Engine-ready, Carbon-free Ammonia Fuel

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NH_3 Fuel: The Key to US Energy Independence
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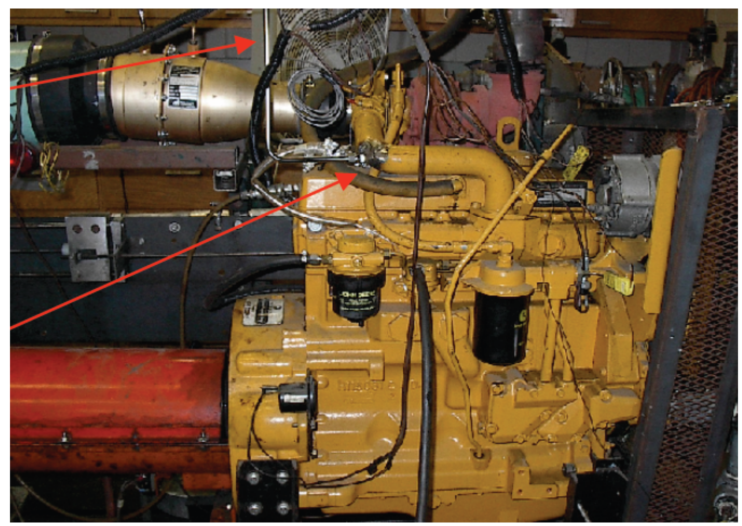
Highlights: NH_3 as a Combustion Fuel

Belgium, 1943: NH_3 & Coal Gas

Canada, 1981: NH_3 & Propane

United States, 2007: NH_3 & Gasoline

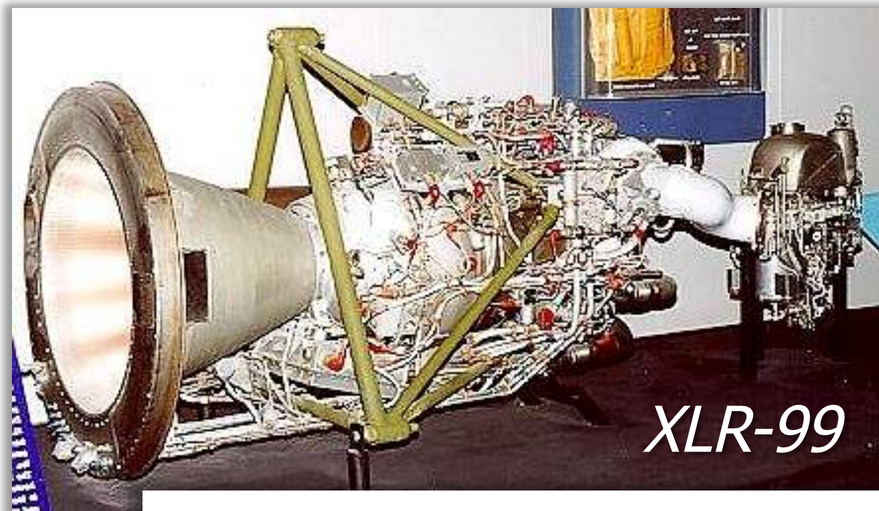


United States, 2008: NH_3 & (Bio)diesel

NH_3 Combustion Concerns

- **Spark ignition**
  - Tight flammability window (6-15% in air)
  - Gets better as temp. increases, worse with altitude!
  - Thermal issues at low engine speeds or startup
  - Air/NH_3 mixing difficult; air displaced by NH_3 vapor
- **Compression ignition**
  - High octane… high autoignition temperature
    - -Diesel: ~210°C
    - -NH_3: 651°C (H_2: 536°C)
- **Combustion (gas) turbine**
  - Low flame speed for ammonia/air, low flame radiance
  - Low heating value → high turbine flow

