

NH₃ Fuel Working Group Meeting with the California Air Resources Board

June 21, 2011



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Agenda

- Background and goals of meeting (5 minutes)
- Introductions (10 minutes)
- Presentation from NH3 Fuel Working Group (55 minutes)
 - Full lifecycle greenhouse gas emissions
 - Multimedia assessment (air, water, waste, etc.)
 - Safety
 - Fueling infrastructure
 - Technology compatibility
 - Implementability / consumer acceptance
- Discuss relevance of NH3 fuel to the State of California (30 minutes)
 - Registration under Low-Carbon Fuel Standard program
 - Market introduction as a sustainable fuel
- Define possible next steps (20 minutes)

Summary of the Case - 1

Ammonia has six strengths that recommend it as a transportation fuel

***Full lifecycle
greenhouse gas
emissions***

1. It is a non-carbon fuel with the potential to have a near-zero GHG footprint

***Multi-media
assessment***

2. It can be made with essentially no environmental impacts; with proper engine controls and exhaust after-treatment, it can be internally combusted with near-zero emissions

Safety

3. Although recognized by authorities as an inhalation hazard, it has an extensive track record of safe use and a clear path to low-risk deployment as a transportation fuel

Summary of the Case - 2

Ammonia has six strengths that recommend it as a transportation fuel

***Fueling
infrastructure***

4. It is already widely distributed; additional infrastructure needed is closer to “last mile” than build-out from scratch; Iowa alone has 800 retail outlets

***Technology
compatibility***

5. It has physical and combustion characteristics that are close to those of propane; it is not quite a “drop-in” replacement for petroleum – but close

***Implementability/
consumer
acceptance***

6. It lends itself to scale-up into a widely used transportation fuel, with prospective economics that can compete with petroleum on a subsidy-free basis; the practical steps needed are readily executable -- no miracles required

Common Denominator Is Hydrogen

- The energy content of chemical transportation fuels comes from both carbon and hydrogen
- In the following sequence of fuels, the importance of carbon as an energy carrier decreases with the carbon-hydrogen ratio until the carbon is gone altogether
 - Diesel fuel → Gasoline → Ethanol → Methane → Hydrogen
- At the low-carbon end of this sequence, where the energy contribution from carbon is small or nonexistent, the challenge can be framed as how to “package” hydrogen in the most economical and environmentally benign way

One good answer – arguably the best answer – is anhydrous ammonia (NH₃)

Comparison of Low-Carbon Options

	Diesel	Natural Gas	Biomethane	Hydrogen	Ammonia
GHG Impact ⁽¹⁾ (gCO ₂ e/MJ)	94.71	67.70-68.00	11.26-13.45	76.1-142.2 (but potentially very low)	Potentially very low
Energy Density (energy units per unit of system mass)	High	Low	Low	Low	High (~50% of petroleum fuels)
Fuel production/ preparation cost	Low	Low	Mid-High	Mid-High	Low-Mid
Transportation cost	Low	Low	Low-Mid	High	Low
Depot and on-board storage cost	Low	High	High	High	Low

(1) Source: Carbon-Intensity Lookup Tables, California Air Resources Board

Lifecycle GHG Emissions - Production

- For most ammonia production processes, the key is hydrogen production; the rest is just reacting hydrogen with nitrogen from the air
 - For every source of “green” hydrogen there will be a corresponding possibility of “green” ammonia
- Since ammonia will have the GHG footprint of its source hydrogen, the GHG intensities of the corresponding versions of hydrogen and ammonia will generally be in the same ballpark; they will differ only on the GHG-intensity of the “hydrogen packaging” process
- In an all-in accounting, the “green ammonia” pathways can be expected to yield LCFS metrics that are at the lower end of the values in the Lookup Tables

Green Ammonia Pathways

Hydrogen Source	Fossil System	Non-Fossil System
Water (electricity)		<ul style="list-style-type: none">• “Spilled” hydro or wind• Stranded wind, solar, ocean energy, geothermal• Solid state ammonia synthesis
Biomass		<ul style="list-style-type: none">• Forestry and agricultural wastes
Methane	<ul style="list-style-type: none">• Natural gas reforming with carbon sequestration• Co-production with methanol	<ul style="list-style-type: none">• Steam reforming of biogas
Coal	<ul style="list-style-type: none">• Hydrogen extraction with carbon capture and sequestration	

