Toward new solid and liquid phase systems for the containment, transport and delivery of hydrogen

By Guido P. Pez

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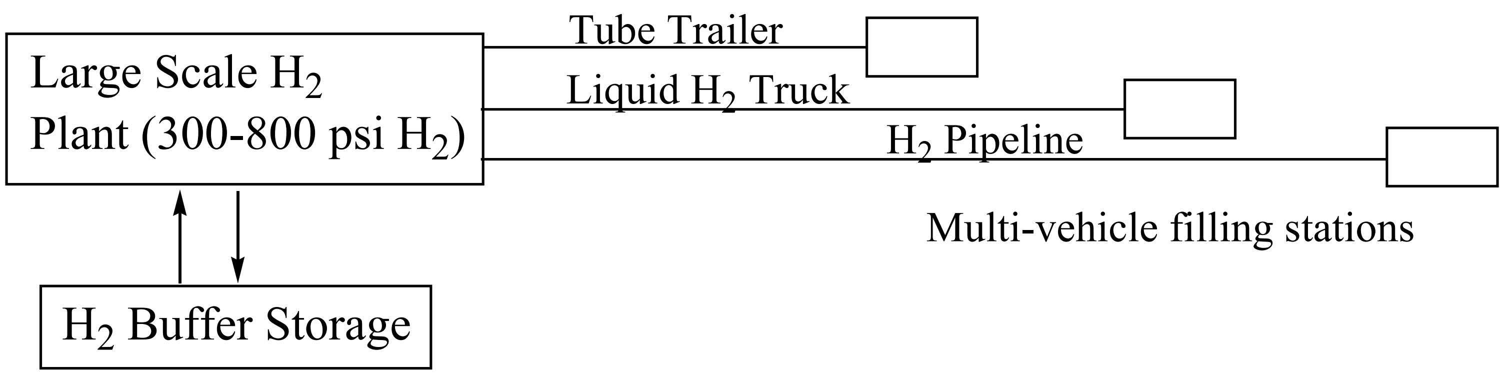
Hydrogen Energy Infrastructure for Fuel Cell Vehicle Transportation

Scenario A: Distributed H_2 from a Large Scale Plant (150-230 tonne/day)



Feedstock: N. gas, Coal, Biomass
Pet. Coke, Resids.
Future: Carbon sequestration
Storage: Underground well?

Output: Depends on the vehicle's H_2 storage technology
Currently H_2 up to >6000 psi for 5000 psi tanks

