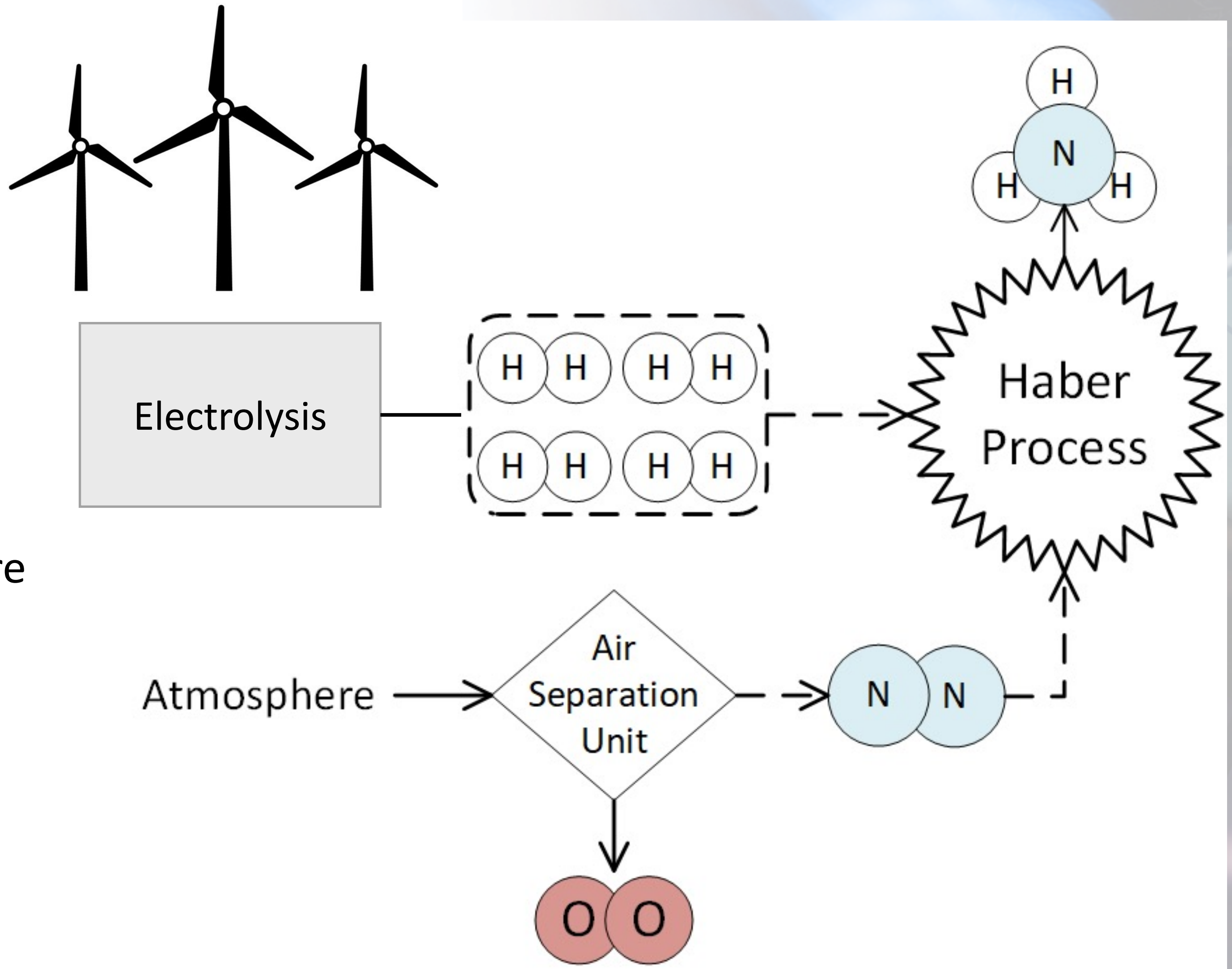
Anhydrous ammonia can also be produced using hydrogen and nitrogen from renewable sources

"Gray" hydrogen and ammonia from natural gas or coal

"Green" hydrogen and ammonia from renewable resources

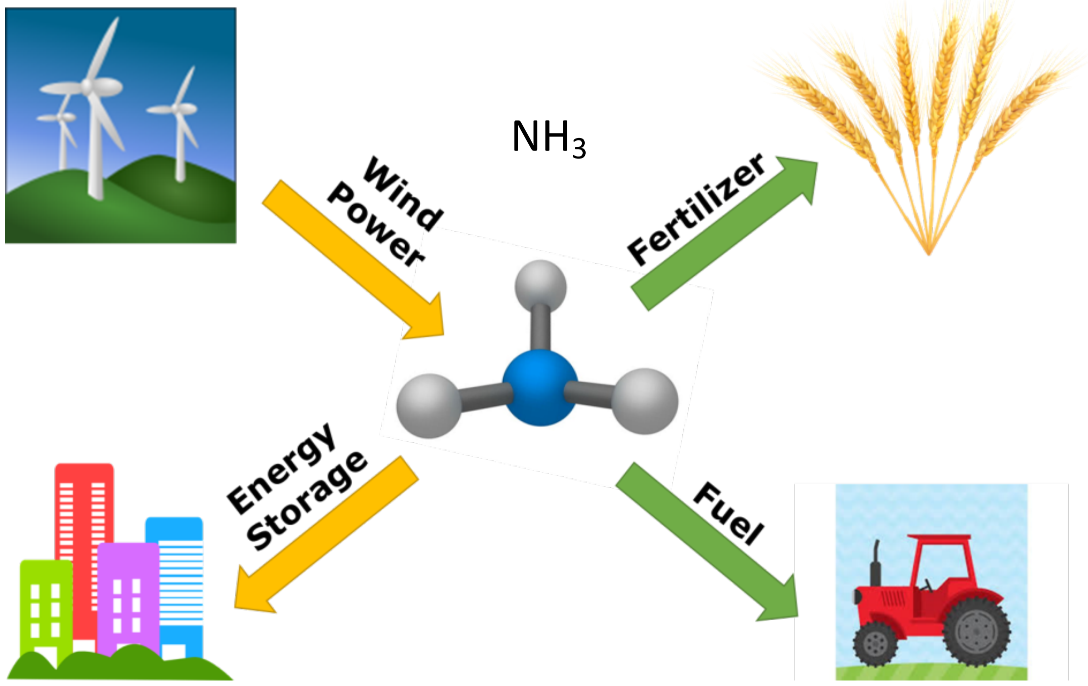
"Blue" hydrogen and ammonia from natural gas or coal with carbon capture and sequestration

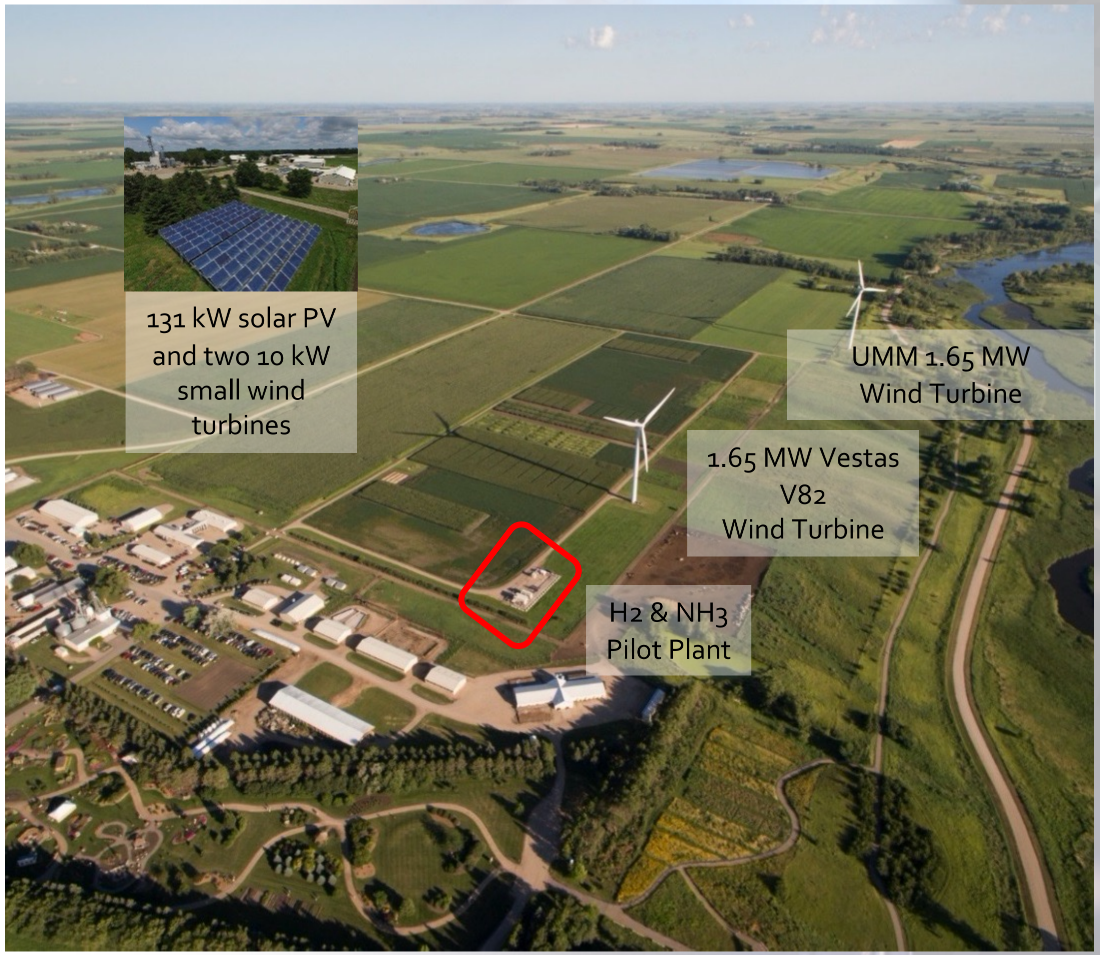
"Pink" hydrogen and ammonia from nuclear power