Lifecycle GHG Emissions - Production

	Energy Application	Energy Type	Energy Amount (kWh/kg H ₂)	GHG Footprint
Gaseous Hydrogen	• Compression	• Electricity	• 2.9 – 3.2 ⁽¹⁾	• Depends on electricity source; could be significant if the default is the state's grid mix
Liquid Hydrogen	• Liquefaction	• Electricity	• 8.0 – 13.4 ⁽¹⁾	
Ammonia	• Nitrogen separation	• Electricity	• 2.3 ⁽²⁾	• ~Zero if a renewable electricity pathway is used
	• Haber Bosch NH ₃ synthesis reaction	• Exothermic chemistry, electricity		• Small or negligible

(1) Source: "Energy requirements for hydrogen gas compression and liquefaction as related to vehicle storage needs", Record 9013, DOE Hydrogen Program Record, July 7, 2009.

(2) Reflects the process energy consumed in ammonia synthesis. Source: "Efficient Ammonia Production", Jim Gosnell, Kellogg-Brown & Root (KBR), Power Point Presentation, NH₃ Fuel Conference II, October 2005.

Lifecycle GHG Emissions – End Use

- Both hydrogen and NH₃ produce oxides of nitrogen when combusted – including the very potent greenhouse gas N₂O
- Oxides of nitrogen produced at power plants or in internal combustion engines are currently reduced to acceptable levels using a catalytic process involving NH₃ or NH₃-related compounds; the NH₃ reacts with the oxides of nitrogen to form N₂ and H₂O
- Using commercially available technology, NH₃ combustion can produce less GHG emissions than hydrogen simply by using a very small slip stream of NH₃ fuel; the Air Resources Board already allows selective catalytic reduction on large diesel truck engines using ammonia (SCR-N)
- Hydrogen engines would require the addition of NH₃ to attain the same GHG emissions level
- It should be noted that NH₃ itself is not a greenhouse gas

Multimedia Assessment - Production

- NH₃ is a naturally occurring, very prevalent compound and is an important part of the earth's nitrogen cycle
 - It is produced and processed daily in the human body and not a carcinogen
 - It is widely applied as a fertilizer and is readily incorporated in natural plant growth cycles and therefore will not have any negative environmental legacy issues
- Issues involving water and waste during NH₃ production will be very similar to those associated with hydrogen
 - Nitrogen (approximately 78% of the air we breathe) for the process is taken from the atmosphere
 - Oxygen is a by-product of the process

Multimedia Assessment - Use

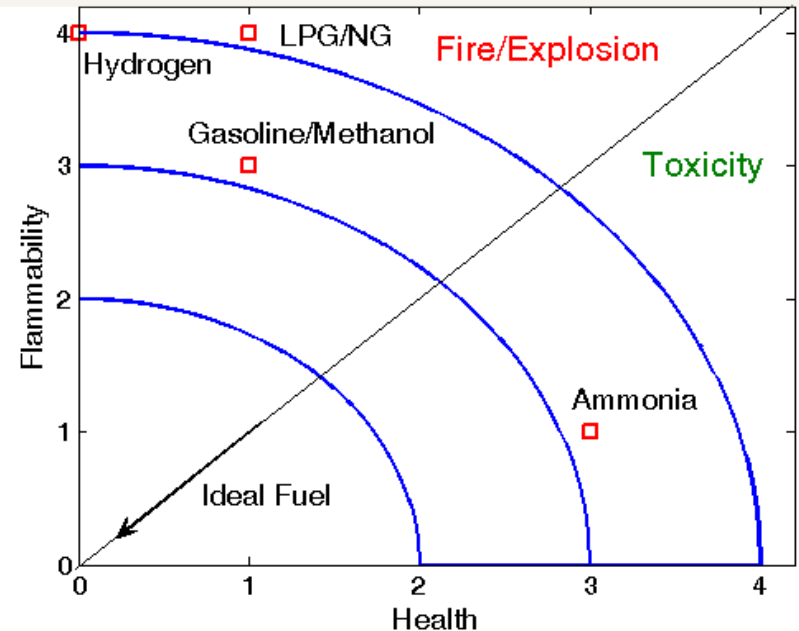
- Under typical conditions, ammonia burns to N_2 and H_2O
- In sub-typical conditions (e.g., cold starts), ammonia combustion could yield unburned fuel and oxides of nitrogen, but commercially available technology can reduce these emissions to acceptable levels
- No particulates are formed in the combustion of ammonia
- Several parties have studied and documented emissions profiles from internal combustion of NH_3 , including members of the proponent team
- There is a consensus among knowledgeable observers that pollutants can meet compliance targets through the application of current engine control and exhaust after-treatment technology

