Comparative Hazards Assessment of Conventional and Alternative Fuels

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Key words

- Comparative – all fuels are hazardous; want to know relative risks
- Conventional – fuels we are used to living with give us a reference point for hazard assessment; thus methane, propane, octane, cetane, etc.
- Alternative – non-petroleum based, preferably even non-carbon containing (but don't rule out for now); thus H_2, NH_3, CH_3OH, and many more exotic proposals

Philosophy

Q: If you accept that the End of Oil is imminent, why not ignore conventional and just compare alternatives?

A1: Can't wait for the End of Oil to compete with oil

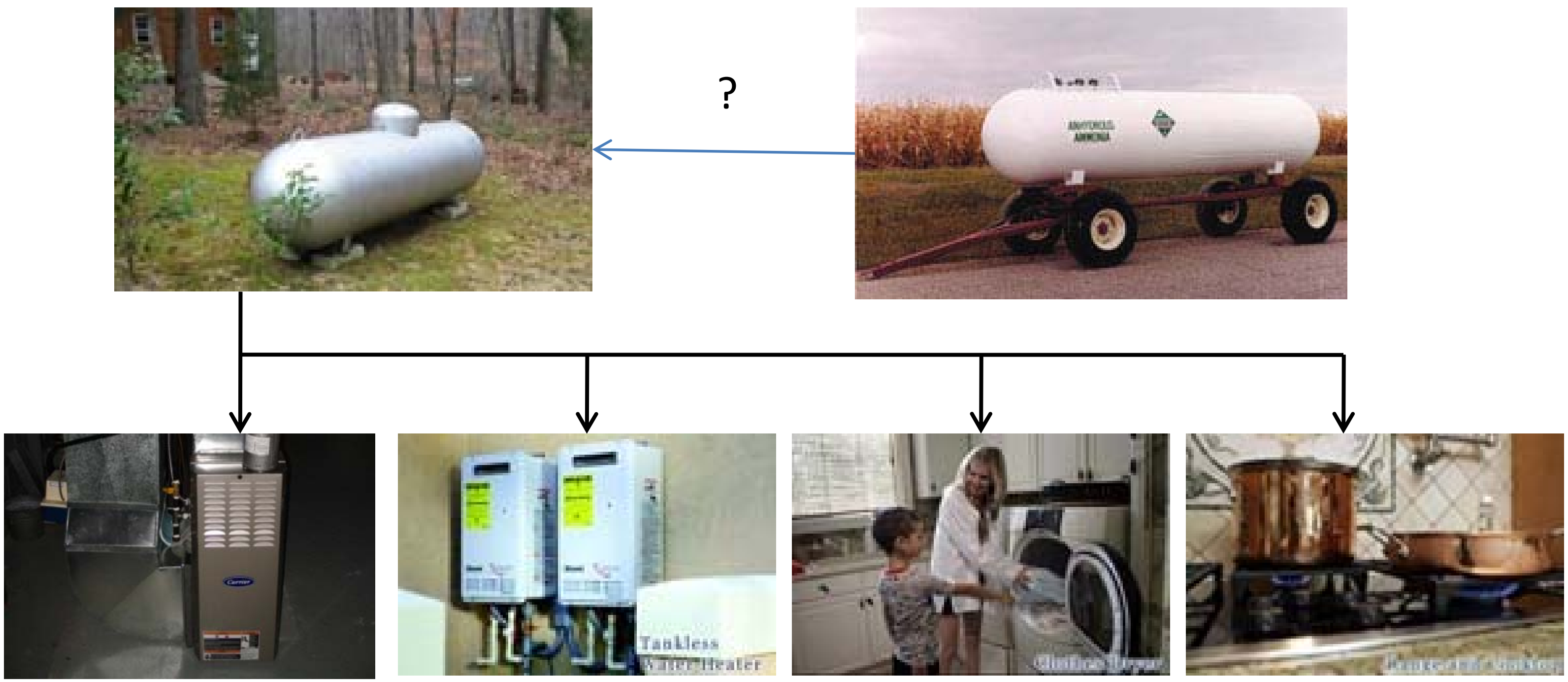
A2: Need to compare that which is unknown with that which is familiar

Apologia

- The task is daunting!
  - Several important alternative and conventional fuels
  - Many different applications
  - Many issues: Toxicity (acute and chronic), fire/explosion, environmental effects, accident scenarios, consequence calculation, risk analysis…
- Advice from Dirty Harry: "A man's got to know his limitations."
- Focus on first-order issues in a specific application that can be taken personally:

Shall I replace propane with ammonia in my home?

