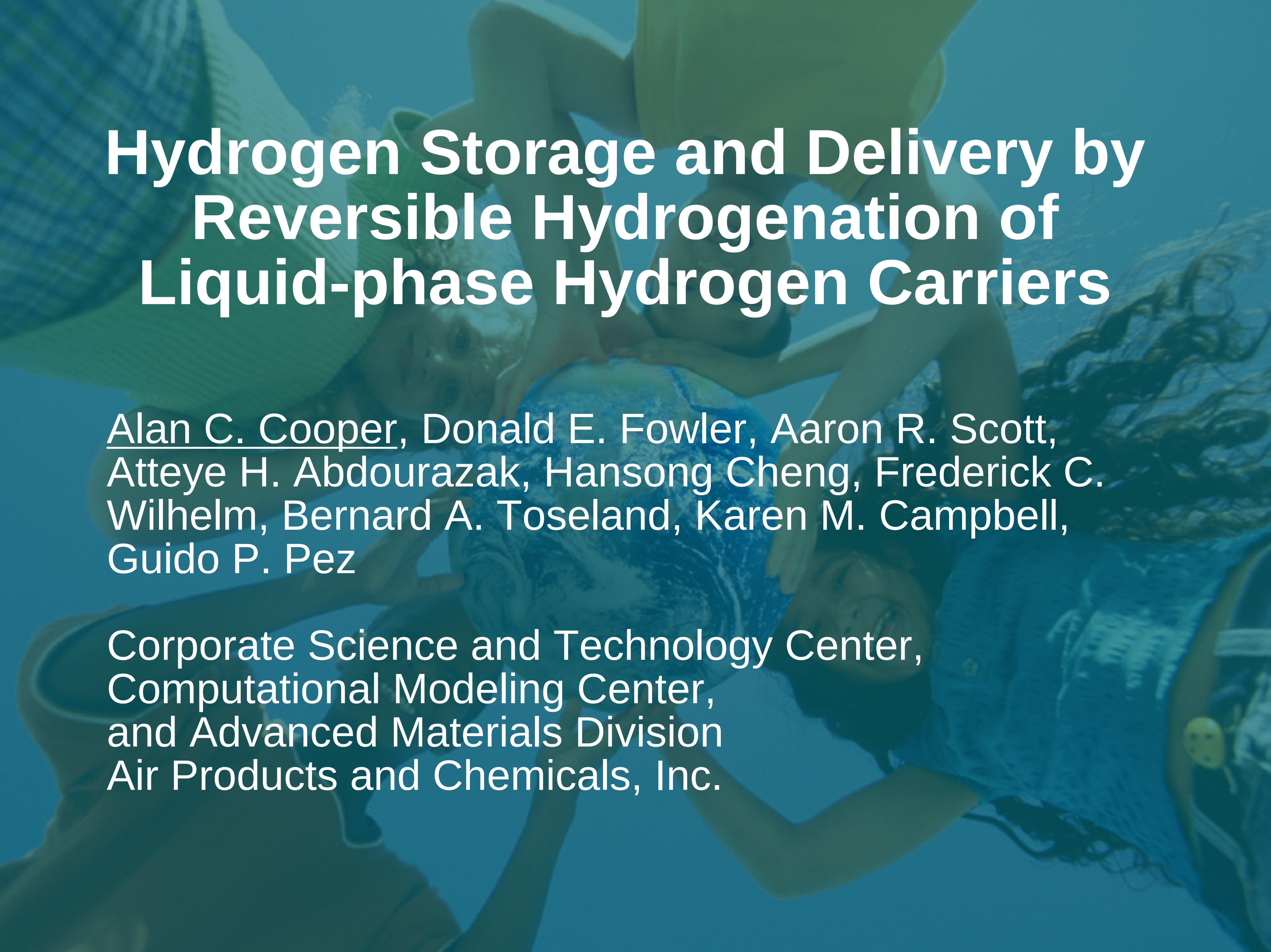

Hydrogen Storage and Delivery by Reversible Hydrogenation of Liquid-phase Hydrogen Carriers

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Fundamental Energetics for Reversibly Containing Hydrogen:

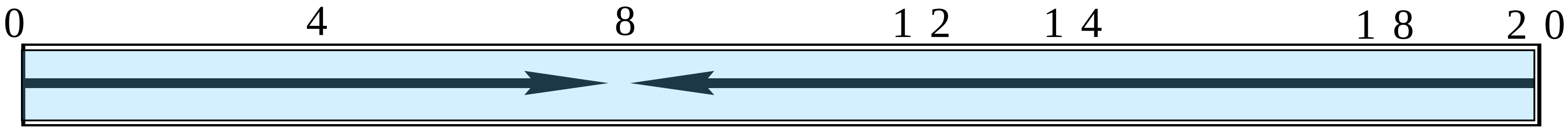
- For H_2 (gas) $\rightleftarrows$ H_2 (contained) equilibrium:

$$\boxed{\Delta G = \Delta H - T\Delta S = -RT\ln K}$$

- For containing H_2 in a spontaneous process:
  - $\Delta G<0$
  - $\Delta H<0$
  - entropy (S) decreases from its' gas phase value (31.1 cal/mole K)