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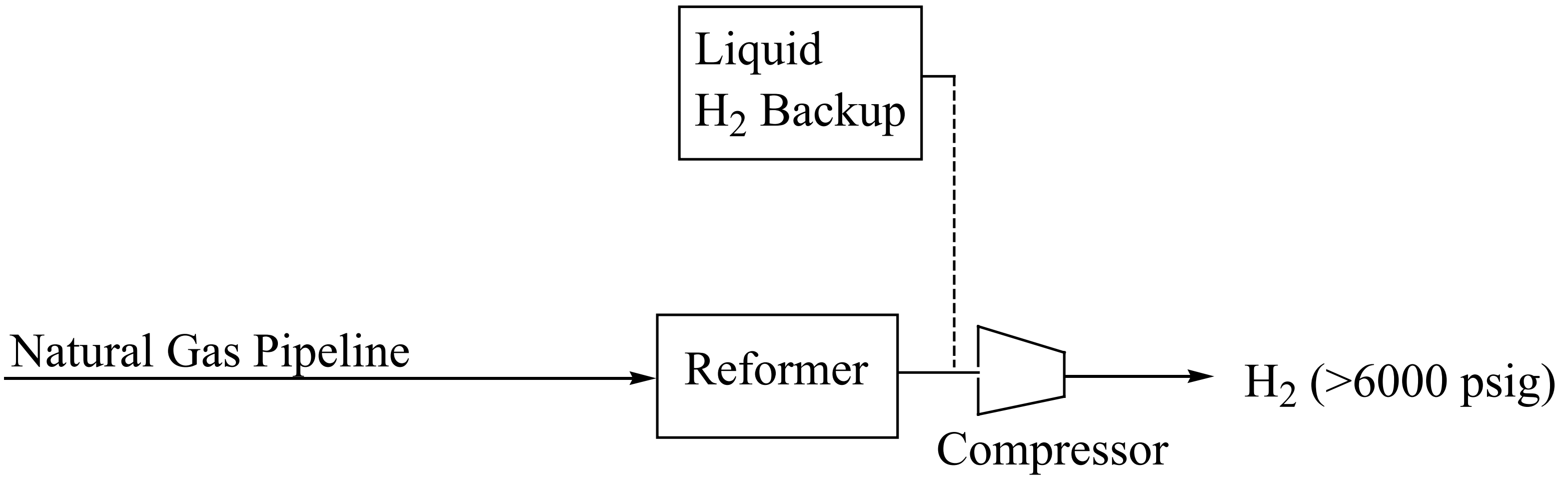
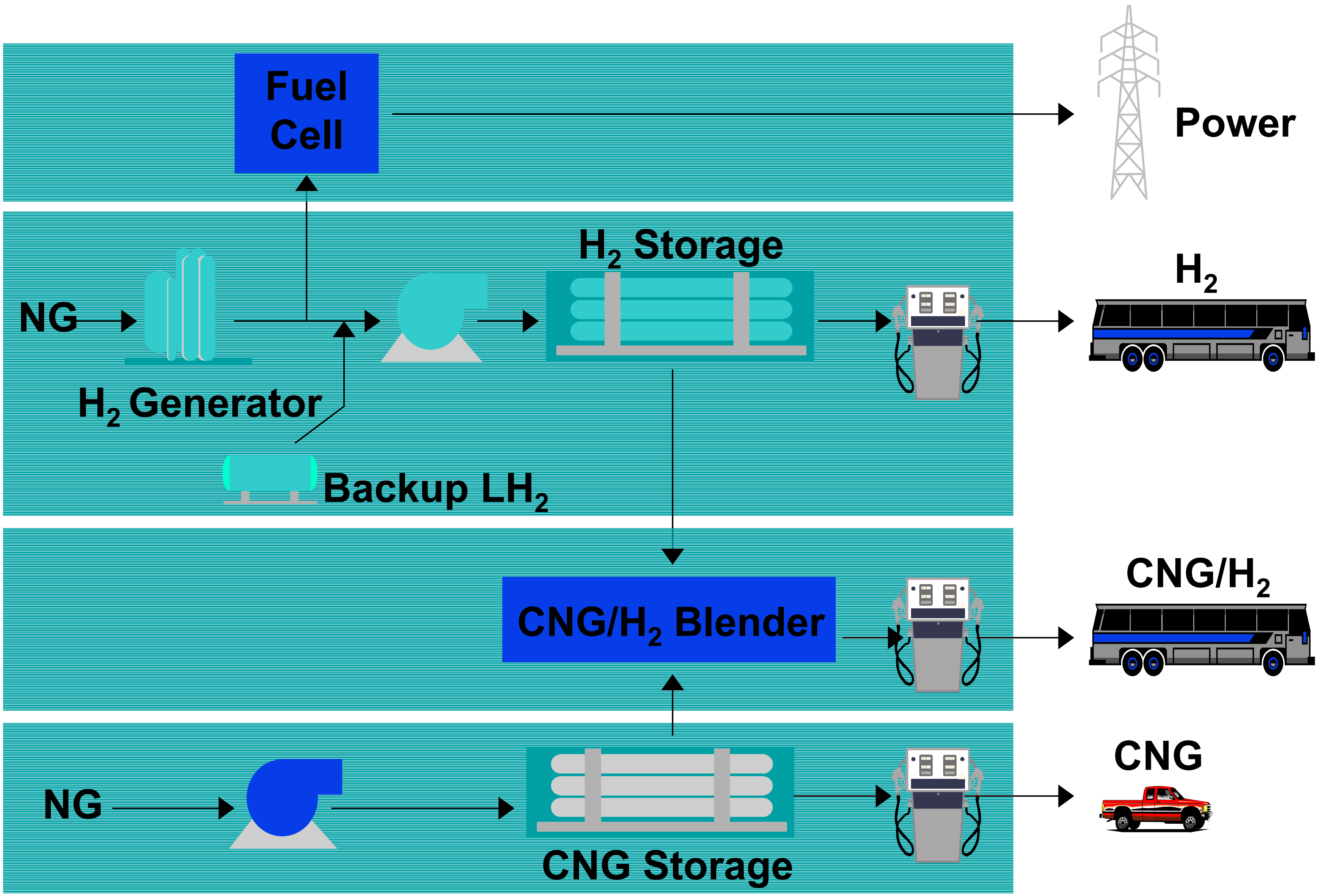
Scenario B: Hydrogen by a small scale reforming of pipeline natural gas and compression