Safety – Overview

NFPA no. 704 classification is a good starting point to assess the safety of fuels

Substance	Health	Flammability	Reactivity
Ammonia	3	1	0
Hydrogen	0	4	0
Gasoline	1	3	0
LPG	1	4	0
Natural Gas	1	4	0
Methanol	1	3	0

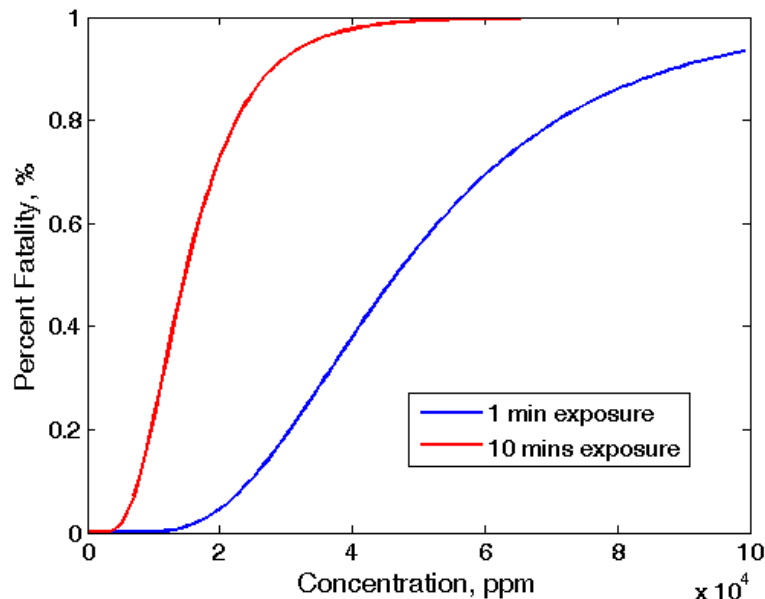
0=No hazard, 4=Severe hazards



- There are serious hazards associated with all fuels
- With the exception of gasoline and methanol health related hazards of fuels other than ammonia are low
- Hazards associated with flammability are low in the case of ammonia
- Ammonia is rated as a toxic substance but NOT as a poison (NFPA Health: 3)
- With ammonia Fire/Explosion hazards of the other fuels are traded with the Toxicity hazard

Safety – Toxicity Hazard

- Ammonia is a toxic substance with the exposure limit of
TWA: 25 ppm 8 hours
- LC50 level for 20 min. exposure is 29,000 ppm