A Successful Combustion Turbine



XLR-99

- "1 million hp"
- Anhydrous NH_3/LOX
- 1.4:1 O_2/NH_3 ratio

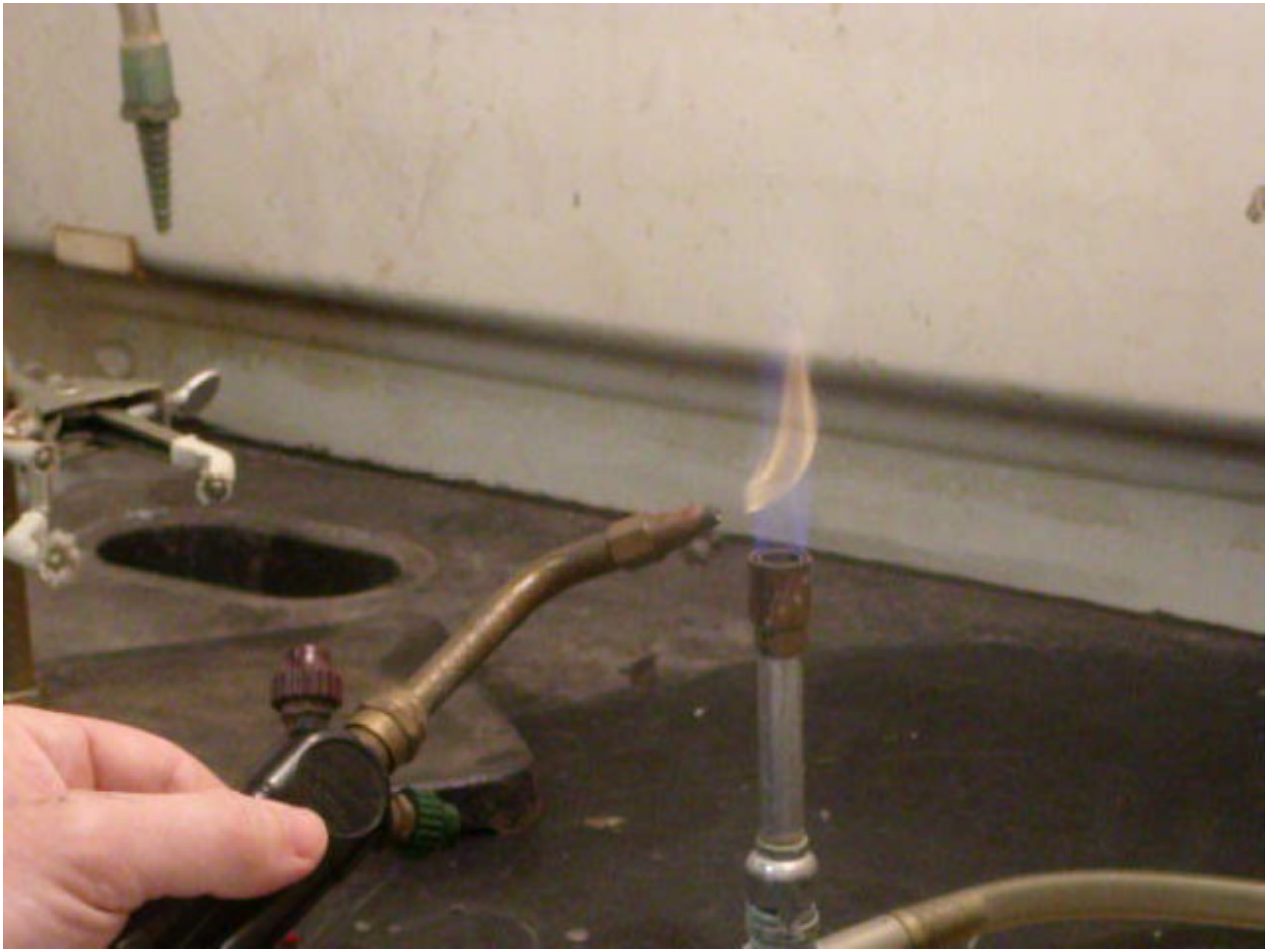
US Air Force

Point of Order...

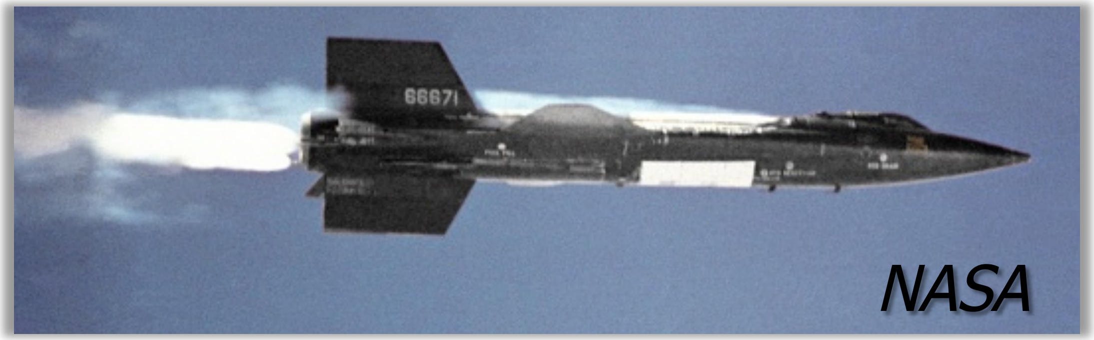
Recreation of an Old Experiment

- **2002: NH_3 fuel for soldier power**
  - Good energy density
  - Crack (99+%) for use in fuel cells
- **One-fuel forward**
  - If you use ammonia in the fuel cell, you need to burn ammonia to crack it
  - Torch tests to determine combustion limits, to be extrapolated to microchannel combustion

Ammonia Torch

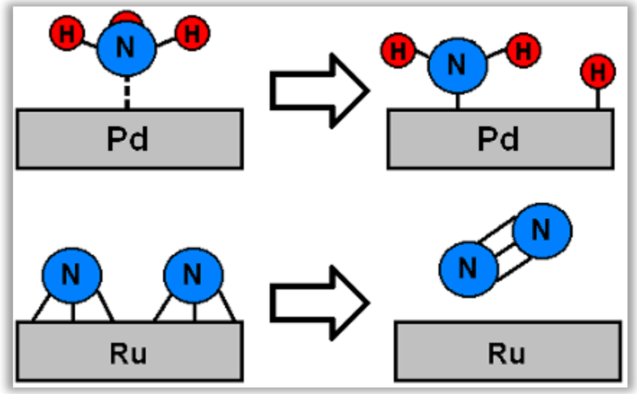


White Flame: Good Flame Speed

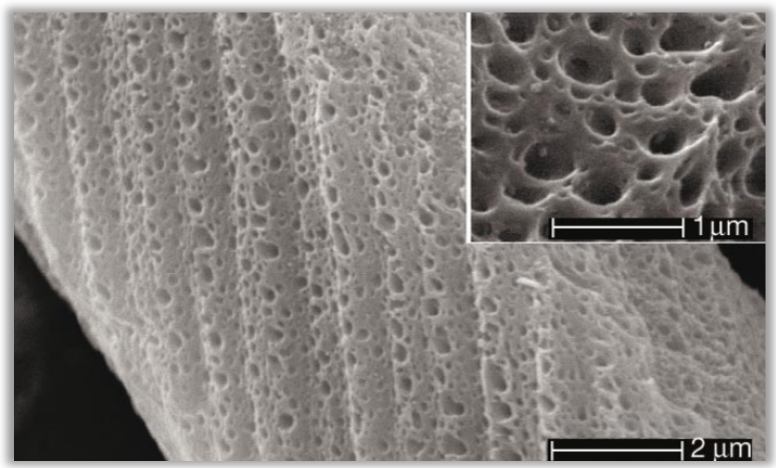


To Reform or to Enrich?

