

Technical Assessment of Organic Liquid Carrier Hydrogen Storage Systems for Automotive Applications

R. K. Ahluwalia, T. Q. Hua, and J-K Peng
Argonne National Laboratory, Argonne, IL 60439

M. Kromer, S. Lasher, K. McKenney, K. Law, and J. Sinha
TIAX LLC, Lexington, MA 02421

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Executive Summary

In 2007-2009, the DOE Hydrogen Program conducted a technical assessment of organic liquid carrier based hydrogen storage systems for automotive applications, consistent with the Program's Multiyear Research, Development, and Demonstration Plan. This joint performance (ANL) and cost analysis (TIAX) report summarizes the results of this assessment. These results should be considered only in conjunction with the assumptions used in selecting, evaluating, and costing the systems discussed here and in the Appendices.

Organic liquid carriers (LC) refer to a class of materials that can be reversibly hydrogenated in large central plants using established industrial methods with high efficiency through recovery and utilization of the heat liberated in the exothermic hydrogenation reaction [1, 2]. The hydrogenated carrier (LCH₂) is delivered to the refueling station for dispensing to the vehicles. On demand, hydrogen is released from LCH₂ in a catalytic reactor on-board the vehicle and the liquid carrier (LC) is recycled to the central plant for rehydrogenation. The challenge has been to find suitable organic carriers that have sufficient hydrogen capacity, optimal heat of reaction (ΔH), rapid decomposition kinetics, low volatility and long cycle life, and that remain liquid over the working temperature range. Air Products and Chemicals Inc (APCI) investigated many candidates for potential liquid carriers but no one material could satisfy all the requirements for a viable hydrogen storage system.

We based our assessment of liquid organic carriers on N-ethylcarbazole (C₁₄H₁₃N), an early APCI candidate molecule, recognizing that a practical storage system cannot be built with this polycyclic aromatic hydrocarbon. The assessment, however, does show the potential of meeting the storage targets with other yet-undiscovered organic liquid carriers that may have the right properties. We analyzed an LCH₂ hydrogen storage system with a capacity of 5.6-kg usable H₂ for its potential to meet the DOE 2010, 2017, and ultimate hydrogen storage targets for fuel cell vehicles [3]. The analysis assumed Year 2009 technology status for the major components and projected their performance in a complete system. The analysis also projected the system cost at production volumes of 500,000 vehicles/year. The presentations by Argonne and TIAX describing their analyses in detail are given in Appendices A and B, respectively. Key findings are summarized below.

On-board Assessments

We developed a trickle-bed reactor model for on-board release of hydrogen from perhydro N-ethylcarbazole ($C_{14}H_{19}N$) and validated the model against APCI's test data. We also developed a model for the on-board hydrogen storage system and evaluated the potential performance of the system with respect to storage capacity and efficiency. Figure 1 shows a schematic of the fuel cell system with organic liquid carrier hydrogen storage. The system includes a circuit with an oil-based heat transfer fluid and a combustor to supply the ΔH for thermal decomposition of perhydro N-ethylcarbazole. It shows one method of integrating the storage system with the fuel cell system by controlling the hydrogen utilization in such a manner that the thermal energy needed for the dehydrogenation reaction is provided by burning the remaining hydrogen with the spent cathode air. Waste heat from the fuel cell stack (or an internal combustion engine power plant) cannot be used for this purpose because hydrogen desorbs rapidly from N-ethylcarbazole only at a temperature ($>200^{\circ}C$) higher than the temperature at which the waste heat is available.

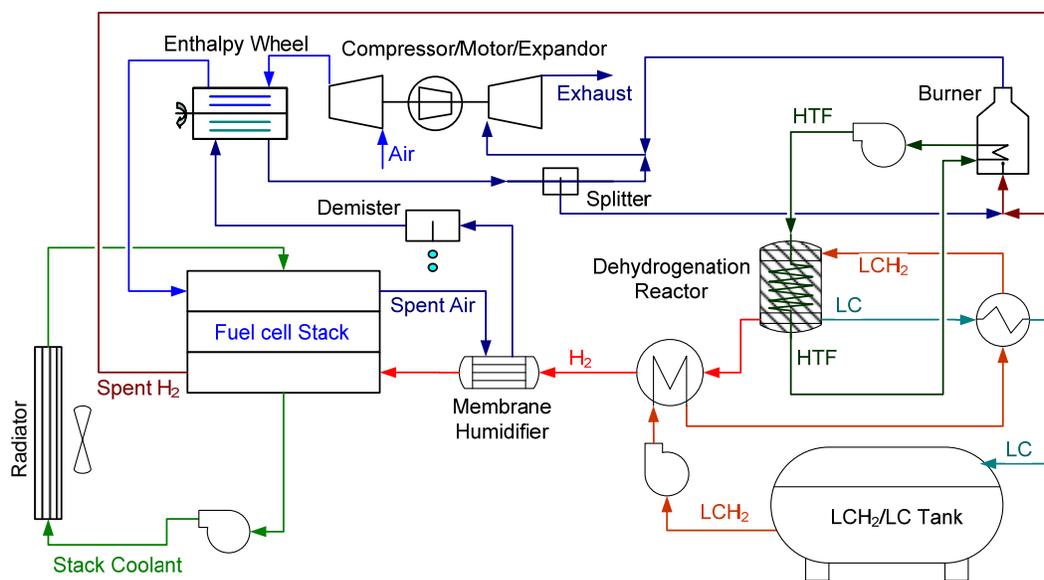


Figure 1 Automotive fuel cell system with organic liquid carrier hydrogen

Our analysis showed that a dehydrogenation reactor with a pelletized, palladium (Pd) on lithium aluminate catalyst produces unacceptably low conversions of the hydrogenated organic liquid carrier due to mass transfer resistances through the pore structure. To achieve conversions $>95\%$, a compact on-board dehydrogenation reactor will likely require dispersing the catalyst on a high surface area support and operating the reactor at a liquid hourly space velocity (LHSV) $>20\text{ h}^{-1}$. To power an 80-kW_e fuel cell system using perhydro N-ethylcarbazole ($\Delta H \approx 51\text{ kJ/mole H}_2$), the reactor needs to produce 2.4 g/s of H_2 , of which 1.6 g/s is electrochemically oxidized in the fuel cell system, and 0.8 g/s is burned to provide the thermal energy needed for the dehydrogenation reaction.

For N-ethylcarbazole (material capacity of 5.8- wt\% H_2), the system-level storage capacities are 4.4 wt\% and $35\text{ g-H}_2/\text{L}$ (on a stored H_2 basis), which translate to 2.8 wt\% and 23 g/L of usable

hydrogen (hydrogen converted to electricity in the fuel cell). These usable storage capacities fail to meet the 2010 targets of 4.5 wt% and 28 g/L.

Our system analysis is based on a volume-exchange tank with a flexible bladder to separate the fresh and spent fuels. Although this concept appears feasible, it has not been demonstrated in practice. We have assumed that an organic liquid carrier with a melting point lower than -40°C will be found so that the fuel and the carrier remain liquid at all ambient conditions. N-ethylcarbazole, however, melts between 66 and 70°C and would require that the tank be heated to prevent solidification. The downflow trickle-bed reactor configuration is likely inappropriate for use on-board vehicles. It would be desirable to build and analyze a compact horizontal flow reactor taking advantages of the recent developments in microchannel heat exchanger technology. Similarly, a more active, robust, non-precious metal catalyst is needed to achieve complete conversion at space velocities exceeding 120 h⁻¹.

