Potential Roles of Ammonia in a Hydrogen Economy:
Public Opinion and Input

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Ammonia Fuel Conference
October 9-10, 2006
Golden, CO

Background

- In 2005, a report titled

  Potential Roles of Ammonia in a Hydrogen Economy

  was completed and placed on the DOE website for public comment
- The purpose of the report was to examine issues related to the use of ammonia as a hydrogen carrier for light duty fuel cell vehicles

  primarily onboard vehicles as a storage medium, but also

  as a carrier for hydrogen delivery (distribution)
- The scope of the report was intended to stay within the bounds of the current program.

Outline

1. Hydrogen storage targets and material properties

2. Brief summary of paper
   - Onboard use of ammonia as storage material
   - Ammonia as a carrier for hydrogen transport

3. Summary of public comments on paper

Hydrogen Storage Requirements

Market expectations of vehicle performance place challenging requirements for onboard hydrogen storage systems

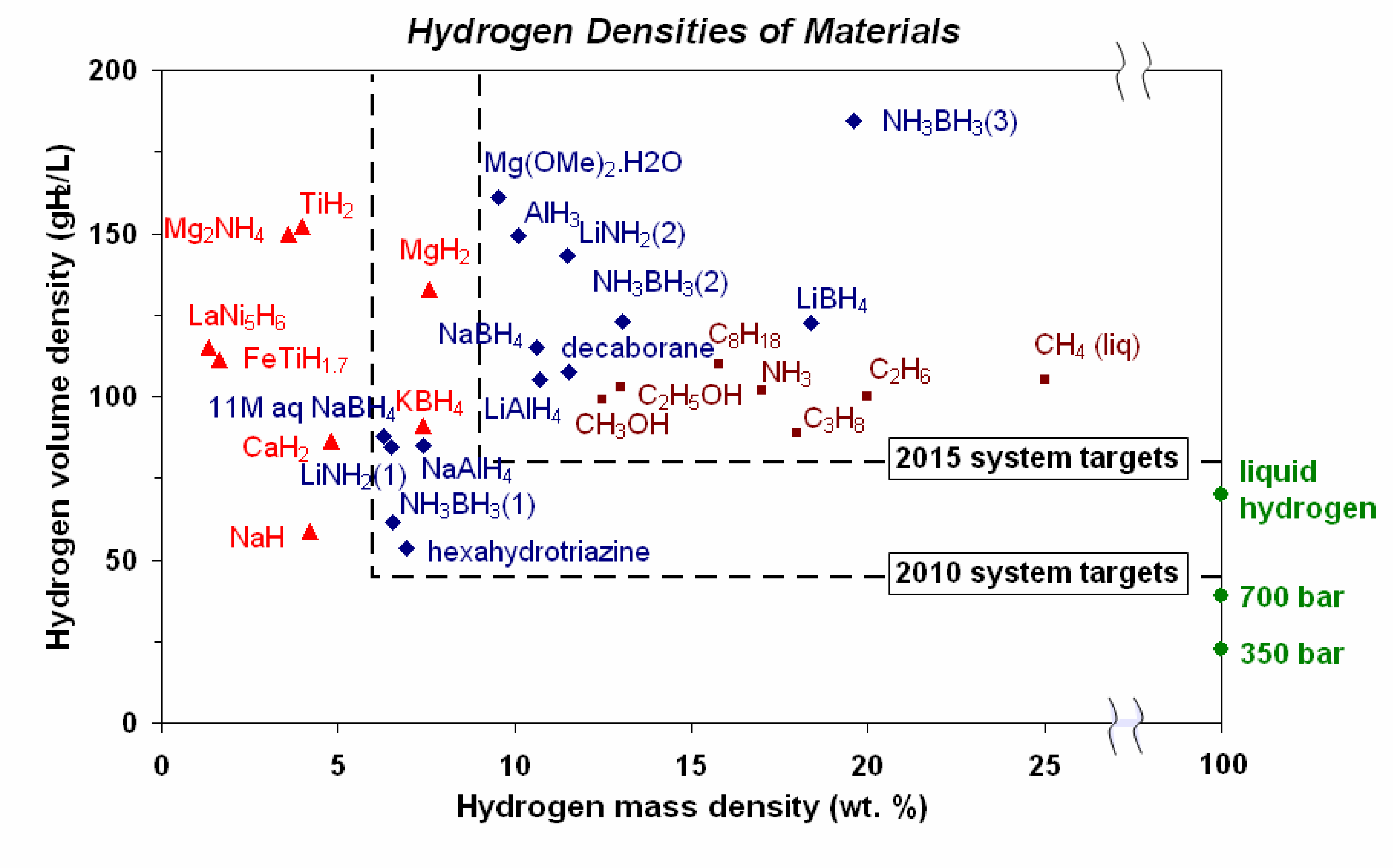
Targets	2010	2015
System Gravimetric Capacity "specific energy"	**6 wt.%** (7.2 MJ/kg) (2.0 kWh/kg)	**9 wt.%** (10.8 MJ/kg) (3.0 kWh/kg)
System Volumetric Capacity "energy density"	**1.5 kWh/L** (5.4 MJ/L) (45 g/L)	**2.7 kWh/L** (9.7 MJ/L) (81 g/L)
Storage system cost	**$4/kWh** (~$133/kg H_2)	**$2/kWh** ($67/kg H_2)