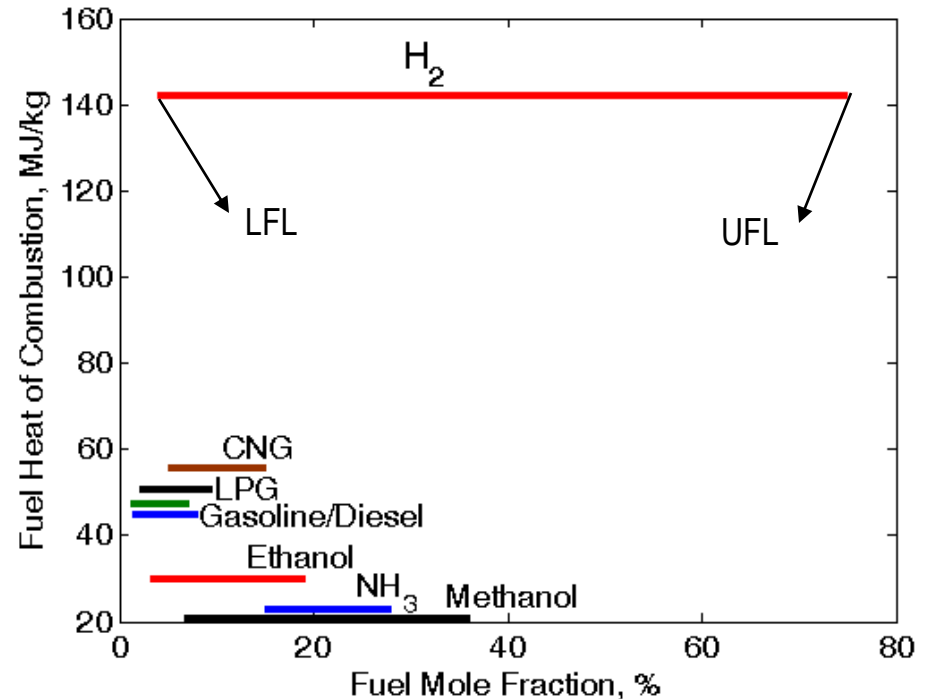
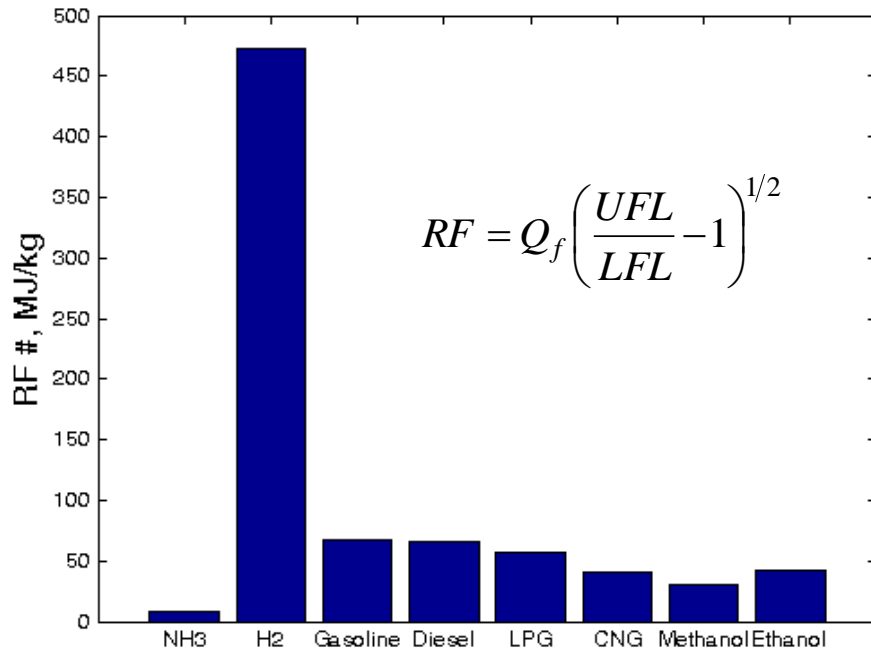
Effect	Ammonia Concentration in Air (by volume)
Readily detectable odor	20-50 ppm
No impairment of health for prolonged exposure	50-100 ppm
Severe irritation of eyes, ears, nose and throat, No lasting effect on short exposure	400-700 ppm
Dangerous, less than ½ hours of exposure may be fatal	2,000-3,000 ppm
Serious edema, strangulation, asphyxia, rapidly fatal	5,000-10,000 ppm

The following are the mitigating factors

- Ammonia is lighter than air – plume moves up quickly, reducing the exposure times
- Perceptible odor at safe concentrations
- The “self-alarming” feature of ammonia is particularly useful since readily detectable odor concentration is well below the fatal level
- Ammonia is NOT a carcinogenic substance

Safety – Fire/Explosion Hazard

- Ammonia has
 - Low heat of combustion
 - Narrow flammability limits
- Fire/explosion hazard for ammonia is very low



- RF index is used to assess the fire/explosion hazard of a flammable substance
- Higher RF # indicates more fire/explosion hazard
- RF number for ammonia is much smaller than the other fuels
- RF # of H2 is almost 100 times larger

Safety – Tank Rupture Hazard

PV Driven Explosions

- Energy associated with high pressure gases
- H₂ and CNG are stored at extremely high pressures resulting in substantial PV energies in the storage vessel

BLEVE's

- Explosive boiling of a saturated liquid
- Both ammonia and LPG are subject to BLEVE events
- Fatal BLEVE events have been reported with both substances