The results from our “reverse engineering” analyses suggest that the on-board storage inefficiency can be largely eliminated if we had a liquid carrier with $\Delta H < 40$ kJ/mol and a catalyst that allows rapid dehydrogenation at temperatures below the temperature at which the waste heat is available from the fuel cell stack. The carrier would also need to have a material capacity >7.5-8 wt% H₂ for the storage system to satisfy the 2017 DOE targets of 5.5 wt% gravimetric and 40 g/L volumetric capacities. The intrinsic material capacity would need to be >11 wt% H₂ to meet the ultimate system target of 7.5 wt%.

Table 1 Summary results of the assessment for organic liquid carrier based hydrogen storage systems compared to DOE targets

Performance and Cost Metric	Units	LCH ₂	DOE Targets		
			2010	2017	Ultimate
System Gravimetric Capacity	wt%	2.8	4.5	5.5	7.5
System Volumetric Capacity	g-H ₂ /L	23.0	28	40	70
Storage System Cost	\$/kWh	15.7	TBD	TBD	TBD
Fuel Cost	\$/gge*	3.27	3-7	2-6	2-4
WTE Efficiency (LHV**)	%	43.3	60	60	60

*gge: gallon gasoline equivalent

**Lower heating value

The results of the cost assessment showed that the LCH₂ on-board storage system will cost \$15.7/kWh. The main contributor to the onboard system cost was the dehydrogenation reactor, which accounted for nearly 40% of the total system cost. In turn, the dehydrogenation reactor cost was primarily driven by the cost of the palladium catalyst. Other high cost components include pumps, the burner, and the LCH₂ medium itself. The results from multi-variable

sensitivity analysis indicated a likely range of \$14 to \$21.5/kWh. Detailed cost results are presented in the Appendix B. The system capacities and cost results are compared to the DOE targets in Table 1.

Off-board Assessments

We constructed a flowsheet for rehydrogenation of N-ethylcarbazole in multi-stage, catalytic, trickle-bed reactors, with regenerative intercooling between the stages to achieve a declining temperature profile. Hydrogen is introduced at multiple quench locations within each stage of a reactor to maintain a nearly isothermal temperature profile. In this manner, H₂ far in excess of the stoichiometric amount (15-21 times, depending on the number of stages) is used to absorb the heat of reaction. The excess H₂ is recovered downstream of the final stage, recompressed, mixed with compressed makeup H₂, and recycled. We considered two scenarios, one in which the heat of reaction is discarded as low-grade waste heat and the second in which an organic Rankine cycle system is used to produce electricity from the waste heat (~1 kWh/kg-H₂ in the liquid carrier).

We estimated that the LCH₂ option has one of the highest well-to-tank (WTT) efficiencies of all hydrogen storage options since regeneration of perhydro N-ethylcarbazole is an exothermic process. The WTT efficiency can be higher than 60% if the waste heat liberated in rehydrogenation can be used to co-produce electricity via the organic Rankine cycle. Our analysis showed that the well-to-engine (WTE) efficiency is 43.3% taking into account the ~68% efficiency of the on-board storage system (i.e., 32% of H₂ produced is burned on-board to provide the dehydrogenation heat of reaction).

The off-board refueling cost of the LCH₂ system was projected to be \$3.27, meeting the 2010 and 2017 targets, as well as the ultimate target of \$2-4/kg. In contrast to the on-board system, sensitivity analysis suggested that there are several viable pathways to reducing the off-board refueling cost. These cost reduction opportunities include reducing the cost of the carrier material, reducing hydrogen production costs, or reducing the size of the liquid carrier storage buffer at the regeneration facilities.

Using a series of simplified economic assumptions, the off-board cost estimated was combined with the on-board system base case cost projection of \$15.7/kWh H₂ to calculate the fuel system ownership cost on a per-mile basis. The results projected an ownership cost of \$0.12/mile for the LCH₂ system. Slightly more than half of this cost was due to the amortized purchased cost of the on-board storage system; the remainder was due to the off-board refueling cost. This projected ownership cost for the LCH₂ system may be compared with about \$0.10/mile for the fuel costs of a conventional gasoline internal combustion engine vehicle (ICEV) when gasoline is at \$3.00/gal, untaxed.

References

1. Cooper, A. and Pez, G., "Hydrogen Storage by Reversible Hydrogenation of Liquid-Phase Hydrogen Carriers," APCI, 2007 DOE H₂ Program Review, May 2007.

2. Toseland, B. and Pez, G., "Reversible Liquid Carriers for an Integrated Production, Storage and Delivery of Hydrogen," APCI, 2008 DOE H₂ Program Review, June 2008.
3. "Targets for onboard hydrogen storage systems for light-duty vehicles," US Department of Energy, Office of Energy Efficiency and Renewable Energy and The FreedomCAR and Fuel Partnership, Revision 4.0, p. 9, Sep. 2009.

APPENDIX A

Performance Assessment of Organic Liquid Carrier Hydrogen Storage Systems



... for a brighter future



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On-Board Hydrogen Storage Systems for Liquid Carriers

R.K. Ahluwalia, T. Q. Hua and J-K Peng

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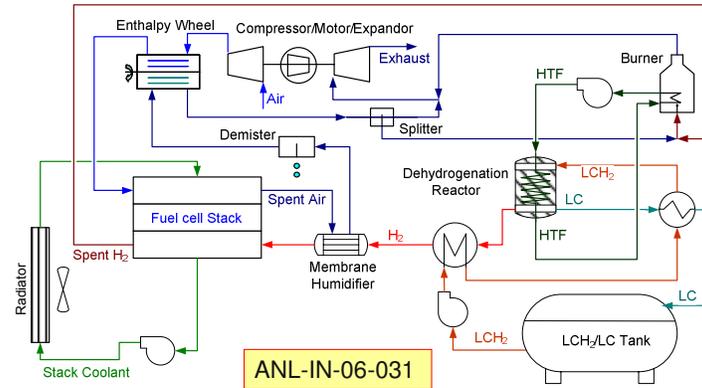
On-Board Hydrogen Storage Systems for Liquid Carriers

Objective: To determine the performance of the on-board system relative to the storage targets (capacity, efficiency, etc)

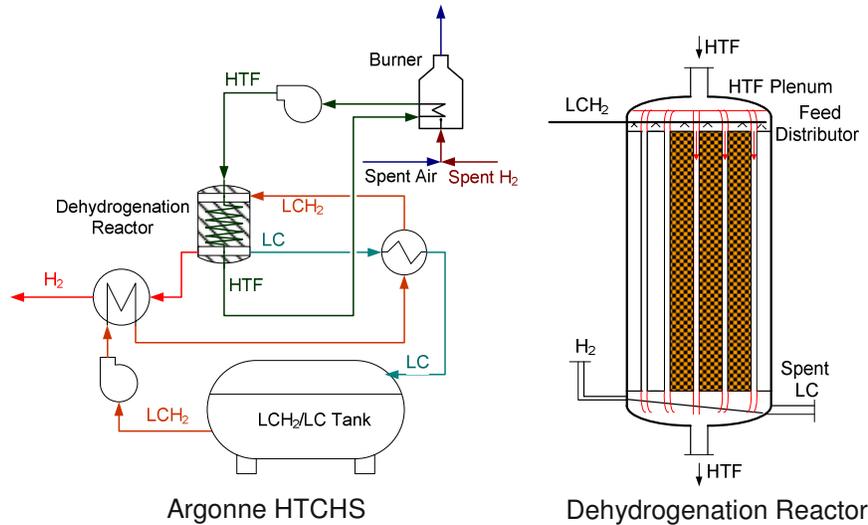
1. On-Board System Configuration
2. Dehydrogenation Reactor
 - Dehydrogenation kinetics
 - Trickle bed hydrodynamics
 - Dehydrogenation reactor model
 - Reactor performance with pelletized and supported catalysts
3. System Performance
 - Storage efficiency
 - Storage capacity