The greater variable contribution to ΔG is from ΔH

Known Enthalpies Ranges for Physical and Chemical Stage



$H_2 + \text{Substrate(S)} \rightleftarrows \text{S-}H_2$

$H_2 + 2\text{S} \rightleftarrows 2\text{S-H}$

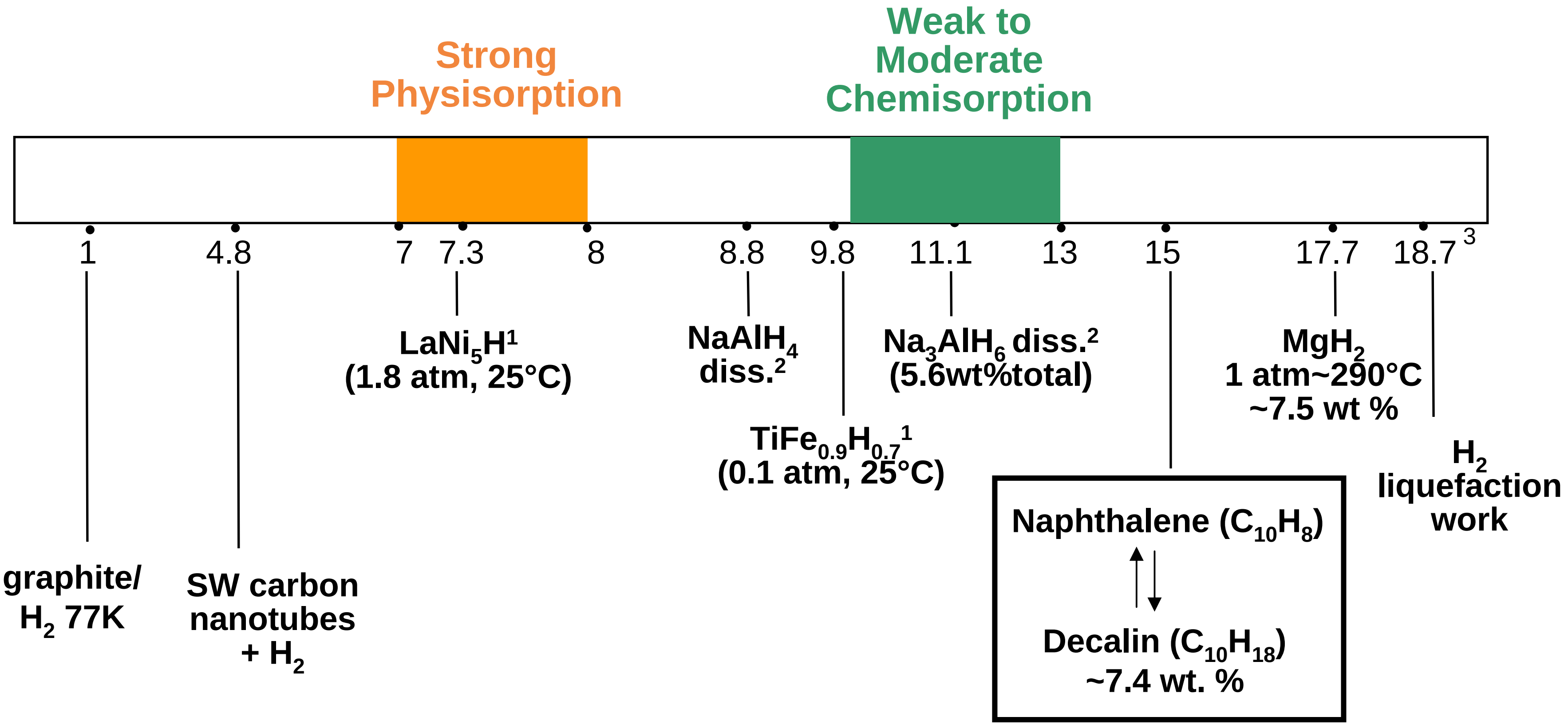
Weakly to strongly physisorbed H_2 on Substrate

Strongly to weakly chemisorbed H_2 on Substrate

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

Ranges for Various H_2 Storage Technologies



Strong Physisorption

Weak to Moderate Chemisorption

1 4.8 7 7.3 8 8.8 9.8 11.1 13 15 17.7 18.7[3]

graphite/ H_2 77K

SW carbon nanotubes + H_2

$LaNi_5H$[1] (1.8 atm, 25°C)

$NaAlH_4$ diss.[2]

$TiFe_{0.9}H_{0.7}$[1] (0.1 atm, 25°C)

Na_3AlH_6 diss.[2] (5.6wt%total)

Naphthalene ($C_{10}H_8$)

