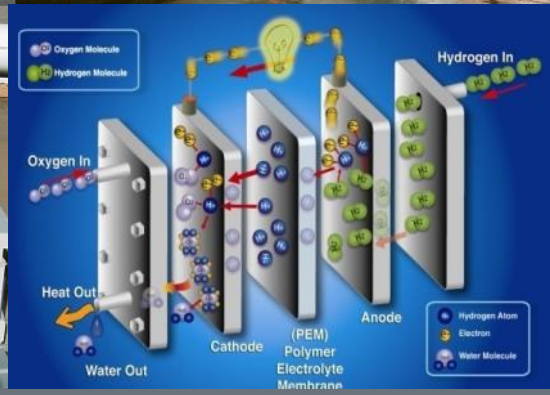
An overview of liquid hydrogen carrier R&D supported by the DOE Fuel Cell Technologies Office

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy



ARPA-E Liquid Transportation Fuels Workshop

Denver, CO

August 27-28, 2015

Ned Stetson, PhD

U.S. Department of Energy
Fuel Cell Technologies Office
Hydrogen Storage Program Manager

Outline

- Definition of an ideal liquid hydrogen carrier
- How liquid hydrogen carriers could fit in the infrastructure
- Overview of key properties needed for an effective carrier
- Overview of DOE supported R&D on liquid carriers
  - Air Products and Chemicals Inc.
  - Hawaii Hydrogen Carriers
  - University of Oregon/Boston College
- H_2 Infrastructure – potential areas liquid carriers could offer advantages

What is not being covered

- Solid or gaseous carriers
- “One-way” carriers –
  e.g., ammonia, hydrocarbon reformation
- Slurries – solid carrier suspended in a slurring agent –
  e.g., ammonia borane or alane (AlH_3) in AR 20 silicon oil

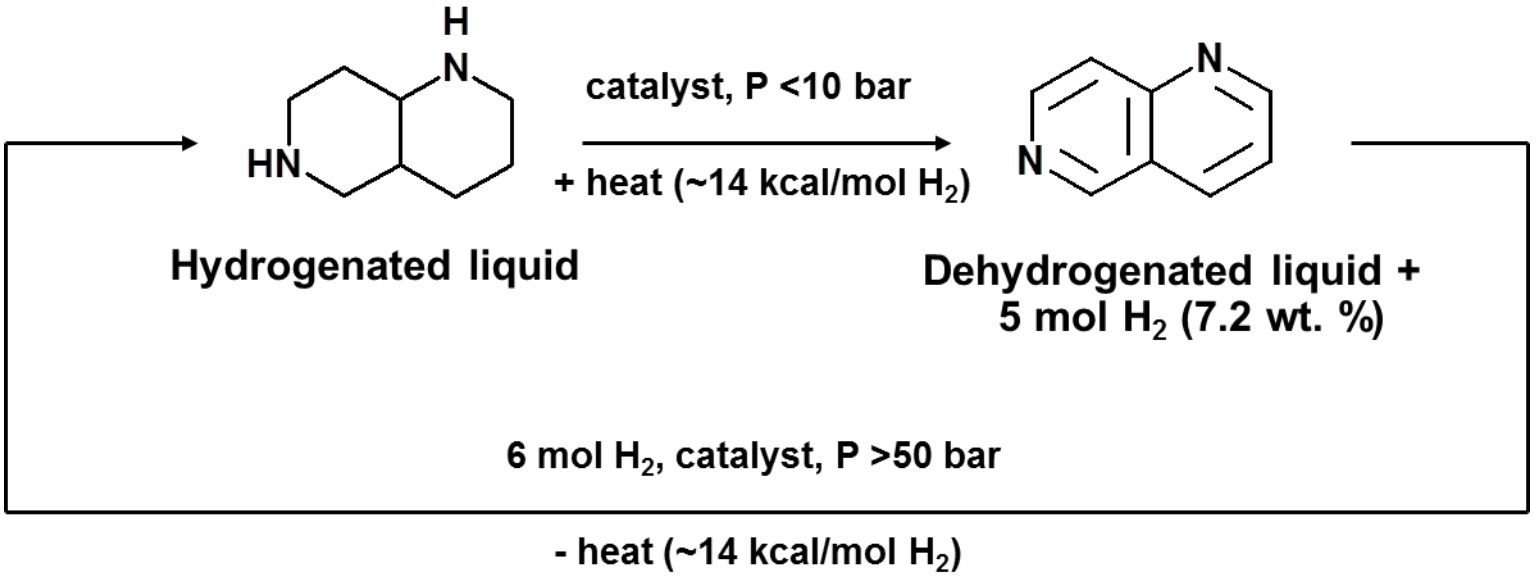
What's an ideal liquid H_2 carrier?

- Stable with little to no release of hydrogen under the range of ambient conditions

$$LQ + H_2 \xleftrightarrow{\text{catalyst}} LQ^*H_2 + \text{heat}$$

- Rapidly able to release hydrogen using available "waste" heat and temperature (e.g., PEM fuel cell)
- Remains in liquid phase throughout all stages of hydrogenation/dehydrogenation and temperature range
- Low volatility and able to be separated from the released hydrogen easily
- Little degradation on cycling (i.e., minimal side reactions and loss of volatile components) – long cycle life

Operation scheme for "2-way" liquid hydrogen carriers

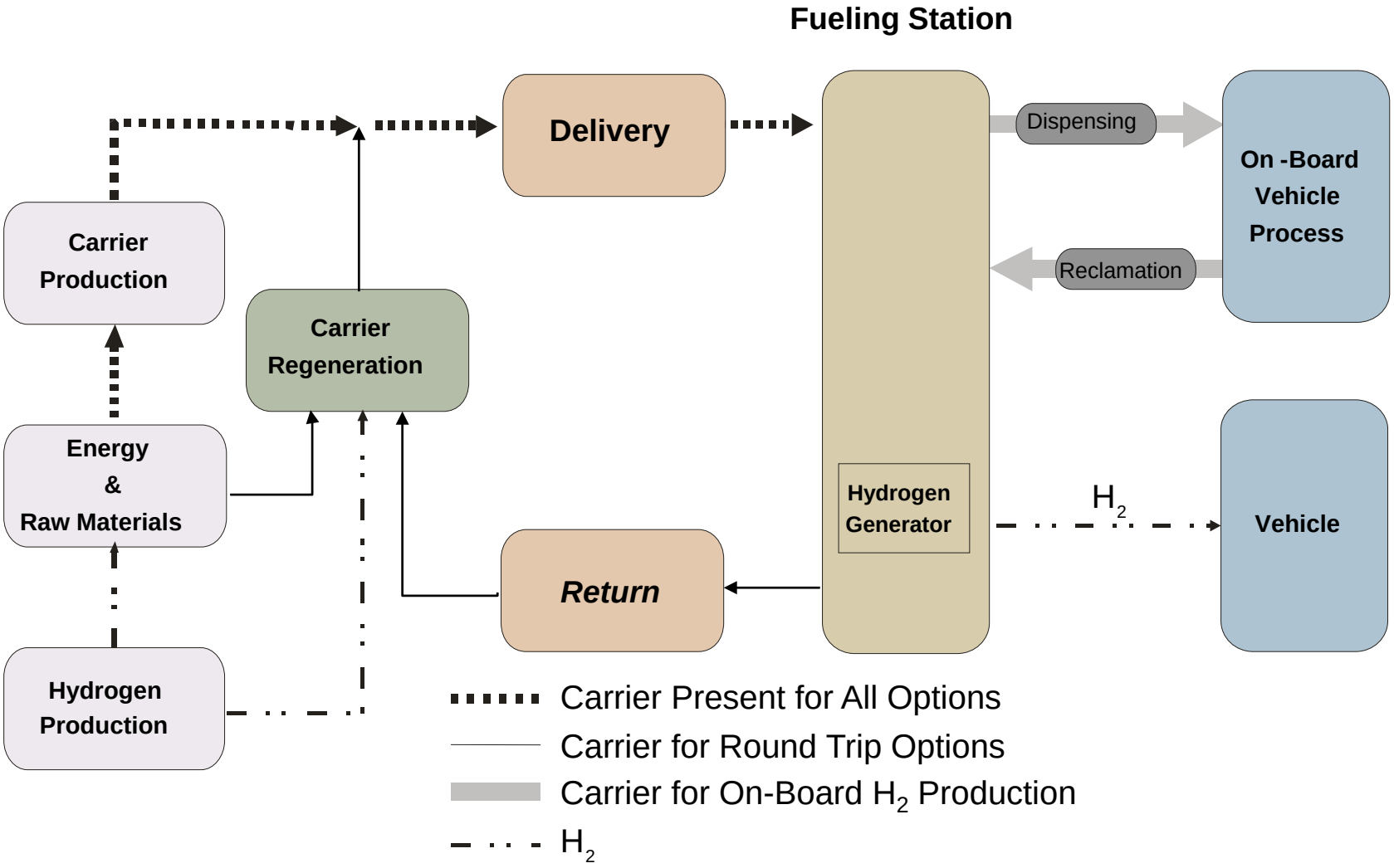


Estimate: ~72 liters of hydrogenated liquid carrier could reversibly store 5 kg of hydrogen at 7 wt.% and 1g/cc density

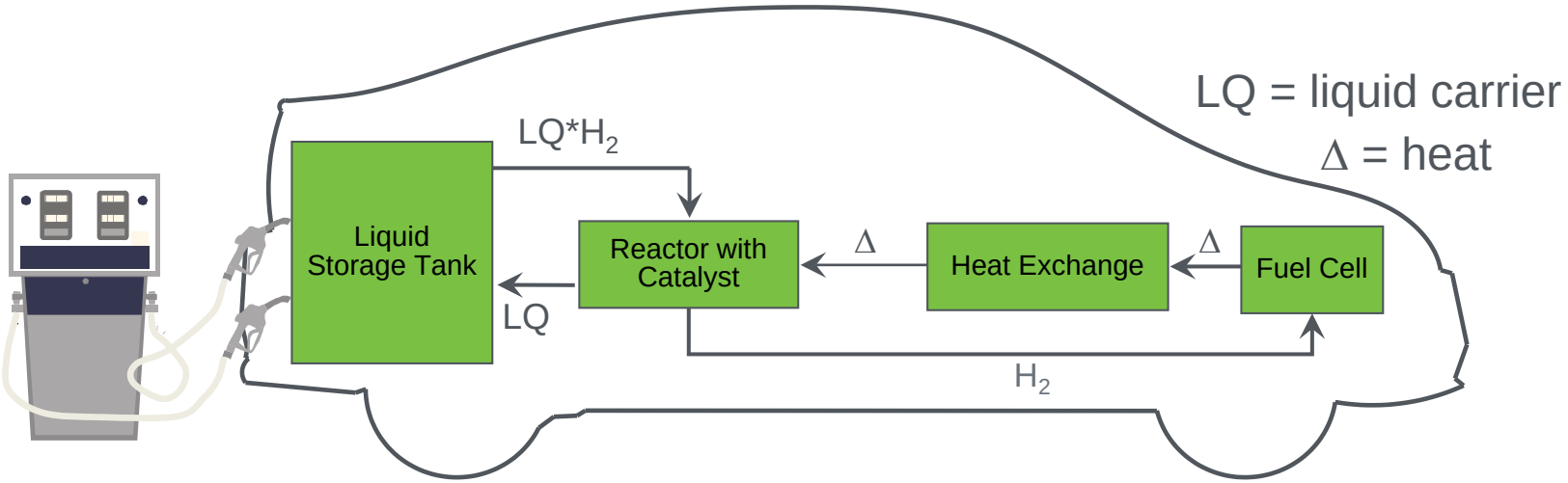
~ 50% of the volume required for 700 bar compressed H_2 at ambient temperatures!