Fuel	TNT equivalent for 1 kg of fuel	Relative Mass Basis	TNT equivalent for 1 MJ of fuel	Relative Energy Basis
Hydrogen @ 10,000 psi	570 g	50	4.1 g	7
Ammonia @ 298 K	11 g	1	0.6 g	1

- No combustion energy is used in the calculations
- Reported ammonia BLEVE's are limited to large industrial systems
- BLEVE's are unlikely in the small tanks of transportation systems
- Melting liners can be used to prevent fire induced BLEVE's

Blast wave and fragment hazards associated with the rupture of a small ammonia tank is negligible
The rupture of GH₂ and CNG vessels present a significant risk

Safety – Ammonia Vehicle Safety Studies

Two comprehensive studies on the safety of ammonia as a transportation fuel exist

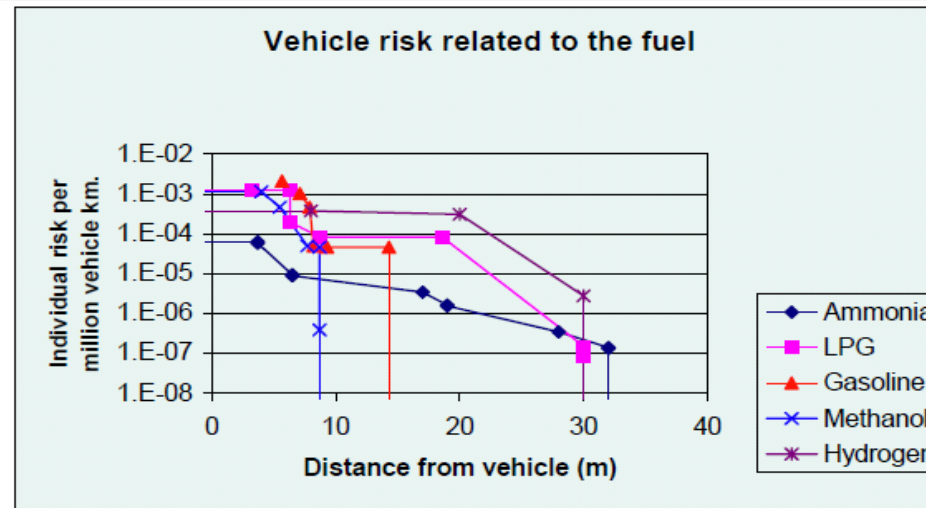


Figure 10 Comparison of individual risk as function of distance to a vehicle

Risk (per million km) is plotted against the distance from the vehicle for various fuels. Flash fire, heat radiation, explosion and toxicity damage modes are included in the calculations

Ref.: "Safety Assessment of Ammonia as a Transport Fuel", RISO National Laboratory, Denmark, 2005

The other study, by Quest Consultants of Norman, OK, came to a similar conclusion: the safety issue is NOT a show stopper for ammonia as a transportation fuel

Safety – Experience Base & Safety Record

- Ammonia is a widely used commodity
- Extensive knowledge base exists in
 - Production of ammonia
 - Transportation of ammonia
 - Storage of ammonia
 - Design of ammonia systems (including a comprehensive list of compatible materials)
 - Safe handling
 - Emergency procedures

- Ammonia is regularly handled by farmers in relatively large quantities
- Ammonia related accidents are rare in agriculture
- By following a set of relatively simple rules, ammonia can be handled safely by people with minimal training

Excellent data base exists on ammonia related accidents

Ammonia has an excellent safety record

NH₃ is overall as safe or safer than any other fuel

Fueling Infrastructure

- The fact that ammonia is handled, stored, and dispensed as a liquid simplifies questions of fueling infrastructure; the challenge and cost is not much different than for petroleum fuels
- Ammonia is already supported with a very extensive distribution infrastructure (ships, barges, rail, thousands of miles of pipeline)
- Ammonia is readily stored in large volumes at moderate pressure (equivalent to propane) and/or huge atmospheric pressure liquid NH₃ tanks; ammonia industry procedures for both types of storage are well established
- The investment required for ammonia to become a transportation fuel is akin to that for electricity and natural gas; essentially the build-out is for the “last few miles” to the point of dispensing
- Dispensing infrastructure itself is widespread throughout the farm belt; adapting dispensing equipment for transportation use does not embody any obvious technical challenge