ASME ICEF 2022 Internal Combustion Engine Fall Conference

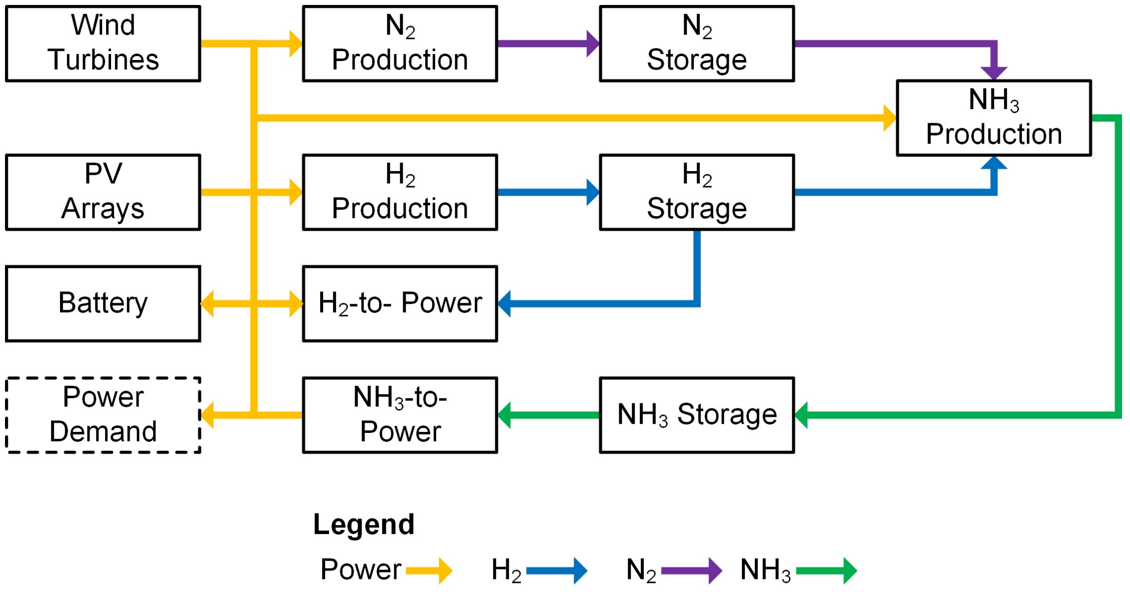
Rural green ammonia has promise to decarbonize agriculture and start a pathway towards a green hydrogen economy

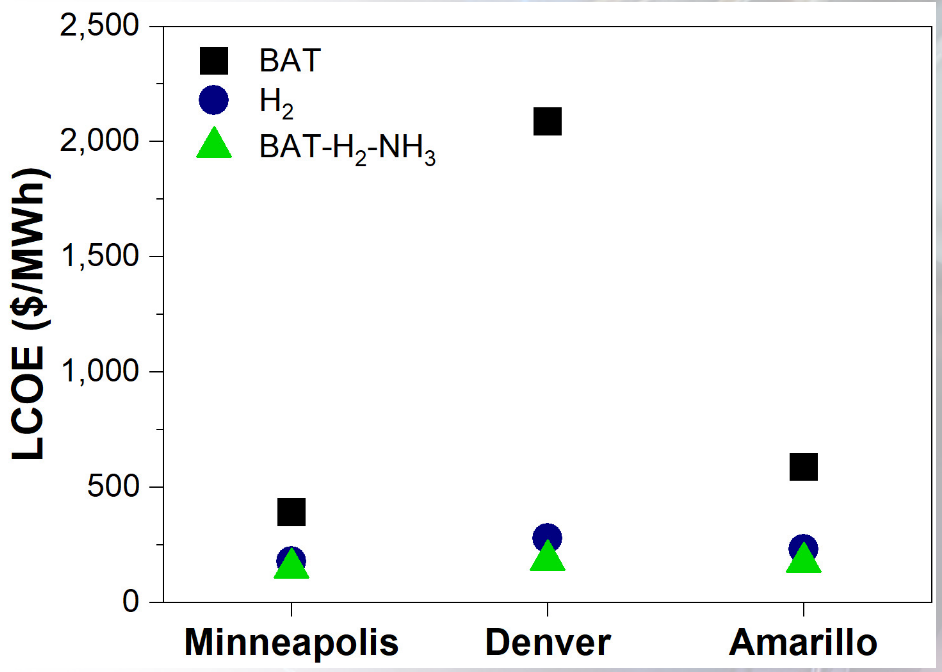




Research shows that ammonia is ideal for long term energy storage and can be mixed with H_2 and batteries to decarbonize electricity production

- 100% wind-solar islanded energy system: No carbon fuels or grid connection
- Residential demand profiles with 10 MW annual average demand
- Optimized sizing and scheduling for lowest levelized cost of energy (LCOE)





Palys & Daoutidis. (2020). *Comput. Chem. Eng., 136*, 106875.

- **Batteries alone prohibitively expensive**
- **Lowest LCOE from combining H_2 and NH_3**

Anhydrous ammonia has lower flammability and higher health hazard than conventional hydrocarbon fuels

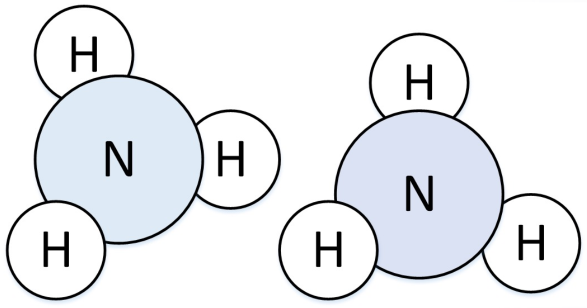
Gasoline

Anhydrous Ammonia

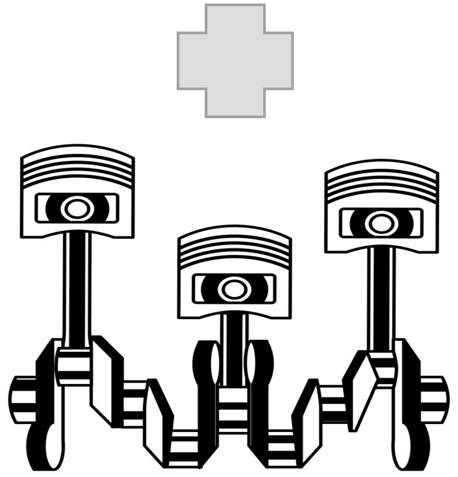
For health and safety reasons, ammonia is NOT appropriate as an alternative for light or heavy-duty on-road transportation

Motivating ammonia for use in off-highway internal combustion engine applications where fuel storage can be safely managed