Air Products presentation at the 2007 Hydrogen and Fuel Cells Technologies Annual Merit Review and Peer Evaluation Meeting, #ST-23, 17 May 2007

Liquid Carrier Pathway



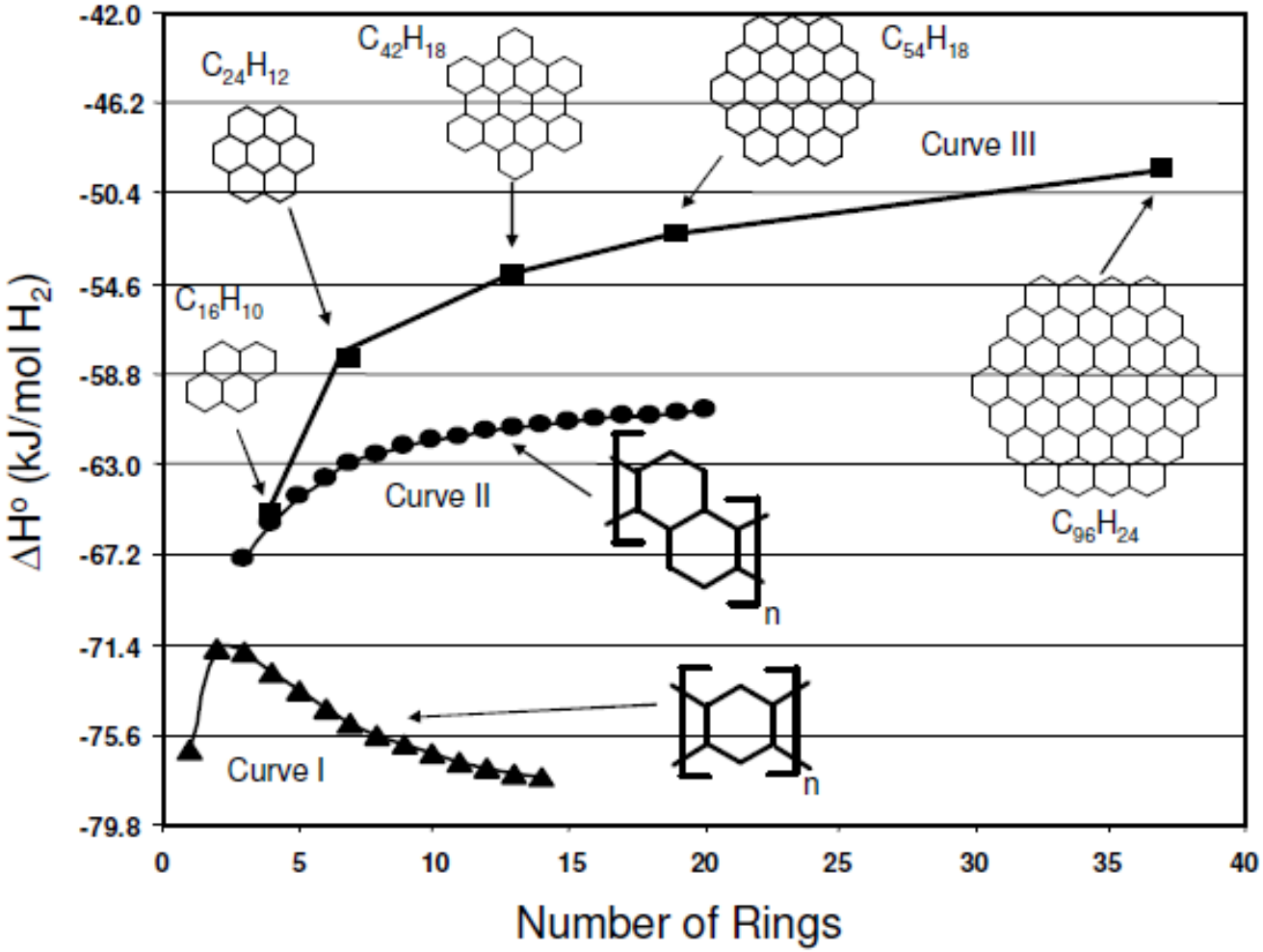
Potential for use onboard vehicles



Currently not a focus area for the DOE-EERE Fuel Cell Technologies Office

Liquid Hydrogen Carrier Development

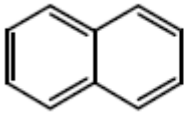
Dehydrogenation enthalpy vs number of rings



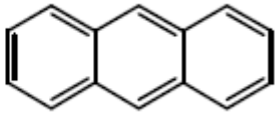
Calculated dehydrogenation enthalpy, $H_D°$ (kJ/mole H_2), for three series of polyaromatic hydrocarbons as a function of the number of rings. The PM3 semi-empirical method was used for the calculations. (*Air Products, Final Report, DOE Award # DE-FC36-04GO14006*)

Aromatic sextet stabilization

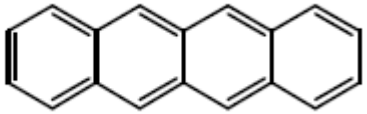
The aromatic stabilization energy of polyaromatic hydrocarbons is determined by the relative number of aromatic sextet structures in the molecules. (*Clar, E. in "Polycyclic Hydrocarbons", Academic Press, NY, 1964, Chapter 16*)



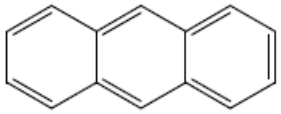
naphthalene



anthracene



tetracene



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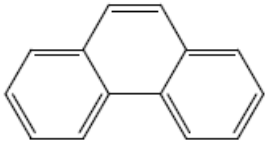
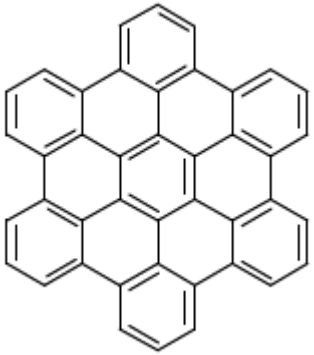
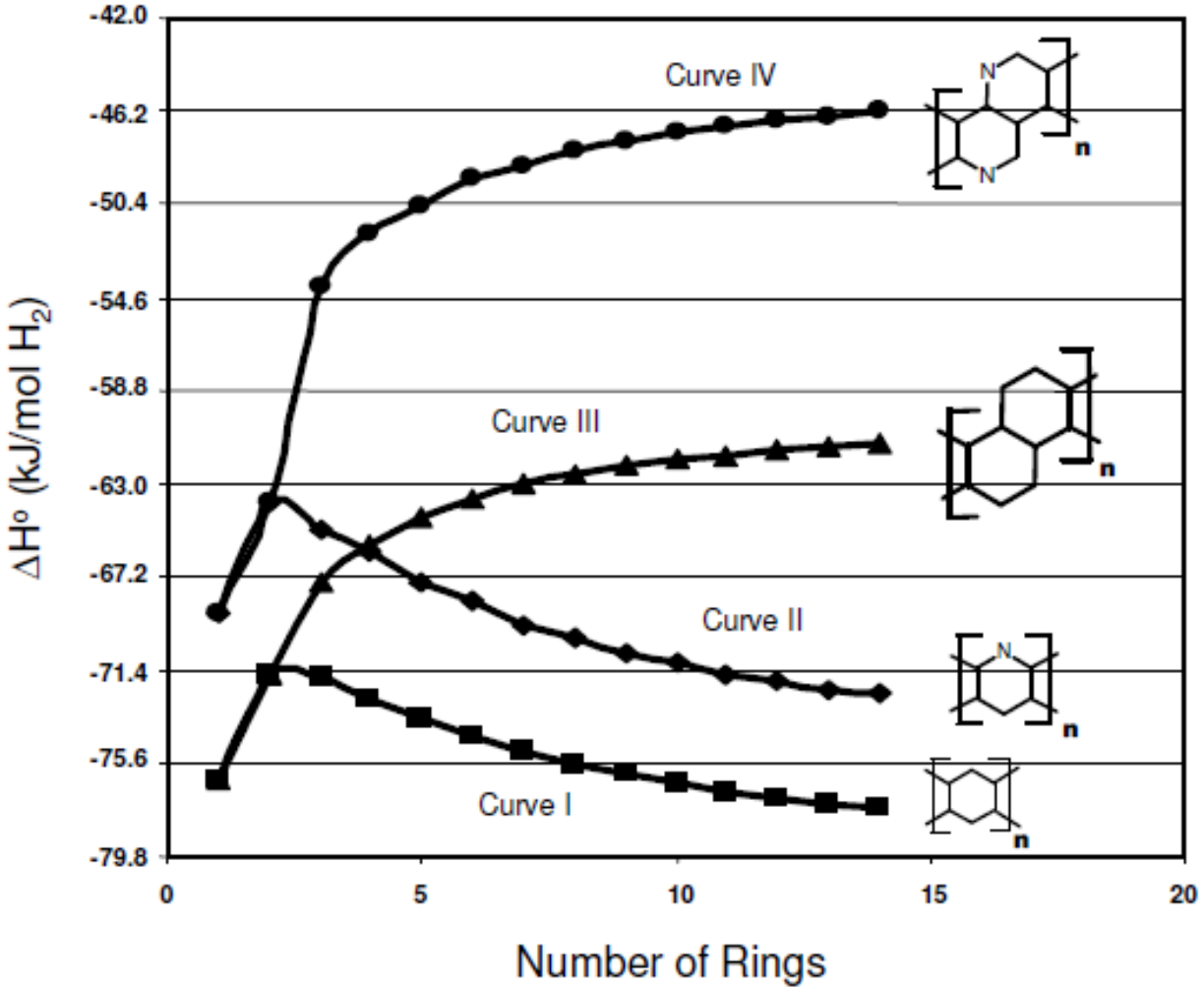