$\uparrow\downarrow$

Decalin ($C_{10}H_{18}$)
~7.4 wt. %

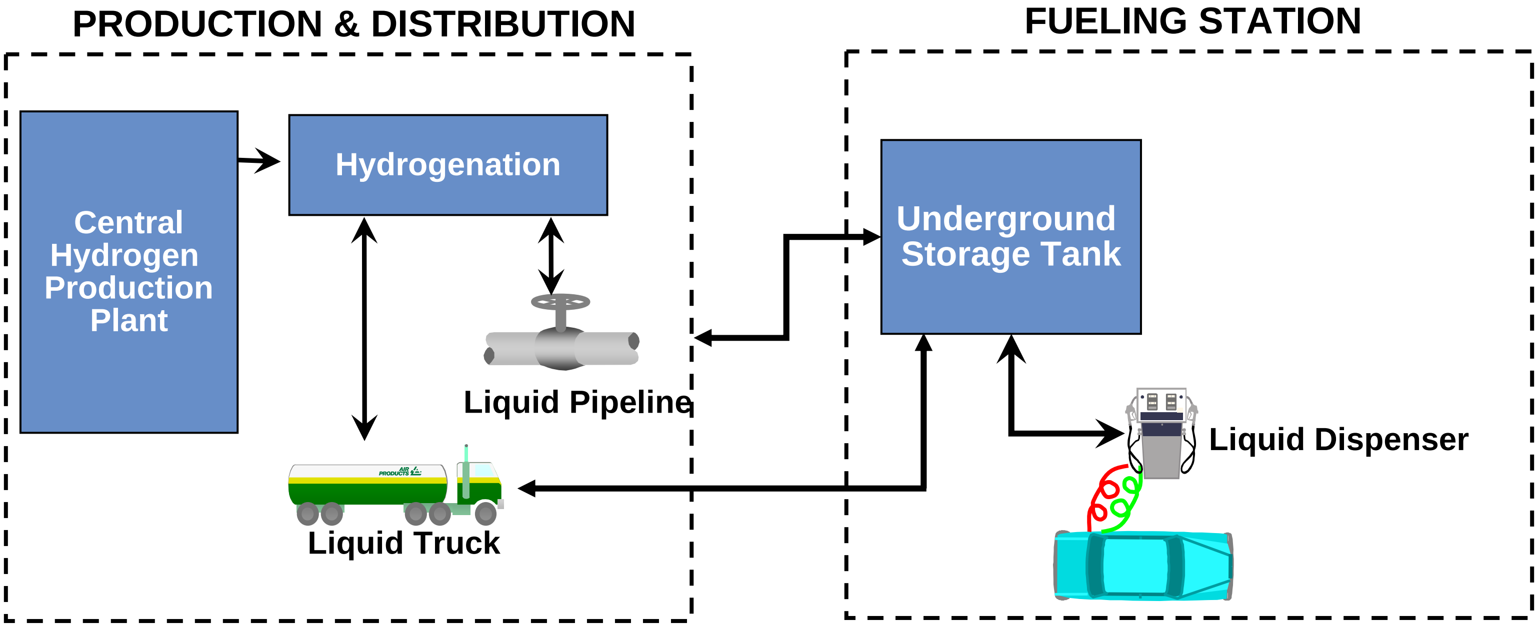
MgH_2
1 atm~290°C
~7.5 wt %

H_2 liquefaction work

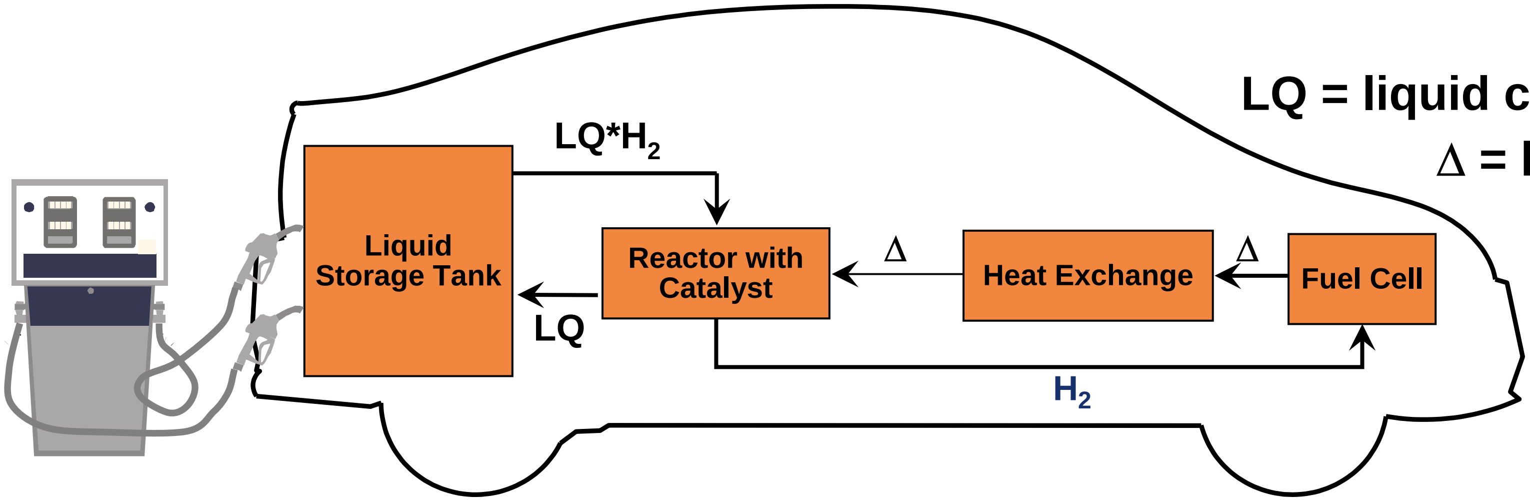
Note: Lower Heating Value for H2 (LHV) = 57 kcal/mole

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

Storage Approach for Delivery to a Fueling Station



Approach: An off-board regenerable liquid carrier for vehicles and stationary H_2 gas delivery



$LQ*H_2$

Liquid Storage Tank

Reactor with Catalyst

Δ

Heat Exchange

Δ

Fuel Cell

LQ

H_2

LQ = liquid carrier

Δ = heat

- Conformable shape liquid tank with design to separate liquids; 22.5 gallons for 5 kg hydrogen at 6 wt. % and unit density
- Heat exchange reduces the vehicles' radiator load by *ca.* 40% (for ΔH of 12 kcal/mol H_2 and 50% FC efficiency)

$$LQ*H_2 + \text{heat } (\Delta H) \underset{\substack{\text{P > 50 atm.} \\ \text{Catalyst}}}{\overset{\substack{\text{Catalyst} \\ \text{P < 10 atm.}}}{\rightleftarrows}} LQ + H_2$$

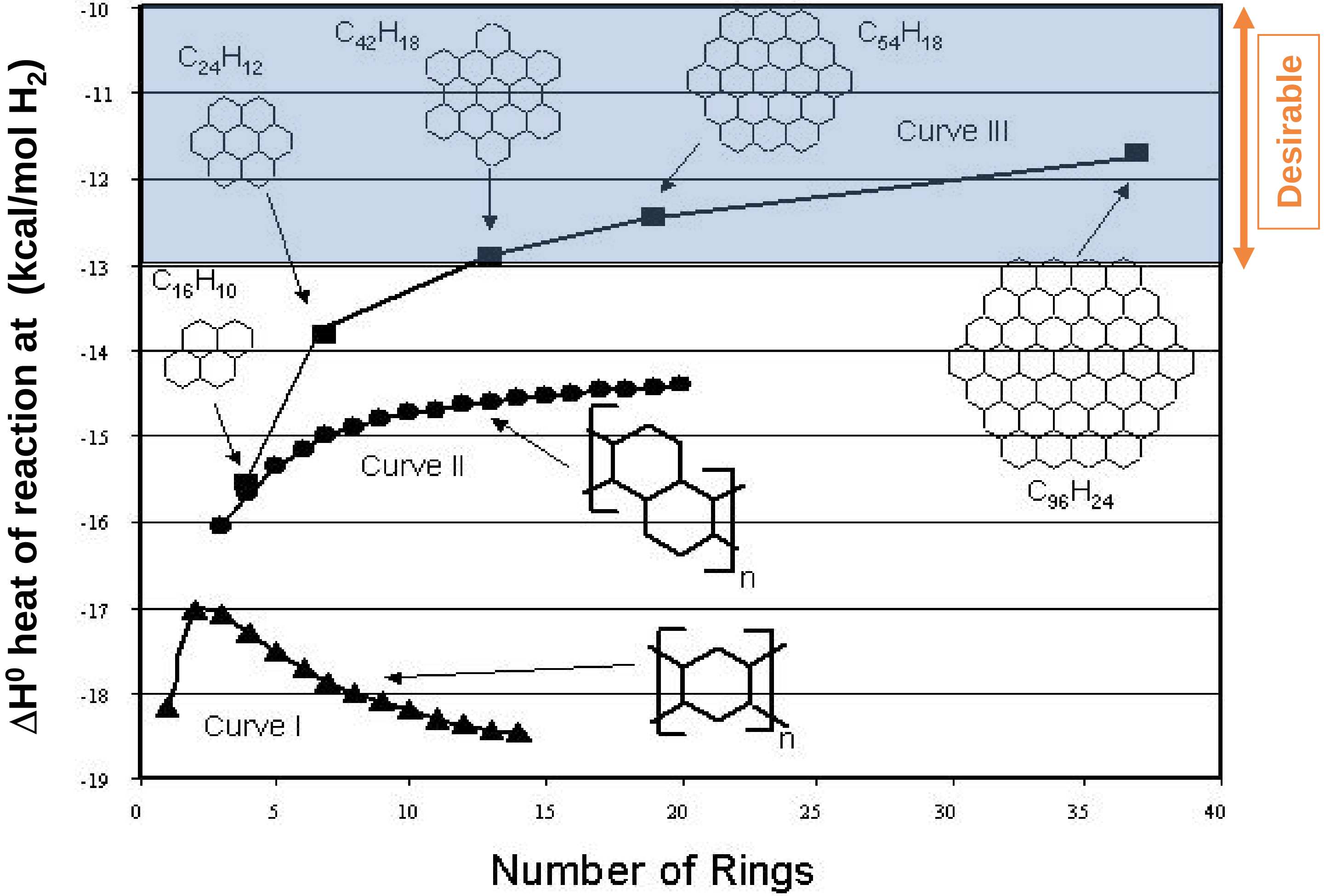
Maximum energy efficiency: by (a) recovering the exothermic (-ΔH) of hydrogenation and (b) utilizing the waste heat from the power source to supply the ΔH for the endothermic dehydrogenation.