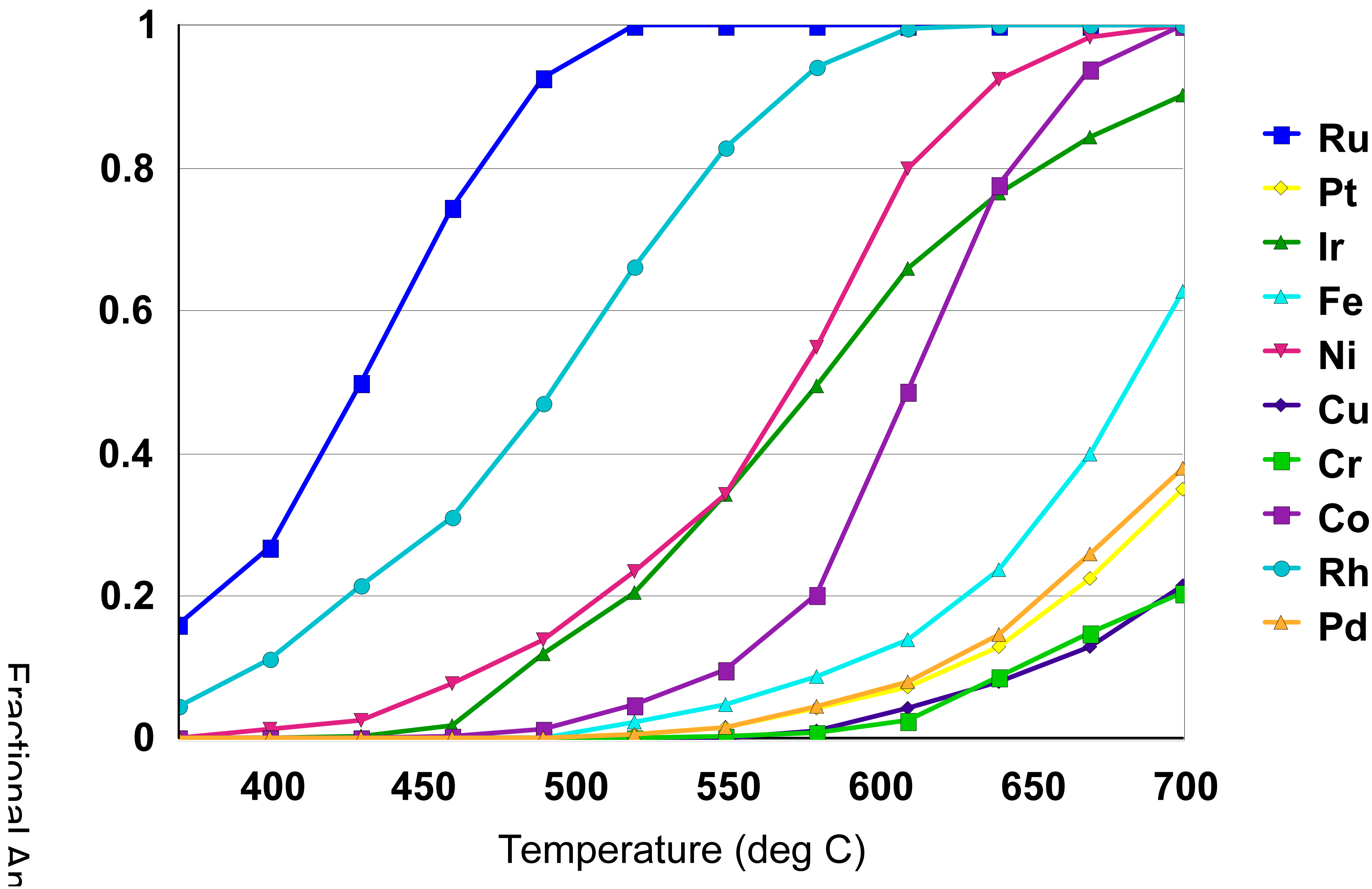
- **Cracking ammonia (reforming)**
  - Temperature will determine catalyst identity/support type
  - 5-10% of NH_3 must be cracked
  - Cold start?



- **Oxygen enrichment**
  - LOX not an option, must use air on the fly
    - -Physical separation of N_2
    - -Molecular sieve (zeolites)
  - Large flows will require large packed beds



Supported Catalysts for Cracking



Supported Catalysts for Cracking

Table 1
Measured TOF for ammonia decomposition over several supported metal catalysts

Catalyst	Dispersion (%)	TOF (s^{-1})	TOF/Ru TOF
0.5 wt% Ru/Al_2O_3	48	6.85	1
1.0 wt% Ni/Al_2O_3	0.9	4.21	0.61
0.5 wt% Rh/Al_2O_3	65	2.26	0.33
1.0 wt% Co/Al_2O_3	2.3	1.33	0.19
1.0 wt% Ir/Al_2O_3	47	0.786	0.11
1.0 wt% Fe/Al_2O_3	0.7	0.327	0.048
1.0 wt% Pt/Al_2O_3	31	0.0226	0.0033
1.0 wt% Cr/Al_2O_3	1.9	0.0220	0.0032
0.5 wt% Pd/Al_2O_3	39	0.0194	0.0028
1.0 wt% Cu/Al_2O_3	5.1	0.0130	0.0019
1.0 wt% Te/Al_2O_3	4.2	<0.0056[a]	<0.00082
1.0 wt% Se/Al_2O_3	2.9	<0.0044[a]	<0.00065
1.0 wt% Pb/Al_2O_3	16	<0.0024[a]	<0.00035

[a]Maximum possible rate, actual rate is below the mass spectrometer detection limit.

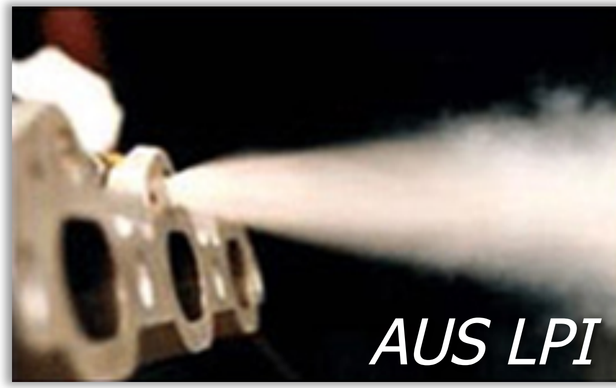
J. Ganley, et. al.
Catalysis Letters,
96 (3-4), p. 117-122 (2004).

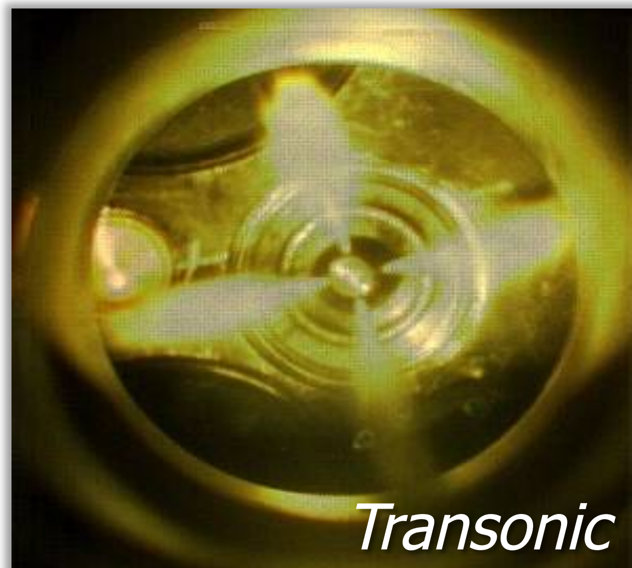
Each Approach Has Drawbacks

- **Catalytic NH_3 Reforming**
  - Precious metals required to avoid dispersion loss
  - Port or plenum injection of fuel, air displacement
  - Liquid NH_3 injection impossible for cracking reaction
- **Oxygen Enrichment**
  - Zeolite/molecular sieve issues
    - Regeneration/N_2 purge required periodically
    - Pressure drop! Calls for turbocharging
    - Automated regeneration controls/timing
  - Fuel/oxidant mixing issues remain
  - Does not allow for liquid NH_3 injection during compression stroke, ox/fuel mixing issues remain

Liquid Injection – What's the Big Deal?