Distributed Power Generation



Agricultural



Locomotive

Marine

Ammonia can be used in both compression ignition and spark-ignited engines

Compression Ignition

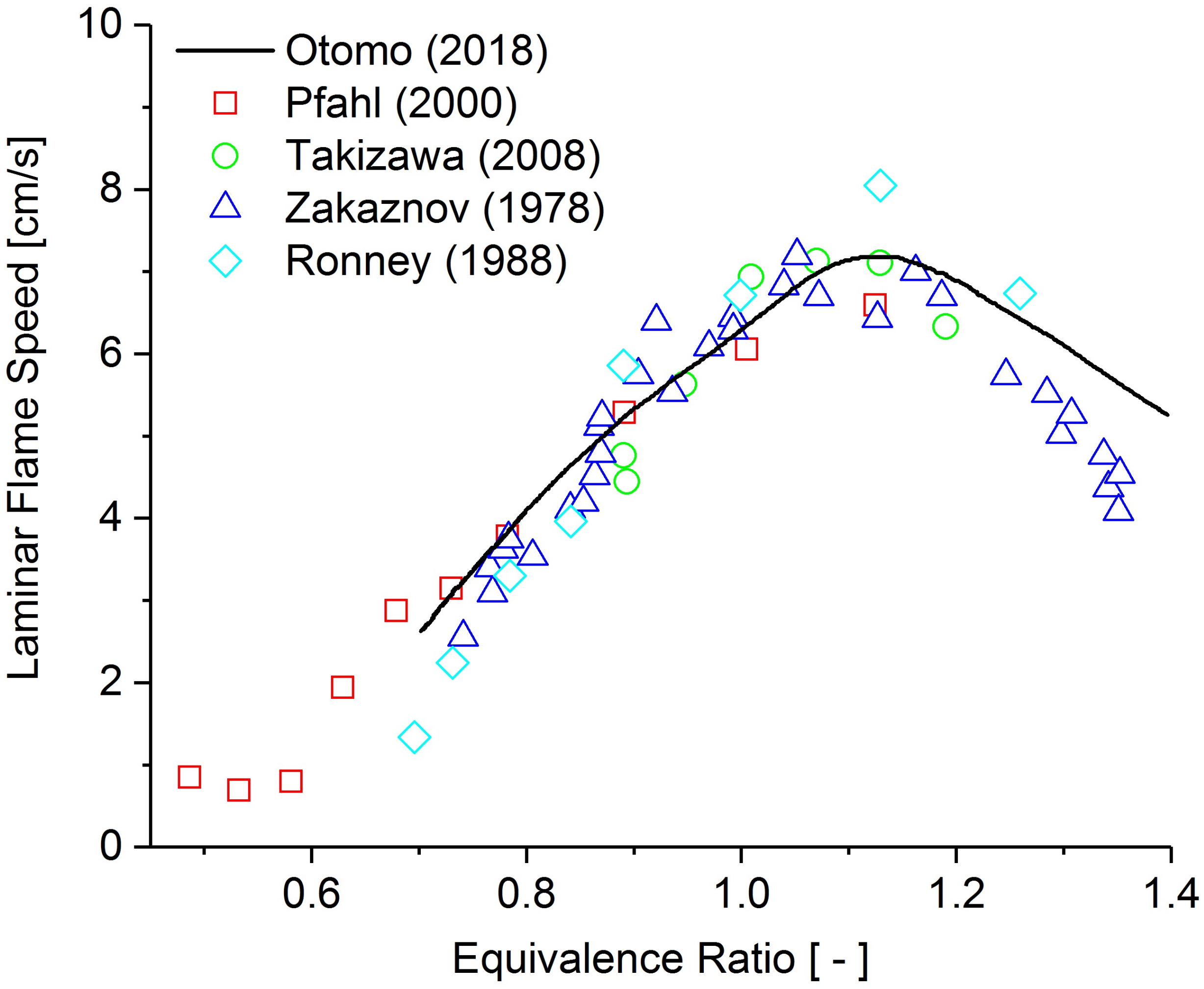
- 100% NH_3 requires high compression ratio (CR > 35:1)
- Dual-fuel strategies
- Minimum ~5% pilot diesel injection for low-speed engines
- Multiple injection strategies for emissions reduction

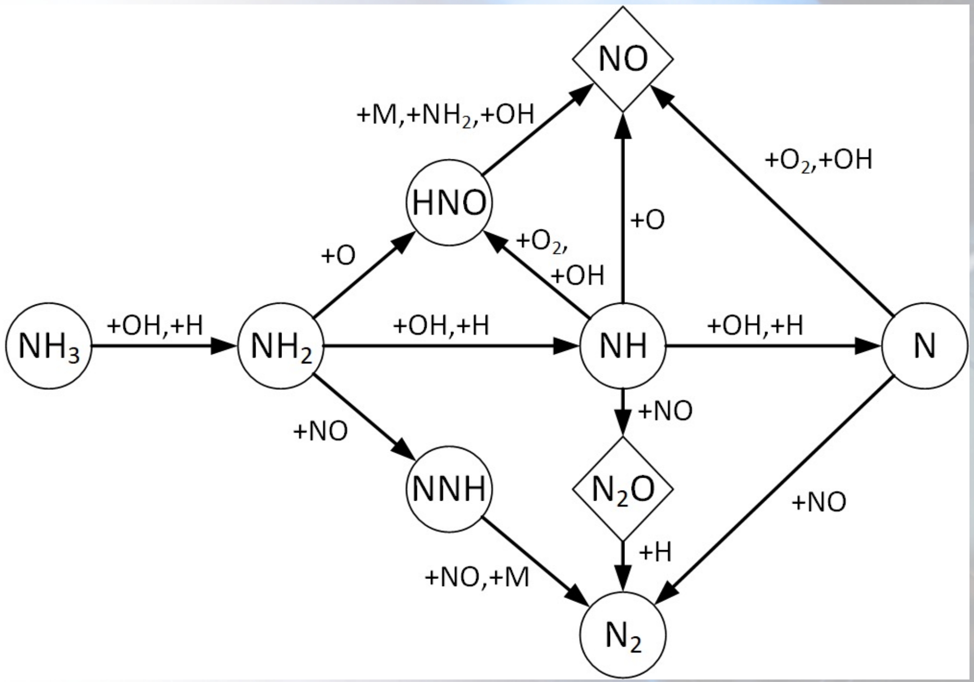
Spark Ignition

- Laminar flame speed low for ammonia alone
- H_2-NH_3 blends from cracking are promising
- Reduced volumetric efficiency
- Stoic-rich aftertreatment may be more effective than lean aftertreatment

- High NO_X and unburned ammonia emissions – N_2O
- Catalytic aftertreatment is expensive – benefit, unburned NH_3 as reductant for SCR for lean engines

Ammonia combustion proceeds through well-known chemistry; the complete mechanism has yet to be determined