Partial List of “Liquid Carrier” Performance Criteria

- **Optimal heat of hydrogenation (10-13 kcal/mole H2), enabling the catalytic dehydrogenation at unprecedented temperatures (<200 °C)**
- **Low volatility (b.p. > 300 °C), enabling the use of these liquids in simplified systems onboard vehicles and reducing exposure to vapors**
- **Low toxicity and environmental impact**
- **Clean catalytic hydrogenation and dehydrogenation, enabling multiple cycles of use with no significant degradation of the molecule**
- **Manufacture of the liquid carriers from low cost, natural source raw materials.**

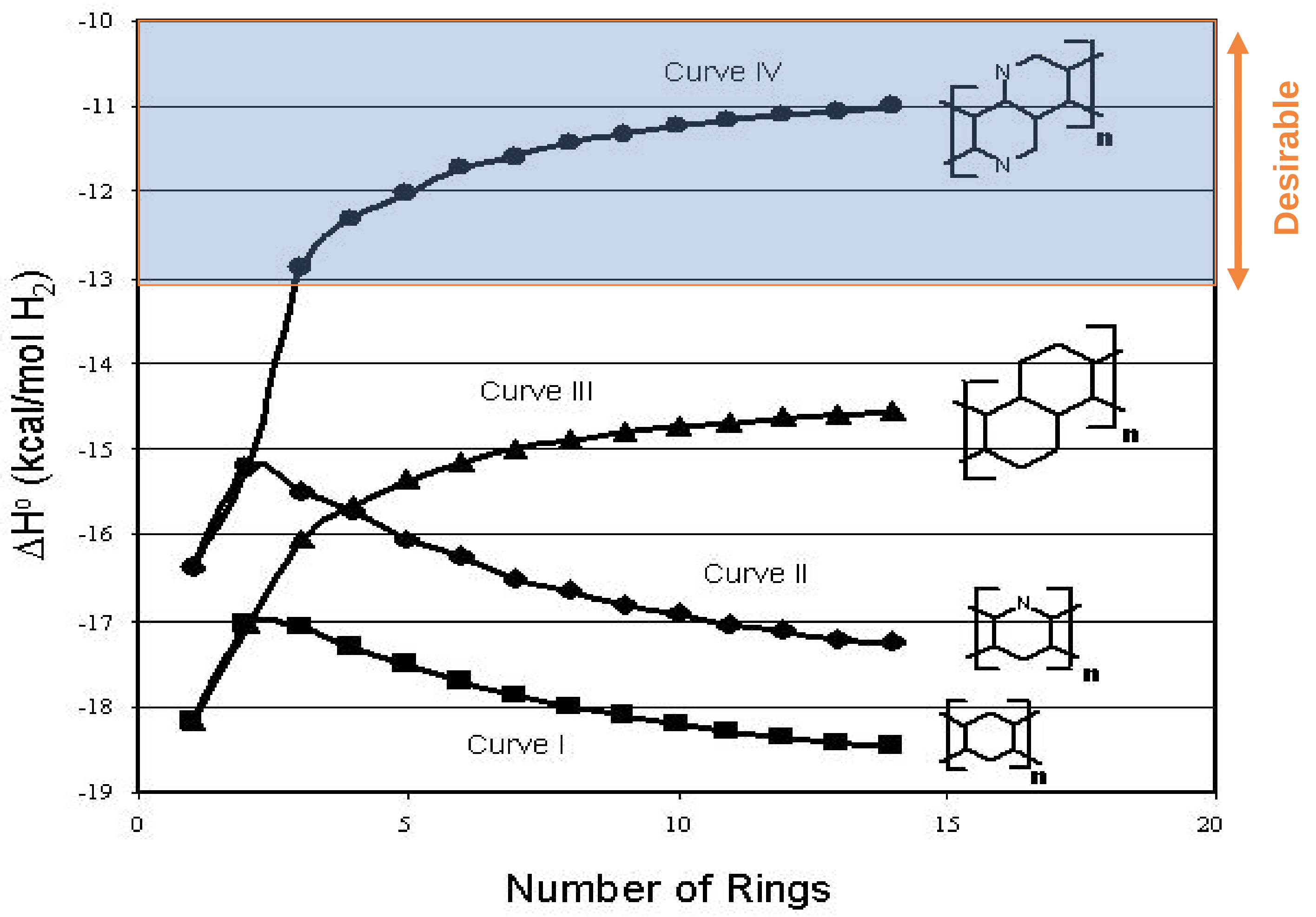
These are not completely satisfied by known organic liquid carriers (eg. cyclohexane, decalin)