Technology Compatibility -- Present

- Ammonia fuel is highly compatible with incumbent vehicle technology
- Ammonia power involves differences in
 - Fuel storage (a low-pressure tank – typically 150 psig – is used; a closed filling system and fill indicator is also required)
 - Pre-combustion fuel preparation (may involve partial or complete phase change (liquid to gas); may involve an in-line reformer to create a mix of hydrogen and ammonia)
 - Emissions control technology (must address NO_x and unburned NH₃)
- Overall, the compatibility challenge is less than that for methane and similar to that for propane
- A small number of heavy-duty spark-ignition NH₃ engines are in use today to power irrigation pumps
- The companies involved in ammonia engine technology are confident that they will have products ready for on-road applications once demand materializes

Technology Compatibility -- Future

- High-Compression Engines
 - Ammonia's internal combustion properties lend themselves to higher-than-conventional compression ratios
 - Such engines can achieve efficiencies that match and could potentially exceed those of diesel engines
 - This higher engine efficiency can partially offset ammonia's lower energy density vs. petroleum fuels (~50 percent)
- Fuel Cell Power Plants
 - The technology for generating hydrogen via ammonia reformation is well known; hence ammonia could be a fuel source for proton-exchange-membrane fuel cells
 - Ammonia is one of the best fuels for solid-oxide fuel cells; initial indications are that very high fuel efficiency could be achieved in such systems

Technology Compatibility -- Future

- On-Board Combustion Turbines
 - Companies exploring the use of on-board combustion turbines to drive generators in hybrid-electric systems recognize ammonia as a desirable fuel in this application

Consumer Acceptance

- Due to NH₃'s widespread, long-term use and proven public acceptance in fertilizer applications throughout the world, it is logical to believe that taking the incremental step of using NH₃ as a fuel will also be socially and environmentally acceptable
- The question of acceptance will play out differently in the light (consumer) and heavy (vocational) vehicle segments
 - Probably best to lead with the vocational segment
 - Can start with public-sector fleets (buses, refuse trucks, etc.)
 - Private-sector fleet proprietors will likely be driven by the economics; if NH₃ is cheaper per mile traveled, slight changes in dispensing procedures won't matter
 - Once dispensing infrastructure is widespread; the safety track record established; and the economic case is manifest; consumer interest is likely to follow

Implementability

- Given the well-established nature of the ammonia industry . . .
- And given the imminent availability of ammonia engine and vehicle systems . . .
- Conversion to ammonia fuel could begin immediately in the transportation sector
- From the LCFS perspective, the question is, how quickly could a supply of low-carbon NH₃ be provided?
- There is no technical challenge; there just needs to be a market for it
 - Producers need to have a reason to invest in “green” production
- It should be noted that low-carbon NH₃ production can be impactfully integrated with renewable electricity generation to the economic benefit of both fuels

Implementation Concept

	Green Production	Fueling Infrastructure	Vehicles/ Engines	Consumer Acceptance
Near-Term	Create a market for the green fuel (LCFS!)	Pilot NH3 hubs	Gain regulatory certification for first generation	Small-fleet demonstrations City fleets as early adopters
Mid-Term	Investment in green fuel production facilities	NH3 corridors along interstate routes in agricultural regions	Refinement and model proliferation	Roll out HD fleets
Long-Term		Widespread development		General use

Discussion/Next Steps

- What is the relevance of ammonia fuel to the State of California?
 - Registration under Low-Carbon Fuel Standard program
 - Market introduction as a sustainable fuel
- What possible next steps might proponents take to foster an ammonia-fuel early adoption program in California?
 - Independently
 - With interested State agencies
 - With interested city administrations

Addendum: Ammonia Fueling Facilities

- Ammonia's physical properties are similar to those of propane; most notably, ammonia's boiling point of -33 degrees C is close to propane's of -42 degrees C
- Ammonia has some distinct material compatibility characteristics, but the materials used to store and dispense ammonia in agricultural and industrial settings are neither exotic nor unusually costly
- This means that the cost of an ammonia fueling facility is likely to be in the same ballpark as that of a propane facility, (circa \$30,000 per refueling site per Clean Fuel USA)