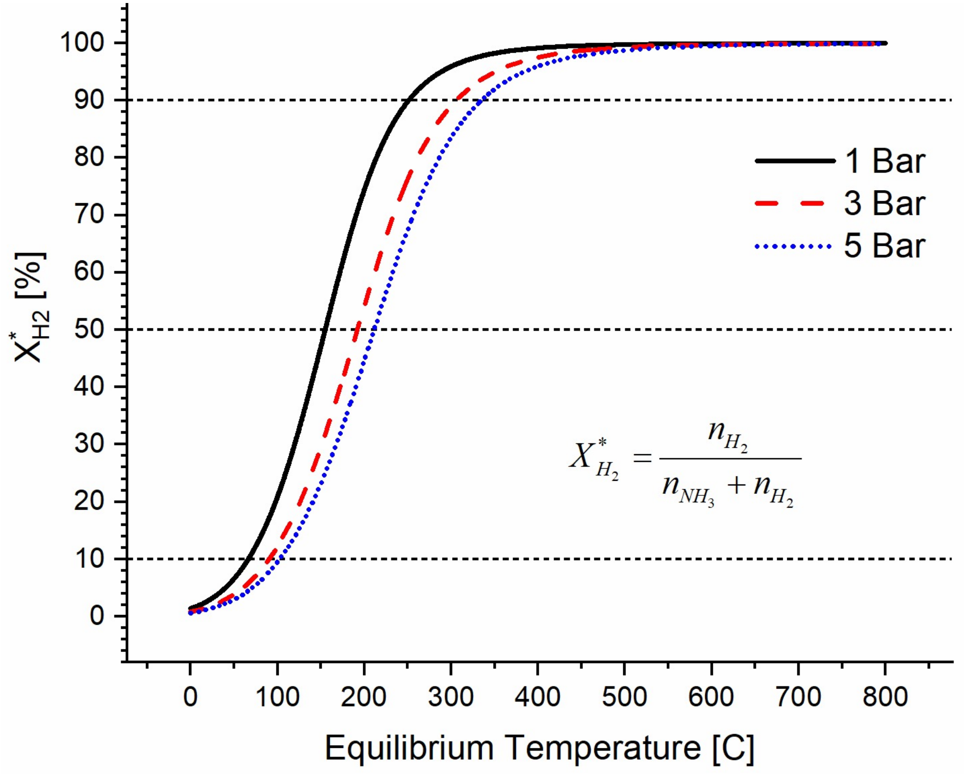




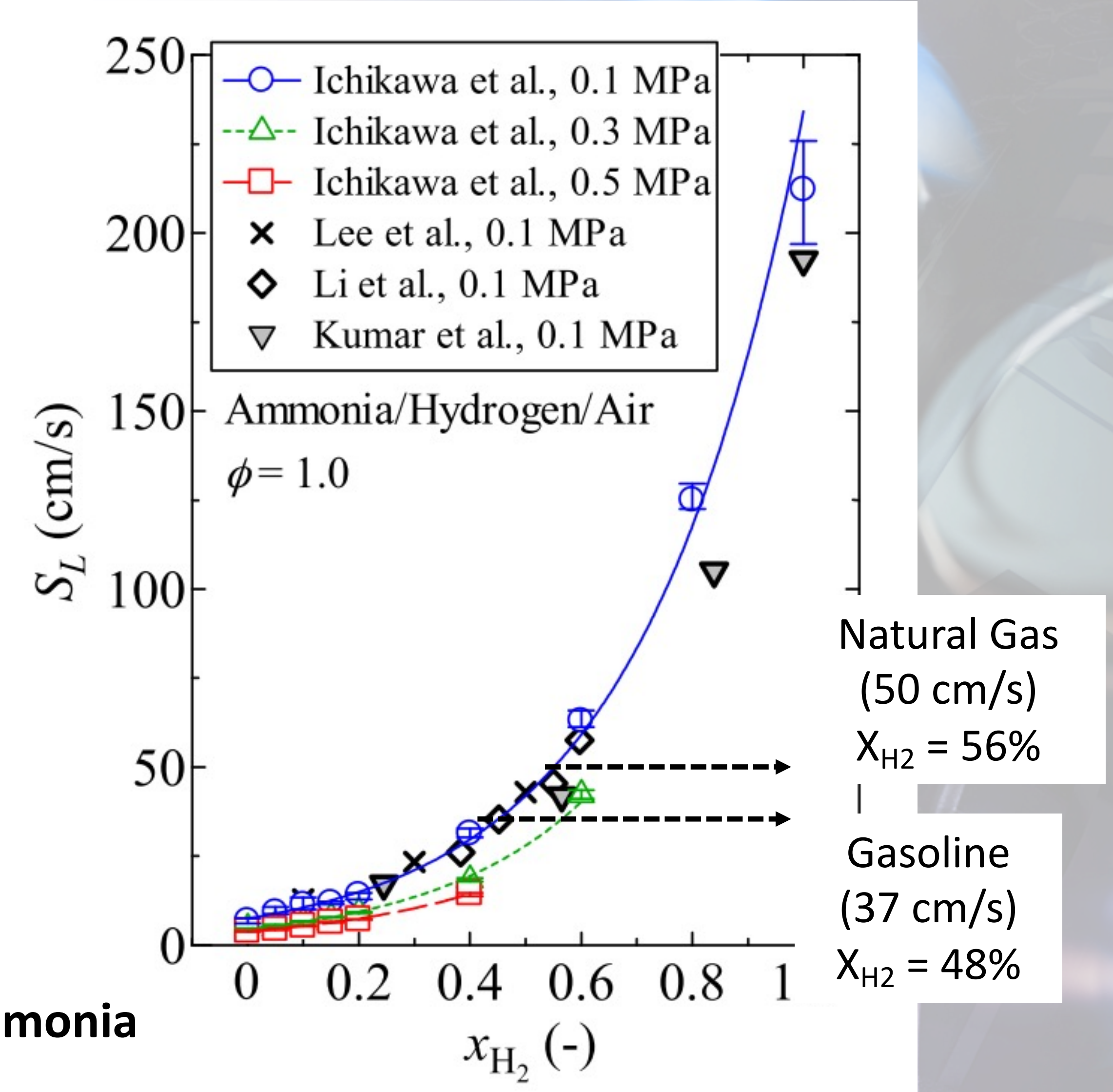
$$NH_3 + \frac{3}{4}O_2 \rightarrow N_2 + \frac{3}{2}H_2O \qquad \left[-317\frac{kJ}{mol}\right]$$

$$NH_3 + \frac{5}{4}O_2 \rightarrow NO + \frac{3}{2}H_2O \qquad \left[-104\frac{kJ}{mol}\right]$$

Though anhydrous ammonia has low flammability, a small amount of hydrogen can sufficiently enhance combustion

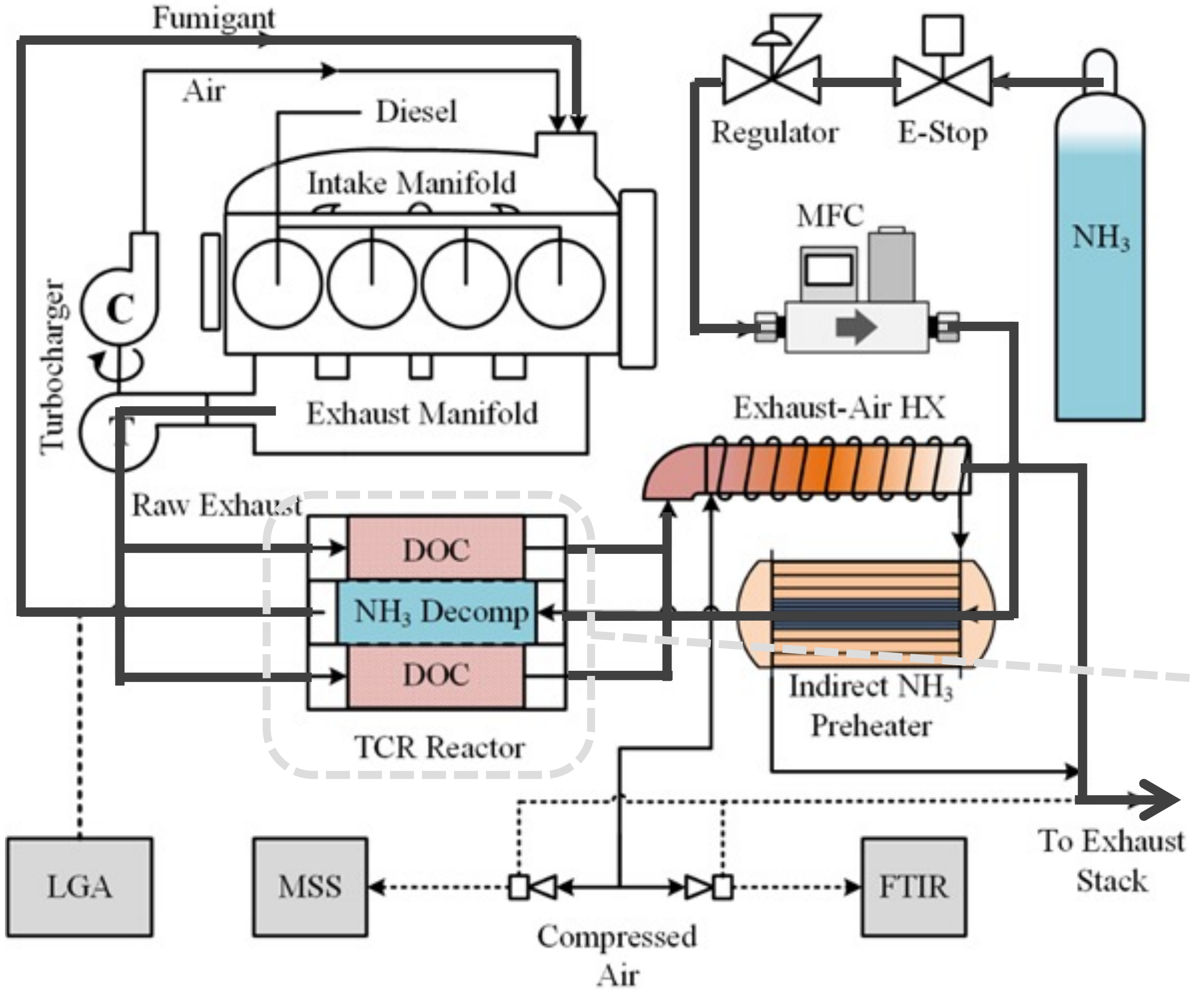


$$2NH_3 \rightarrow N_2 + 3H_2 \quad \left[45.8\frac{kJ}{mol}\right]$$

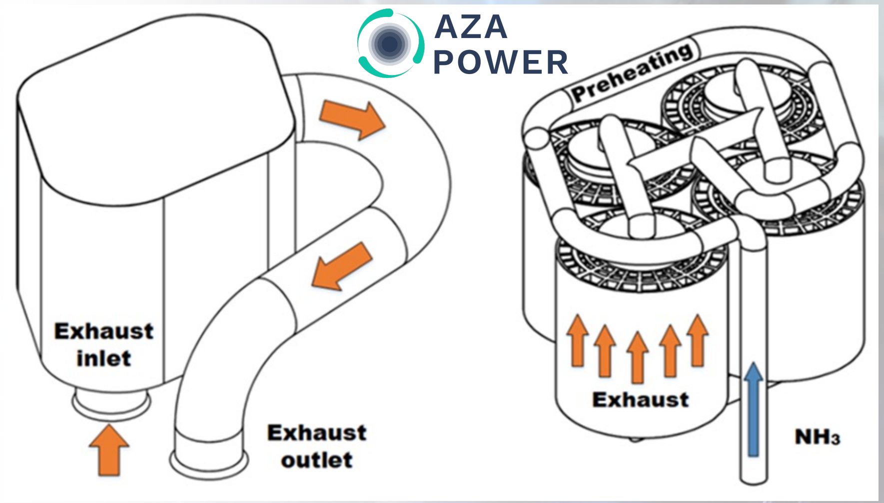


Use waste exhaust heat to partially decompose ammonia = thermochemical recuperation (TCR)