TARGETS ARE SYSTEM TARGETS- MATERIAL CAPACITY MUST BE HIGHER!

Explanations at www.eere.energy.gov/hydrogenandfuelcells/

FreedomCAR & Fuel Partnership

Hydrogen storage program focused on high capacity materials with the potential to meet system targets.



Brief summary of:

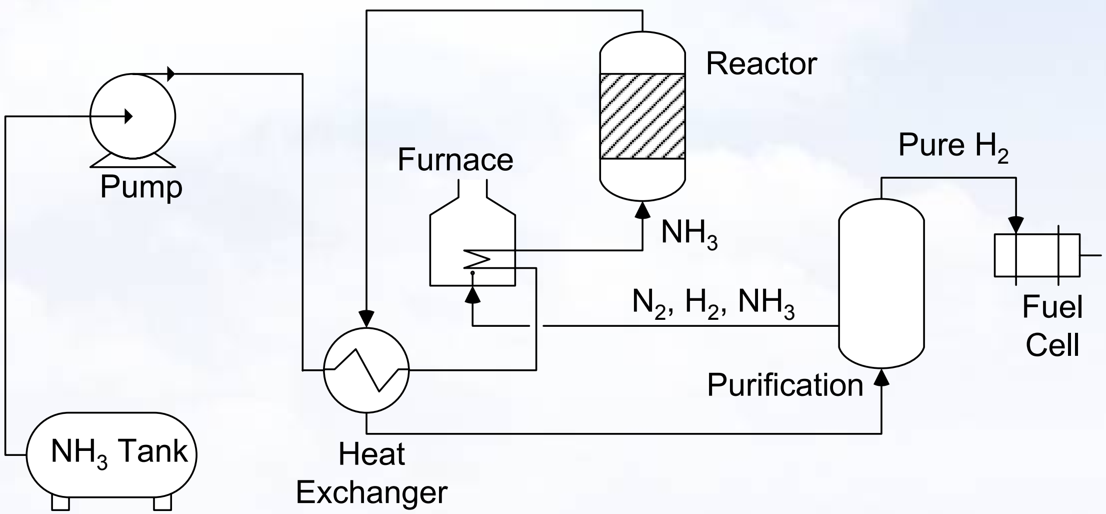
Potential Roles of Ammonia in a Hydrogen Economy

Some ammonia properties relevant to use as a hydrogen carrier (from report)

• H_2 volumetric density:	102 g H_2/liter
• H_2 gravimetric density:	17 wt.%
• Production efficiency:	~60-65% H_2 energy/NG energy
	~35-40% H_2 energy/coal energy
• Production cost from NG:	~\$3.00/kg H_2 (gge)
• Production cost from coal:	~\$5.00/kg H_2

- Theoretical adiabatic efficiency
  for thermocatalytic decomposition: ~85%
  (the theoretical best you can do to get H_2 from NH_3)

Conceptual ammonia cracking reactor



Equilibrium conversion efficiencies

Temperature (°C)	Unconverted NH_3 1 bar	Unconverted NH_3 10 bar
400	0.88%	7.91%
500	0.26%	2.55%
600	0.10%	1.00%
700	0.047%	0.47%
800	0.025%	0.25%
900	0.015%	0.15 %