Fuel Cell System with H₂ Stored in a Liquid Carrier: Argonne FCS-HTCH

- Once-through anode gas system with controlled H₂ utilization
- Burner uses depleted air split-off from spent cathode stream
- Burner exhaust expanded in gas turbine to recover additional power

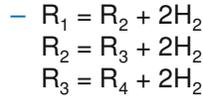


Argonne HTCHS: High-Temperature Chemical Hydrogen Storage System



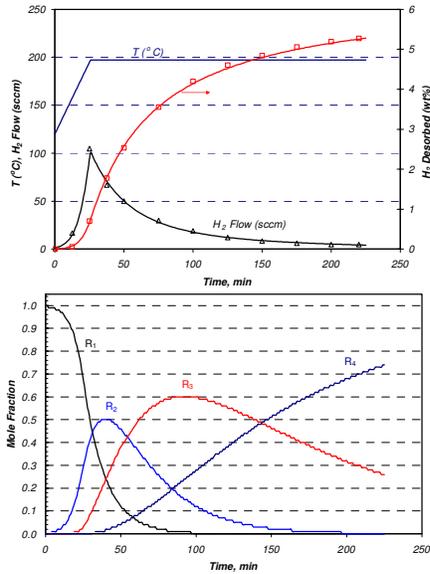
Dehydrogenation Kinetics (Batch Reactor)

Sequential reaction kinetics



Kinetic constants from batch reactor data

- APCI Patent
US 2005/0002857
- 8 g N-ethylcarbazole, 20-cc reactor volume
- Powder catalyst: 0.2-g 4% Pd on Li aluminate
- Heating from 50°C to 197°C at 3°C/min
- P = 1 atm
- 96% conversion: 5.6 wt% H₂



Trickle Bed Reactor Hydrodynamics Neural Network Model

Parameter	Re _l	Re _g	Fr _l	Fr _g	We _l	X _l	X _g	St _l	St _g	Sc _l	Sc _g	Ga	Ca _l	Ca _g	Bi	Pe _l	Pe _g	ρ _{g,l}	α	d _{p,r}	Φ	ε	
Slip factors: f _s , f _v	√	√	√	√	√	√	√																
Ergun constants: E ₁ , E ₂																					√	√	√
Liquid-catalyst mass transfer coefficient	√	√						√		√		√									√		
Volumetric liquid-side mass transfer coefficient		√			√			√	√	√			√	√							√	√	
Volumetric gas-side mass transfer coefficient	√	√		√				√			√											√	
Liquid-wall heat transfer coefficient	√			√	√			√									√	√			√		
Bed radial thermal conductivity	√			√	√											√	√	√					
Wetting efficiency	√	√	√		√	√	√	√					√						√	√	√	√	√
Pressure drop	√	√			√	√							√								√	√	√
Liquid holdup	√	√			√	√															√		

Re Reynolds number

Fr Froude number

We Weber number

X Lockhart-Martinelli number

St Stokes number

Sc Schmidt number

References: Ind. Eng. Chem. Res., 37 (1998), 4542-4550

Ind. Eng. Chem. Res. 42 (2003) 222-242

Chem. Eng. Sci., 54 (1999) 5229-5337

Ga Galileo number

Ca Capillary number

Pe Peclet number

Bi Biot number

ρ Density

α Bed correction factor

d_p Catalyst diameter

d_r Reactor diameter

Φ Sphericity factor

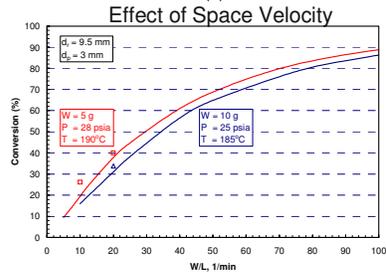
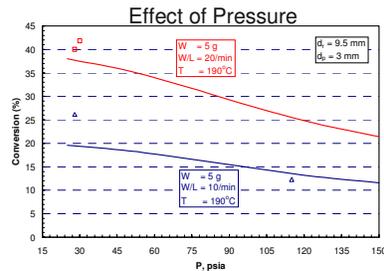
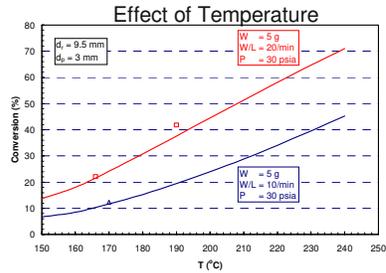
ε Void fraction

Subscripts:

l Liquid g Gas

Tubular Trickle Bed Reactor Comparison with APCI Data

- Models written on GCtool platform
 - First-order kinetics with internal & external mass transfer
 - Trickle bed hydrodynamics
 - ODEs for T and species flow
- TBR data for 5% Pd on alumina catalyst, kinetic data for 4% Pd on Li aluminate



Conversion with Pelletized Catalysts

- Reactor Parameters
 - Pellet diameter = 3 mm
 - Bulk density = 800 kg/m³
 - HX tube diameter = 3/8"
 - AL 2219-T81 construction
- Analysis Method

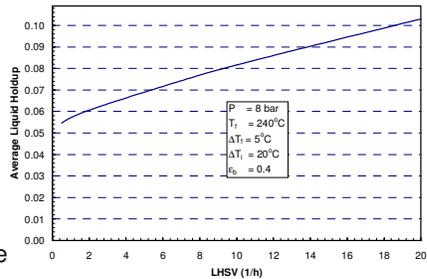
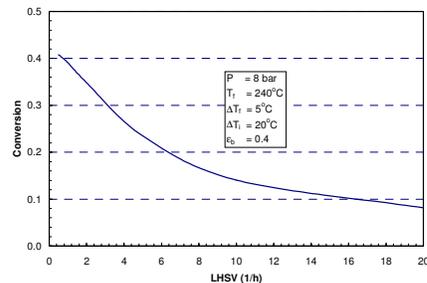
Variable	Constraint
LCH ₂ flow rate	1.6 g/s ^a H ₂ to FCS ^b
HTF flow rate	$\Delta T_f = 5^\circ\text{C}$
No. of tubes	$Q = (Q_s + 61) \text{ kW}^c$

^a2.4 g/s total H₂ for N-ethylcarbazole

^b80-kWe FCS

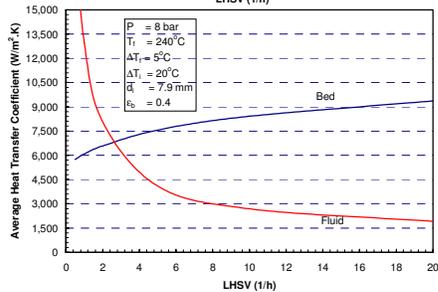
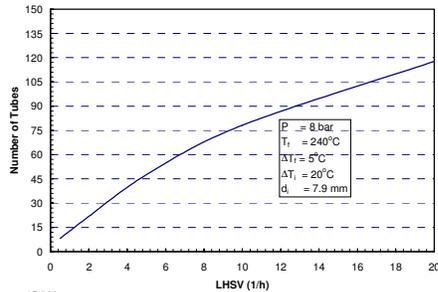
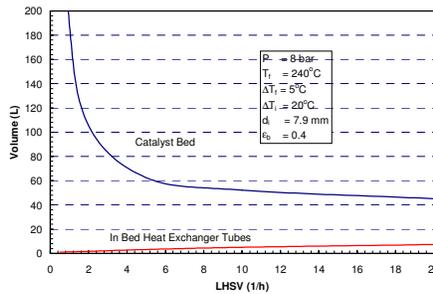
^c $\Delta H = 51 \text{ kJ/mol}$ for N-ethylcarbazol