Dual-fuel compression ignition engine combustion of ammonia-hydrogen mixtures enabled by thermochemical recuperation (TCR)



- John Deere 4045HF475 CI engine
- Modified ISO 8178-C1 8-mode test
- TCR installed on engine
- Diesel replaced to 50% (LHV)
- PM-based diesel oxidation catalyst (DOC)

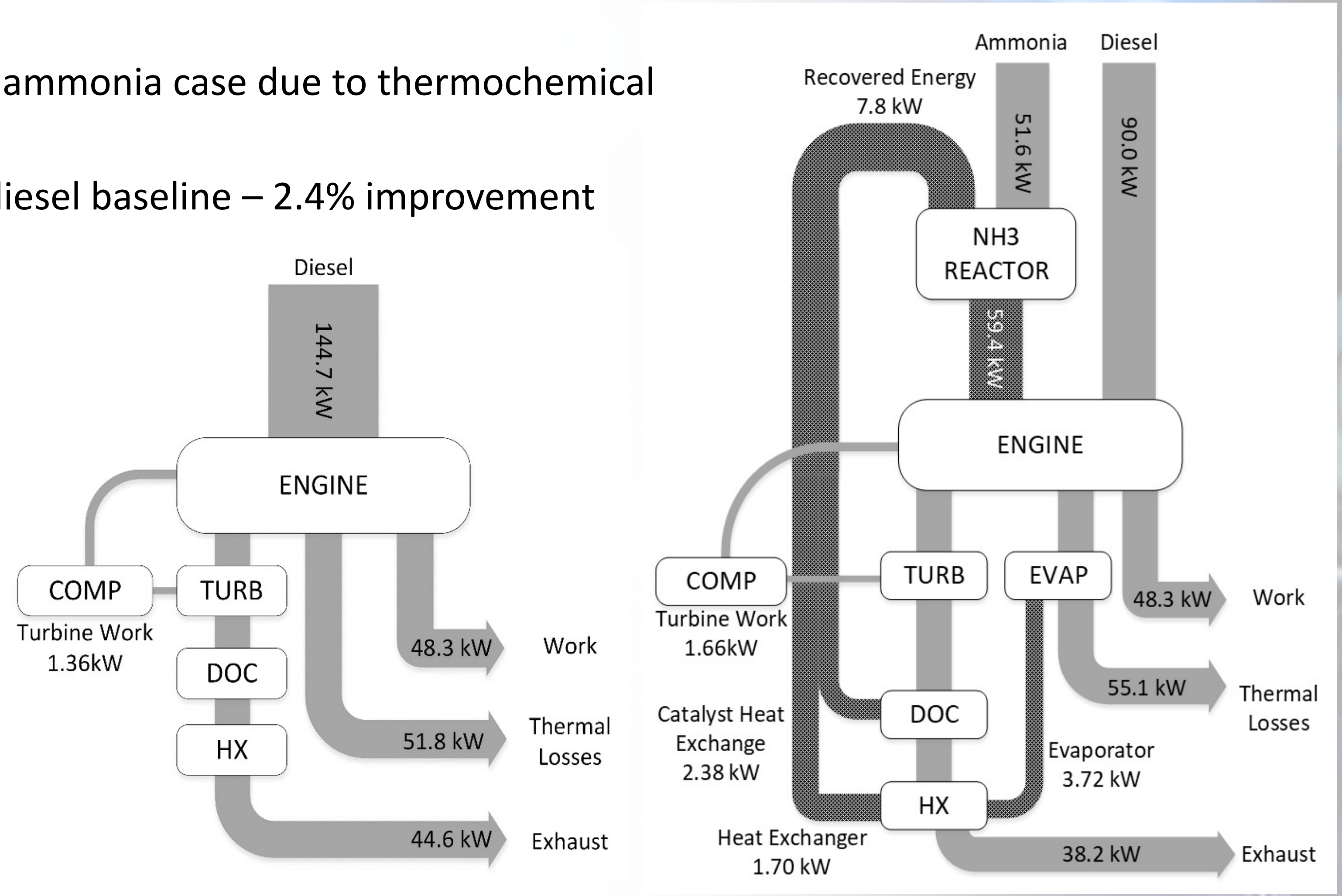


Northrop, W.F. (2020) Engine Fuel-Reforming Reactors, Systems, and Methods, US Patent 10,815,123.

Kane, Seamus P., and William F. Northrop. 2021. "Thermochemical Recuperation to Enable Efficient Ammonia-Diesel Dual-Fuel Combustion in a Compression Ignition Engine" *Energies* 14, no. 22: 7540. https://doi.org/10.3390/en14227540

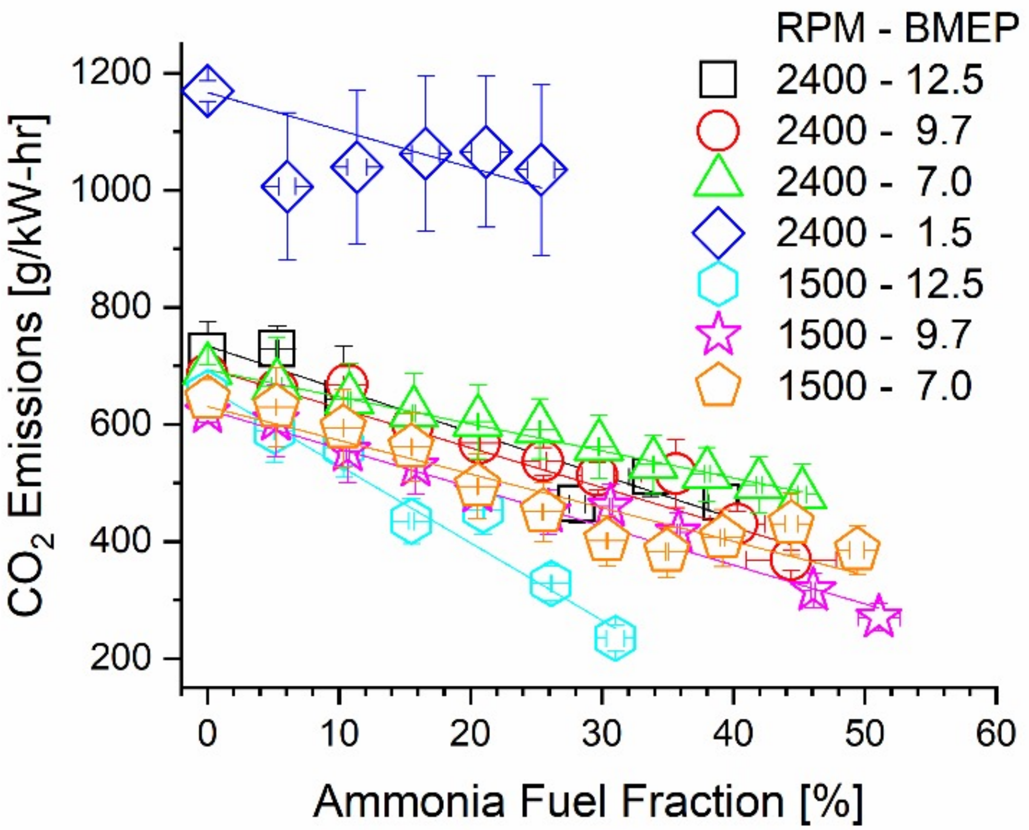
In a practical application TCR improved thermal efficiency and enable higher ammonia fraction

- 3.5 kW less input fuel for ammonia case due to thermochemical recuperation.
- 34.1% BTE vs. 33.3% for diesel baseline – 2.4% improvement



Kane, S. P., Zarling, D., and Northrop, W. F., ASME ICEF 2019. https://doi.org/10.1115/ICEF2019-7241

CO_2 emissions decrease linearly as a function of diesel replacement with ammonia