- **Injection timing control, compression ratio tuning**
- **Thermodynamics?**
  - Vaporization heat – emissions
  - Vap. heat not wasted at tank
  - Potential to cool exhaust valves
- **Less displacement of air by fuel vapor**
  - Fuel takes up less space
  - Reduces power loss
  - Reduces need for turbo





Summary of Motivating Factors

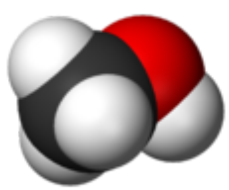
- **Burn NH_3 w/o carbon-bearing promoters**
- **Overcome drawbacks of cracking**
  - Cold start, vapor handling
  - Catalyst cost/cracker volume (your choice)
- **Overcome oxygen enrichment issues**
  - Pressure drop, mixing oxidant/fuel
  - Membrane/sieve cycling and management
- **Enhance flame speed, combustibility**
- **Liquid fuel injection, if possible**

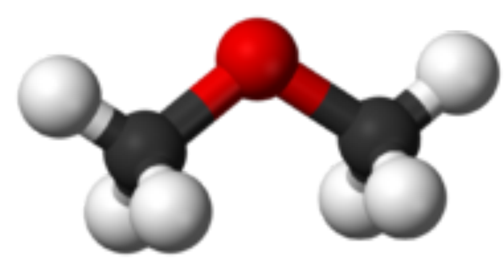
Combustion Enhancers

- **Goal 1: increase fuel flame speed**
  - This is a kinetic effect – reducing reaction barrier
  - Increase reaction rate: flame propagates faster
  - Good enhancers: gasoline, propane, methane, H2
  - (side note: O_2 increases reactive energy transfer – fewer inerts to soak up collision energy of radicals)
- **Goal 2: increase net heating value of fuel**
  - This is a thermodynamic effect – broken-bond energy
  - Raise internal energy of mixture: wider flammability range
  - Better performance at low engine speeds & cold start
  - (side note: oxygen enrichment reduces total volume of gas heating, and associated thermal sink)
- **Some of the best: H_2 C_2H_2 C_3H_8 C_4H_{10}**

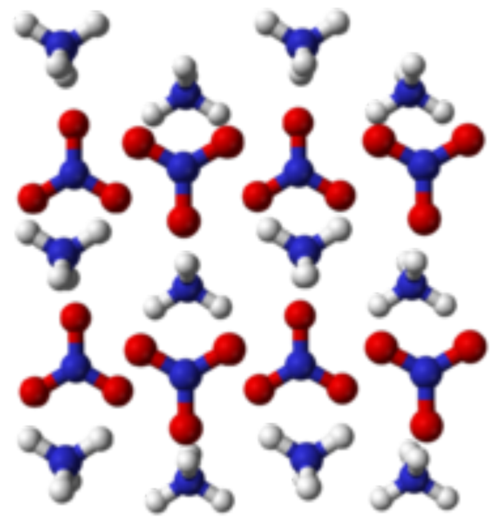
Oxygenated Additives

- **A new twist: add oxygen as well as a fuel**
  - Benefit: oxygen is included, assists oxidation of fuel
  - Detriment: oxygenated fuel = lower energy content
- **Several oxy-fuels strike a fair balance**
  - Methanol
  - Ethanol
  - Dimethyl Ether (DME)





Ammonium Nitrate (AN)



- **NH_4NO_3**
  - Carbon-free
  - Reactive, oxidizer
  - Not flammable, not an explosive
  - Our second favorite fertilizer
- **Made from ammonia & oxygen**

$$4\ NH_3 + 5\ O_2 \rightarrow 4\ NO + 6\ H_2O$$

$$2\ NO + O_2 \rightarrow 2\ NO_2$$

$$3\ NO_2 + H_2O \rightarrow NO + 2\ HNO_3$$

$$HNO_3 + NH_3 \rightarrow NH_4NO_3$$

Ammonia and AN

- **AN is extremely miscible w/anhydrous NH_3**
  - Saturation: ~80 wt% AN in NH_3 at 25°C
  - Reduces vapor pressure of solution
  - Creates a combustible liquid
- **Exceptional oxygenation**