PEM FC's require <0.1 ppm NH3 concentration

Conceptual ammonia tank for onboard hydrogen storage

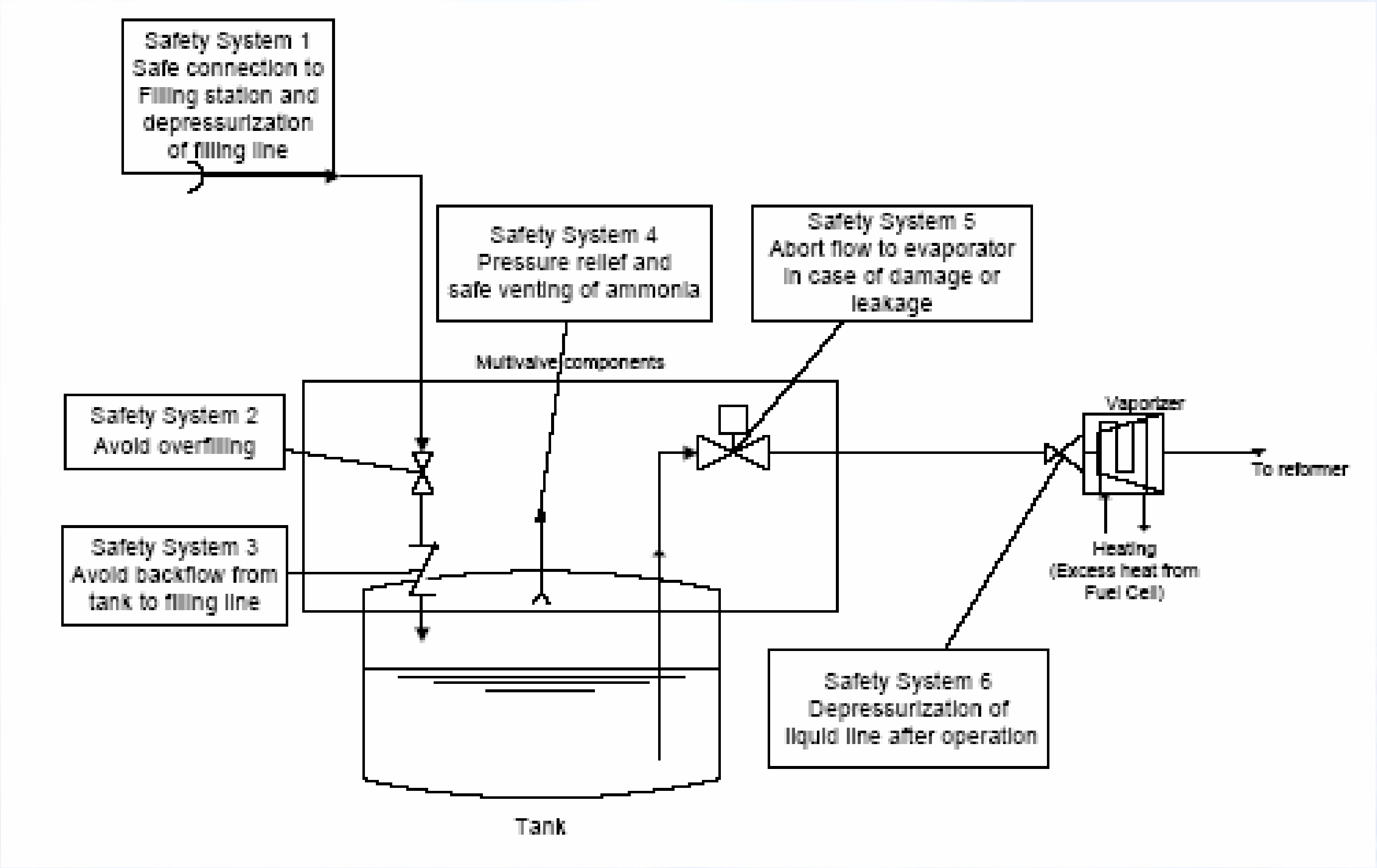
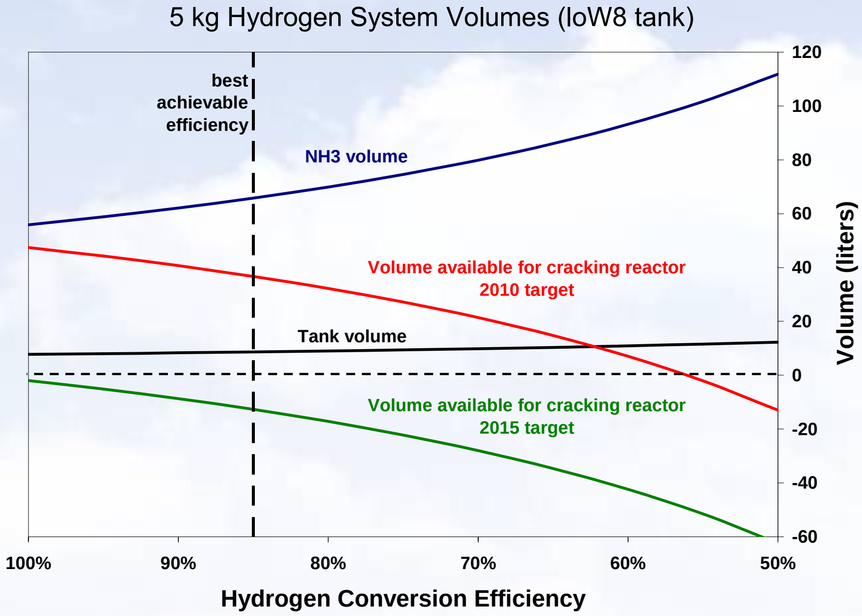
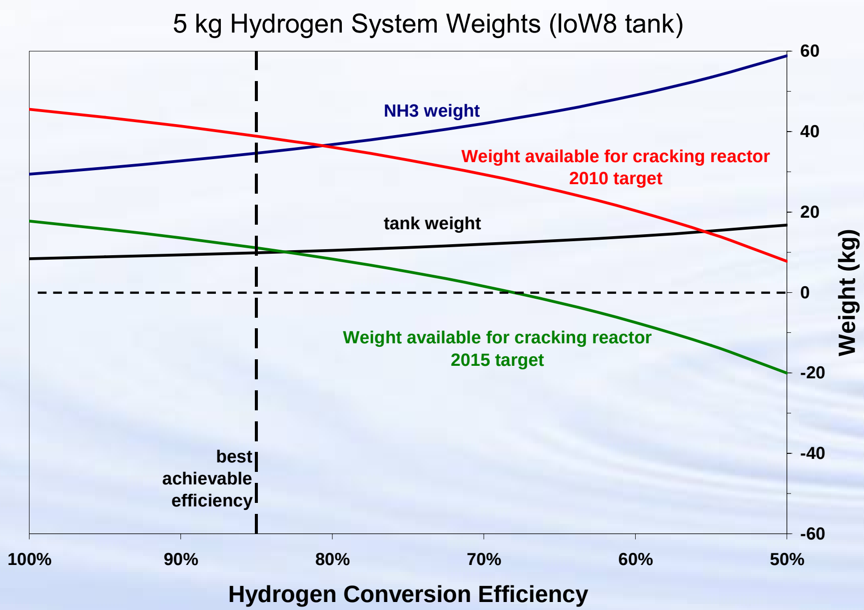