Enthalpies of Hydrogenation as a function of fused aromatic rings



Fused multi-ring aromatic systems desirably lower ΔH

Enthalpies of Hydrogenation as a function of N substitution



Inclusion of N heteroatoms can greatly lower ΔH

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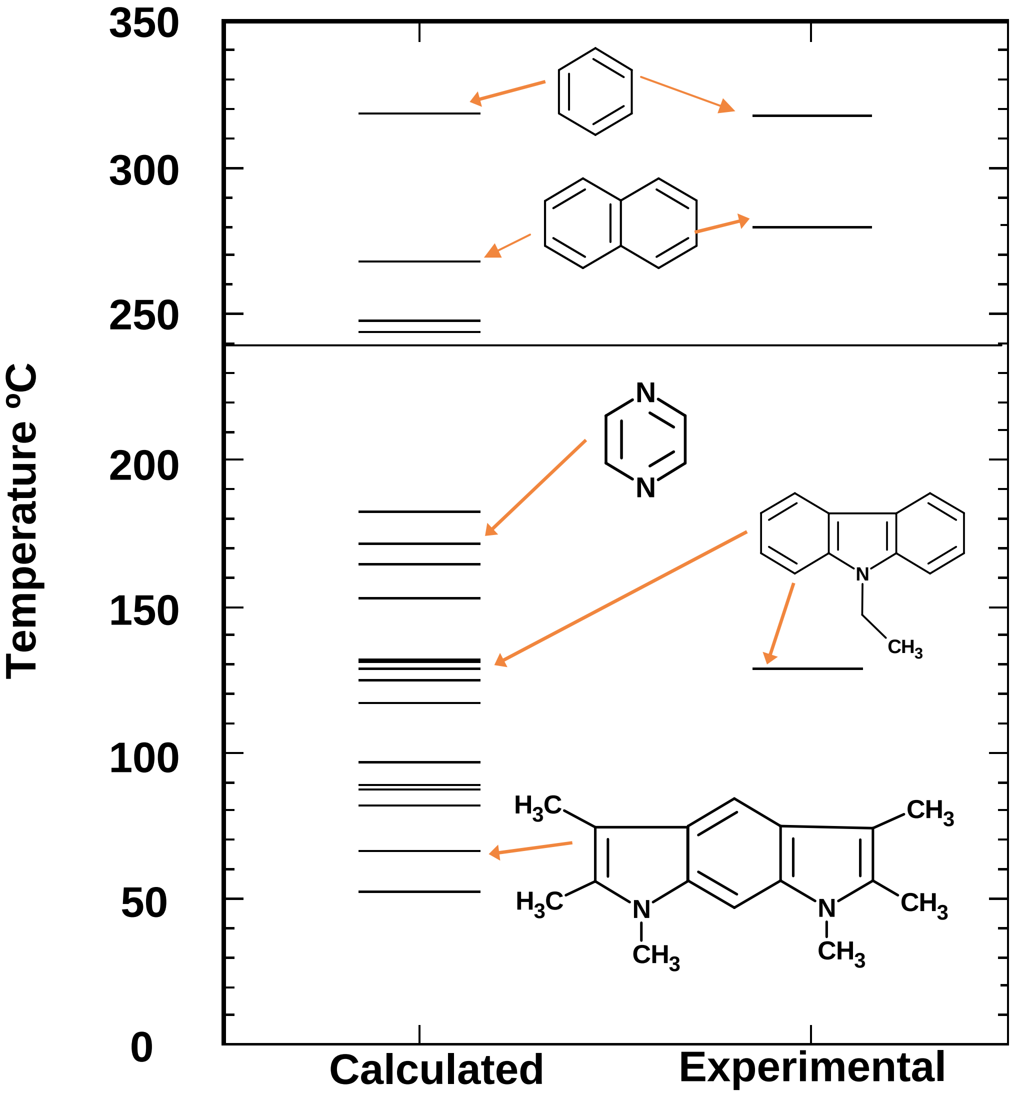
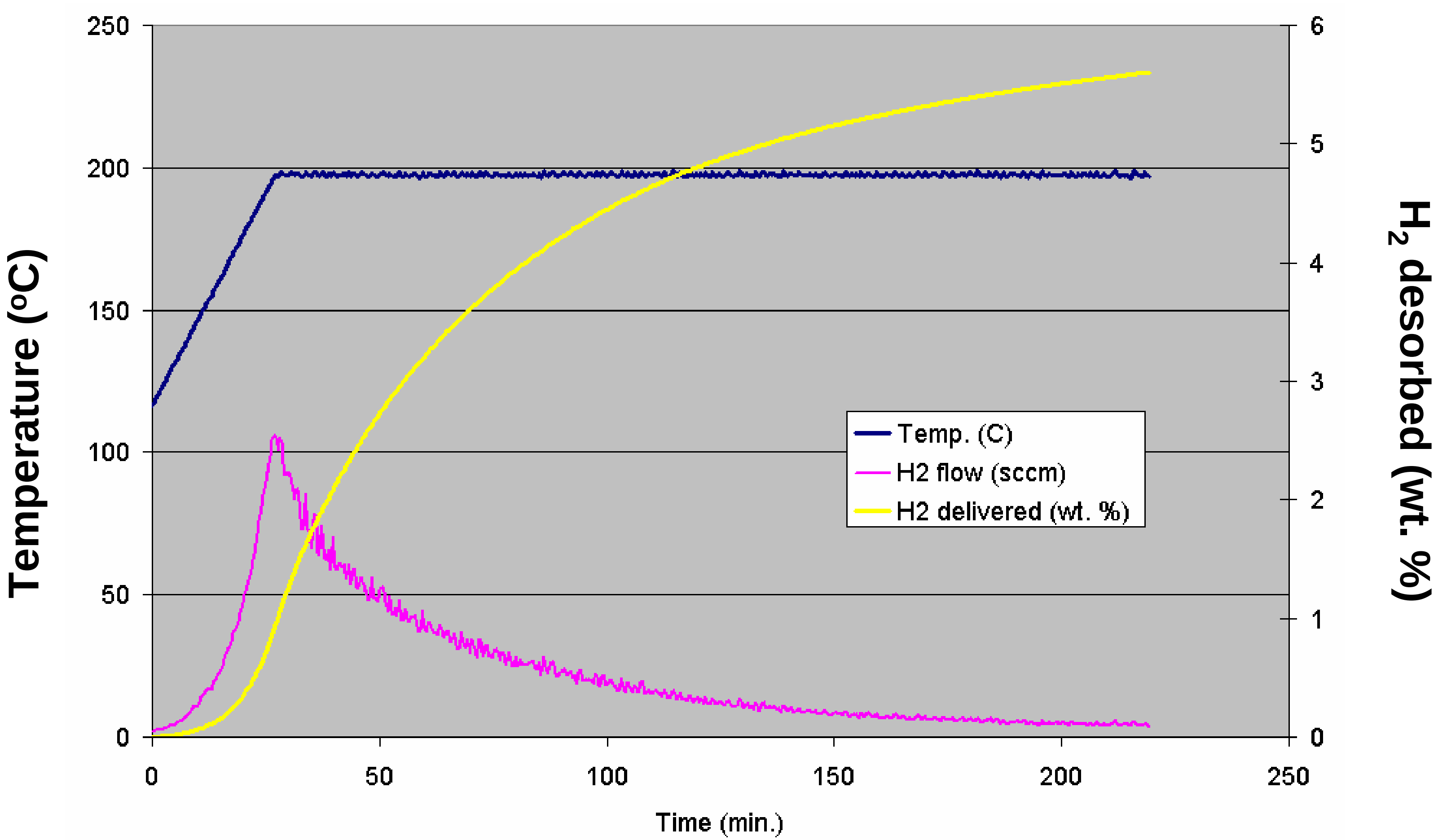
Dehydrogenation temperature for 95% conversion at 1 atm. H_2 pressure