Substitute ammonia for propane in home?



Air heating　　Water heating　　Clothes drying　　Cooking

Bottom line

- Propane:
  - Low toxicity
  - High fire/explosion hazard
- Ammonia
  - High toxicity
  - Low fire/explosion hazard

On balance, ammonia looks attractive after fail-safe appliances are developed.

NFPA Hazard Ratings

	Propane	**Ammonia**
Health	2	3
Flammability	4	1
Reactivity	0	0
Special		Corrosive

Degree of hazard increases with rating number. ↑

4 – Very dangerous
3
2
1
0 – Safe

Propane is more dangerous than ammonia.

NFPA definitions

- Health
  - Ammonia (3) – Short exposure could cause serious temporary or residual injury
  - Propane (2) – Intense or continued exposure could cause temporary incapacitation or residual injury
- Flammability
  - Ammonia (1) – Must be preheated before ignition can occur
  - Propane (4) – Will rapidly or completely vaporize at atmospheric pressure and normal ambient temperature, or readily disperse in air and burn readily

Minimum Ignition Energy

- Parameter that mainly determines relative flammability (higher is safer)
- Propane: 0.26mJ
- Ammonia: 14mJ (values from 8-700mJ are cited)
- Depends on such factors as oxygen concentration and proximity of catalytic surfaces

Maximum Flame Velocity

- Another parameter that characterizes flammability (lower is less flammable)
- Propane: 0.40m/s
- Ammonia: 0.23m/s
- Depends on many factors; other things equal, lower for ammonia

Conclusion on flammability

- Values of such parameters as lower and upper flammability limits, flash point, and auto-ignition temperature do not seem to say much about relative hazard.
- Minimum ignition energy and maximum flame velocity are more relevant, but not simple—various values reported.
- Nevertheless, it seems clear from all reports:

Ammonia is difficult to ignite, and thus safe, with respect to fire/explosion hazard.

Is this good or bad?

- Ammonia is relatively non-flammable
- Problematic for a combustion fuel
- Exhaust emissions of unburned ammonia carry toxicity risk
- For open flame burning in a home, exhaust emissions must be extremely low *without fail*

Low flammability of ammonia is basically a good thing—engineering can solve the emissions problem.

The problem with ammonia

$$NH_3 + H_2O \rightarrow NH_4^+(aq) + OH^-(aq)$$

- Ammonia reacts with water to form a strong caustic (basic) solution that destroys tissue, especially eyes, nose, throat, and lungs.
- Ammonia is “toxic” only in the same sense that being burned by a fire is toxic.
- Inhalation and eye exposure are the main risks.

Toxicity standards

- Given in concentrations
- ppm or mg/m^3
- Convert using $[mg/m^3]=M\cdot[ppm]/V_M$
- M is molecular weight [g/mol]
- V_M is molar volume [L/mol], 22.4 for ideal gas at STP
- $1L = 10^{-3}m^3$ and ideal gas $V_M = RT/p$

Acronyms

- OSHA
  - PEL: Permissible Exposure Limit, 8hr TWA (Time-Weighted Average)
- ACGIH
  - TLV-TWA: Threshold Limit Value, 8hr TWA
  - TLV-STEL: 15min TWA (Short-Term Exposure Limit)
- NIOSH
  - REL-TWA: Recommended Exposure Limit, 10hr TWA
  - REL-STEL: 15min TWA
  - IDLH: Immediately Dangerous to Life or Health
- Europe, Canada, others have their own standards, similar in spirit but different in detail

Ammonia vs. Propane

Property	Concentration [ppm]	
	Ammonia	Propane
PEL-TWA	50	1000
TLV-TWA	25	1000
TLV-STEL	35	
REL-TWA	25	
REL-STEL	35	
IDLH	300	2100*

* Based on 10% of the lower explosive limit for safety considerations even though the relevant toxicological data indicated that irreversible health effects or impairment of escape existed only at higher concentrations

What does this mean?