Standard NH_3 Combustion: $4\ NH_3 + 3\ O_2 \rightarrow 6\ H_2O + 2\ N_2$

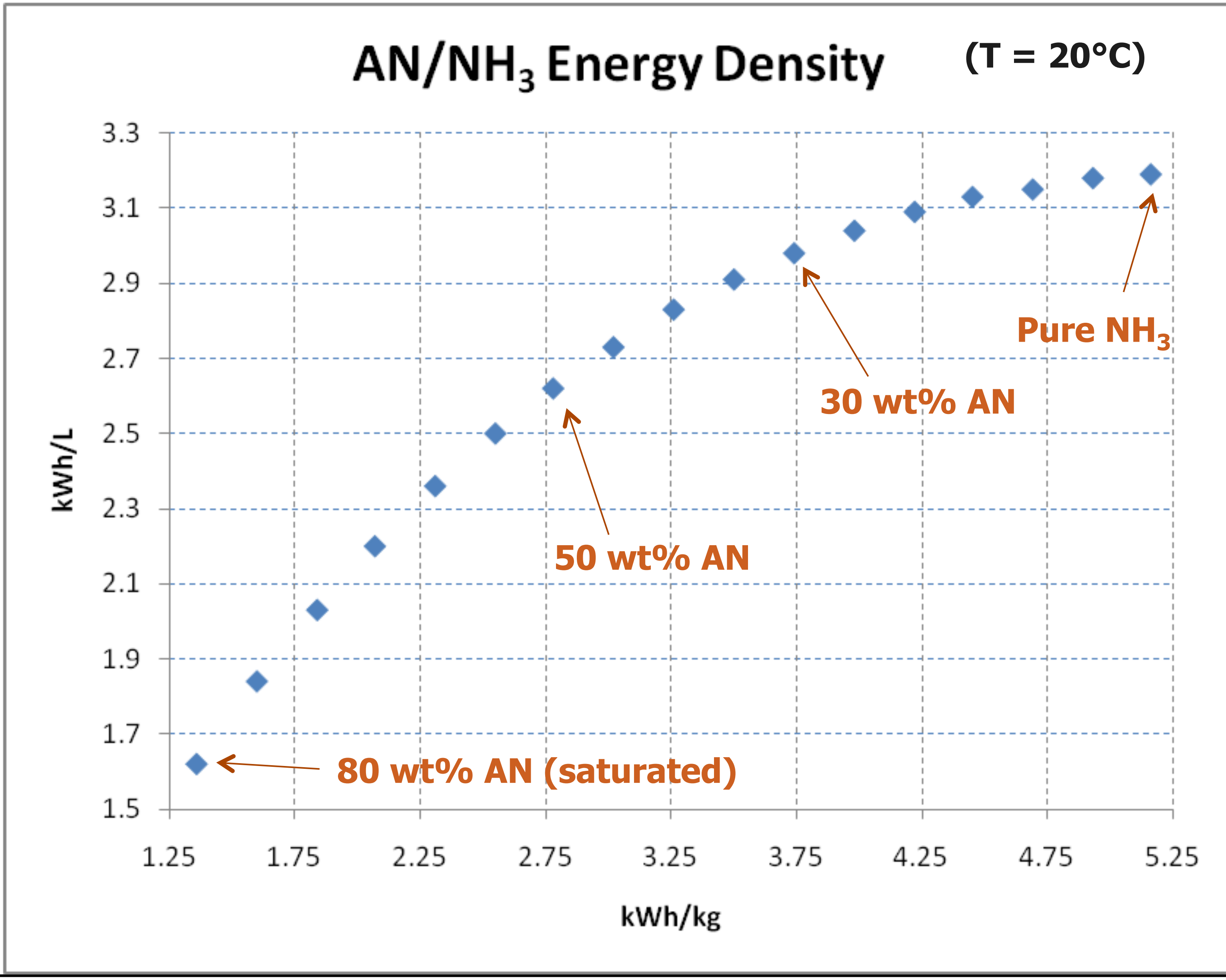
Fuel:O_2 ratio = 1.3:1

AN/NH_3 Combustion: $2\ NH_3 + NH_4NO_3 + O_2 \rightarrow 5\ H_2O + 2\ N_2$