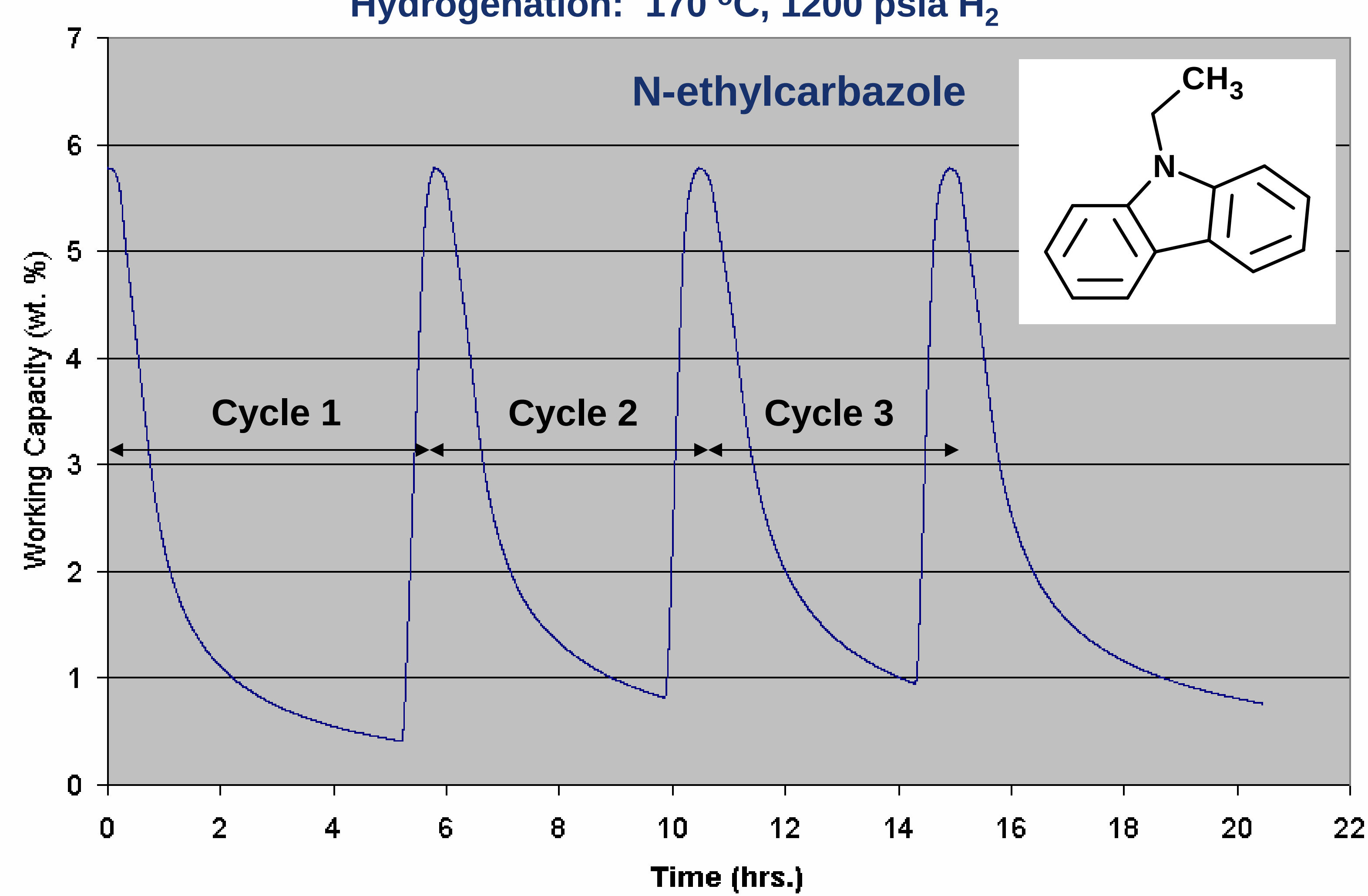
Flow Measurement of Hydrogen Generation from N-ethylcarbazole



GC/MS analysis after run termination showed loss of 5.7% wt H_2

Results: Cycling Studies

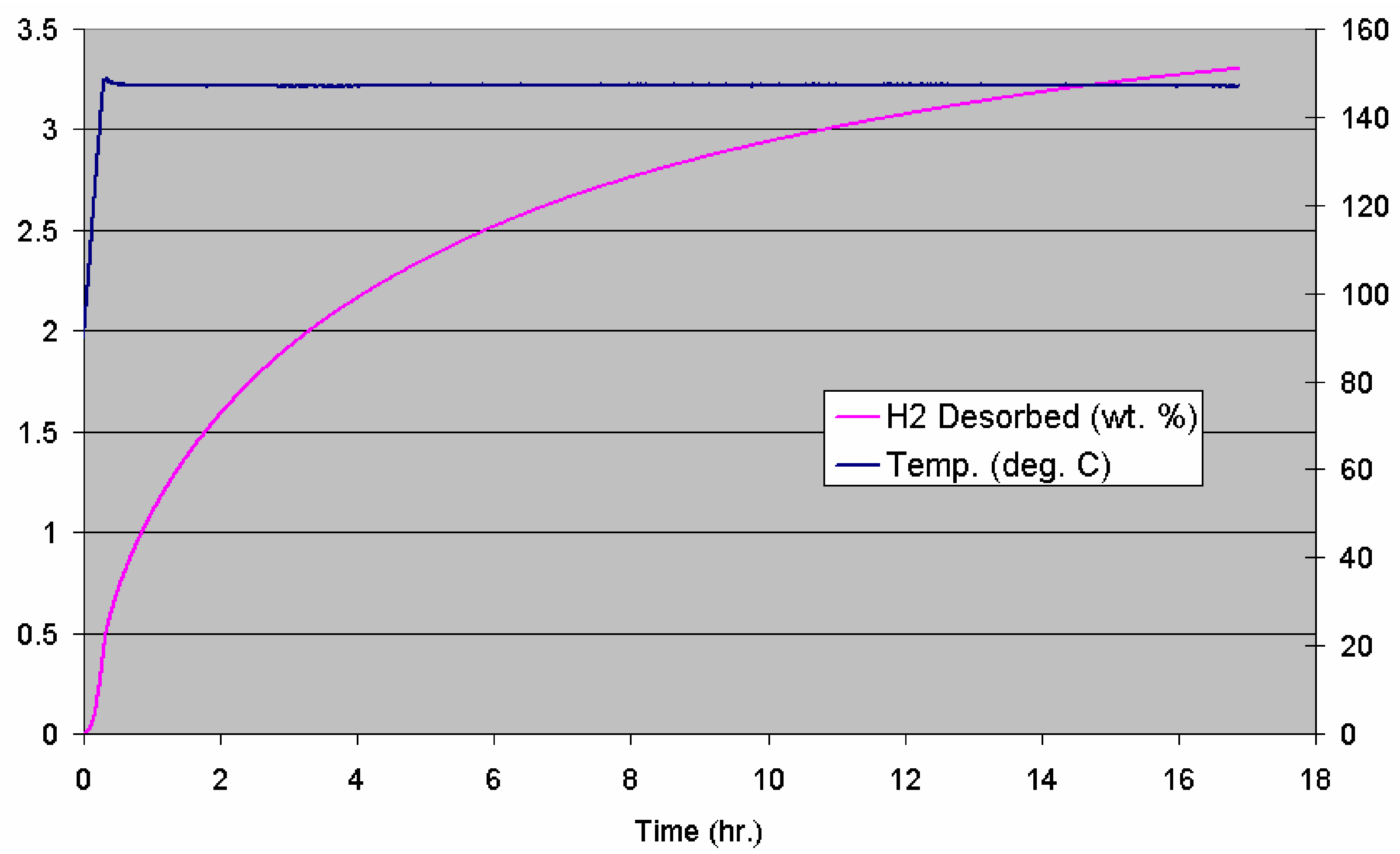
Dehydrogenation: Ramp from 25 °C to 200 °C, 15 psia H_2
Hydrogenation: 170 °C, 1200 psia H_2