phenanthrene



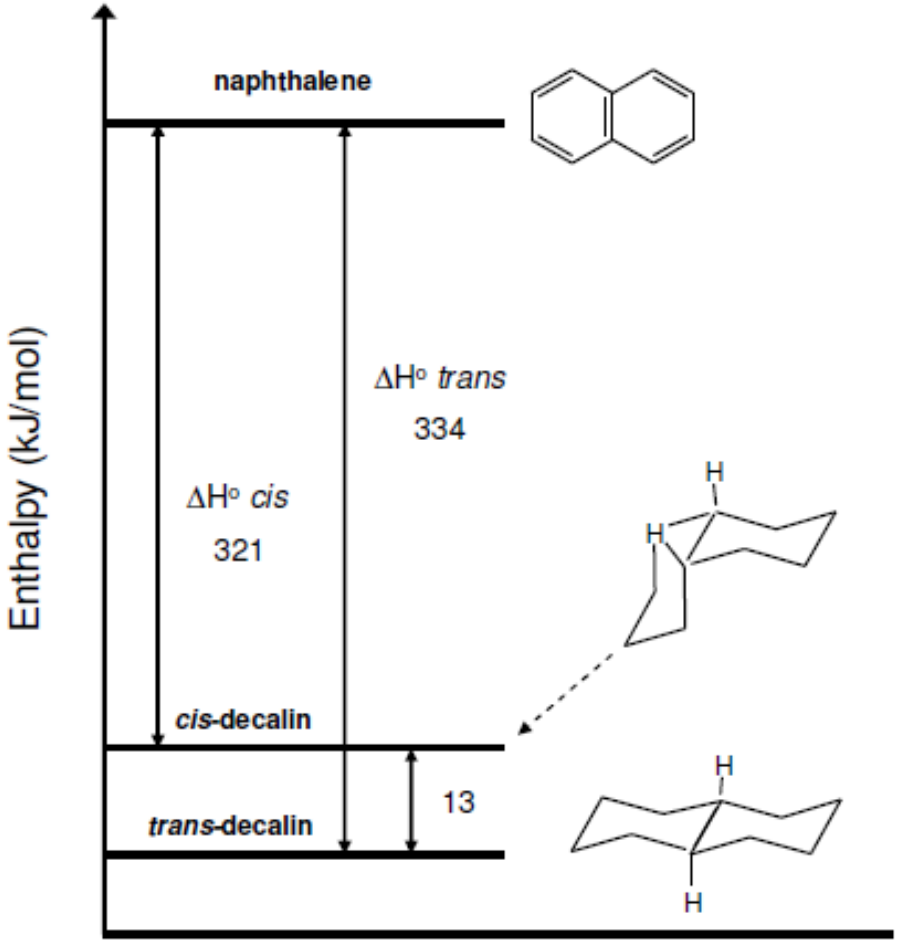
hexabenzocoronene

Effect of heteroatoms in the rings



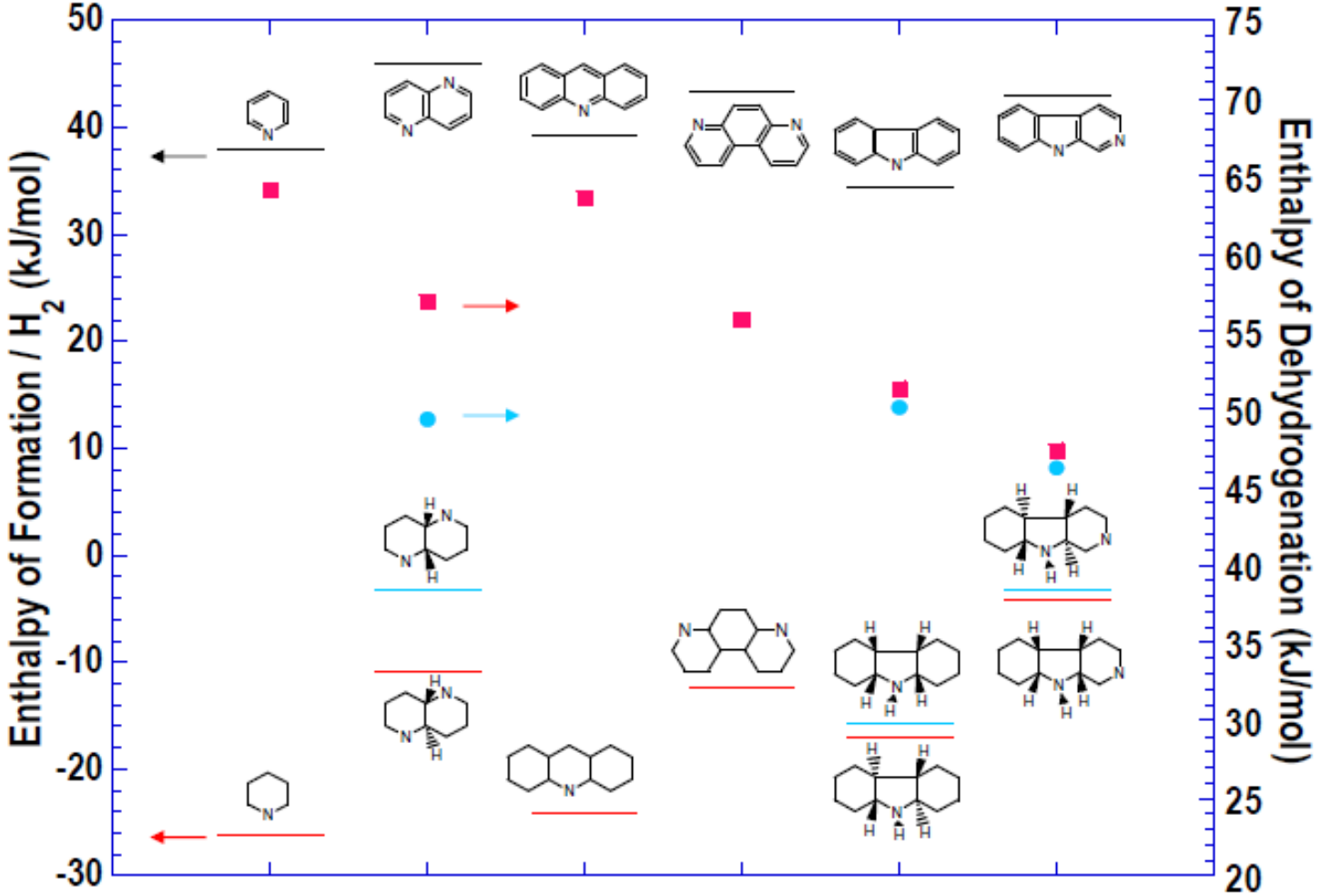
Calculated dehydrogenation enthalpy, $H_D°$ (kJ/mole H_2) for N-heterocycles and the corresponding polyaromatic hydrocarbons (PM3 method) (*Air Products, Final Report, DOE Award # DE-FC36-04GO14006*)

Impact of *cis-trans* isomerization



Cis-trans isomerism in naphthalene and the relative energetics (*Air Products, Final Report, DOE Award # DE-FC36-04GO14006*)

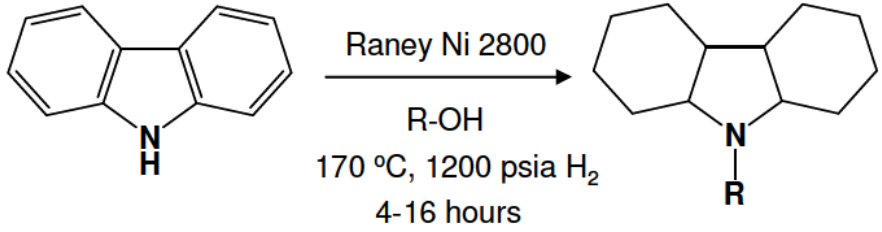
Survey of standard enthalpies of formation and dehydrogenation



Standard enthalpies of formation, Hf° and standard dehydrogenation enthalpies, HD°, (kcal/mole H2) of N-heterocyclic aromatic and cycloaliphatic molecule pairs. (*Air Products, Final Report, DOE Award # DE-FC36-04GO14006*)

Alkylated carbazoles

Molecule	Formula	Melting Point	Theoretical Capacity (wt.%)
Carbazole	$C_{12}H_9N$	250°C	6.7
N-methylcarbazole	$C_{12}H_9N\text{-}CH_3$	90°C	6.2
N-ethylcarbazole	$C_{12}H_9N\text{-}CH_2CH_3$	70°C	5.7

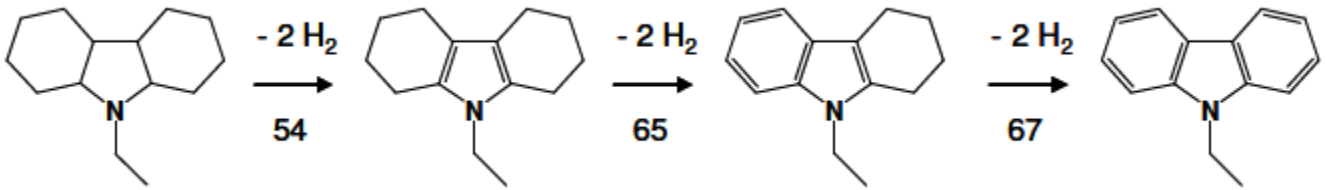


Yields of nickel-catalyzed hydrogenation and N-alkylation of carbazole.
(*Air Products, Final Report, DOE Award # DE-FC36-04GO14006*)

Alkyl group	Yield of perhydro-N-alkylcarbazole	Yield of partially hydrogenated N-alkylcarbazole	Hydrogenated carbazole
Methyl	98%	2%	0%
Ethyl	97%	3%	0%
n-propyl	97.5%	2.5%	0%
iso-propyl	59%	7%	34%

Dehydrogenation conditions

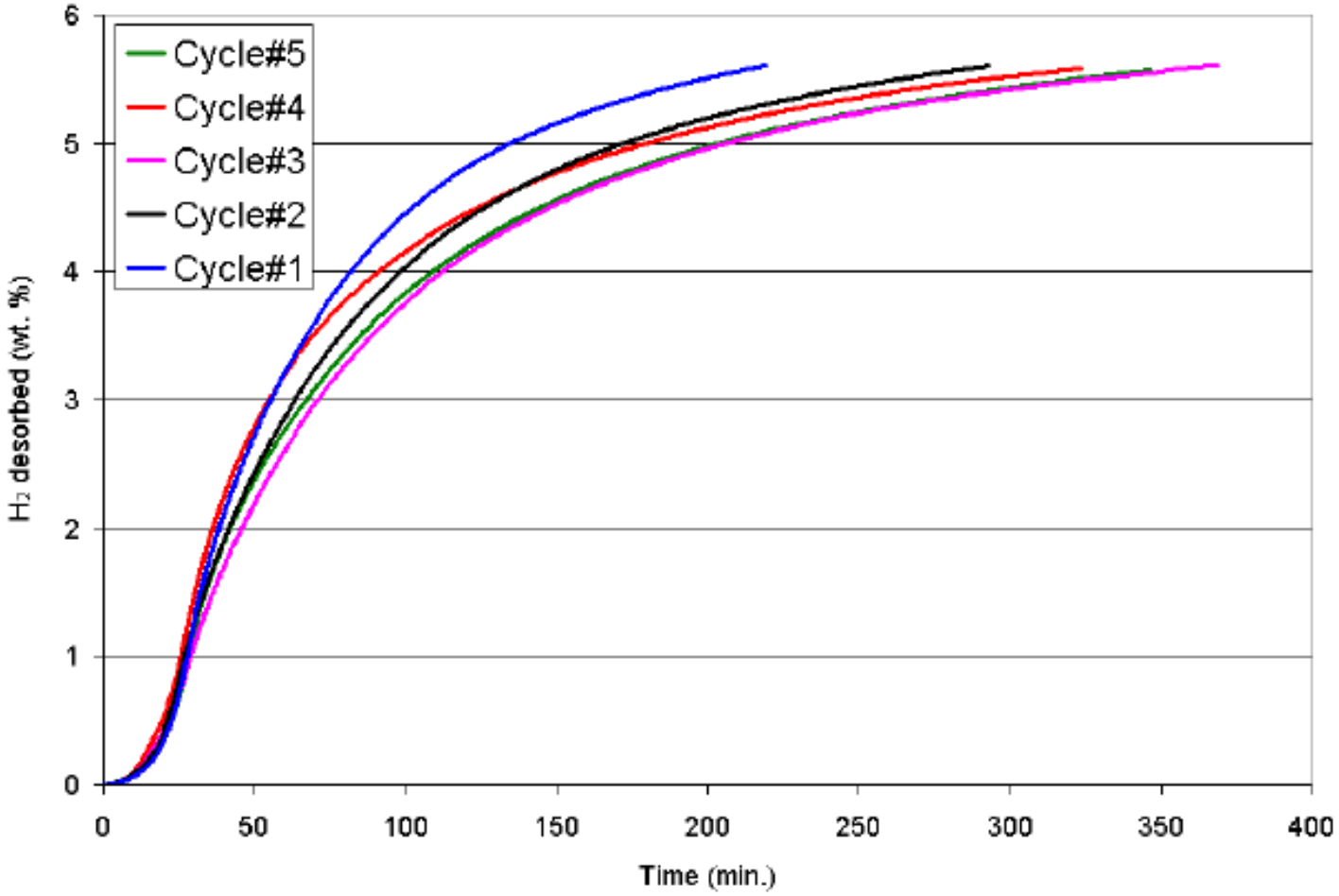
- Typical dehydrogenation experimental conditions for perhydro-N-alkylcarbazole performed by Air Products:
  - the dehydrogenation catalyst was slurried (1-5 wt.%) in liquid perhydro-N-alkylcarbazole
  - 1 atm. initial hydrogen pressure
  - temperature ramped at a controlled rate up to 150-200 °C
  - slurry stirred at 500-800 rpm
  - rate of hydrogen release from the reactor measured with a flow meter