H_2 Production: 100-400 kg/day; 4-5Kg H_2/fill-up

CO_2 sequestration – not practical

Nevada Hydrogen Project



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Relative Economics* of Central (Scenario A) and "Local" (Scenario B) H_2 Production by SMR from Nat. Gas

The H_2 Cost in $/Kg is approximately equivalent to $/gallon gasoline

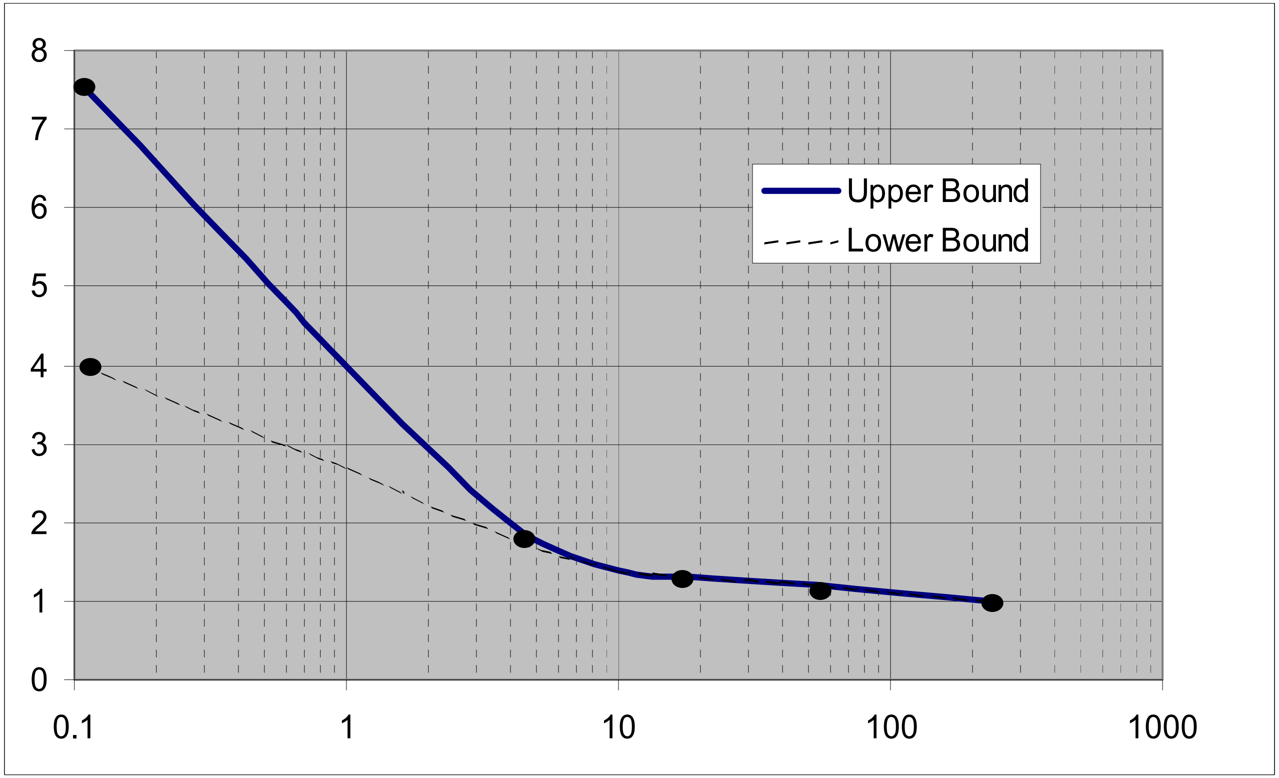
	Scenario A (H_2: 150 tonne/day)			Scenario B (H_2: 0.329 tonne/day)
	Liquid H_2 $/kg	Pipeline $/kg	Tube Trailer $/kg	$/kg
H_2 production	2.21	1.00	1.30	
H_2 delivery	0.18	2.94	2.09	
H_2 fueling	1.27	1.07	1.00	
Total	3.66	5.00	4.39	4.40

While the cost of H_2 as produced at a large plant seems attractive ($1.00/Kg), at the filling station the transport and fuelling expenses predominate, rendering "local" H_2 production at least comparable.