➔ Rapid hydrogenation and cycling stability

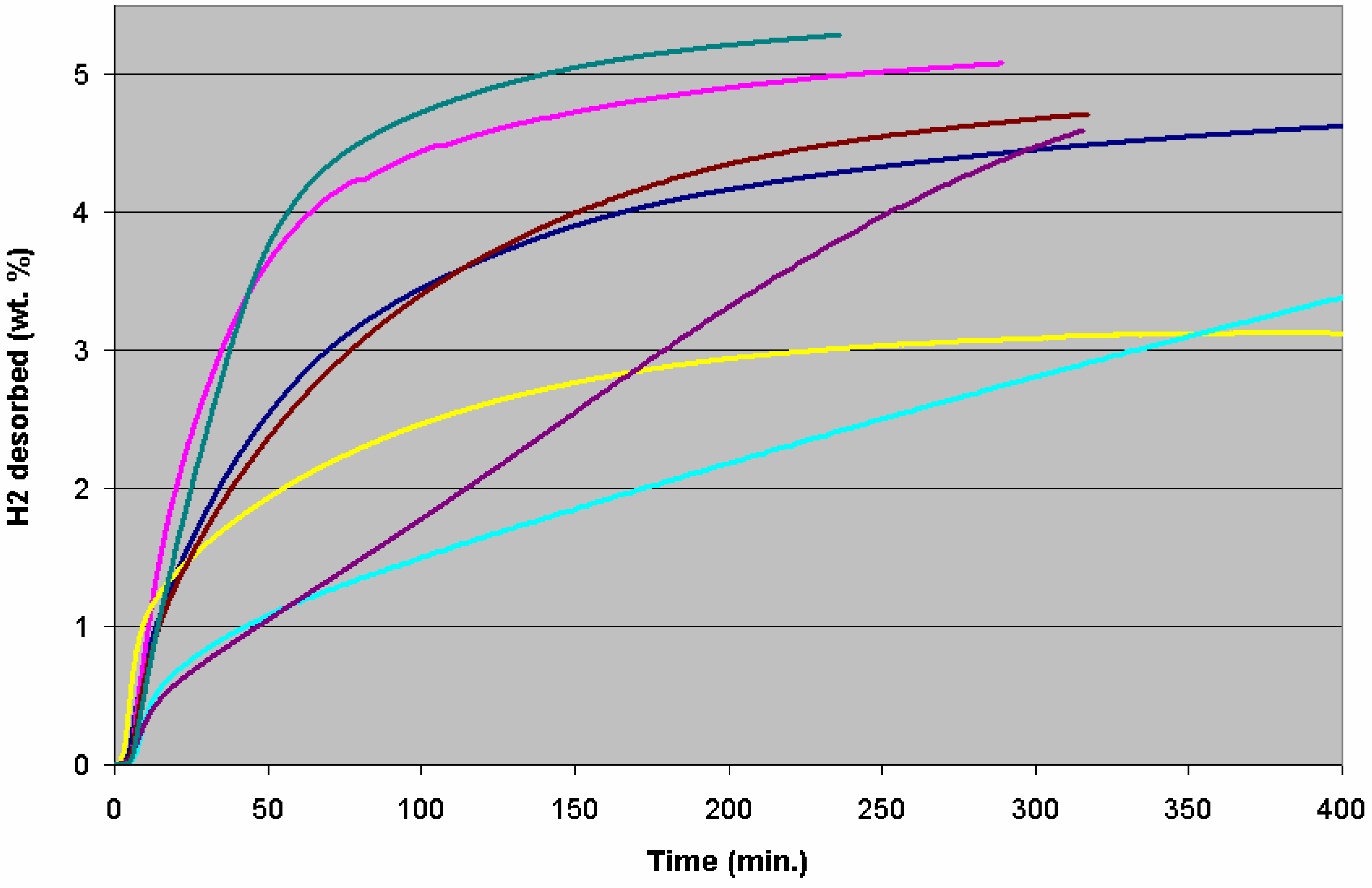
N-ethylcarbazole Dehydrogenation:

(Ramp from 25 ^oC to 150 ^oC, 15 psia H_2)