LHSV=volumetric flow rate/reactor volume



Heat Transfer

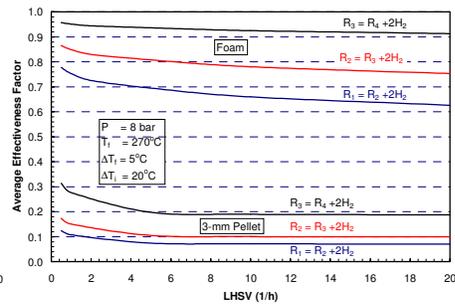
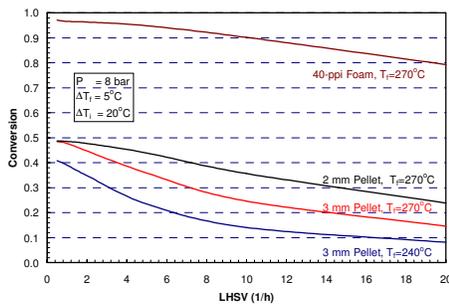
- Reactor size is not heat transfer limited
 - High h because of tube-side liquid flow and shell-side two-phase trickle flow
 - Can be a concern if the catalyst is very active



Conversion with Dispersed Catalyst

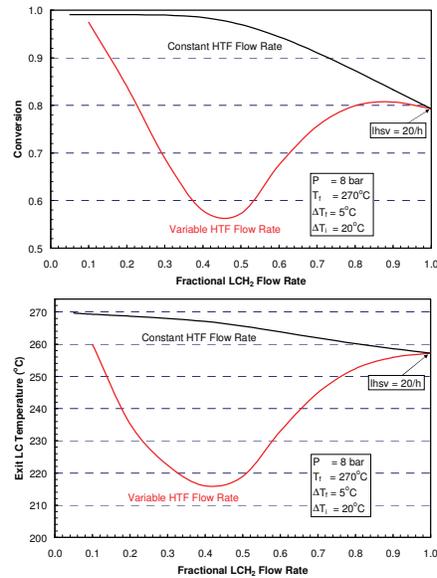
- Low conversion with pellets because of mass transfer limitations
 - Effectiveness factors for the three reactions: 0.08 - 0.3
- Marked improvement in catalyst effectiveness if supported on foam although the wetting efficiency decreases
 - 40-ppi Al-6101 foam, 92% porosity
 - 50- μm catalyst washcoat, 224 kg/m^3 bulk density
 - Trickle flow on foam has not been demonstrated

ANL-IN-07-019



Part-Load Performance

- Higher conversion with constant HTF flow rate especially at low loads
- Transient performance
 - Actual conversion on a drive cycle may be higher or lower than the steady-state value
 - Response time
 - Pressure control?
 - Buffer storage?



Argonne HTCHS: System Analysis

Dehydrogenation Reactor

- T_R function of P(H₂), conversion, ΔH, ΔS, and ΔT_{eq}
- Trickle flow, 20 h⁻¹ LHSV
- Catalyst supported on 40-PPI foam
- HX tubes with 90° inserts
- AL-2219-T81 alloy, 2.25 SF
- 2 cm insulation thickness

Heat Transfer Fluid

- XCEL THERM ®
- 5°C ΔT in DeH₂-HX, T_{HTF} - T_R = 50°C

HEX Burner

- Non-catalytic, spent H₂ and 5% excess spent air
- Counterflow microchannel, inconel
- 100°C approach temperature

H₂ Cooler

- LCH₂ coolant, T_{outlet} = T_{FC}
- Counterflow, microchannel, SS

Recuperator

- LC/LCH₂ HX, T_{LCH₂} = T_R - 10°C
- Counterflow, microchannel, SS

LC Radiator

- T_{LC} = 70°C
- Integrated with FCS radiator
- W and V not included in HTCHS

LCH₂/LC Storage Tank

- Single tank design, HPDE construction
- 10-kg H₂ storage, 10% excess volume

Pumps

- HTF pressure head: 1 bar
- LCH₂ pressure head: 8 bar

H₂ Separation

- Coagulating filter

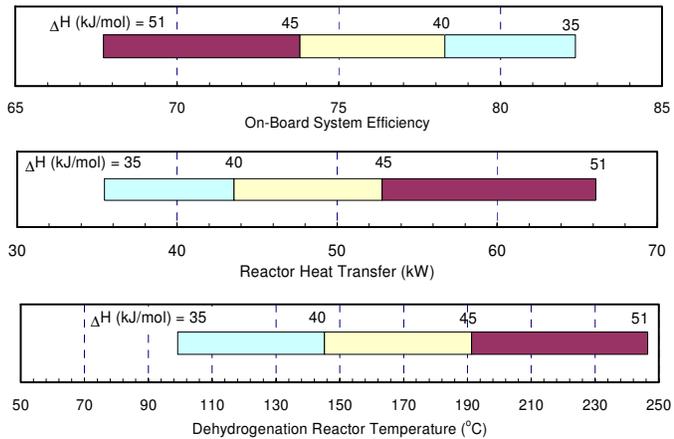
H₂ Buffer Storage

- 20 g H₂ at 80°C, P(H₂)
- AL-2219-T81 alloy tank, 2.25 SF

Miscellaneous

On-Board Storage System Efficiency

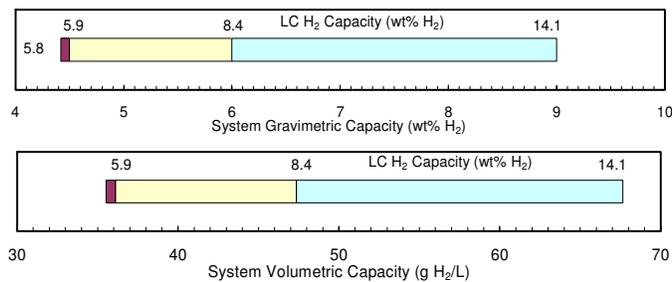
- Storage system efficiency defined as fraction of H₂ liberated in dehydrogenation reactor that is available for use in fuel cell stack
- Efficiency could be ~100% if $\Delta H < 40$ kJ/mol and $T_R < T_{FC}$



- LC: 0.95-1.2 g/cc, 5.8 wt% H₂
- 95% conversion
- DeH₂ LHSV: 20 h⁻¹
- ΔT_{eq} : 50°C
- Burner HX: 100°C approach T
- 2 g/s net H₂ output
- P(H₂): 8 bar
- 0.8-1.4 kWe HTF pump
- Start-up energy not included

Reverse Engineering: H₂ Storage Capacity

- System capacity presented in terms of stored H₂
 - Recoverable H₂: 95% intrinsic material capacity (conversion)
 - Usable H₂ = Storage system efficiency x Recoverable H₂
- System capacity with N-ethylcarbazole: 4.4% wt% H₂, 35 g/L H₂ (H₂ stored basis); 2.8% wt% H₂, 23 g/L H₂ including losses
 - 95% conversion, 67.7% storage system efficiency