GC-MS analysis of intermediates indicate hydrogen released in steps of 2 hydrogen molecules. Scheme above includes calculated electronic energy change (DE; kJ/mol H2) for the stepwise dehydrogenation of perhydro-N-ethylcarbazole

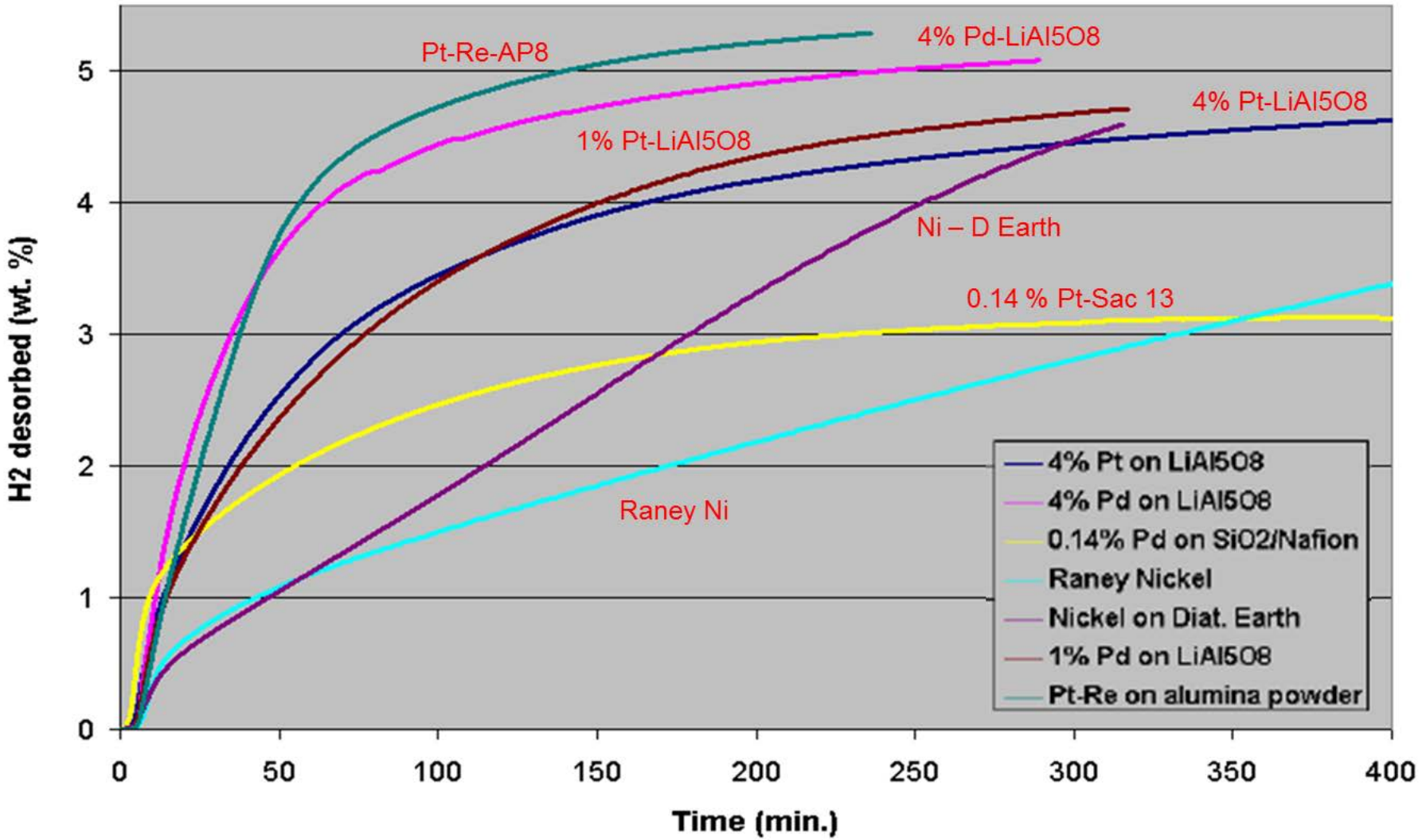
Air Products, Final Report, DOE Award # DE-FC36-04GO14006

Stability with cycling



Five sequential dehydrogenation steps of hydrogenation/dehydrogenation cycling experiments of N-ethylcarbazole. (*Air Products, Final Report, DOE Award # DE-FC36-04GO14006)*

Effect of catalyst on dehydrogenation performance



Overlay of perhydro-N-ethylcarbazole hydrogenationation data for a range of catalysts.
(*Air Products, Final Report, DOE Award # DE-FC36-04GO14006)*

Effect of catalyst, H_2 release rate and temperature on H_2 purity

Dehydrogenation of perhydro-N-ethylcarbazole with palladium/platinum on alumina. The table shows the temperature and hydrogen flow rate at the time when the samples were analyzed.

Pd on alumina

Temp (°C)	H_2 Flow (sccm)	Methane Conc. (ppm)	Ethane Conc. (ppm)
144	5.0	177	2
147	6.4	164	10
149	7.3	137	19
152	8.1	99	31
154	9.0	80	34
197	45.0		1
197	39.0		13
197	35.0		23
197	30.0		23
197	26.0		25
197	5.0		44
197	4.6		47
197	4.4		48
197	4.1		47
197	3.9		48

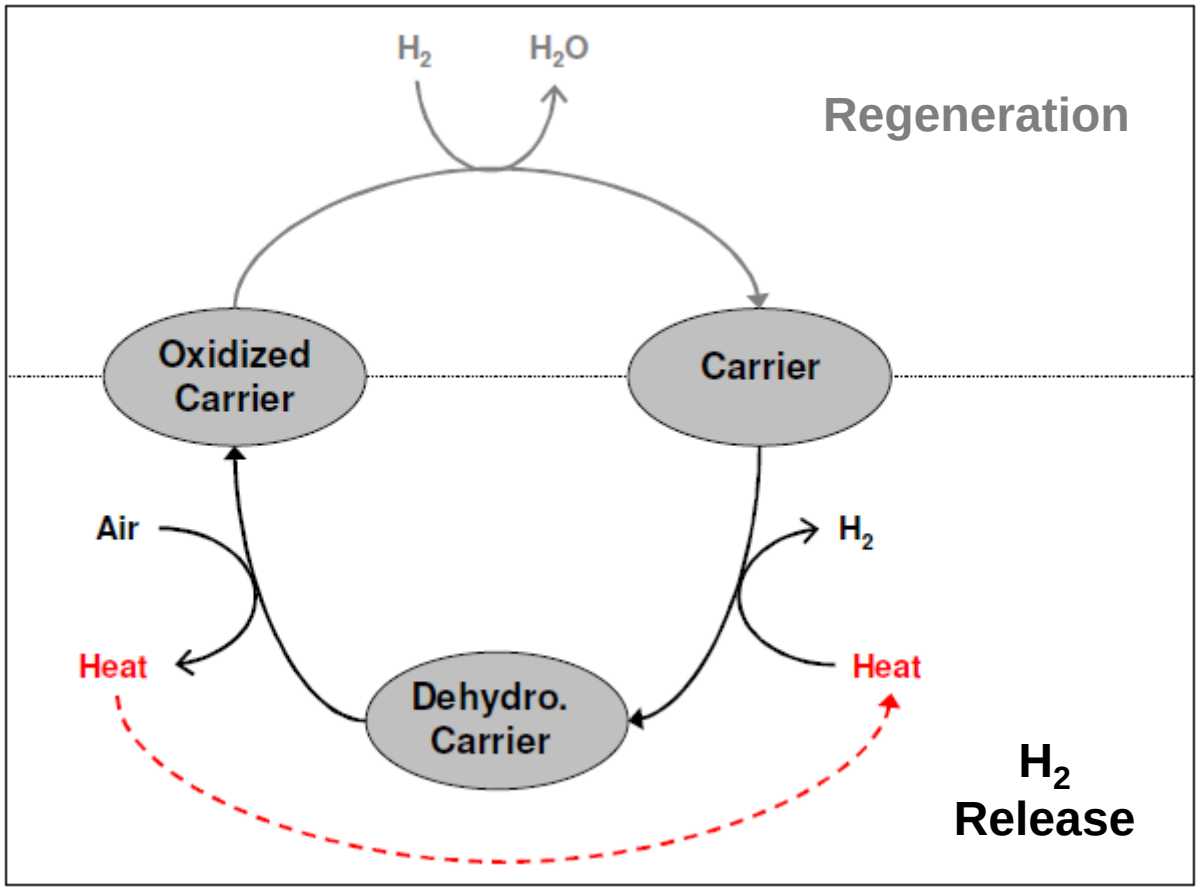
Pt on alumina

Temp (°C)	H_2 Flow (sccm)	Methane Conc. (ppm)	Ethane Conc. (ppm)
144	5	196	44
147	6.4	194	163
153	7.3	188	374
155	8.1	178	631
157	9	169	991
197	58		2723
197	45		2865
197	32.9		3327
197	22.8		4146
197	17.5		5093
197	5		7244
197	4.8		7350
197	5.5		7398
197	4.9		7355
197	4		7343

Air Products, Final Report, DOE Award # DE-FC36-04GO14006

How to supply the heat of enthalpy without consuming stored hydrogen?