*From "Hydrogen Supply: Cost Estimate for Hydrogen Pathways – Scoping Analysis" D. R. Simbeck, E. Chang, SFA Pacific, Inc.NREL NREL/SR-540-32525, July 2002

Relative Cost of H_2 by SMR as a function of plant size/production rate

Cost Index



H_2 Production Rate (tonne/day)

[See also data in J. M. Ogden's "Prospects for Building a Hydrogen Energy Infrastructure" Annu. Rev. Energy Environ., 1999, 24, p 239.]

Challenge: **How to reduce the H_2 delivery and H_2 fuelling costs?**

Key: Hydrogen "containment" – i.e. in an idealized situation "capturing" H_2 so that it's no more costly to transport and store than conventional fuels, such as Diesel oil.

Also a "H_2 containment" or storage that makes H_2 as a vehicular fuel economically feasible.

Energetics for Reversibly Containing Hydrogen Fundamentals

For H_2 (gas) $\rightleftharpoons$ H_2 (contained) equilibrium:

$$\Delta G = \Delta H - T\,\Delta S = -RT\ln K$$

For containing H_2 in a spontaneous process:

$\Delta G < O$, $\Delta H < O$ and the entropy (S) decreases from its' gas phase value (31.1 cal/mole K)

Entropy change, $-\Delta S \approx$ 25-30 kcal/mole – from "free" to "bound" H_2.

The greater variable contribution to ΔG is from ΔH.

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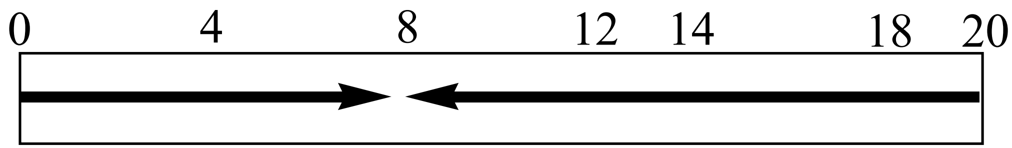
Range of H_2-Containment Enthalpies (- ΔH, kcal/mole H_2)



Weakly to strongly physisorbed H_2 on Substrate

$$H_2 + \text{Substrate(S)} \underset{}{\overset{K}{\rightleftharpoons}} \text{S-}H_2$$

(H_2 molecule intact)

Strongly to weakly chemisorbed H_2 on Substrate

$$H_2 + 2\text{S} \overset{K}{\rightleftharpoons} 2\text{S-H}$$

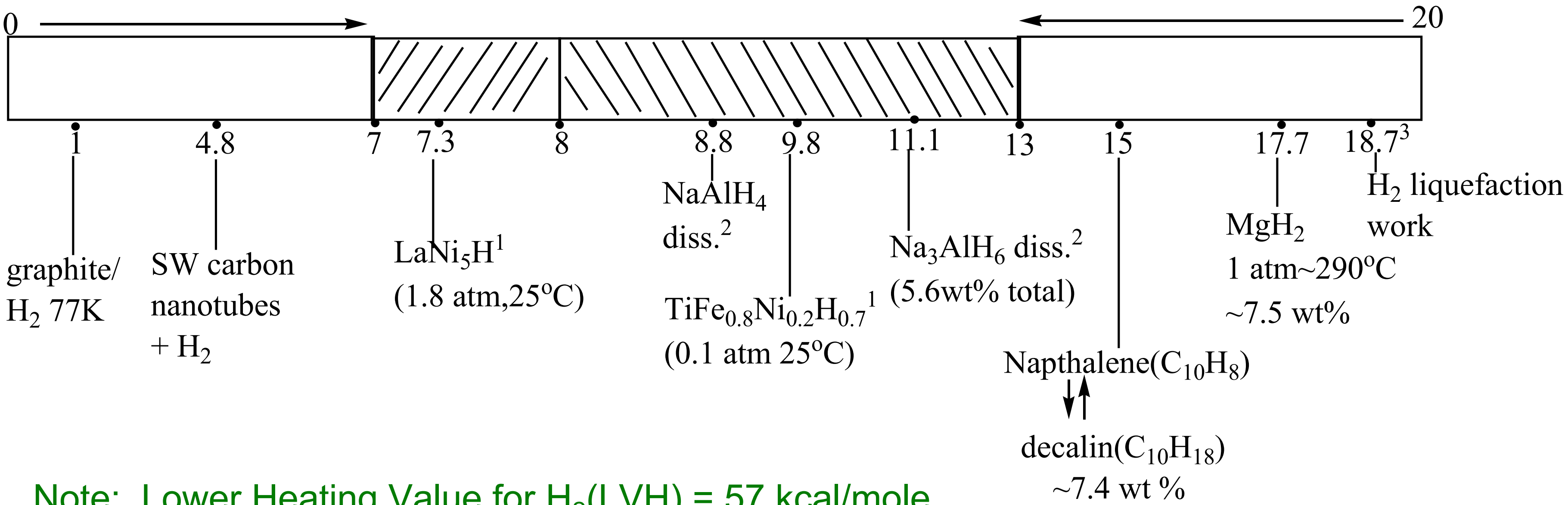
(H-H bond ruptured)