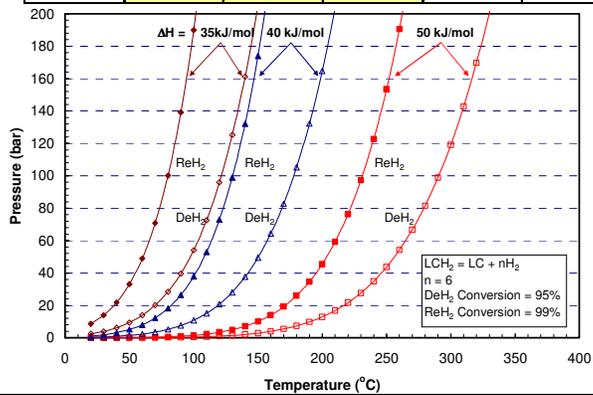


- LC: 0.95-1.2 g/cc
- LC tank: 10% excess volume
- ΔH_2 LHSV: 20 h⁻¹
- ΔT_{eq} : 50°C
- Burner HX: 100°C approach
- 2 g/s net H₂
- 20-g H₂ buffer
- P(H₂): 8 bar

Need Catalysts Active at Low T and $35 < \Delta H < 40$ kJ/mol

Minimum DeH₂ and Maximum ReH₂ Temperatures

ΔH	DeH ₂ Pressure			ReH ₂ Pressure	
	3 bar	4 bar	8 bar	100 bar	200 bar
50 kJ/mol	151°C	160°C	183°C	231°C	262°C
40 kJ/mol	66°C	73°C	92°C	130°C	155°C
35 kJ/mol	24°C	30°C	46°C	80°C	102°C



Summary

- Dehydrogenation reactor will need a supported catalyst
 - Desirable to have LHSV > 20 h⁻¹ for >95% conversion
 - May need $\Delta T > 50^\circ\text{C}$ for compact HX ($\Delta T = T_{\text{HTF}} - T_{\text{R}}$)
- Need $\Delta H < 40$ kJ/mol for >90% on-board storage efficiency
- Material capacities to meet system storage targets

Material Capacity	System Capacity ^a	
	Gravimetric	Volumetric
wt% H ₂	wt% H ₂	g-H ₂ /L
5.8	4.4	35.1
5.9	4.5	36.1
8.4	6.0	47.4
14.1	9.0	67.6 ^b

^aStored H₂ basis

^bH₂ buffer has to decrease for 81 g/L volumetric capacity

WTT Efficiency and Greenhouse Gas Analysis of Hydrogen Storage with an Organic Liquid Carrier

T. Q. Hua and R. K. Ahluwalia

December 18, 2008



U.S. Department of Energy

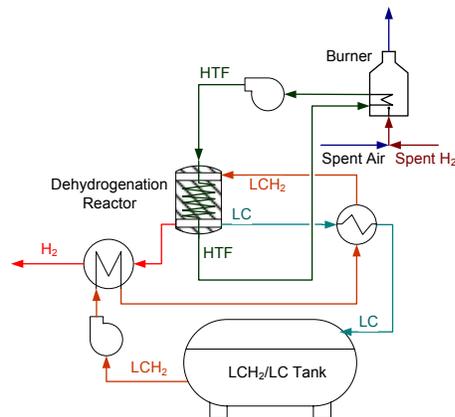
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On-board Hydrogen Storage with Organic Liquid Carrier (N-ethylcarbazole)

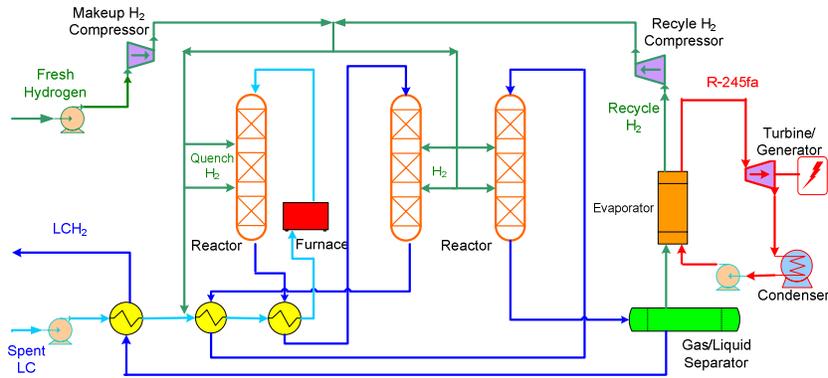
Reference: R. Ahluwalia, T. Hua, J-K. Peng and R. Kumar, "System Level Analysis of Hydrogen Storage Options," DOE Program review 2007, ST-31

- Dehydrogenation reactions are endothermic ($\Delta h \sim 51$ kJ/mole H_2)
 - $C_{14}H_{25}N \rightarrow C_{14}H_{21}N + 2H_2$
 - $C_{14}H_{21}N \rightarrow C_{14}H_{17}N + 2H_2$
 - $C_{14}H_{17}N \rightarrow C_{14}H_{13}N + 2H_2$
- Heat of reaction provided by burning a fraction of H_2 produced on-board
 - System storage efficiency = 68%
 - Need $\Delta H < 40$ kJ/mol for >90% on-board storage efficiency
- Net gravimetric capacity = 2.8 wt%, net volumetric capacity = 23 g/L



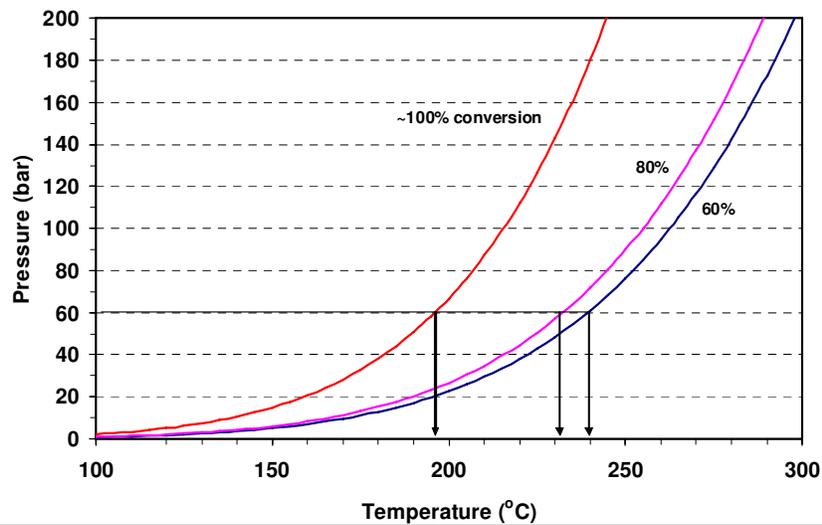
Off-board Regeneration

- Multi-stage hydrogenation reactors with declining T profile, H₂ quench, and inter-stage regenerative cooling
- Hydrogenation reactions are exothermic. Waste heat (~150 °C) can be recovered to produce low grade steam or electricity (Organic Rankine cycle)



Hydrogenation Operating Map

- Hydrogenation/dehydrogenation model validated with APCI's test data



Operating Conditions and Process Energy Consumption (Per kg H₂ hydrogenated in LC)

Parameter	1-Stage	3-Stage
Temperature, °C	196	240/232/196
Pressure, bar	60	60
Cumulative Conversion	1.0	0.6/0.8/1.0
H ₂ Circulation Ratio	21.7	16.2
Electricity (H ₂ compression), kWh	2.0	1.7
Thermal, MJ	0.8	0.8
Electricity (co-production), kWh	-0.9	-0.9