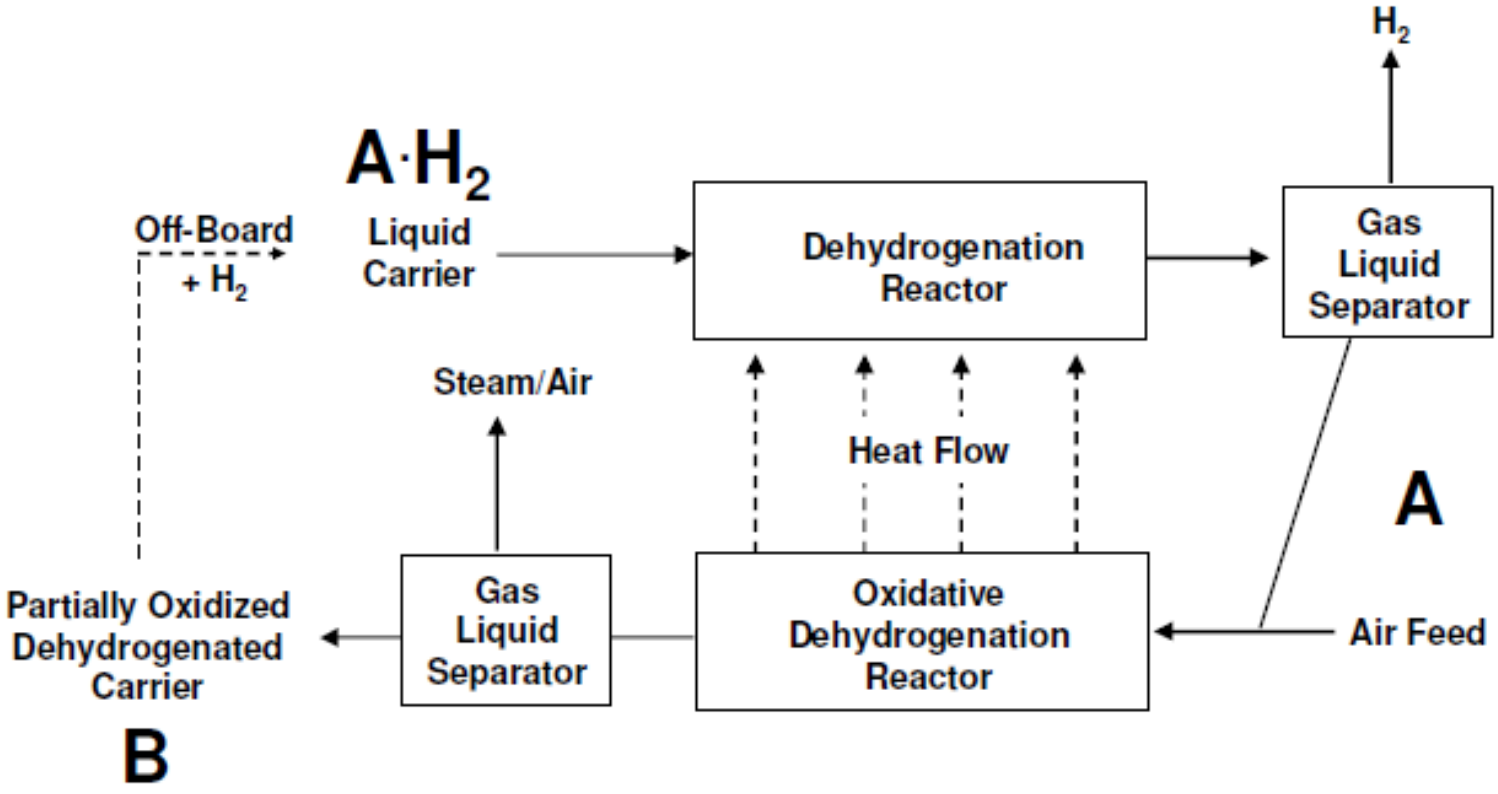
Potential solution – Development of an Autothermal concept



A general schematic of one autothermal carrier cycle

Air Products, Final Report, DOE Award # DE-FC36-04GO14006

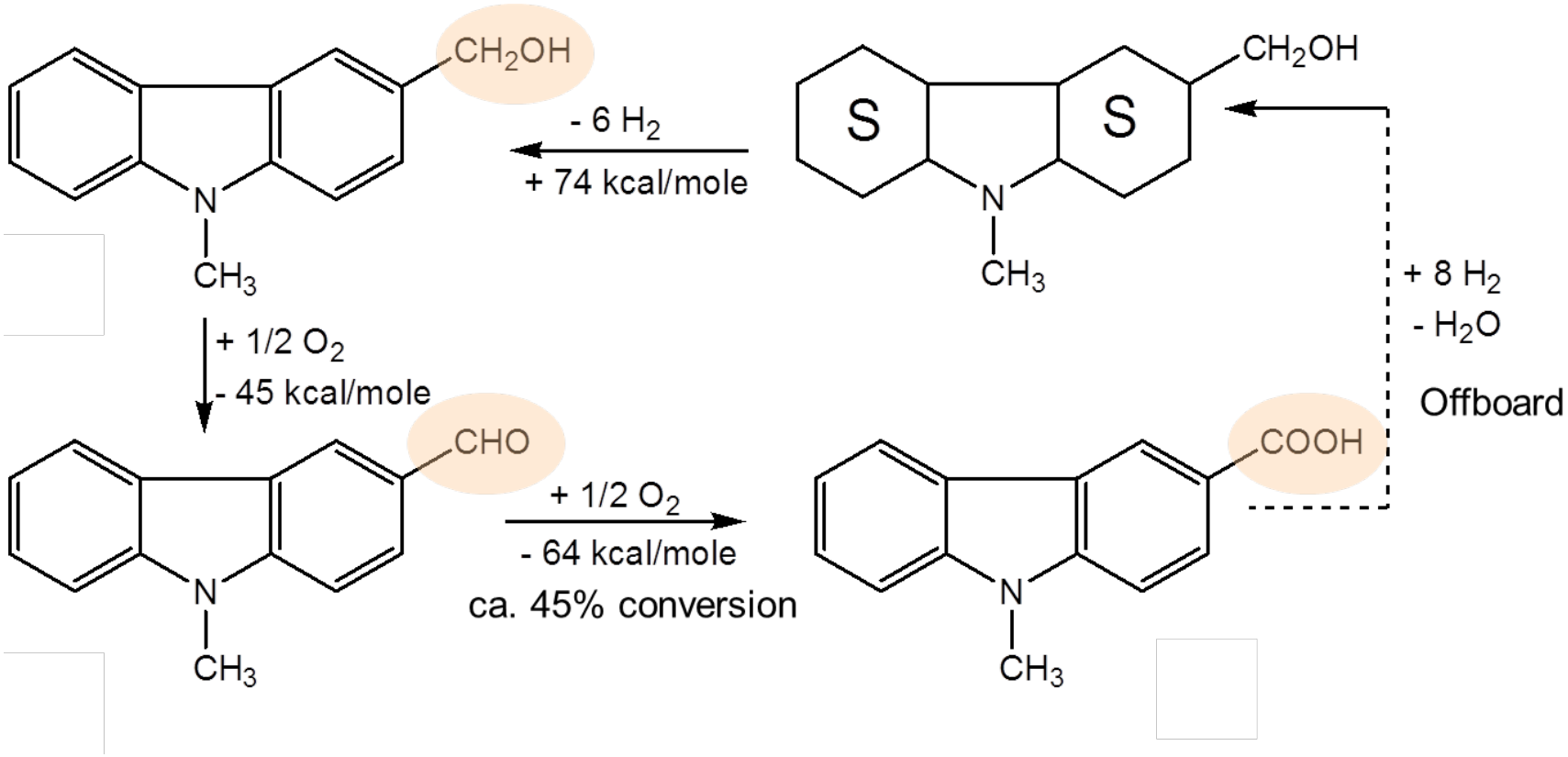
Autothermal concept



Autothermal dehydrogenation reactor system schematic.

Air Products, Final Report, DOE Award # DE-FC36-04GO14006

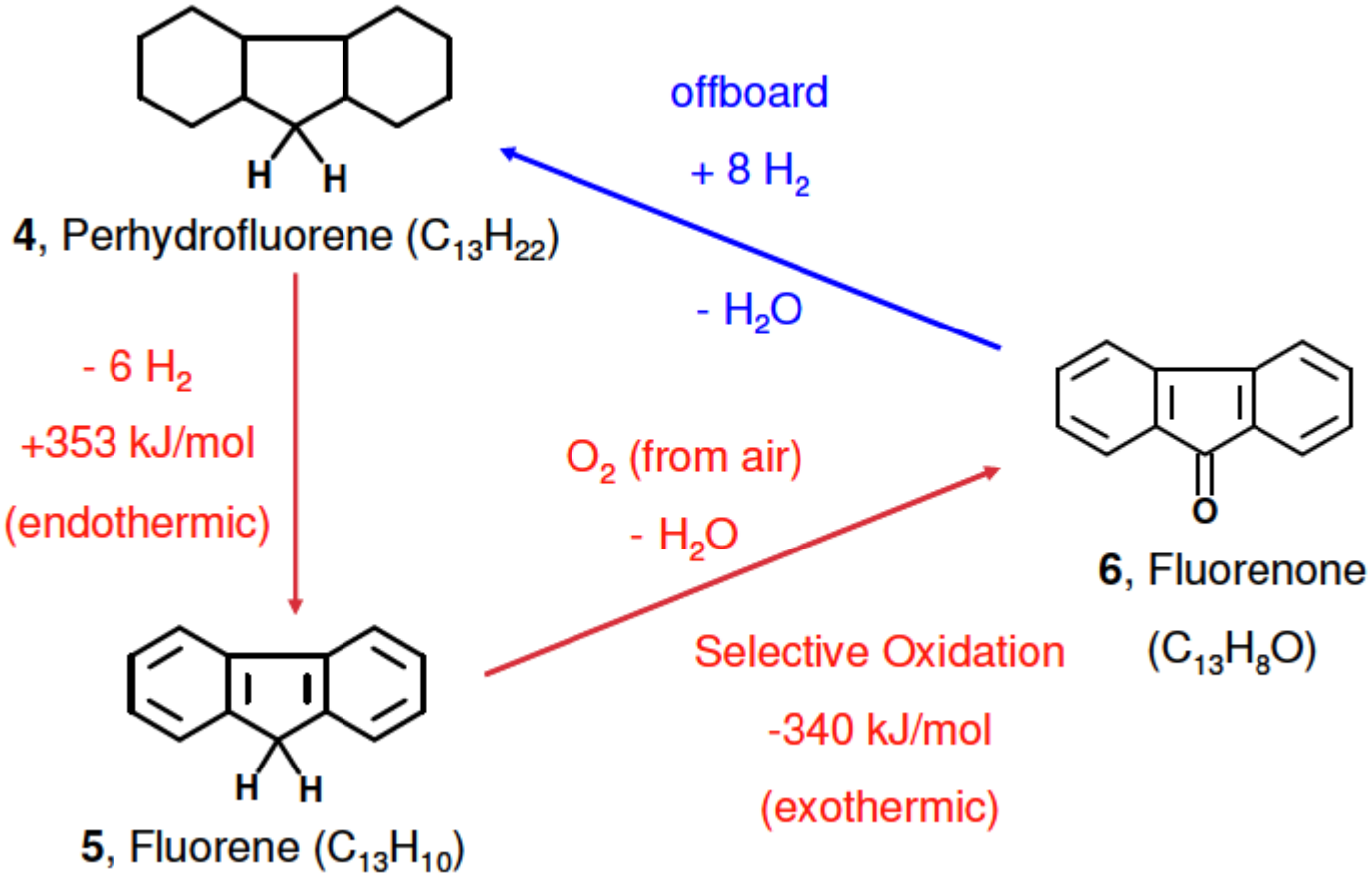
Autothermal concept



- 5.4 wt.% H_2 (material basis) with no external input of heat
- Only partial conversion to the fully oxidized product is necessary for autothermal operation
- Highly selective catalytic chemistry is known for all of these steps

Air Products presentation at the 2007 Hydrogen and Fuel Cells Technologies Annual Merit Review and Peer Evaluation Meeting, #ST-23, 17 May 2007

Autothermal concept



The perhydrofluorene/fluorene/fluorenone, dehydrogenation, selective oxidation and re-hydrogenation cycle.