Where $\ln K = -\Delta H/RT + \Delta S/R$

H_2 containment in porous solid, reversible by H_2 pressure

H_2 containment in a solid or liquid by temperature and/or H_2 pressure reversible chemistry

Observed and Desirable H_2-Containment Enthalpies (-ΔH, kcal/mole H_2)



Note: Lower Heating Value for H_2(LVH) = 57 kcal/mole

Desired (-ΔH) ranges: 7-8 kcal/mole H_2-Strong Physisorption
: 8-13 kcal/mole H_2 – Weak to Moderate Chemisorption

For desired ≥6.5 wt% H_2 for system (DOE). Consider:

- Single-wall carbon nanotubes/H_2 pressure tank
- Napthalene $\underset{}{\overset{5H_2}{\rightleftharpoons}}$ Decalin as an example of a liquid phase hydrogen carrier

1. G. Sandrock, J. of Alloys and Compounds 293-295 (1999) 877
2. B. Bogdanovic, G. Sandrock, MRS Bulletin 2002, 712
3. W. Peschka, "Liquid Hydrogen Fuel of the Future" Springer-Verlag p. 65

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Hydrogen Storage with Single Wall Carbon Nanotubes (SWNT's)

- A. Dillon, M. Heben *et al*[1]: H_2 (ads, 300 torr, 0°C) desorption 25°C with ΔH=-4.7 kcal/mole H_2 by TPD

- Claims of a slow adsorption of H_2 by SWNT materials at high pressures (10-100 ~ atm) eg. 5-7%[2], 4.2%[3], .05%[5]

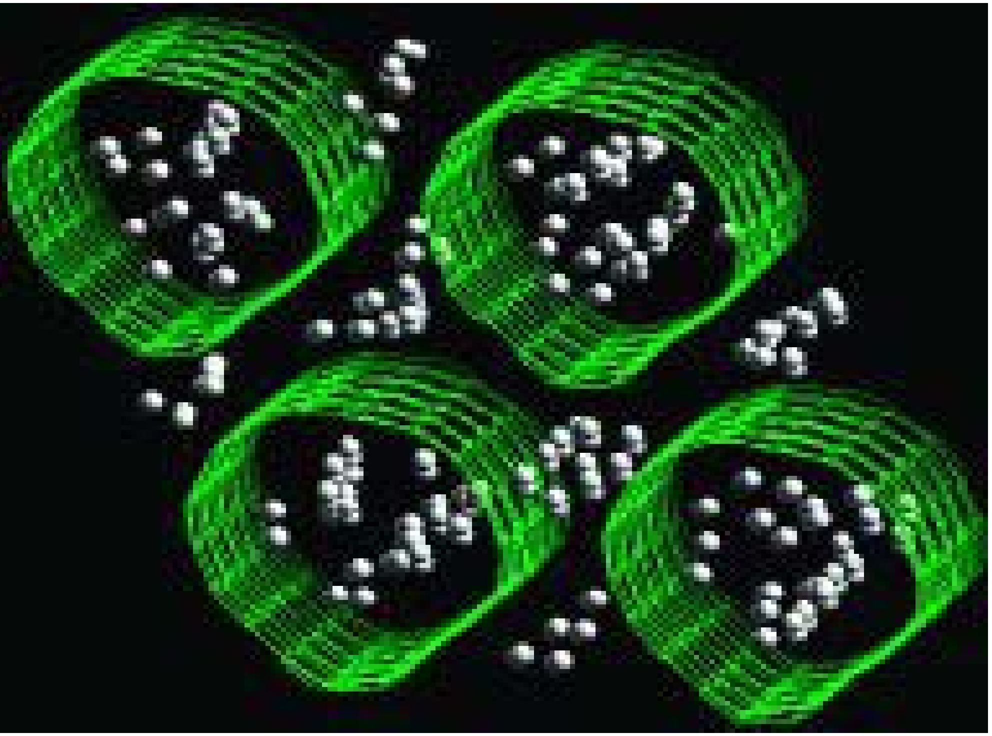
- Up to 8 wt% H_2 in SWNT's at 77K[4]