Primary Energy Consumption and WTT Efficiency (Per kg H₂ to Fuel Cell)

Process	Primary Energy (MJ)
H ₂ Production by SMR	260
Hydrogenation of LC	29
Delivery	2
Electricity Co-production	-16
WTT Efficiency, %	43.2

Note: energy consumption and WTT efficiency include on-board system storage efficiency of 68%

FCHtool Analysis of Greenhouse Gas Emissions

■ g/kg H₂ hydrogenated in LC

Process	VOC	CO	NO _x	PM10	SO _x	CH ₄	N ₂ O	CO ₂	GHGs
H ₂ Production (SMR)	1.55	3.62	7.34	2.20	2.71	29.93	0.06	14,068	14,774
Regeneration	0.06	0.17	0.64	0.70	1.29	0.92	0.01	603	627
Delivery	0.01	0.03	0.02	0.01	0.02	0.03	0.00	21	22
Total	1.6	3.8	8.0	2.9	4.0	30.9	0.1	14,692	15,423

■ g/kg H₂ delivered to fuel cell

Process	VOC	CO	NO _x	PM10	SO _x	CH ₄	N ₂ O	CO ₂	GHGs
H ₂ Production (SMR)	2.28	5.35	10.84	3.25	4.01	44.21	0.09	20,780	21,823
Regeneration	0.08	0.25	0.94	1.04	1.90	1.36	0.01	891	926
Delivery	0.01	0.04	0.03	0.02	0.03	0.04	0.00	31	32
Total	2.4	5.6	11.8	4.3	5.9	45.6	0.1	21,702	22,781

APPENDIX B

Cost Assessment of Organic Liquid Carrier Hydrogen Storage Systems



Analyses of Hydrogen Storage Materials and On-Board Systems

H₂ Storage using a Liquid Carrier:
Off-board and On-board System Cost Assessments

September 14, 2010

Matt Kromer
Stephen Lasher
Kurtis McKenney
Jayanti Sinha
Jeff Rosenfeld

TIAX LLC
35 Hartwell Ave
Lexington, MA
02421-3102
Tel. 781-879-1708
Fax 781-879-1201
www.TIAXLLC.com
Reference: D0268

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TIAX has been engaged since 2004 in an ongoing effort to perform onboard and offboard analysis of hydrogen storage system costs

Technology Focus	2004-2007	2008-2010
On-Board Storage System Assessment	<ul style="list-style-type: none"> Compressed Hydrogen <ul style="list-style-type: none"> 350-bar 700-bar Metal Hydride <ul style="list-style-type: none"> Sodium Alanate Chemical Hydride <ul style="list-style-type: none"> Sodium Borohydride (SBH) Magnesium Hydride (MgH₂) Cryogenic Hydrogen <ul style="list-style-type: none"> Cryo-compressed 	<ul style="list-style-type: none"> Compressed Hydrogen <ul style="list-style-type: none"> 350-bar – update 700-bar – update Chemical Hydride <ul style="list-style-type: none"> Liquid Hydrogen Carrier (LCH₂) Cryogenic Hydrogen <ul style="list-style-type: none"> Cryo-compressed – update Liquid Hydrogen (LH₂) – WIP Activated Carbon MOF-177
Off-Board Fuel Cycle Assessment	<ul style="list-style-type: none"> Compressed Hydrogen <ul style="list-style-type: none"> 350-bar 700-bar Chemical Hydride <ul style="list-style-type: none"> Sodium Borohydride (SBH) 	<ul style="list-style-type: none"> Compressed Hydrogen <ul style="list-style-type: none"> 350-bar – update 700-bar – update Chemical Hydride <ul style="list-style-type: none"> Liquid Hydrogen Carrier (LCH₂) Ammonia Borane Cryogenic Hydrogen <ul style="list-style-type: none"> Cryo-compressed Liquid Hydrogen (LH₂) – WIP

Note: Previously analyzed systems will continually be updated based on feedback and new information.



Over the course of this project, we have evaluated on-board and off-board hydrogen storage systems for 11 storage technologies.

Analysis To Date		cH ₂	Alanate	MgH ₂	SBH	LCH ₂	CcH ₂	LH ₂	AC	MOF-177	Cold Gas	AB
On-Board	Review developer estimates	√	√		√	√	√	√	√	√		
	Develop process flow diagrams/system energy balances (ANL lead)	√	√		√	√	√	√		√		
	Performance assessment (ANL lead)	√	√		√	√	√	√*		√		
	Independent cost assessment	√	√		√	√	√	√*	√*	√*		
Off-Board	Review developer estimates	√		√	√	√	√	√			√	√
	Develop process flow diagrams/system energy balances	√		√	√	√					√	√
	Performance assessment (energy, GHG) ^a	√			√	√					√	
	Independent cost assessment ^a	√			√	√		√			√	
Overall	Ownership cost projection ^a	√			√	√		√		√	√*	
	Solicit input on TIAX analysis	√	√		√	√	√	√*	√	√		
	Analysis update	√			√		√	WIP		WIP		

* Preliminary results under review.

^a Work with SSAWG, ANL and SSAWG participants on WTT analysis.

☐ = Not part of current SOW

WIP = Work in progress



This report summarizes TIAX's assessment of the off-board fuel cost and the onboard high-volume (500,000 units/yr) manufactured cost of hydrogen storage systems using a liquid hydrogen carrier (LCH₂)

◆ **Scope:**

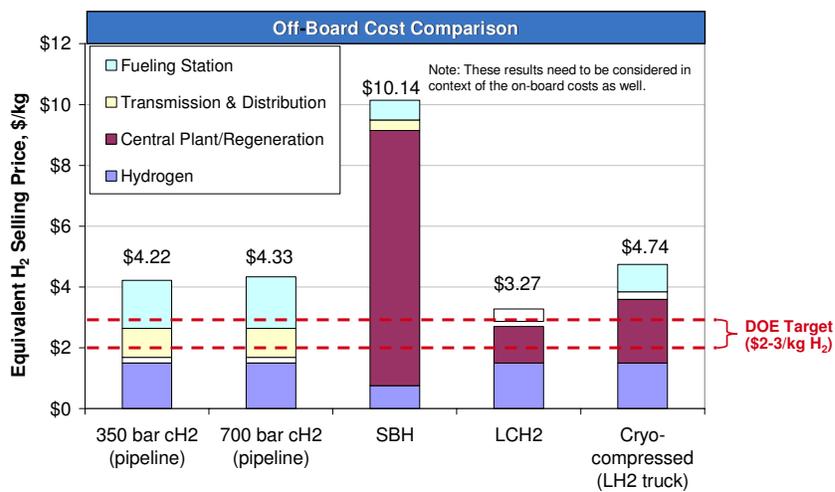
- **Onboard LCH₂ Storage System:** Cost estimates for an onboard storage system using 5.8 wt% N-ethylcarbazole
- **Off-board Fuel Costs:** Cost estimates for the price of hydrogen generated from steam-methane reforming of natural gas and transported in an N-ethylcarbazole liquid hydrogen carrier medium

◆ **Approach:**

- Onboard cost analysis is based on an onboard system design developed by Argonne National Laboratory to meet critical performance criteria.
- Onboard costs are projected from bottom-up estimate of raw material costs and manufacturing process costs, plus purchased components balance-of-plant components
- Off-board cost estimates use a modified version of the H2A Components model to incorporate design parameters provided through discussions with industry



The results of this study project a liquid hydrogen carrier (LCH₂) fuel cost of \$3.27/kg H₂, close to the DOE target of \$2-3/kg H₂.