Slow catalytic dehydrogenation rate at 150 ^oC

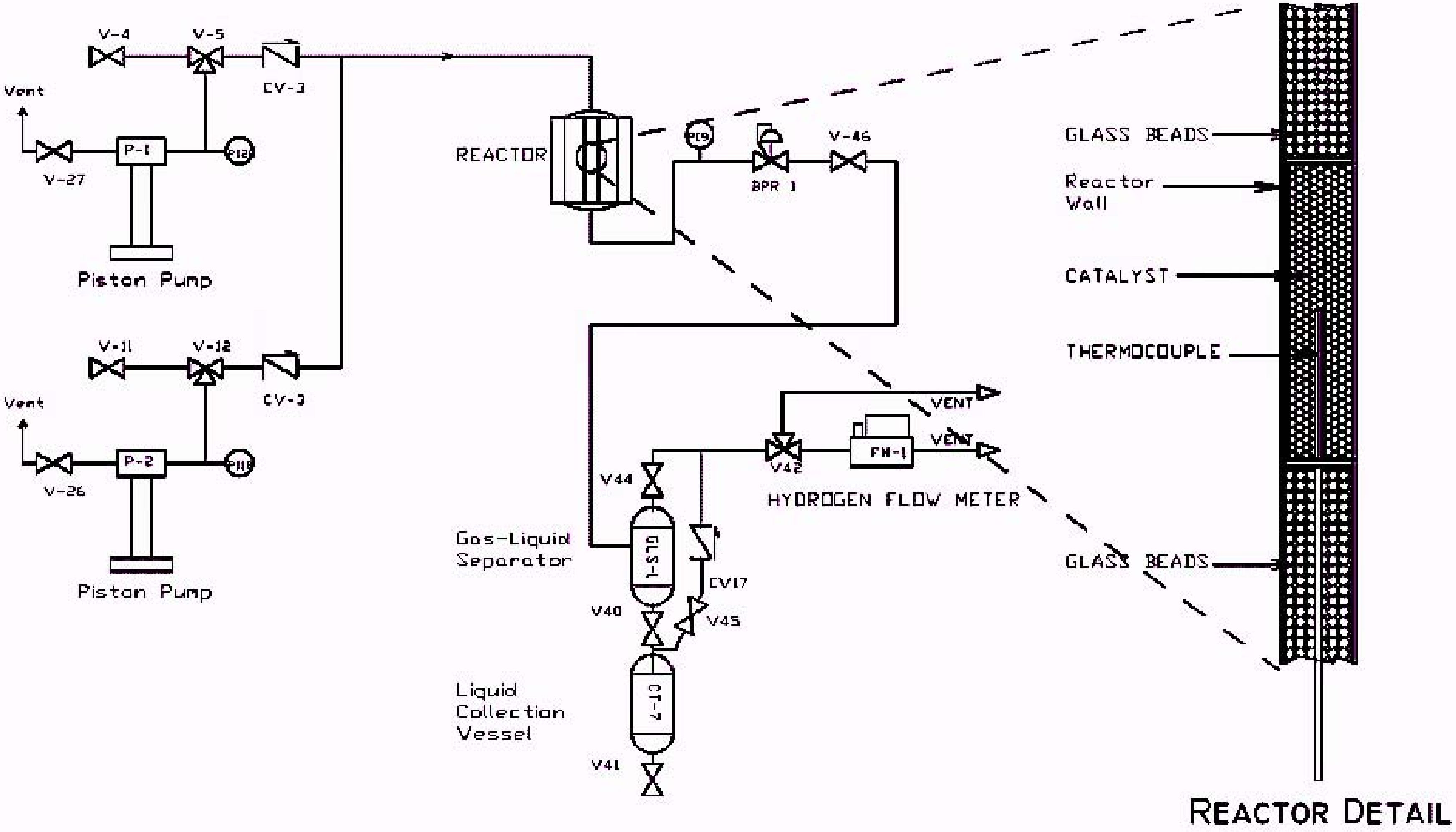
Dehydrogenation Catalyst Screening



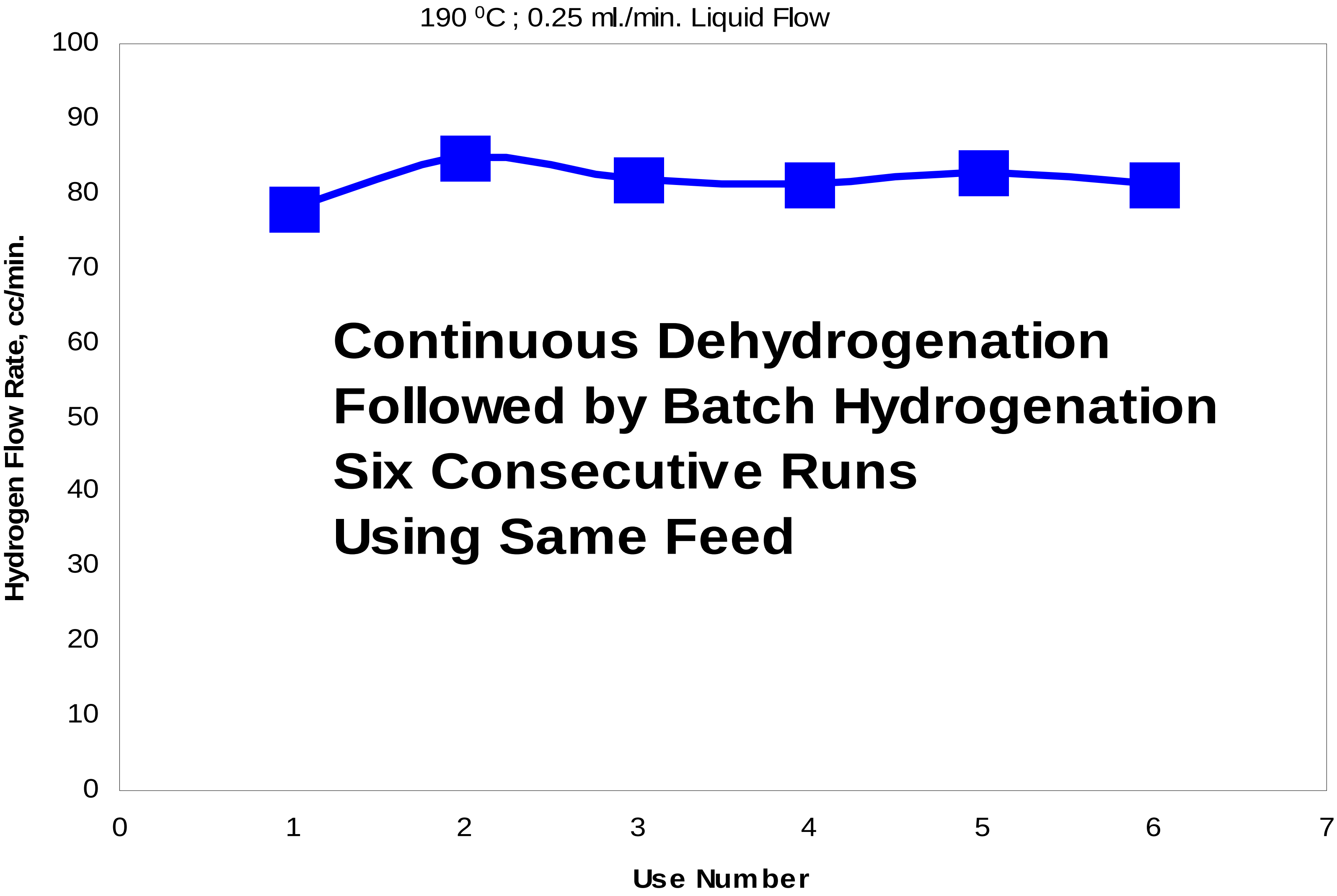
Over 40 catalysts screened in last 3 months

CONTINUOUS PACKED BED REACTOR

(DOWNFLOW OPTION)



Packed Bed Dehydrogenation Demonstration



190 ^{0}C ; 0.25 ml./min. Liquid Flow

Continuous Dehydrogenation
Followed by Batch Hydrogenation
Six Consecutive Runs
Using Same Feed

H_2 Quality from Continuous Flow Dehydrogenation Experiments

Component	Mole %
Hydrogen	99.9+
Methane	0.0013%
Ethane	0.0083%
Carbon Monoxide	ND
N containing compounds	ND
C3’s	ND
C4’s	ND
C5’s	ND
C6’s	ND

ND – Non Detectable

Dehydrogenation Video Clip

Perhydro-N-ethylcarbazole

Pd/Al_2O_3 catalyst

Temperatures: 100-200°C

Technical Challenges: Molecule and Catalyst

- **Development and testing of new liquid carriers:**
  - **optimal heats of hydrogenation**
  - **increase hydrogen capacity**
  - **modify substrate melting points (eg. by the use of mixtures of multiple substrates)**
- **Development of new dehydrogenation catalysts:**
  - **increase rates at low temperatures**
  - **selective dehydrogenation**
  - **transfer of catalyst knowledge to reactor design activities**

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