  Difficulties: 1) SWNT purity, length, opening etc.
  2) Errors in high pressure H_2 sorption measurements[5]

- For H_2 in internal space between tubes, 0.3wt % at 90atm, with ΔH=-4.8 kcal/mole[6]

1. Nature 386 377 (1997);
2. Y. Chen *et al* 78 2128 (2001)
3. C. Liu *et al*, Science 286 1127
4. Y. Ye *et al* Appl. Phys. Lett. 74 2307 1999
5. G. G. Tibbetts, Carbon 39 (2001) 2291
6. M. Shrinaiski *et al* Chem. Phys. Lett. 367 (2003) 633

Modeling of H_2 Adsorption in SWNT Bundles



H. Cheng, G. P. Pez, A. C. Cooper
***J. Am. Chem. Soc.* 123, 5845 (2001)**

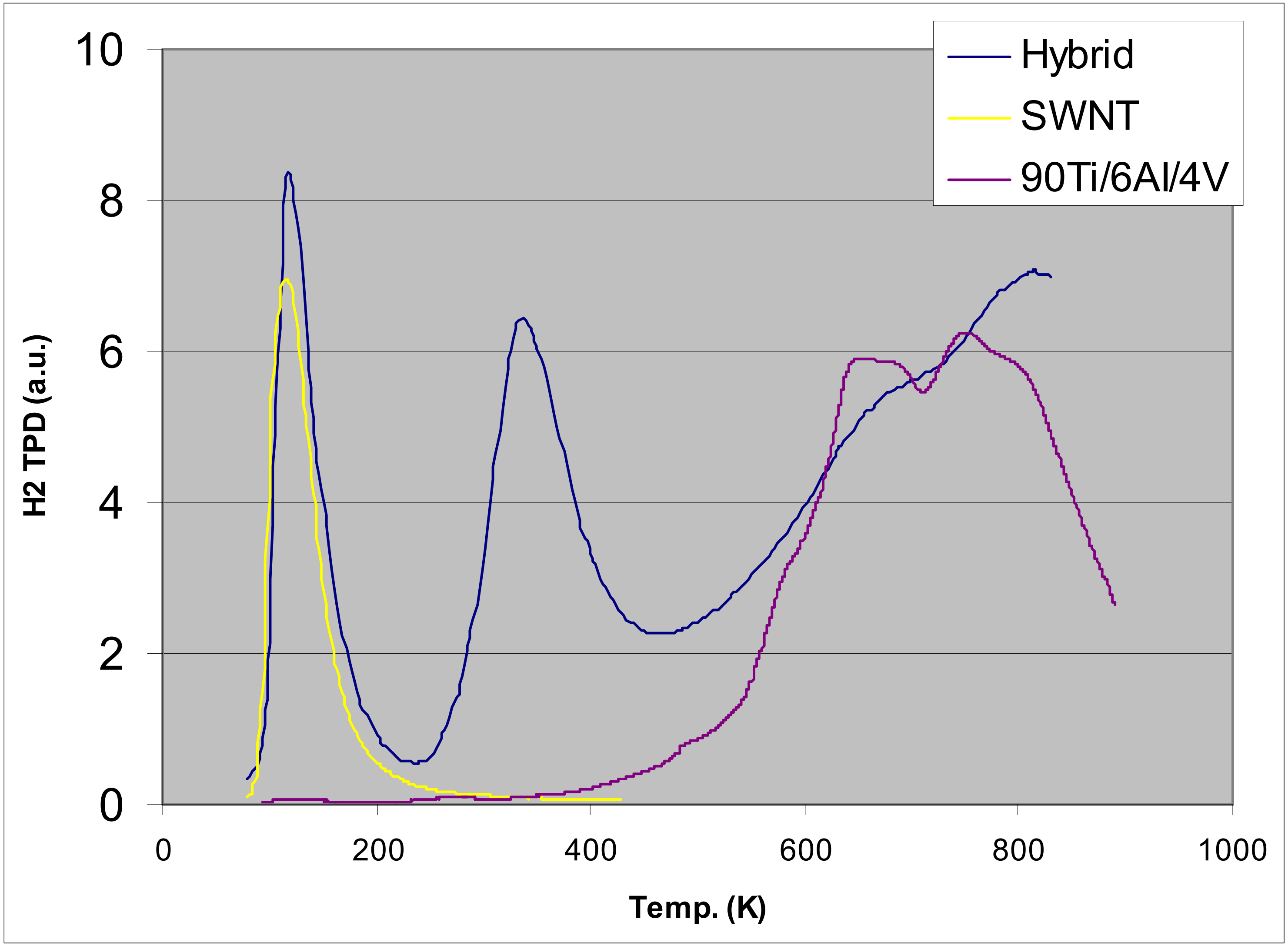
M. K. Kostov, H. Cheng, A. C. Cooper, G. P. Pez