AIHA Guidelines

ERPG Level	Definition	Ammonia conc. [ppm]
1	No more than mild, transient effects for up to 1 hr exposure	25
2	Without serious, adverse effects for up to 1 hr exposure	200
3	Not life threatening up to 1 hr exposure	1000

AIHA – American Institute of Industrial Hygenists

ERPG – Emergency Response Planning Guidelines

CCOHS Chemical Profile

Effects of short-term (acute) exposure

- Noticeable by smell at 0.6 to 53ppm
- 24ppm/2-6 hours is lowest exposure at which nose and throat irritation is noticed
- 30ppm/10min faintly irritating to 2/6 volunteers
- 50ppm/10min moderately irritating to 4/6
- 72ppm/5min irritation noticed by 5/10 volunteers
- 134ppm/5min noticed by 10/10 volunteers
- >1500ppm/"brief" exposure causes severe damage

CCOHS – Canadian Centre for Occupational Health and Safety

Consequences of acute exposure

- Brief exposure (1min?) > 1500ppm
- Pulmonary edema – fluid in lungs
- Symptoms (tightness in chest and difficulty breathing) may not appear for 1-24 hours
- Complete recovery may occur
- Long-term respiratory/lung disorders have also been observed

Eye contact

- 50ppm/5min not irritating
- 72ppm/5min irritating to a few volunteers
- 700ppm is immediately and severely irritating
- At higher exposures there is a high risk of permanent debilitating injury including possible permanent blindness

Effects of long-term (chronic) exposure

- No significant differences in lung function for 58 workers exposed to 9.2ppm ammonia for average of 12.2 years compared to controls with very low exposure (less than 1ppm).
- There is no credible evidence that ammonia can cause cancer.
- Ammonia does not accumulate in the body.

Conclusion: Safe exposures

- 10ppm continuous (days, weeks, years)
- 25ppm for many hours
- 100ppm for an hour
- 200ppm for less than an hour
- 300ppm for less than a minute

Use these levels for engineering design.

Example: Incomplete combustion

- Open ammonia burner in a residential space, operating continuously
- What must be the combustion efficiency?
- Assume:
  - Ammonia concentration must remain < 10ppm
  - Room volume V = 200m^3
  - Ventilation rate Q_v = 3V/hr = 0.17m^3/s
  - Ammonia fuel supply rate Q_m = 100mg/s
  - Combustion efficiency η (value TBD)
  - Mixing factor (ventilation efficiency) k = 0.5

Example (ctd.)

- Let C_m be the ammonia concentration in the room in [mg/s]
- Then $C_{ppm} = (V_M/M)C_m$ where V_M = 22.4L/mol and M = 17.03g/mol
- Total mass of ammonia in room = VC_m
- Rate of accumulation = $V(dC_m/dt)$
- Rate ammonia enters room = $(1 - \eta)Q_m$
- Rate ammonia leaves room = kQ_vC_m

Example (ctd.)

- Mass balance: $V(dC_m/dt) = (1 - \eta)Q_m - kQ_vC_m$
- At steady state, $dC_m/dt = 0$, then $(1 - \eta)Q_m = kQ_vC_m$,

  $\eta = 1 - kQ_vC_{ppm}\, M/(Q_mV_M)$

  $\eta = 1 - 0.5\cdot 0.17\cdot 10\cdot 17.03/(100\cdot 22.4) = 0.9935$

Combustion must be at least 99.35% efficient, <u>without fail</u>. Probably can be done—but challenging!

Compare propane at C_{ppm} = 1000 (and higher mass flow proportional to molecular weight) and assume k = 0.1 (less efficient mixing): then minimum η = 87.1%

Odor thresholds

- Ammonia: 0.6 – 53ppm; geom. mean 17ppm
- Although the ammonia odor threshold varies widely, it is below the TLV-STEL, and thus should provide adequate warning
- Propane: odorless
- Ethyl mercaptan additive: 0.1 – 1ppb
- Extreme sensitivity to propane additive ethyl mercaptan provides a reference point for leakiness of existing plumbing technology (it's very good!)

Gas bouyancy

- Ammonia relative density (Air = 1): 0.59
- Propane relative density: 1.56
- In most cases this is an advantage to ammonia—leaked gas will rise and disperse, not accumulate in low places

Conclusion

- Propane has much higher fire/explosion hazard; Ammonia has higher toxicity hazard.
- Overall, ammonia can be less hazardous, with the proviso that:
- The toxicity hazard must be mitigated by development of fail-safe systems.
- Requirements for ammonia systems can be estimated and compared with performance of existing propane systems to assess feasibility.