Note: See footnotes and details in the Off-board Cost Assessment section.



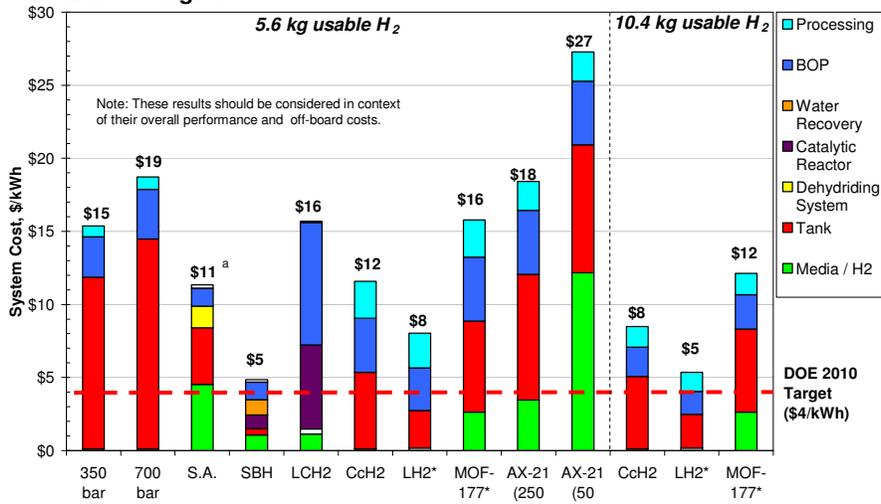
The LCH₂ fuel cost projection is lower cost than both compressed and cryo-compressed hydrogen fuel cost projections.

- ◆ The equivalent H₂ price from LCH₂ is 1.1-1.6 times more expensive than the DOE target, but it is 25 to 40% cheaper than cH₂ pipelines or cryo-compressed options
- ◆ Additional LCH₂ off-board cost reductions are possible if:
 - Carrier material cost is at the low end of the potential cost range of \$2-12/gal
 - Working capital in the system is reduced (i.e., less LCH₂ storage and higher on-board efficiencies)
 - Steam or electricity by-products may be used or sold at the regeneration facility
- ◆ In addition, LCH₂ has the potential to be more attractive than the other hydrogen options due to:
 - Relative ease of transport and dispensing
 - Smaller capital investment than cH₂ pipelines, especially for small-medium volumes
 - No boil-off issues and lower overall energy use and GHG emissions than LH₂ pathway¹

¹ Well-to-Wheel energy use and GHG emissions to be determined by ANL.



The LCH₂ on-board storage system cost is projected to be 4 times higher than the DOE 2010 target.



^aDenotes preliminary estimate, to be reviewed prior to completion of TIAX's cost analysis.

^bThe sodium alanate system requires high temp. waste heat for hydrogen desorption, otherwise the usable hydrogen capacity would be reduced.



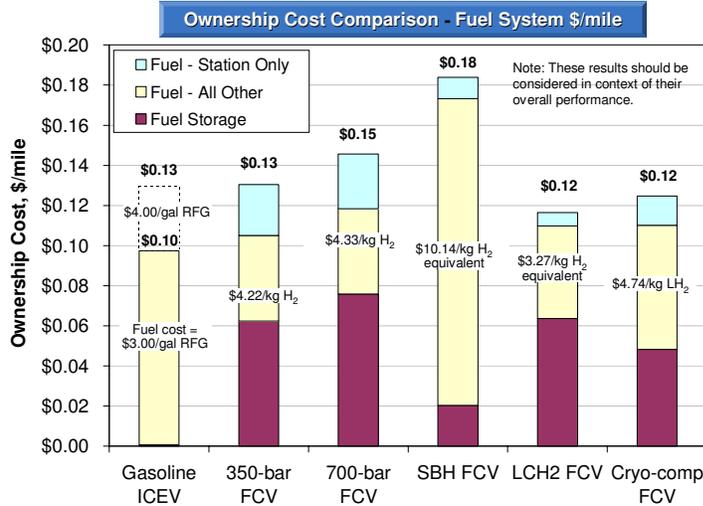
There is currently no clear path to achieving on-board storage system cost targets with the LCH₂ system.

- ◆ The LCH₂ system evaluated here was \$15.7/kWh, almost 4 times more expensive than the DOE 2010 target of \$4/kWh
- ◆ Substantial cost reductions/performance improvements are needed for the on-board reactor and BOP components
- ◆ Even assuming an improved LCH₂ material with 6.7 wt% H₂ and 100% on-board storage efficiency, cost is reduced by less than 5% (see Appendix). However, these changes do offer significant weight and volume reductions.
- ◆ On-board conversion reactor performance and system design has not been proven
 - 95% conversion efficiency assumed in this study vs. only 85% demonstrated (double pass) for a continuous reactor with thin-film catalyst¹
 - Trickle bed reactor hydrodynamics on foam has not been demonstrated²
 - The proposed system design uses an unproven single-tank concept with a flexible bladder separating the spent carrier material from the hydrogenated material. A two tank system may be necessary to ensure the system's technical functionality
 - The onboard storage efficiency does not account for the energy needed to maintain the dehydrogenated carrier above its melting point of 70 °C

¹ "Reversible Liquid Carriers for an Integrated Production, Storage and Delivery of Hydrogen", Toseland, B. and Pez, G., 2008 DOE H₂ Program Review
² "System Level Analysis of Hydrogen Storage Options", Ahluwalia, R.K. et al., 2007 DOE H₂ Program Review, May 2007



When on-board and off-board costs are combined, we see that the LCH₂ system has potential to have roughly the same ownership cost as a gasoline ICEV.



Note: All fuel costs exclude fuel taxes.



When the on-board and off-board fuel system costs are combined, the LCH₂ system has potential to be competitive with other fuel options.

- ◆ The LCH₂ system evaluated here is 1 to 3 cents per mile cheaper than our assessment of compressed H₂ storage systems with pipeline delivery
 - Different assumptions for annual discount factor, markups, annual mileage and fuel economy would yield slightly different results
 - Note that the impact of on-board storage system weight and volume were not taken into account, but the heavier LCH₂ system would likely result in lower fuel economy than the cH₂ system
- ◆ The LCH₂ system is also ~1 cent/mile cheaper than a conventional ICEV when only the fuel system is considered and gasoline is \$4/gal
 - However, when the whole vehicle, including the powertrain purchased cost, is included, the conventional gasoline ICEV will likely be noticeably cheaper (see Appendix)
 - Note that a detailed assessment of the FCV and ICEV maintenance and other non-fuel operating costs has not been conducted

However, even ownership cost is not the whole story: WTW energy use/GHG emissions, vehicle performance impacts and other metrics must be considered.



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This cost assessment is based on a liquid carrier (N-ethylcarbazole) being developed by Air Products (APCI) to reversibly adsorb and desorb hydrogen.