***Phys. Rev. Lett.* 89(14), 6105 (2002)**

The Energies (Kcal mol $^{-1}$) of Adsorption of H_2 in SWNT's

Temp, K	endohedral	exohedral
77	-3.94	-4.79
300	-7.51	-6.75
600	-3.86	-10.91

H_2 Temp. Programmed Desorption Using (a) SWNT (b) Ti:Al:V alloy (c) SWNT/Ti:Al:V alloy hybrid



Water Reactive Hydrogen Generating Systems

Sodium Borohydride in KOH Solutions
(Millenium Cell Corp.[1])

$$NaBH_4 + H_2O/NaOH \xrightarrow{\text{catalyst}} NaBO_2 + 4H_2$$

ΔH^o = -12.7 kcal/mol H_2; ΔG^o = -76 kcal/mole $NaBH_4$

Spontaneous H_2 release

Direct reversal not possible.
Need multi-step process back to $NaBH_4$[2]

Lithium Hydride, Magnesium Hydride Dispersions in a Fluid
(Safe Hydrogen Co. [3])

$$MgH_2 \text{ (slurry)} + 2H_2O \longrightarrow 2H_2 + Mg(OH)_2$$

ΔH^o = -33.1 kcal/mol H_2; ΔG^o = -77 kcal/mole MgH_2

Spontaneous H_2 release as above, the ΔH^o energy is lost

Direct reversal not possible.

Need an easily reversible liquid system.

1. S. Amendola *et al* US 6,534,003
2. S. Amendola *et al* US 6,433,129
3. R. K. Konduri *et al* WO 02/066369A1

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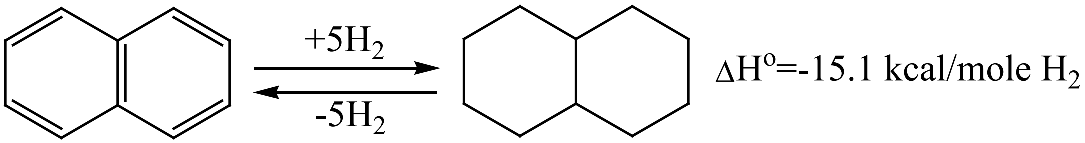
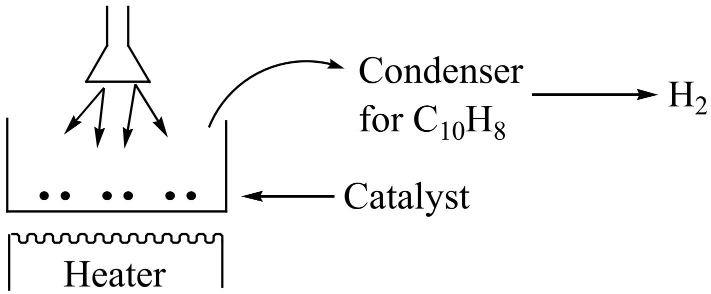
Prospects for a Liquid-Phase Press./Temp. Reversible Hydrogen Carrier

Hydrogen and energy storage [1] by a reversible catalytic hydrogenation of napthalene $C_{10}H_8$ to decalin $C_{10}H_{18}$ (a "liquid organic hydride"[2])