Fuel:O_2 ratio = 3:1

(represents 70 wt% AN in NH_3)

Effect on Energy Density



Vapor Pressure Effect

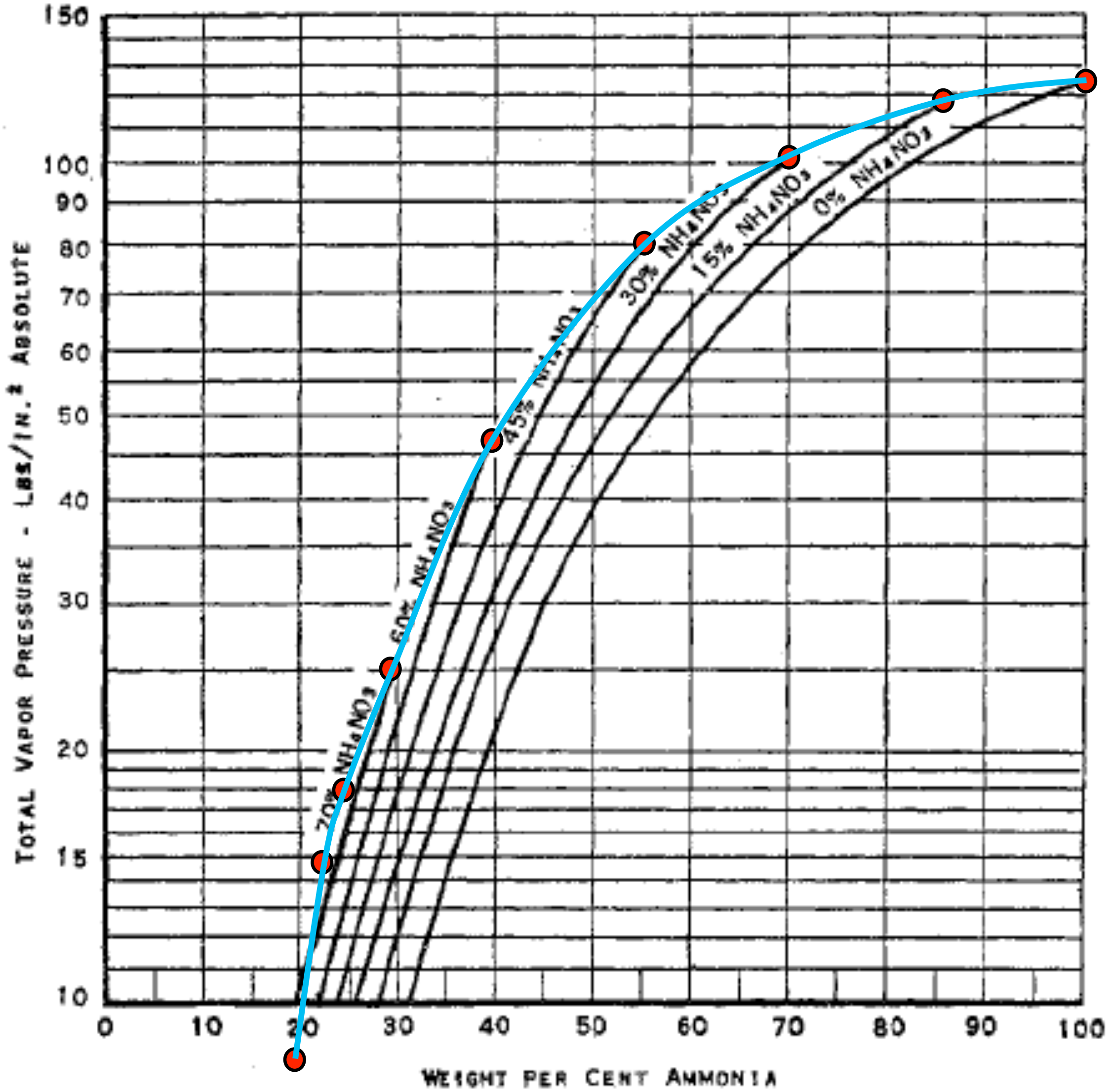
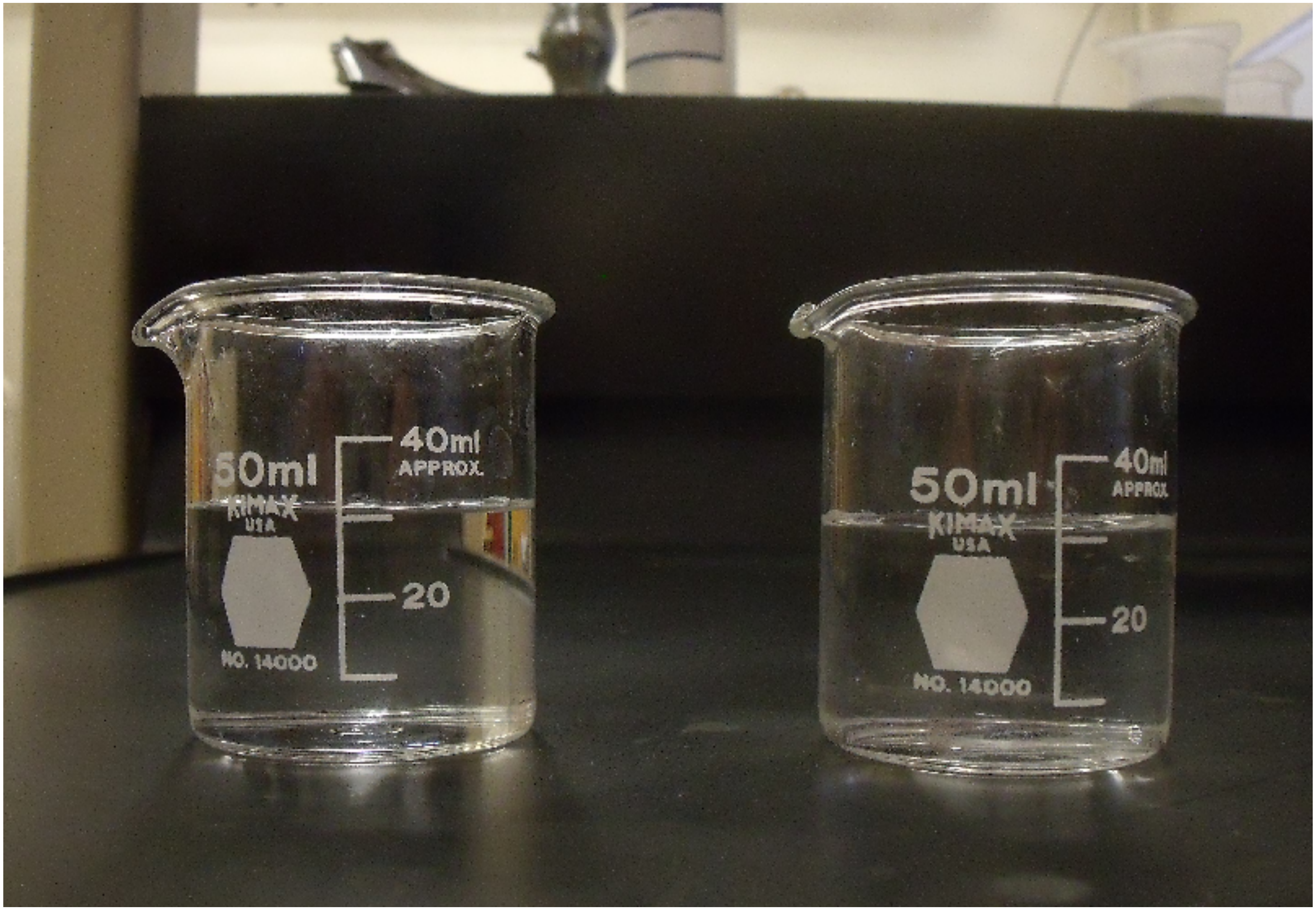