TCR enables up to 50% replacement of diesel fuel by energy

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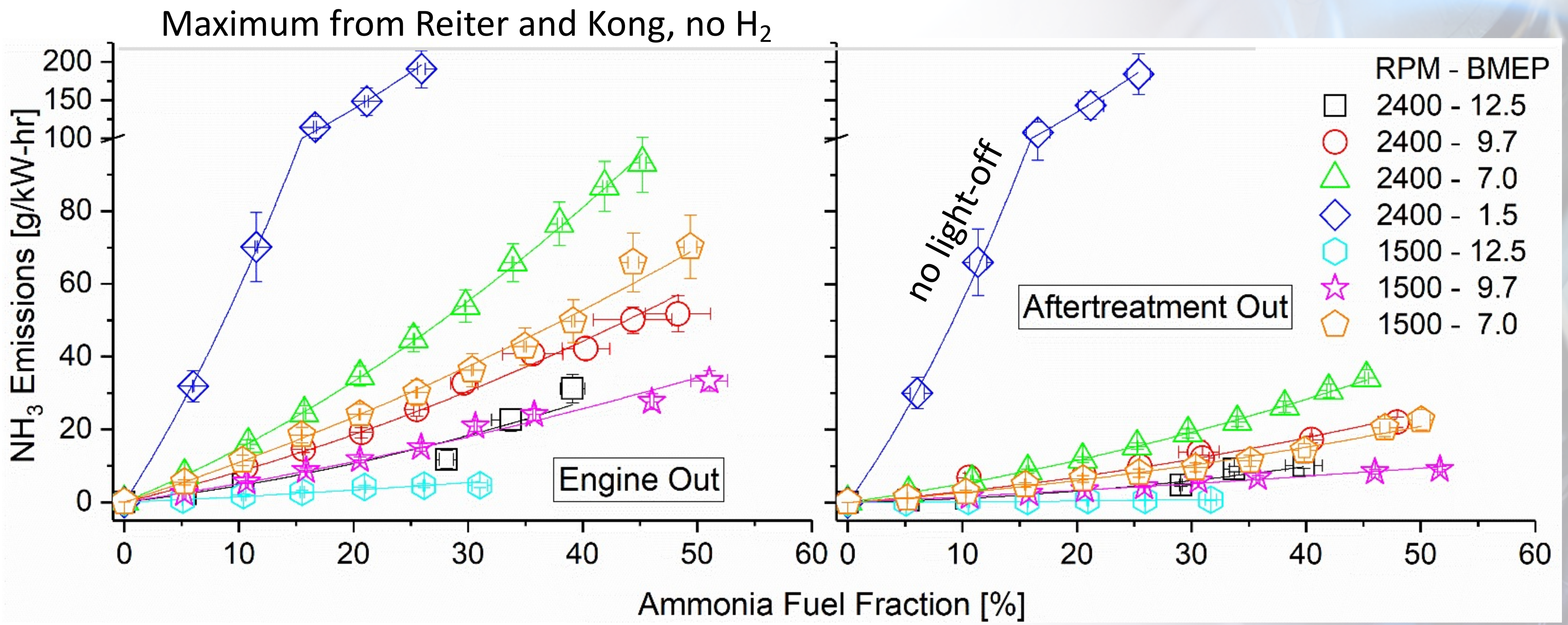
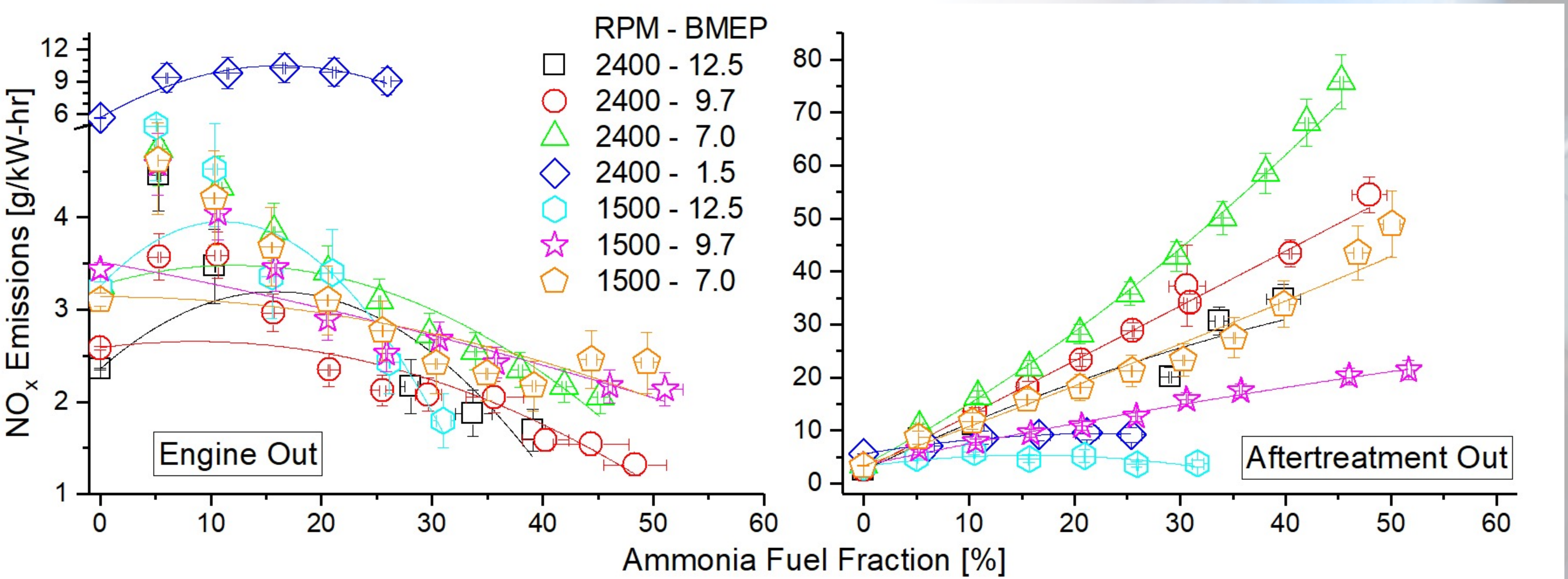
NH_3 emissions are improved compared to previous studies and PM-based DOE can oxidize NH_3 for higher load cases



Reiter, A.J.; Kong, S.C. Combustion and emissions characteristics of compression-ignition engine using dual ammonia-diesel fuel. 2011, *Fuel 90*, 87–97, doi:10.1016/j.fuel.2010.07.055.

Kane, Seamus P., and William F. Northrop. 2021. "Thermochemical Recuperation to Enable Efficient Ammonia-Diesel Dual-Fuel Combustion in a Compression Ignition Engine" *Energies* 14, no. 22: 7540. https://doi.org/10.3390/en14227540

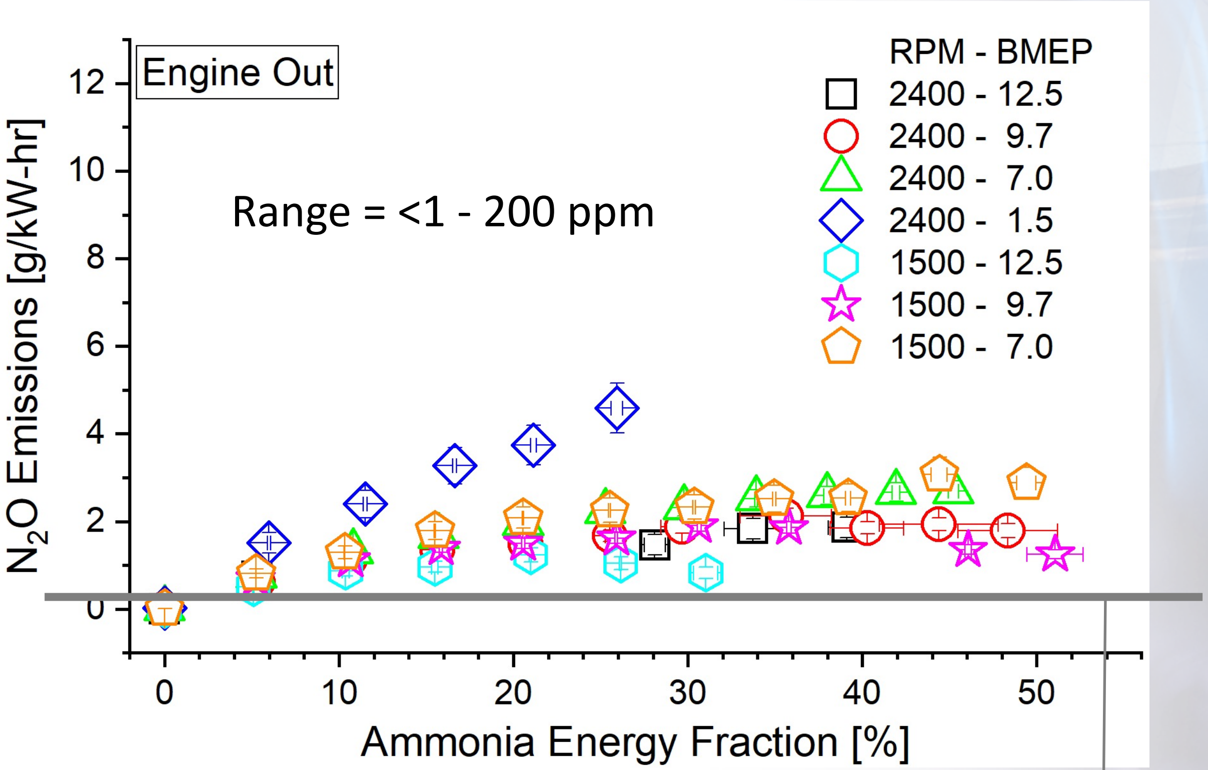
NO_X emissions are reasonable from the engine out location, but NH_3 oxidation on PM-based DOC favors NO instead of N_2