Air Products, Final Report, DOE Award # DE-FC36-04GO14006

Dehydrogenation reactor considerations

For packed-bed reactor designs, two different reaction rate limitations were anticipated:

1) incomplete catalyst utilization caused by “drying out” of the catalyst surface, and
2) a reduction of the intrinsic reaction rate due to the effect of diffusion through the porous catalyst to the active metal sites, as measured by the effectiveness factor.

Alternative reactor designs investigated included:

1) Metal catalyst monoliths prepared from corrugated 0.05 mm iron/chromium foils coated with a tightly-adhering gamma alumina washcoat
2) Wicking microchannel reactor
3) Suspended slurry microchannel reactor – considered the most promising

Air Products, Final Report, DOE Award # DE-FC36-05GO15015

Air Products conclusions

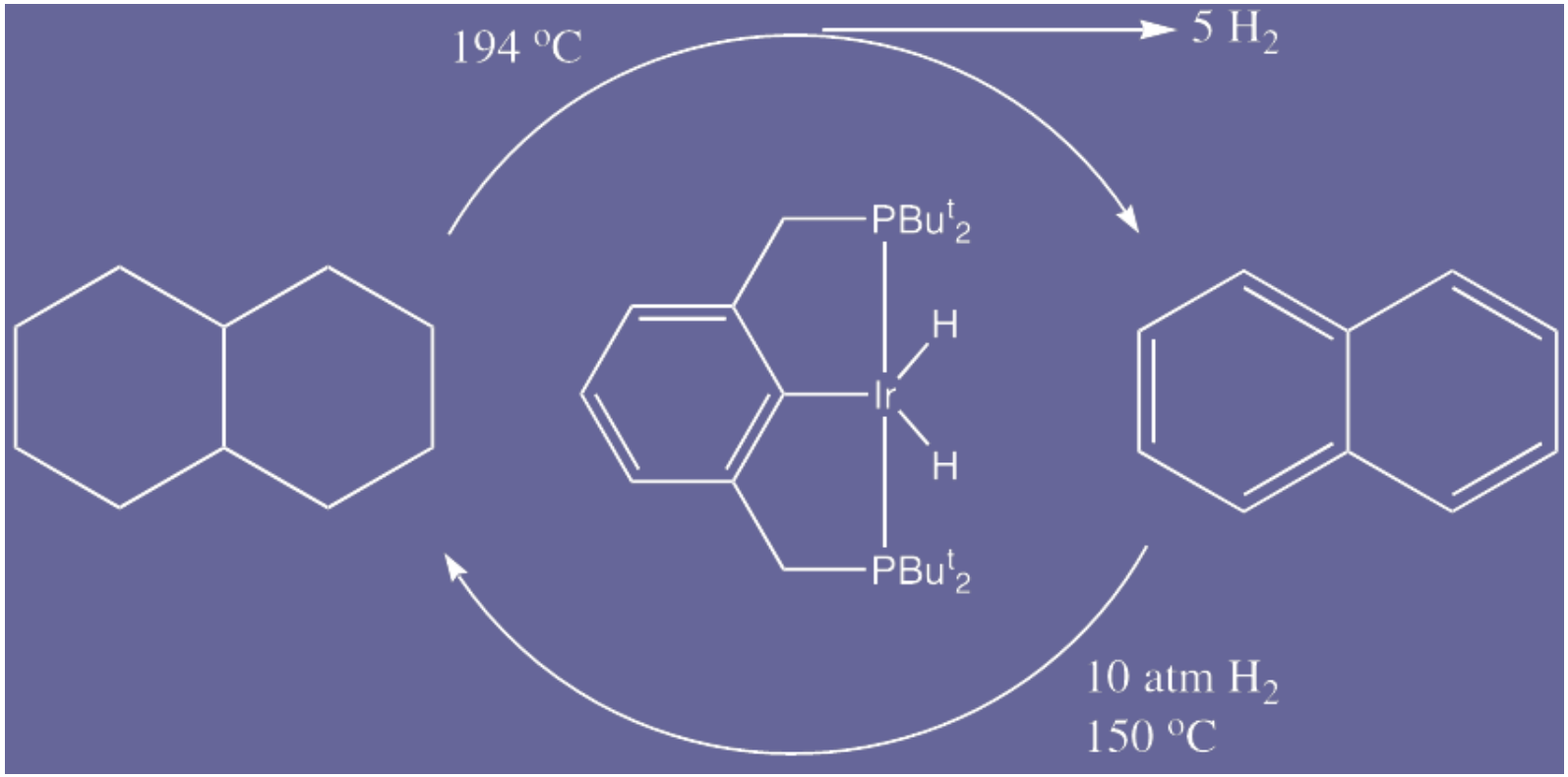
H_2 liquid carrier economics are considered to be favorable, ***in the range of $0.85 – $4.50/kg H_2 delivery cost***, provided that certain targets can be achieved. Specific recommendations include:

- reducing the liquid carrier cost to less than $10/gallon,
- lowering the carrier melting point,
- meeting a catalyst productivity target of >1,000,000 kg LOHC processed per kg of catalytic metal,
- and reducing the carrier loss rate to <2% per year.

Air Products, Final Report, DOE Award # DE-FC36-05GO15015

Homogeneous Catalyst Development

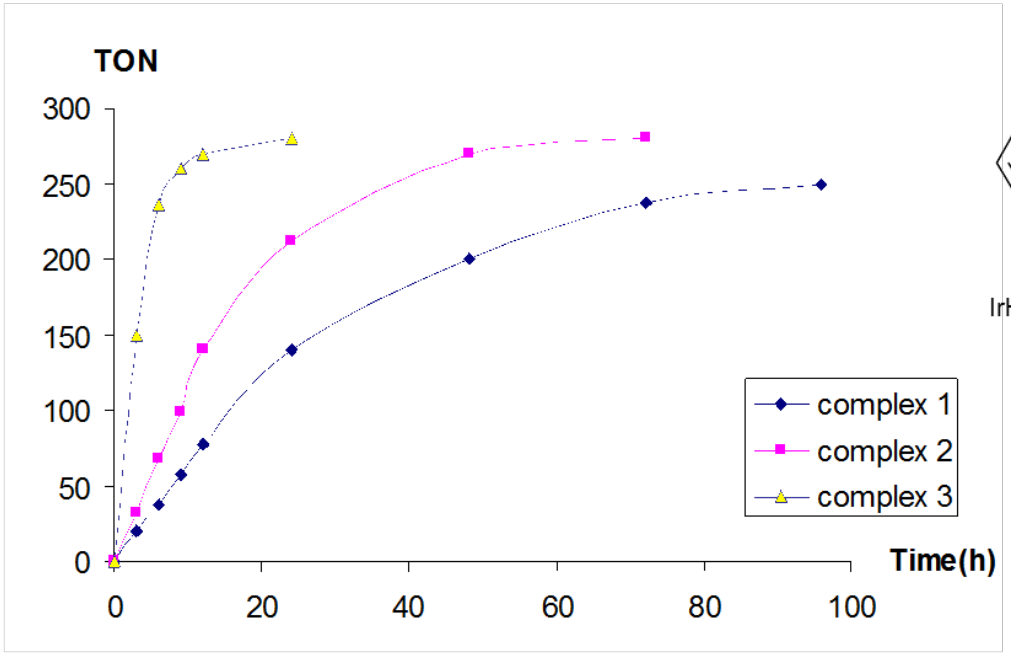
Use of Homogeneous catalysts

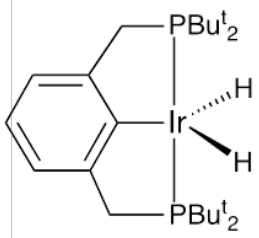


- First homogenous aliphatic dehydrogenation catalyst
- 3 orders of magnitude higher activity than heterogeneous catalyst temperatures as low 100 ˚C
- Two-way catalyst

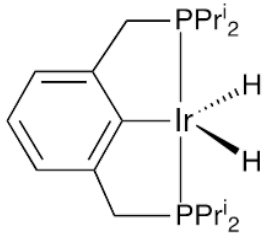
Hawaii Hydrogen Carriers presentation at the 2012 Hydrogen and Fuel Cells Technologies Annual Merit Review and Peer Evaluation Meeting, #ST-098, 17 May 2012

Homo- vs heterogeneous catalysts

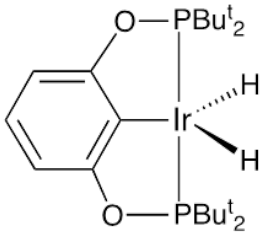




$IrH_2\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t_2)_2$ (1)



$IrH_2\{C_6H_3\text{-}2,6\text{-}(CH_2PPr^i_2)_2$ (2)

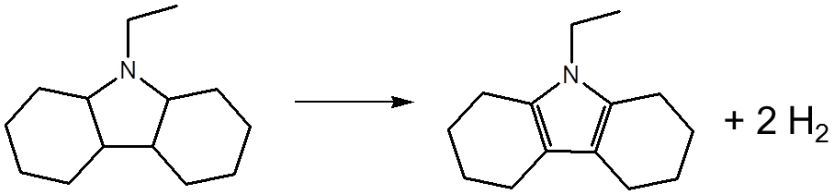


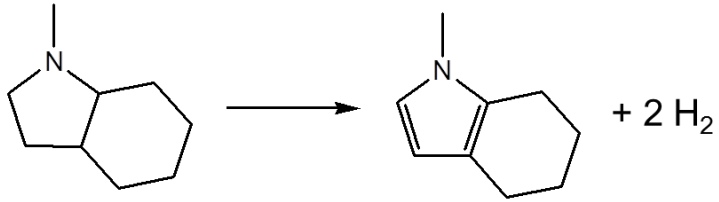
$IrH_2\{C_6H_3\text{-}2,6\text{-}(OPBu^t_2)_2$ (3)

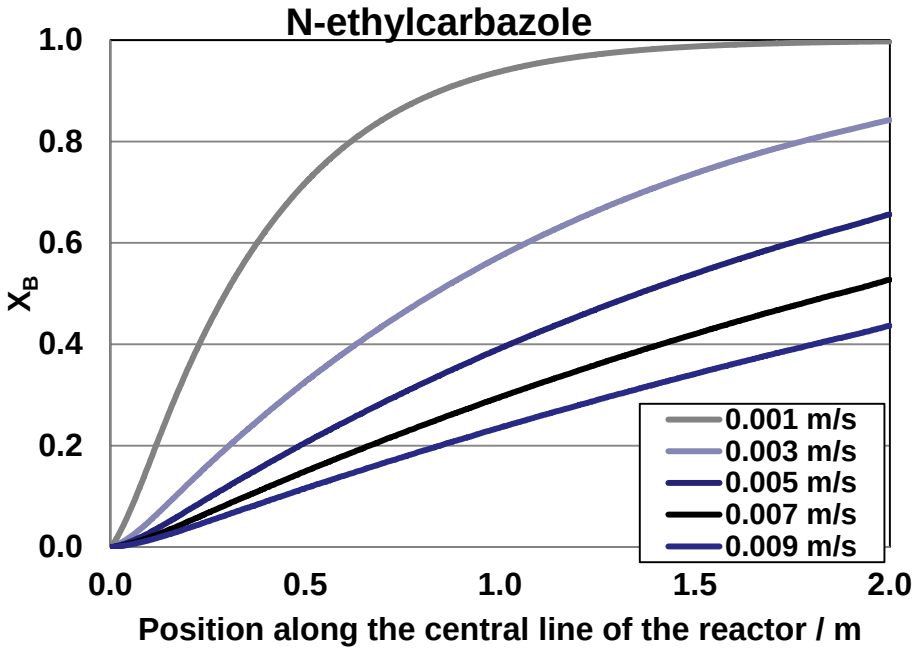
Dehydrogenation of N-ethylperhydrocarbazole using homogeneous Ir PCP pincer catalyst gives **higher rates of dehydrogenation at 2 orders of magnitude lower loadings than heterogeneous catalysts**