Figure 5. Total Vapor Pressure in the System Ammonium Nitrate–Ammonia–Water at 20° C.

E. Worthington, R. Datin, D. Schutz, *Ind. and Eng. Chem.*, **44** (4), p. 910-913 (1952).

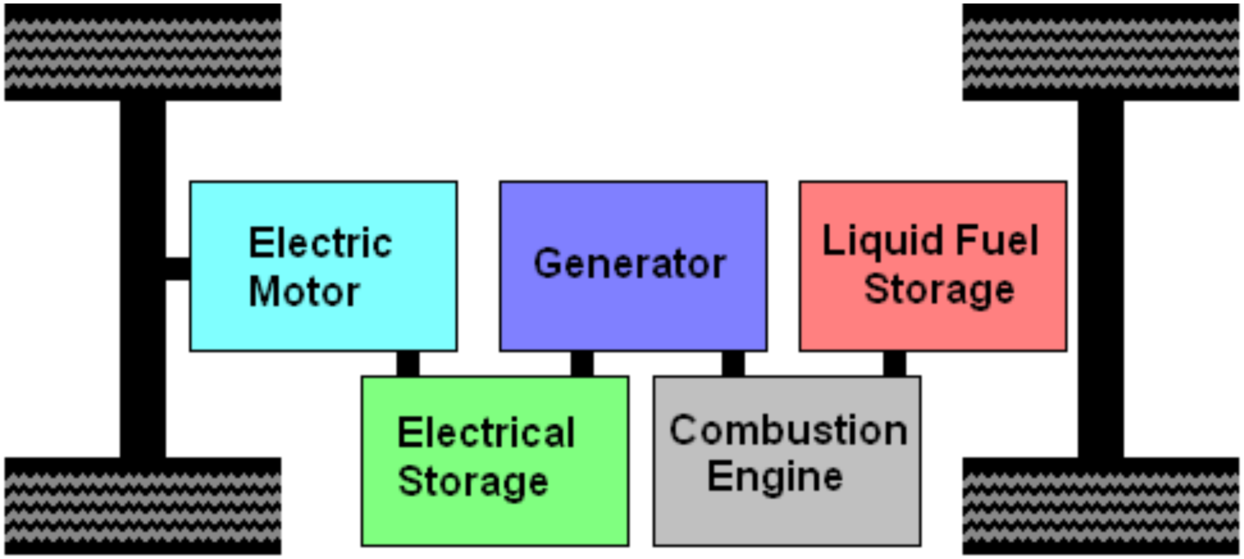
Saturated AN in NH_3 vs. Tap Water



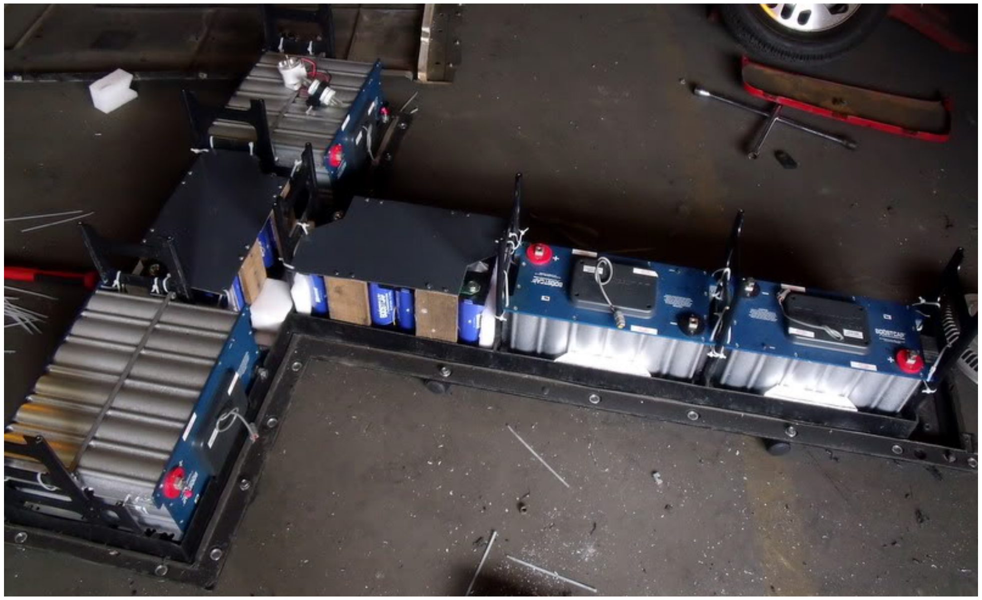
Saturated AN in NH_3 vs. Tap Water

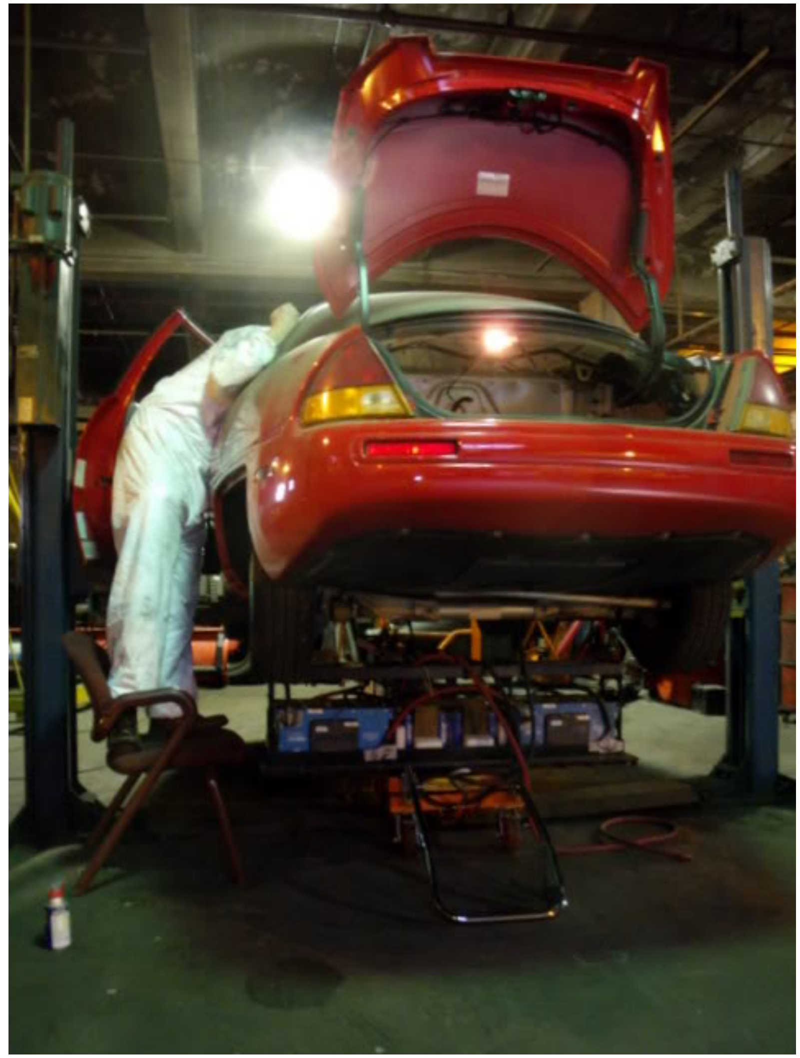
Saturated AN in NH_3 vs. Tap Water

Conversion of GM EV_1



Ultracapacitor-only Buffer





Ready for Transplant

AN/NH3 Fuel Blend Testing

Fuel Blend Testing

- **Initial test: 20 wt% AN in NH_3**
  - Small (100 mL fuel tank)
  - Liquid injector activated with 12 V battery
  - Spray liquid from injector into pilot (propane) flame
- **Mixture burned with orange-blue flame**
- **Plain ammonia liquid did not ignite, occasionally quenched pilot flame**
  - Showed that mixture would burn from injector
  - Next step: try in an engine

Test Engine

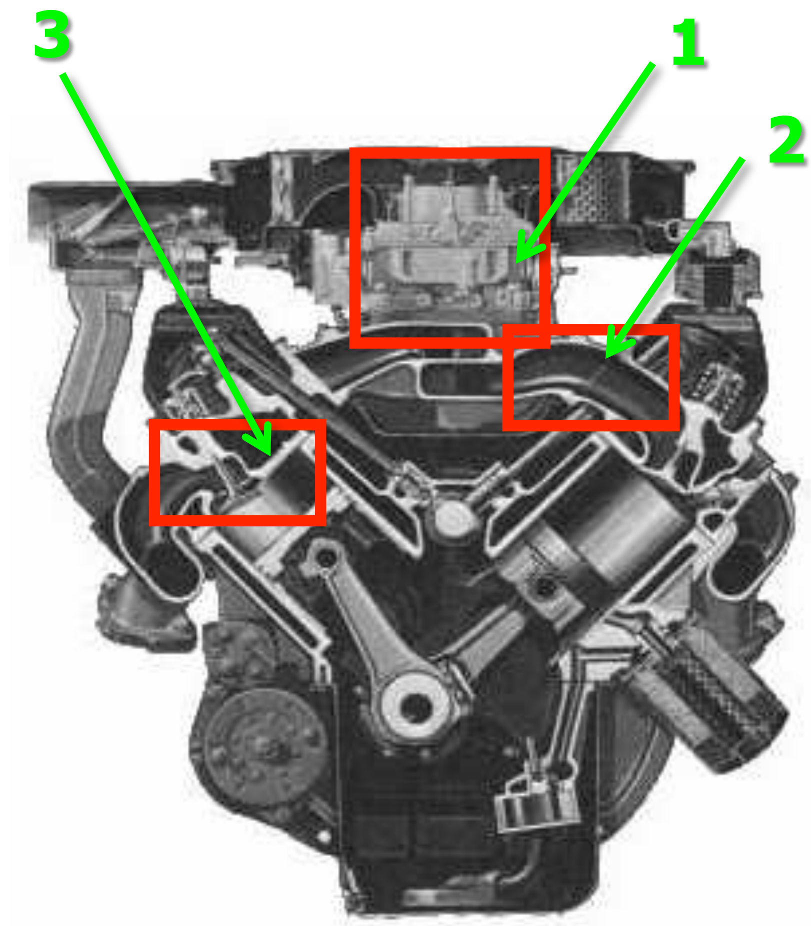
- **Toyota diesel (4 cyl., 2.5 L)**
  - Original compression 18:1
  - Modified to 15.5:1 for ammonia blend (goal 13.5:1)
  - Drilled & tapped for standard spark plugs