Unburned ammonia and hydrogen have potential to be used as reductants in downstream SCR; No urea needed

Kane, Seamus P., and William F. Northrop. 2021. "Thermochemical Recuperation to Enable Efficient Ammonia-Diesel Dual-Fuel Combustion in a Compression Ignition Engine" *Energies* 14, no. 22: 7540. https://doi.org/10.3390/en14227540

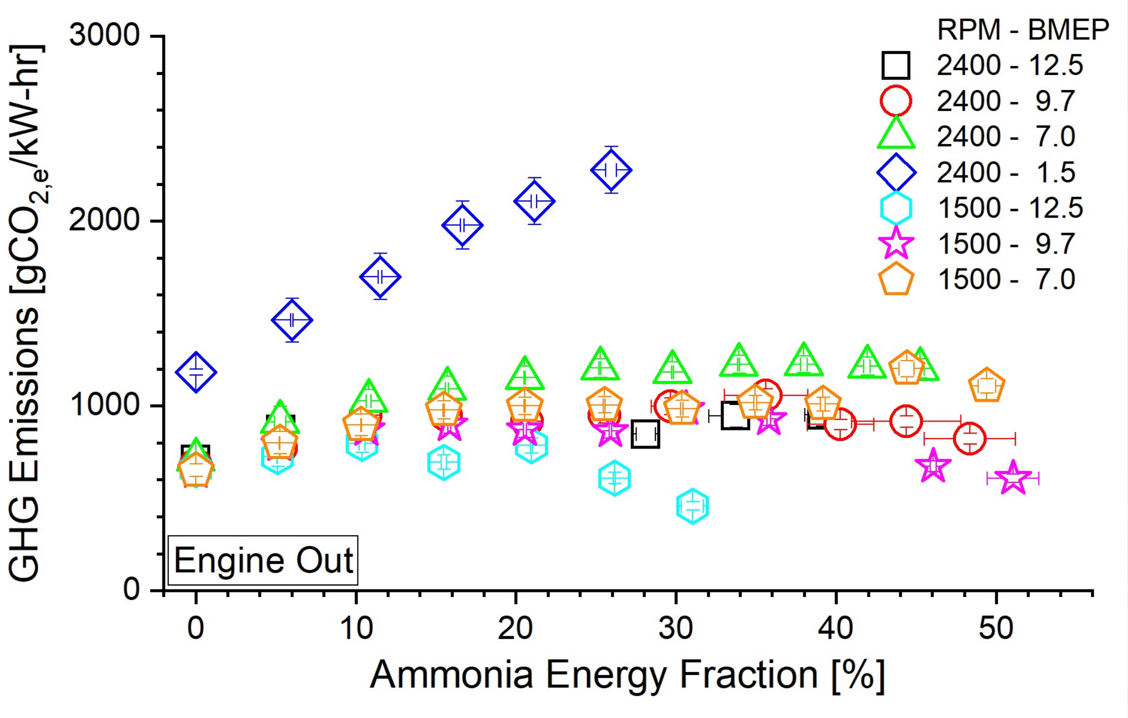
N_2O is also produced by both the engine (and the DOC) as a function of ammonia fueling



EPA GHG N_2O Standard = 0.135 g/bkW-hr

Kane, Seamus P., and William F. Northrop. 2021. "Thermochemical Recuperation to Enable Efficient Ammonia-Diesel Dual-Fuel Combustion in a Compression Ignition Engine" *Energies* 14, no. 22: 7540. https://doi.org/10.3390/en14227540

N_2O has a greenhouse gas potential approximately 298 times that of CO_2 on a 100-year timescale

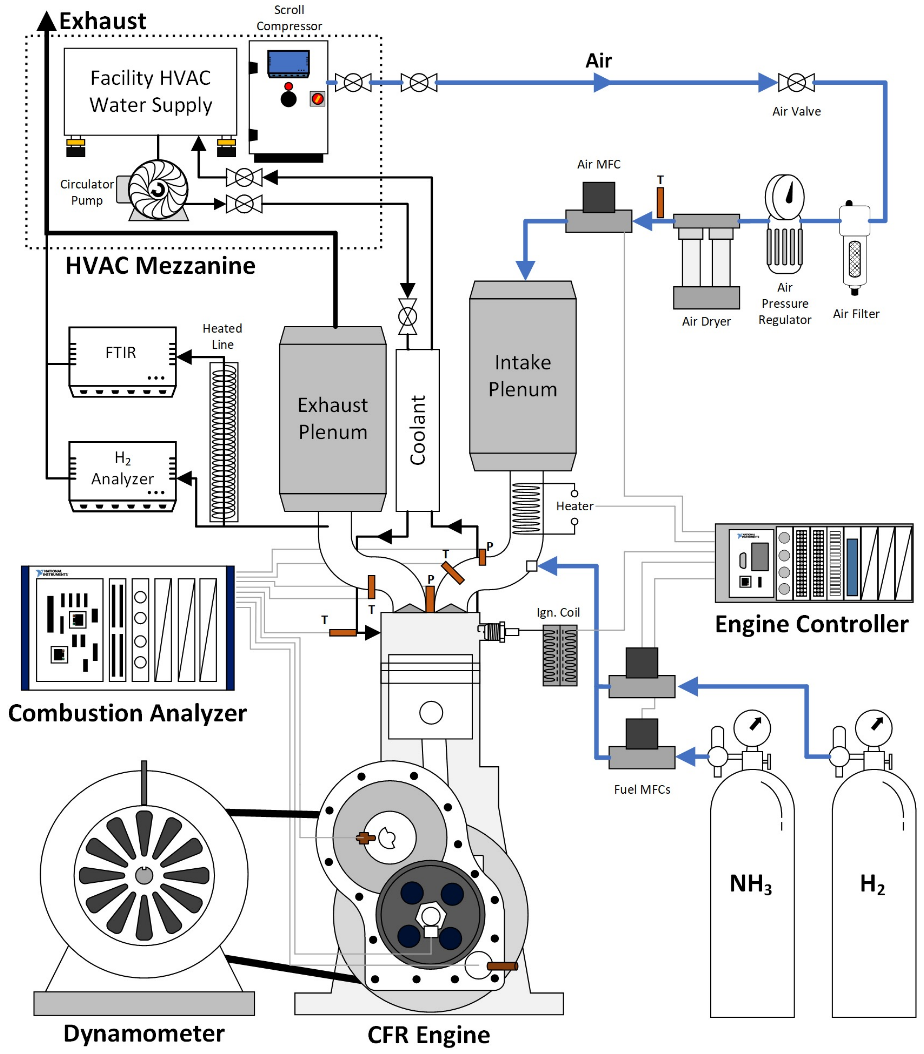


N_2O formation is favored in lean engine combustion and by aftertreatment catalysts at low temperature

- N_2O emissions must be controlled from both lean ammonia combustion and aftertreatment
- THC and CO from dual fuel still require mitigation

Kane, Seamus P., and William F. Northrop. 2021. "Thermochemical Recuperation to Enable Efficient Ammonia-Diesel Dual-Fuel Combustion in a Compression Ignition Engine" *Energies* 14, no. 22: 7540. https://doi.org/10.3390/en14227540

Spark ignition engine combustion of ammonia-hydrogen mixtures



Lean combustion and aftertreatment favors N_2O formation, what about SI operation?