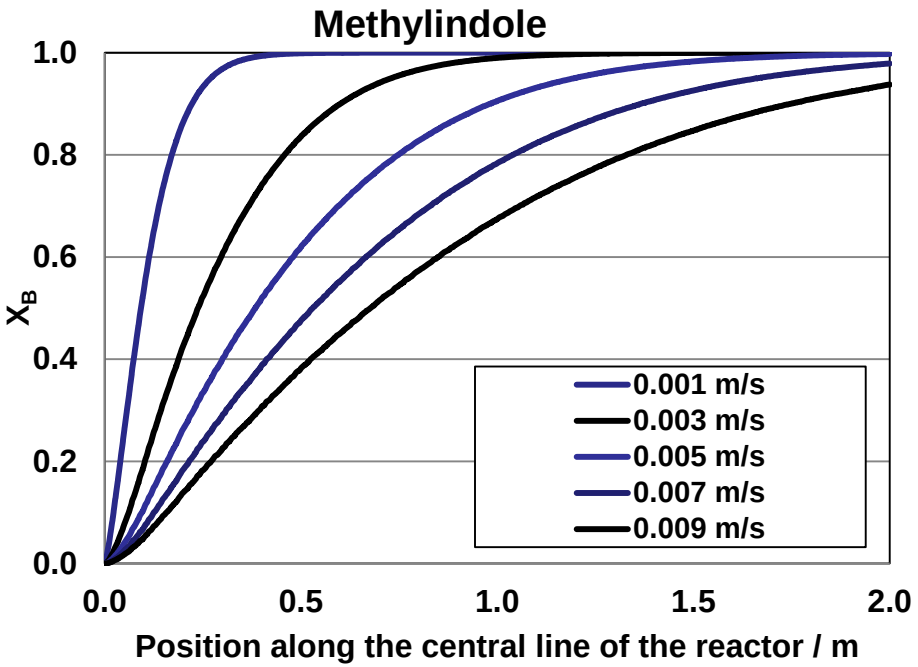
Hawaii Hydrogen Carriers presentation at the 2012 Hydrogen and Fuel Cells Technologies Annual Merit Review and Peer Evaluation Meeting, #ST-098, 17 May 2012

Alternative liquid carriers









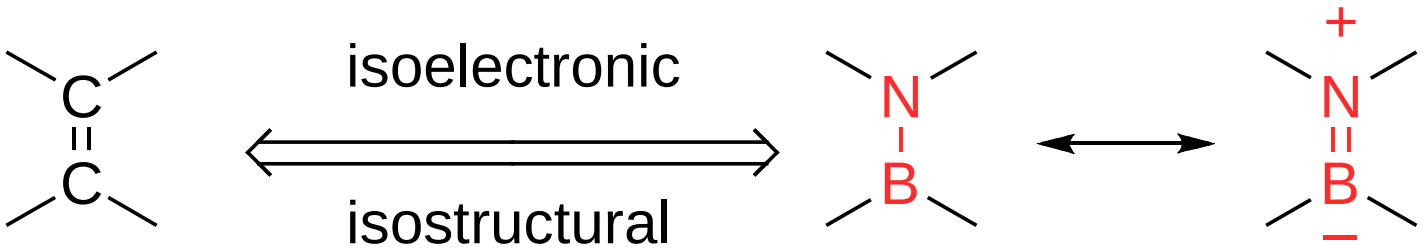
- Fixed reactor geometry and conditions
- Require near 100% conversion
- 5x improvement in H_2 production

MPHI gives higher throughput

Hawaii Hydrogen Carriers presentation at the 2012 Hydrogen and Fuel Cells Technologies Annual Merit Review and Peer Evaluation Meeting, #ST-098, 17 May 2012

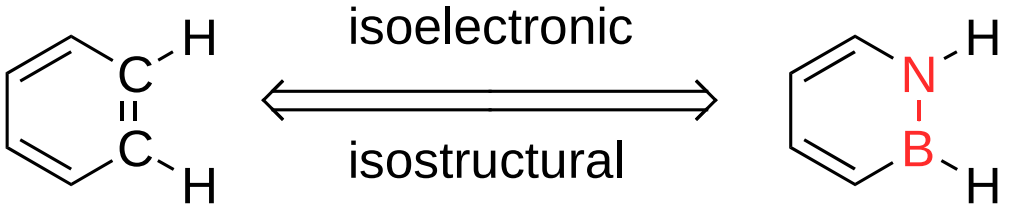
Liquid Hydrogen Carrier Development through B-N substituted heterocycles

B-N substituted heterocycles



benzene

1,2-dihydro-1,2-azaborine

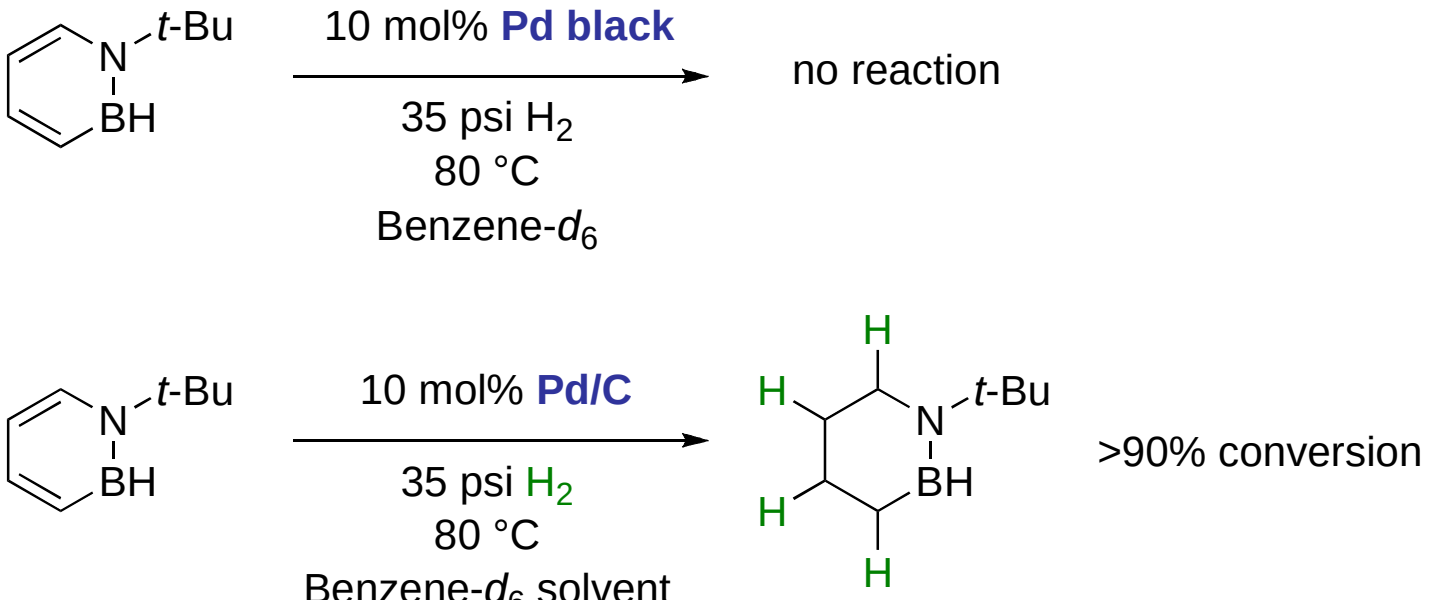


Research objectives:

- liquid-phase
- gravimetric density (> 6 wt. %)
- volumetric density (> 4.5 vol. %)
- favorable thermodynamics (H_2 absorption and desorption)
- efficient and easy regeneration (reversibility)
- Couple *exothermic* H_2 desorption from *BN* with *endothermic* H_2 desorption from *CC*

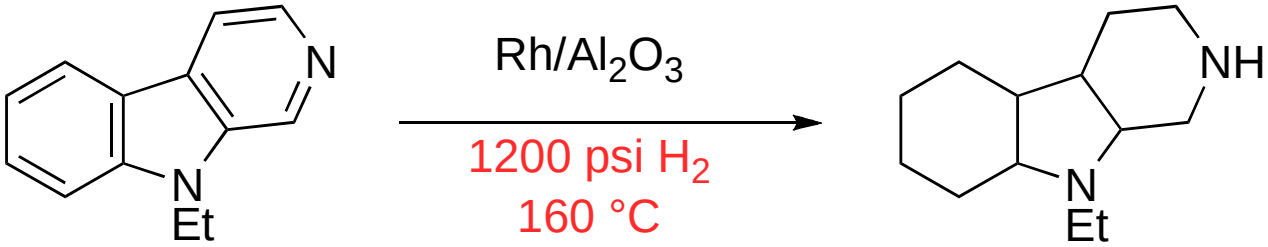
University of Oregon presentation at the 2009 Hydrogen and Fuel Cells Technologies Annual Merit Review and Peer Evaluation Meeting, #ST-016, 21 May 2009

Ease of hydrogenation for CBNs



Benzene-d_6 is not hydrogenated!

VS.

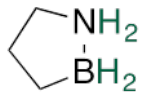


University of Oregon presentation at the 2009 Hydrogen and Fuel Cells Technologies Annual Merit Review and Peer Evaluation Meeting, #ST-016, 21 May 2009