Test Fuel Blend

- **30 wt% AN in NH_3**
  - Standard 5 gallon new propane tank with dip tube
  - 99% AN powder
- **Ammonia transferred as vapor, condensed with ice bath**

Stepwise Testing Strategy

- **1: Plenum injection**
  - Single injector, simple setup
  - Lean mix in cyls. 1 & 4
- **2: Port injection**
  - 4 injectors, better tuning
  - Even fuel/air mix per cyl.
- **3: Direct injection**
  - Liquid spray into cylinder
  - Best control for power and emissions



Test 1: Plenum Injection

- **Fire up engine on 118 octane race fuel**
  - Added injector, 0.034” orifice into plenum
  - Warm up engine sufficiently
  - Switch to nitrate/ammonia fuel blend
  - Verify sustained engine run/operation
- **Results**
  - ~ 6 min warm-up time, confirmed by dyno
  - Fuel evacuation time determined to be 55 seconds
  - 1500 rpm set point for race fuel led to AN/NH_3 stall
  - 2000 rpm set point gave sustained 1250 rpm AN/NH_3
  - Ran for 5 minutes, then manually shut down

Test 1 Conclusion

- **Ammonia fuel blend ran the engine as intended**
  - Slightly rough running, due to cyls. 1&4 running lean
  - No ammonia smell in exhaust
- **Ran as expected, leading into Test 2**

Test 2: Port Injection

- **4 Injectors, one per intake runner**
  - 0.020” orifice size
  - Fuel rail made to connect all injectors to fuel supply
- **Results**
  - Engine started on race fuel, ran choppy
  - Raised up to operating temperature, switched to ammonia fuel blend
  - Engine ran the same for about 30 seconds, then got progressively worse
  - Manually shut down engine to investigate
- **Probable issue: improper atomization due to angle of injector to air flow path**

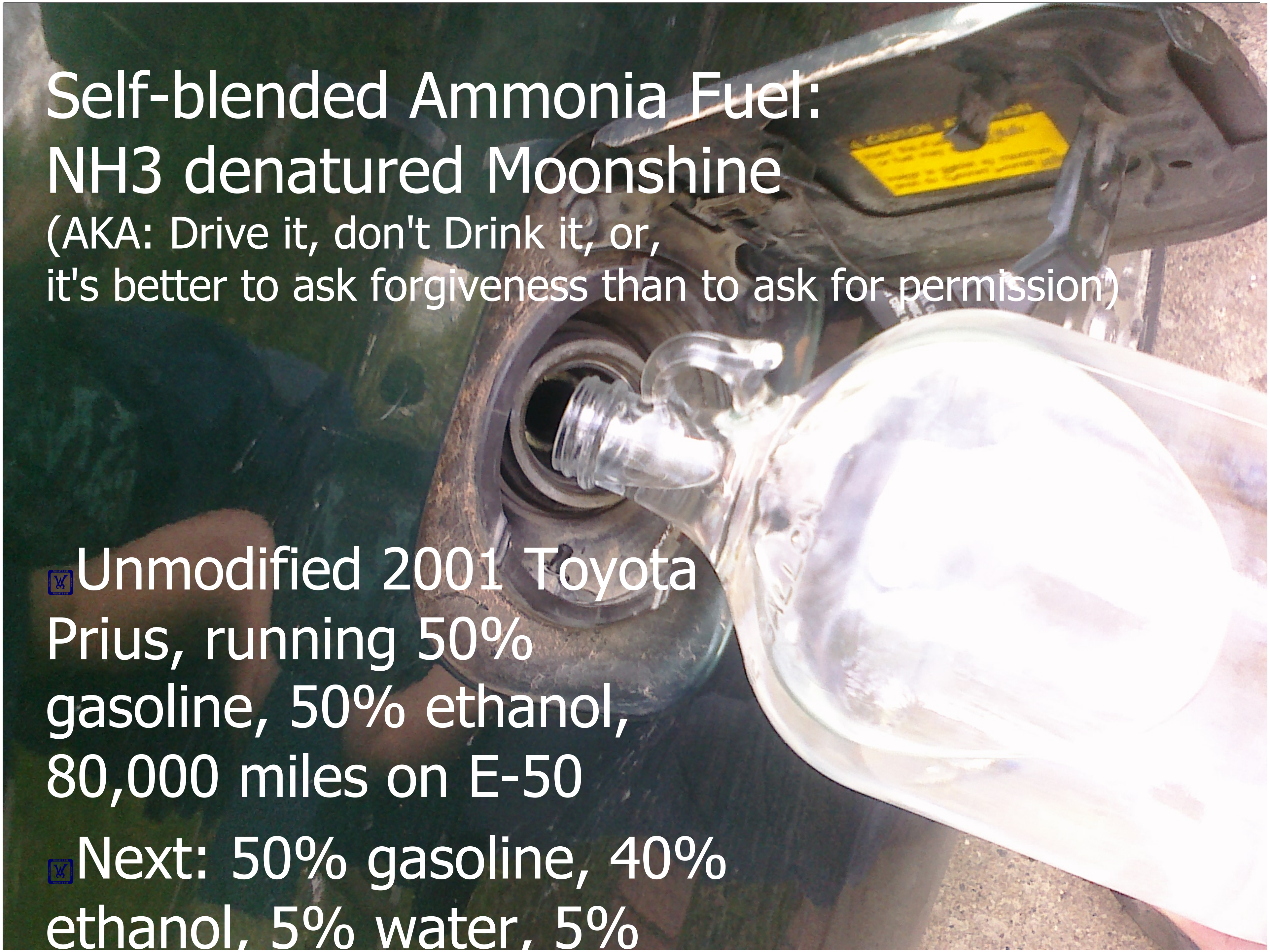
Test 2 Conclusion

- **Engine started, but ran roughly even on race fuel**
- **Disassembly showed that one intake valve had stuck in valve guide, resulting in bent push rod**
- **Waxy residue composed of salt/oil emulsion around other intake valve stems**
- **Therefore, direct injection is required to prevent salt precipitation during fuel vaporization**

Next Steps

- **Test 3 is being planned**
  - Must replace the bent push rod
  - Will reopen the engine and complete investigation
- **This engine should be a good platform for future tests to determine optimum AN/NH_3 fuel blend compositions, injector locations, and spark timing**
- **OEI has offered to assist with plans to integrate ammonia fuel blend genset into EV_1**

Questions?



Self-blended Ammonia Fuel:
NH3 denatured Moonshine

(AKA: Drive it, don't Drink it, or,
it's better to ask forgiveness than to ask for permission)

- Unmodified 2001 Toyota Prius, running 50% gasoline, 50% ethanol, 80,000 miles on E-50
- Next: 50% gasoline, 40% ethanol, 5% water, 5%