CFR engine with compressed air supply

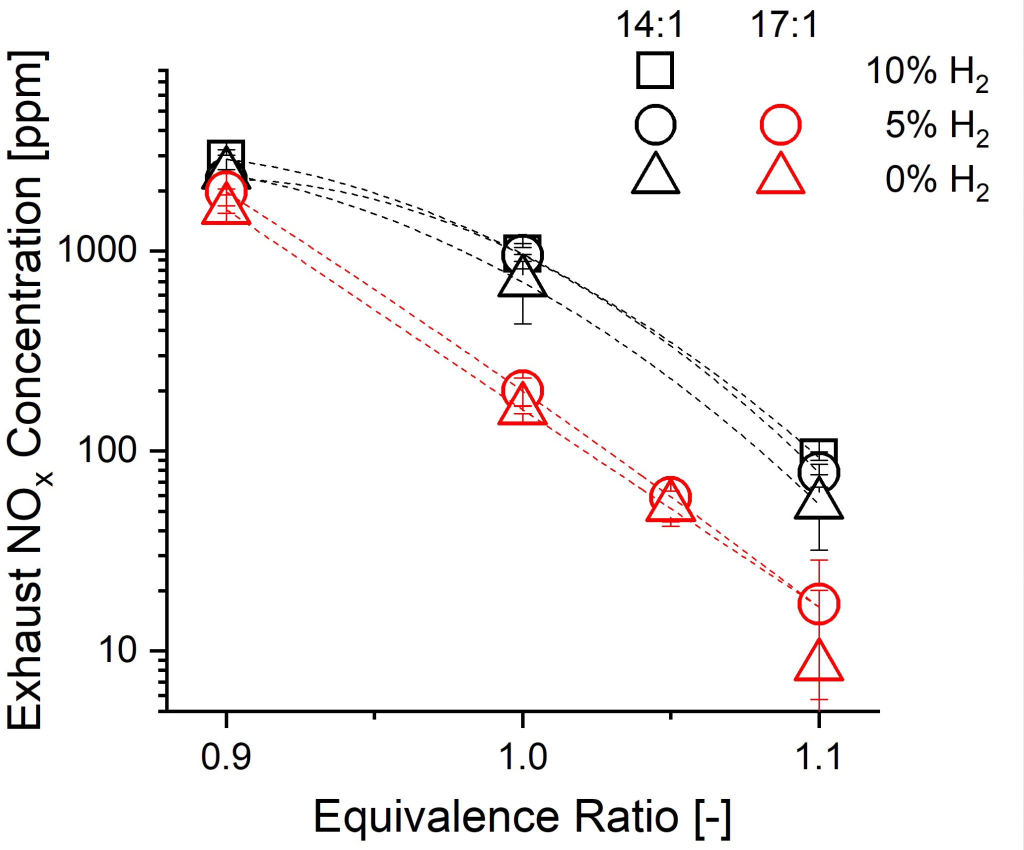
Air heating, gas mixture control, and compression ratio (CR)

Range of experiments:

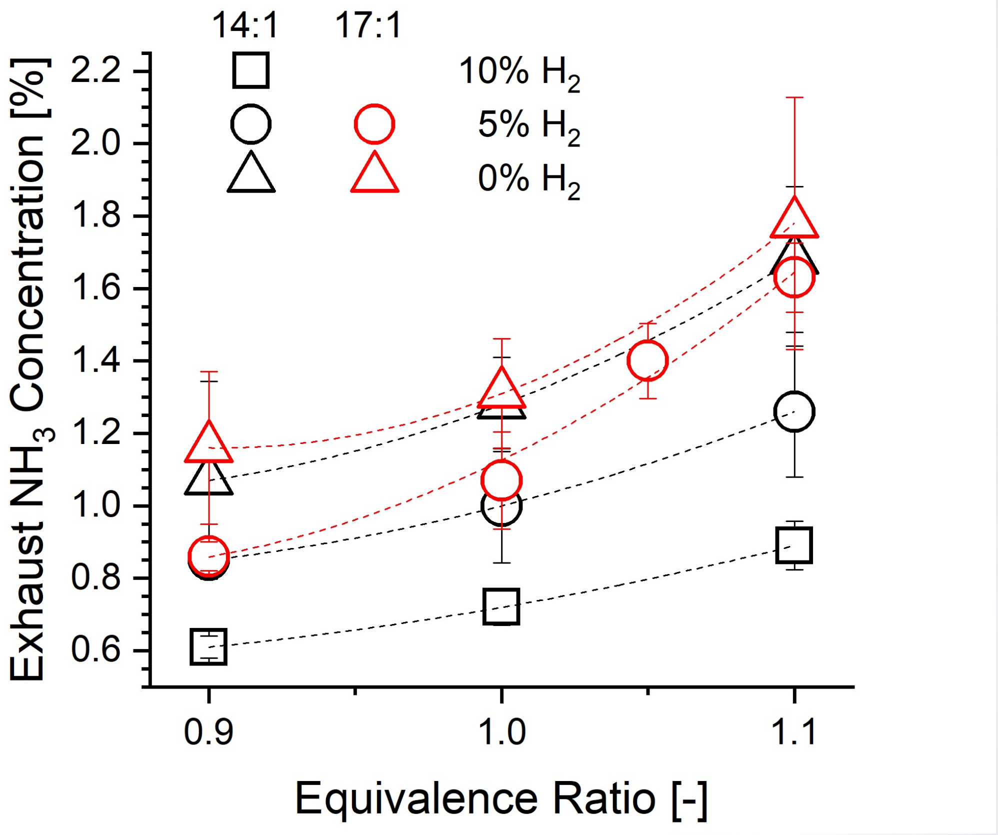
- Equivalence ratio = 0.9, 1.0, 1.1
- H_2% of fuel = 0, 5, 10
- CR = 14, 17

Constant intake pressure = 1 bar

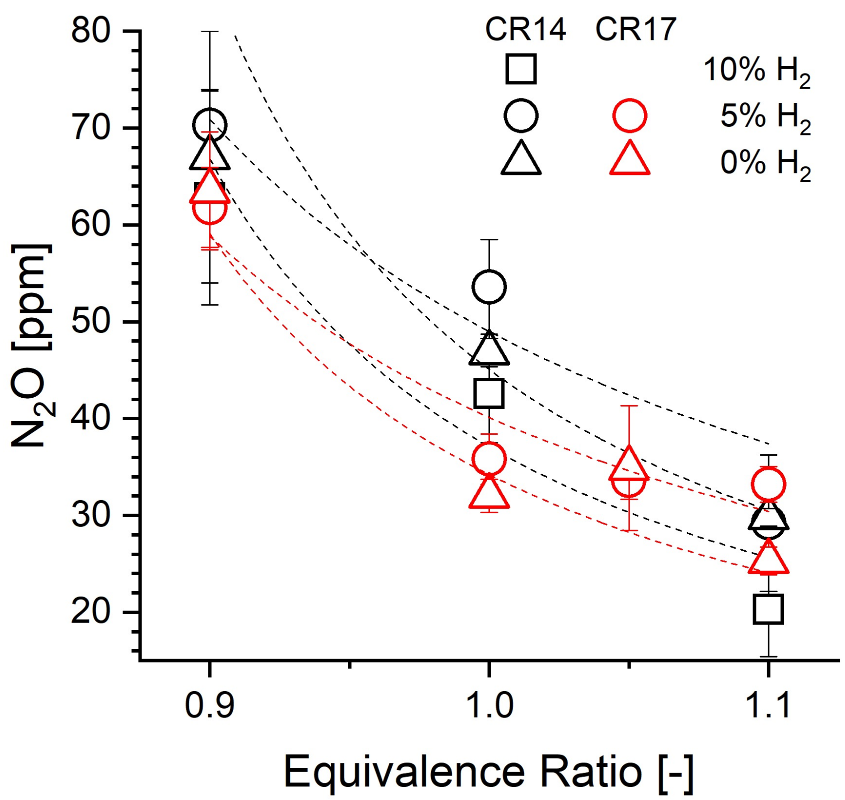
Rich operation appears to control NO_X well in SI mode independent of H_2 percentage



A NO_X vs NH_3 tradeoff exists with equivalence ratio; increasing hydrogen concentrations appear to defeat it

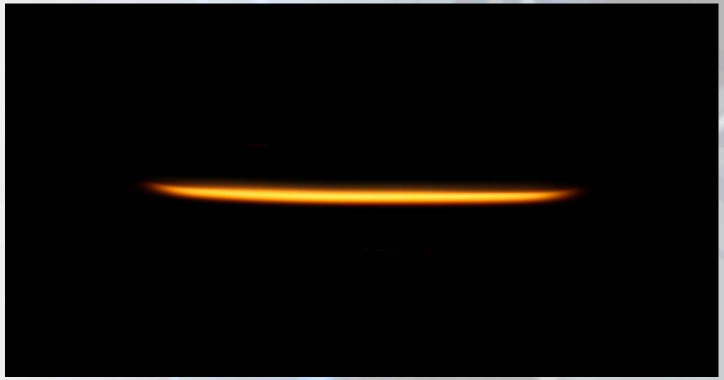


N_2O emissions considerably lower than previous diesel work and decreases with equivalence ratio – More promising than lean operation



Ammonia combustion in engines is far from optimized for use in engines though promising trends are emerging

- NH_3 low reactivity and flame speed can be enhanced with low H_2 concentrations
- Fundamental combustion studies for refining chemical mechanisms and NH_3 flames needed
- Dual-fuel diesel operation can be enhanced by hydrogen addition and TCR
- NO_X from dual-fuel diesel combustion can be controlled; N_2O is a key challenge
- Stoichiometric and rich SI combustion is promising with as little as 5% H_2 addition
- Advanced combustion modes due to ammonia's unique chemistry compared to HC's should be studied



Ammonia-H_2 Counterflow Flame at UMN MERL

Thank You

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