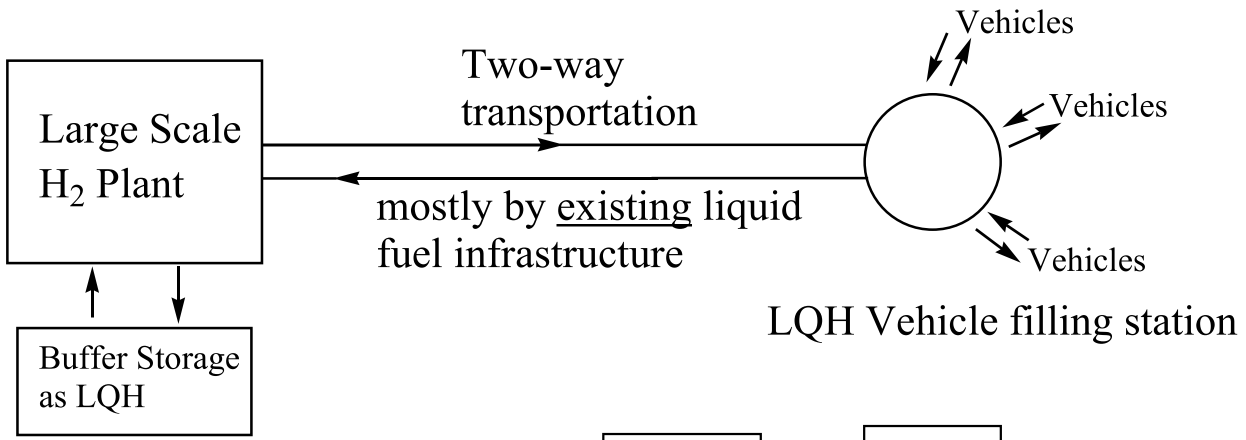
High conversion of $C_{10}H_{18}$ in membrane reactor at ~320°C[2]
Efficient H_2 evolution from $C_{10}H_{18}$ from 195°C to 400°C under "wet-dry multiphase" conditions [3-5]



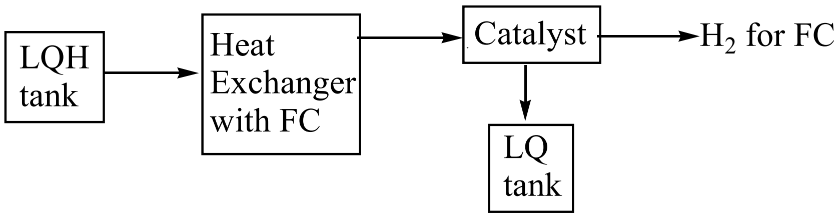
But what if a "liquid hydride" could be made fully reversible at lower temperatures i.e. with - ΔH^o <<15 kcal/mole?

1. E. Newson, *et al,* Int. J. Hydrogen Energy, 23 905 (1998)
2. R. O. Loufty, *et al*, Proc. of Int. H_2 Energy Forum, (2000) 335-340
3. N. Kariga, *et al*, Appl. Cat A, 233, (2002), 91-102
4. S. Hodoshima, *et al*, Suiso Enerugi Shisutemu 25, (2000), 36-43
5. S. Hadoshima, *et al,* Int. J. Hy Energy, 28, (2003), 197-204

Scenario for a Temp/Press-Reversible "Liquid Hydride" (LQH)



In fuel cell (FC) vehicle
or stationary power source:



Need: The LQH dehydrogenation at T<fuel cell temperature, to supply ΔH (react) and sensible heat.

Assuming an LQH carrying 6wt% H_2, d=1g/cc 4Kg H_2 (sufficient for FC vehicle 400 mile range) is equivalent to 18 gallons of the "liquid hydride" fuel.

The temperature/H_2-pressure reversible LQH composition – a synthetic chemist's challenge!

Conclusions and Recommendations

- While hydrogen can be produced most economically at large central plants, the hydrogen infrastructure's storage transportation and delivery costs contribute very significantly to its price at vehicle filling stations.

- More effective H_2 containment storage – key to a step-out reduction in H_2 infrastructure costs

- Challenge of H_2 containment expressed in $-\Delta H$ of H_2 "capture". Ideally $-\Delta H$ = 6-8 kcal/mole H_2 (physical, H_2 bond intact) potentially realizable with a porous carbon material (eg. SWNT) or 8-13 kcal/mole H_2 (chemical, H_2 bond ruptured) ideally using a "liquid hydride" (LQH)

  Concept: A temperature/pressure reversible liquid hydride (LQH) of ~6wt% H_2 capacity, by largely utilizing the existing liquid fuel infrastructure could greatly lower the barrier to an extensive H_2 distribution system, and make possible lower cost delivered hydrogen.

  Concept: A LQH that preferably delivers the H_2 at less than the FC's operating temperature would also provide an effective on-board H_2 fuel storage. eg. 18 gal LQH delivering 4 Kg H_2.

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Air Products & Chemicals, Inc.