Series of CBNs investigated

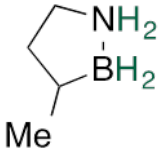
1) liquid phase

A



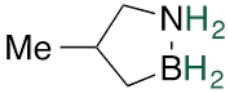
Mw = 71

B



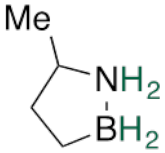
Mw = 85

C



Mw = 85

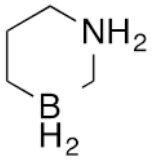
D



Mw = 85

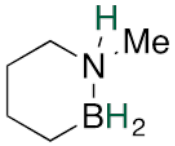
2) potentially reversible

E



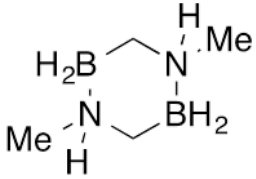
Mw = 85

F



Mw = 99

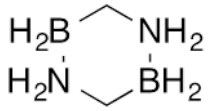
G



Mw = 114

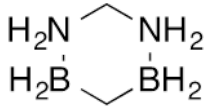
3) high capacity

H

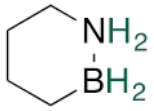


Mw = 86

I

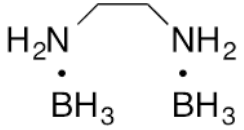


J



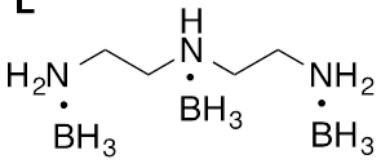
Mw = 85

K



Mw = 88

L



Mw = 145

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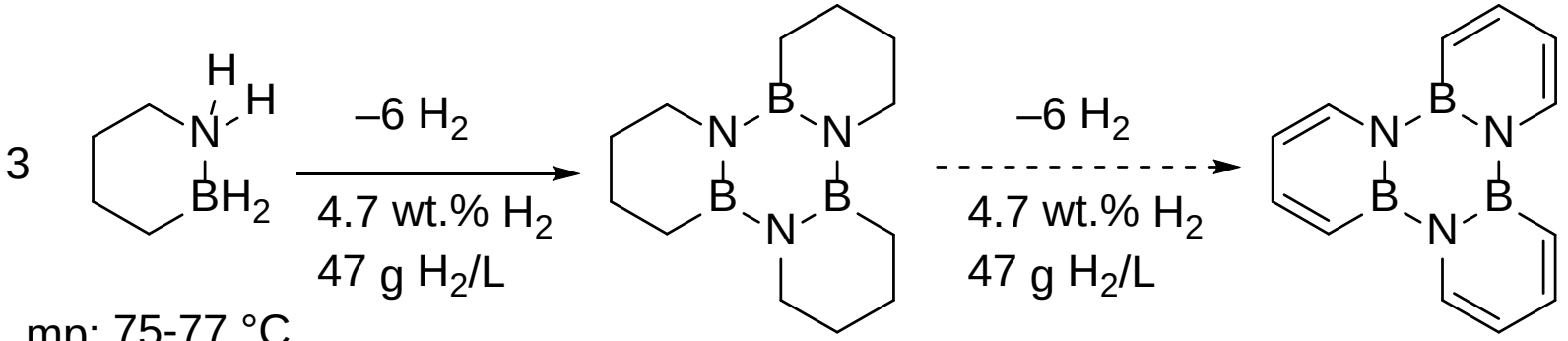
Potential high capacity materials



mp: 75-77 °C
d: 1.00 kg/L

Overall (–6 H_2)
ΔH(gas) = –83.1
Δ H(liquid) = –59.6
Δ G(gas) = –107.3

Per mol H_2:
Δ G(gas) = –17.8
Δ H(liquid) = –10.0
Δ G(THF) = –13.6

Overall (–6 H_2)
Δ H(gas) = +102.3
Δ H(liquid) = +102.8
Δ DG(gas) = +49.4

Energies in kcal/mol @ 298K

Gas Phase: G3MP2

Liquid Phase: G3MP2 (gas) + BP*0.025 (Trouton's rule)

overall potential:
9.4 wt.%; 94 g H_2/L, potential **liquid phase** starting material at operating T

Per mol H_2:
ΔG(gas) = –4.8
ΔH(liquid) = +4.0
ΔG(THF) = –3.6

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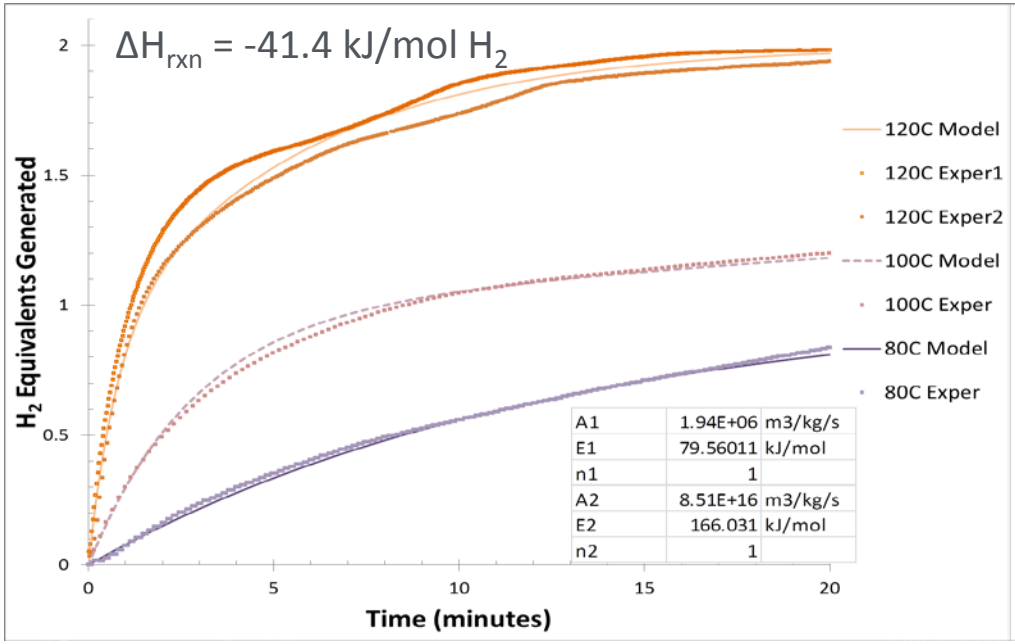
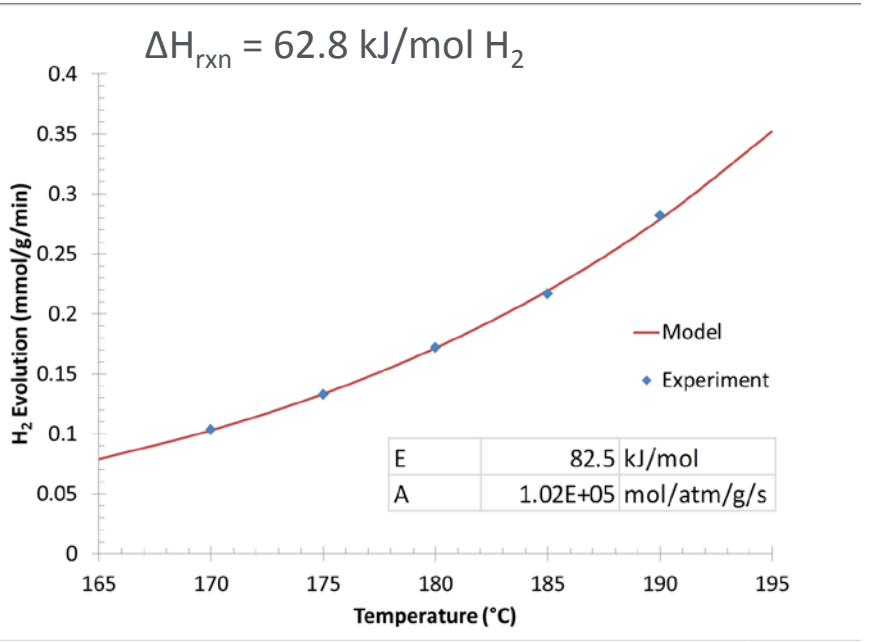
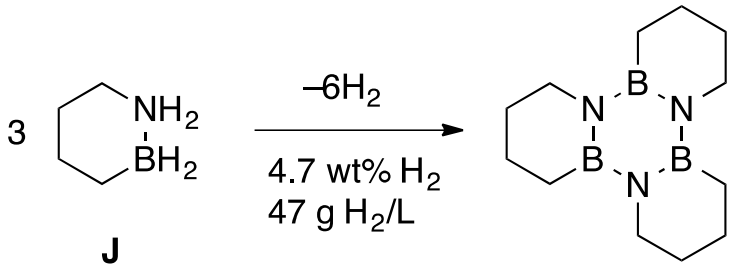
Exo/Endothermic reactions for CBNs

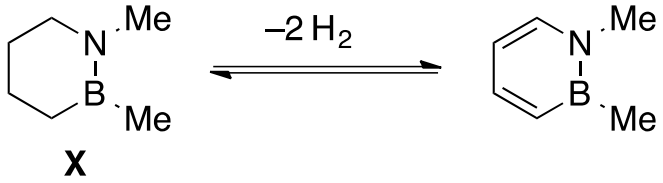
Exothermic Reaction



Endothermic Reaction







Thermodynamic Coupling Performed with Properties of Actual CBN Materials

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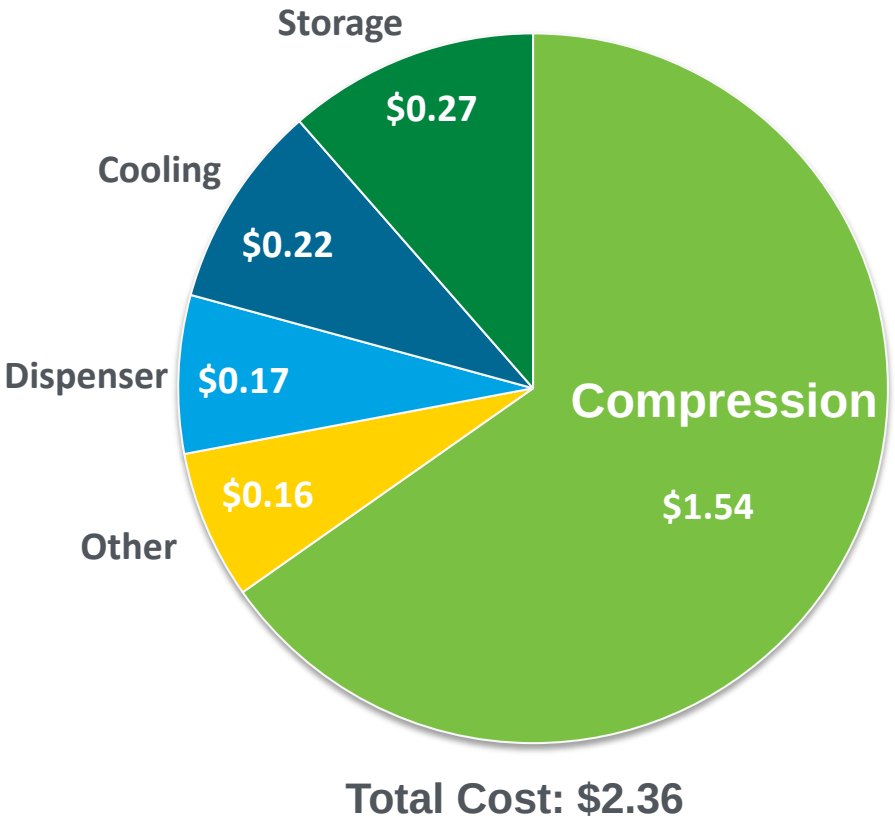
H_2 Infrastructure considerations

Can liquid hydrogen carriers address key cost and performance issues of the hydrogen infrastructure?

- Transport/delivery
  - Capital cost of delivery equipment
  - Payload for delivery
- Forecourt
  - Storage
  - Compression

Hydrogen Delivery Critical Costs

H_2 Compression, Storage and Dispensing (CSD) Cost Breakdown



*Based on the pipeline scenario

- 2020 goal for H_2 cost at the pump is **<$4/gge** *(production and delivery cost included)*
- **Compression** and **storage** are **75%** of the cost of H_2 station dispensing costs.

Compression is a key challenge for the cost of delivering and dispensing H_2

Reference information availability

- Air Products' reports available through the DOE Office of Science and Technology Information (*www.osti.gov)*
  - **Design and Development of New Carbon-based Sorbent Systems for an Effective Containment of Hydrogen -** DOE Award No. DE-FC36-04GO14006
  - **Reversible Liquid Carriers for an Integrated Production, Storage and Delivery of Hydrogen -** DOE Award Number DE-FC36-05GO15015

- FCTO Annual Progress Reports: http://energy.gov/eere/fuelcells/annual-progress-reports
- FCTO Annual Merit Review Proceedings: http://energy.gov/eere/fuelcells/annual-merit-review-proceedings

Thank you!