Fig. 2 from Risø R-1504(EN)

Requirements for onboard reactors are challenging





- maximum flow rate of ~2 g H_2/sec needed for 100 kW fuel cell
  - ~1 liter NH_3/min into reactor
  - ~1340 std liters H_2/min output
  - H_2 output pressure of ~3-8 bar
- <0.1 ppm NH_3 impurity in H_2 stream
- start-up time equivalent to H_2 system
- volume, weight as shown in plots

In summary, the viability of ammonia-based onboard storage systems would depend on:

1. Development of high power, small volume, lightweight and efficient integrated ammonia cracking/purification systems capable of supplying hydrogen at ~1400 slm and with ammonia pass-through of <0.1 ppm.

2. Development of lightweight tanks capable of sustaining the weight and vapor overpressure of anhydrous ammonia and with proven long-term integrity in an ammonia environment.

3. Addressing all of the safety issues associated with working with ammonia and ammonia-containing systems.

Ammonia as a carrier for hydrogen delivery

Requirements and targets for hydrogen carriers

- High effective hydrogen densities (carrier, not system)

2010	6.6 wt.%	13 g/liter
2015	13.2 wt.%	27 g/liter

- Hydrogenation-dehydrogenation processes should be simple, energy efficient and cost effective

2010	70% energy efficiency*
2015	85% energy efficiency*

- Carriers should be safe and environmentally benign
- Contribution to fuel cost should be reasonable

2010	$1.70 per gge*
2015	$1.00 per gge*

* From hydrogen production point through dispensing at refueling site

Ammonia as a carrier for hydrogen delivery

- Positive attributes
  - Good hydrogen densities (meets targets)
  - One-way liquid carrier
  - Estimated transport costs appear to be within target
  - Some existing infrastructure and handling experience
- Issues to be resolved
  - Production and cracking processes need to be improved
    - Energy efficiency improvements, particularly with coal as feed stock
    - Overall energy efficiency (production X cracking) relatively low
    - Better catalysts, efficient reactor designs
  - Inexpensive and reliable purification schemes
  - Analysis needed to better understand life cycle efficiencies, economics and safety issues surrounding ammonia use

Public comments to paper

Overall summary of public comments

- 10 responses received
  - 7 responses strongly advocated the use of ammonia (or ammonia-containing compound) as a fuel or hydrogen carrier
  - 2 responses were against the use of ammonia either as a fuel or as an energy carrier
  - 1 response suggested multiple R&D paths to determine best alternative fuel option.
- Some recurring themes
  - Existing infrastructure
  - Use of ammonia as fuel rather than hydrogen carrier
    - Particularly with ICEs
    - Direct ammonia fuel cells
  - Interim or transitional fuel towards pure hydrogen economy
  - Safety, handling issues of ammonia not show-stoppers
- Some suggested alternatives
  - Partial cracking for improved efficiency in ICEs
  - Ammonia production from coal
  - Hydrolysis of guanidine or ethanol guanidine solutions

Many, diverse safety-related comments

- “. . . nasty and toxic stuff . . . don’t recommend using it . . .”
- “Safety and handling of ammonia is well established technology in the agricultural community.”
- “. . . underestimates ammonia safety record . . .”
- “. . . many of the risks are perceived, not real . . .”
- “safety issues can be addressed . . .”
  – encapsulating in highly ammoniated salt
  – engineered pressure tanks
  – porous monolith inside tank
- Danish study on ammonia safety cited (Nijs Jan Duijm, et. al.)
  – this in-depth study provided specific safety-related comments and suggestions

Quotes from "Safety Assessment of Ammonia as a Transport Fuel" by Nijs Jan Duijm, et. al.

"**The conclusion is that the hazards in relation to ammonia need to be controlled by a combination of technical and regulatory measures.**

The most important requirements are:

– Advanced safety systems in the vehicle

– Additional technical measures and regulations are required to avoid releases in maintenance workshops and unauthorised maintenance on the fuel system.

– Road transport of ammonia to refuelling stations in refrigerated form

– Sufficient safety zones between refuelling stations and residential or otherwise public areas.

When these measures are applied, the use of ammonia as a transport fuel wouldn't cause more risks than currently used fuels (using current practice)." ***(From abstract)***

"The acceptance of ammonia will not be based on the results of numerical risk analysis, but will also be influenced by the public's perception of the threats of ammonia, and people tend to be more horrified by toxic substances than by fires. This public perception cannot and should not be ignored or dismissed." ***(p. 40)***

Many comments on onboard vs. off-board use of ammonia

- General agreement against onboard use of ammonia as a hydrogen storage material
  - "... rather than onboard reforming, more practical to consider forecourt reforming and hydrogen storage onboard ..."
- Consensus view that onboard use of ammonia could be as a fuel
  - Particularly with ICEs, but also with ammonia tolerant fuel cells or direct ammonia fuel cells
  - Partial cracking could be used to improve efficiency of ICEs
  - Potential for combining ammonia with ethanol or gasoline
- Potentially an intermediate fuel or transition technology until fuel cells become competitive
  - "... Shipping ammonia rather than natural gas allows C sequestration at central plants..."
- Within a hydrogen economy framework, ammonia could be used as a delivery carrier
  - "...ammonia provides a viable solution to delivery infrastructure..."

Hydrolysis of guanidine as an onboard hydrogen storage carrier

$$\underbrace{HN{=}C(NH_2)_2}_{59\ g} + 2H_2O \rightarrow 3NH_3 + CO_2$$

15.25 wt% H_2 $\longrightarrow$ (as NH_3)

$$\underbrace{HN{=}C(NH_2)_2 + 2H_2O}_{59\ g \ + \ 36\ g}$$

9.47 wt% H_2 $\longrightarrow$ (as NH_3)

Fuel Cell Water Balance for Chemical Hydrogen Storage Systems
By T. Abdel-Baset, DaimlerChrysler
with input from R. Kumar, ANL, D. Masten, GM, FreedomCAR and Fuel Partnership Fuel Cell Tech Team, DOE Hydrogen Program

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$\downarrow$

8.0 wt% H_2 (as H_2)

at max. theoretical efficiency

Summary

- Onboard cracking of ammonia for hydrogen fuel cell vehicles appears to be very challenging and would require an intense R&D effort
- Ammonia has potential application as an energy carrier, particularly during the transition towards a hydrogen economy
- The use of ammonia as a hydrogen carrier is being investigated further by DOE’s Hydrogen Delivery Program and the FreedomCAR and Fuel Partnership’s Hydrogen Delivery Technical Team
- Further work needs to be done, particularly a “well to wheels” analysis which would include
    - Safety
    - Environmental impact
    - Energy efficiency
    - Cost
    - Infrastructure
    - Feedstock availability

For more information, see

www.hydrogen.energy.gov