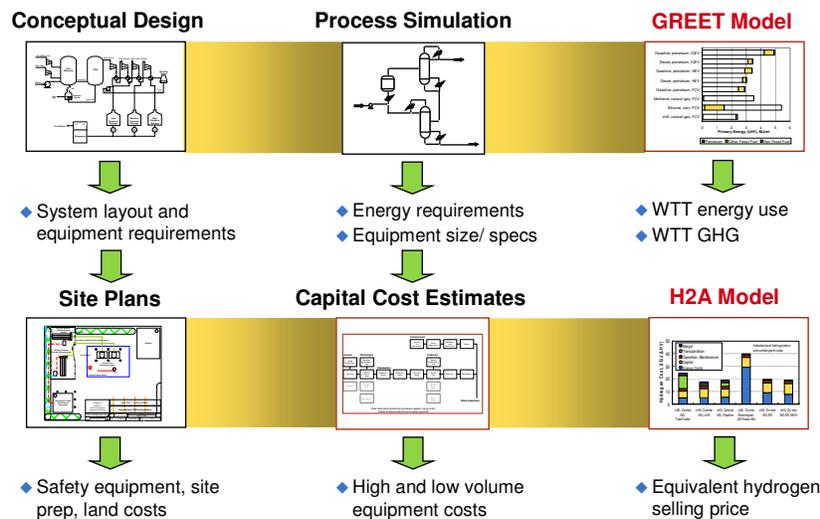
- ◆ Despite having a moderate hydrogen storage density of 5.8 wt% (3.7 wt% net¹), N-ethylcarbazole has many positive attributes, including:
 - Regeneration (i.e., hydrogenation) process adsorbs H₂ at a pressure of 60 bar, which does not add significantly to capital and energy costs at the regeneration facility
 - No additional reactants besides hydrogen are required
 - Regeneration process produces low-quality steam that can be used as a by-product or to generate electricity (not included in this cost analysis)
 - The hydrogenated carrier can be stored and transported in tanks designed for standard hydrocarbons (e.g., gasoline, diesel)
- ◆ Dehydrogenation of the carrier on-board the vehicle adds some complexity and cost to the on-board storage system
 - Thermal requirements during the dehydrogenation process are significant (~25 MJ/kg H₂) and the temperature requirement (240-270 °C) is significantly greater than current PEM operating temperatures²
 - The dehydrogenated carrier must be kept above a melting point of 70 °C necessitating insulated or heated storage and transport tanks

¹ Assuming 95% conversion efficiency in the dehydrogenation reactor and 68% on-board storage efficiency (i.e., 32% of the stored H₂ must be burned to generate the heat required for on-board dehydrogenation).

² If dehydrogenated at the fueling station, natural gas will likely provide the thermal energy required for dehydrogenation.



Our off-board assessment makes use of existing models to calculate cost and performance for each technology on a consistent basis.

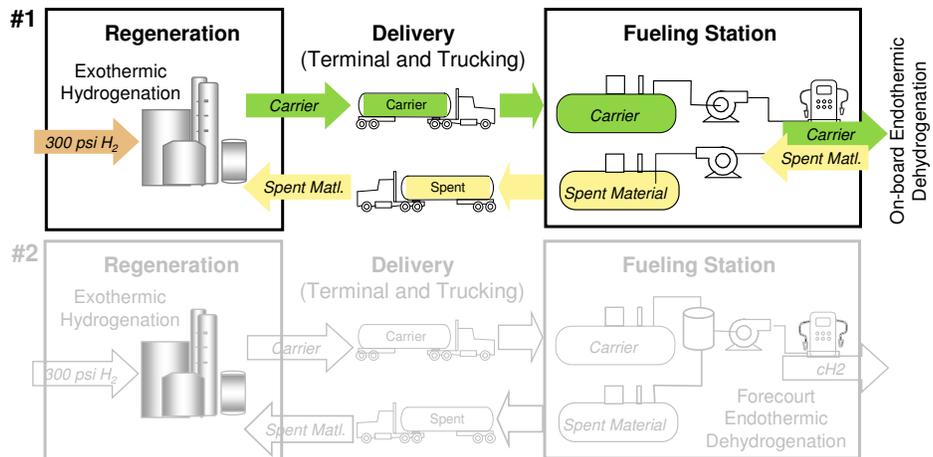


The H2A Carrier model was used to allow for direct cost comparison to compressed, liquefied, and sodium borohydride (SBH)-based H₂ options.

- ◆ Most financial assumptions are maintained from the original H2A Model
- ◆ New calculation tabs were added as part of the DOE Delivery Project
 - Regeneration – calculates material regeneration costs based on capital and operating costs of a central plant
 - Storage Terminal – calculates required storage for fresh and spent materials
 - Trucking – calculates trucking costs for all novel carriers
 - Fueling Station – calculates fueling station costs for fueling vehicles with novel carrier
- ◆ Calculation tabs were populated with inputs based on industry and developer feedback
 - TIAX made initial estimates consistent with H2A methodology
 - Model and estimates were reviewed with developers (primarily APCI)
 - Model inputs and results were updated



The off-board assessment for novel carriers requires evaluation of regeneration, delivery and forecourt technologies.



This analysis assumes that the LCH₂ will be employed for on-board storage as illustrated in Pathway #1 above.



The regeneration facility includes equipment and material for hydrogenation, purification and storage.

- ◆ Hydrogen
 - Hydrogen is purchased as a pure gas at 20 bar for \$1.50/kg (H2A Central Plant target)
 - No losses are assumed
- ◆ Material Storage Tanks
 - Storage for a 10-day plant shutdown and a 120-day summer peak period (10% above average demand) is included for hydrogenated material
 - Equal amount of storage included for dehydrogenated material
 - Two quarantine tanks are included for substandard material (five days of material)
 - Assumed cost: \$0.42/gal (based on similar tanks in H2A)
- ◆ Carrier Material
 - N-ethylcarbazole is estimated to cost between \$2-12/gal; \$7/gal used for baseline (industry estimate, in 2008\$)
 - Material replacement is estimated to be 0.1% of plant throughput (APCI estimate)
 - Material allocation equals that required to fill all hydrogenated storage tanks
- ◆ Capital Cost
 - Includes: compressors, reactors, tankage, distillation, heat exchangers, fluid power equipment, and power and instrumentation (combination of H2A and industry cost estimates)
 - Range of 50-150% of estimated equipment capital cost used for sensitivity analysis
- ◆ Catalyst Loading and Replacement
 - Assumed initial catalyst cost is \$170/kg and cost for replacement catalyst is \$155/kg (industry estimate)
 - Catalysts lifetime based on material processed: 350,000-1,000,000 kg_m/kg_c; 500,000 baseline (industry estimate)



Capital cost estimates are derived from developer feedback and baseline H2A model assumptions.

Regeneration Plant Capital Equipment	Installed Cost (\$millions)	Basis
Carrier Material	\$258	Personal communication with APCI, 2008
Indirect Capital (permitting, project contingency, engineering, site prep, land)	\$155	H2A Baseline
Storage (Including quarantine)	\$41.7	Personal communication with APCI, 2008
Piping & Instrumentation	\$25.7	Personal communication with APCI, 2008
Catalyst	\$21.3	Personal communication with APCI, 2008
Compressors	\$14.8	H2A Baseline
Pumps	\$6.8	Personal communication with APCI, 2008
Reactor	\$1.5	Personal communication with APCI, 2008
Heat Exchangers	\$1.4	Personal communication with APCI, 2008
Distillation	\$0.2	Personal communication with APCI, 2008
Total	\$526	



The ability of the liquid carrier to be transported in relatively standard, insulated tank trucks makes for cost efficient transportation.

- ◆ Transport capacity: determined by the liquid carrier yield (3.7 wt% net) and the mass of material that can be transported within an insulated aluminum trailer (24,750 kg GVW)
- ◆ Insulation: will be able to maintain the temperature of the carrier for up to 1 day
- ◆ Trailer cost: \$90,000 based on quotes from Heil and Polar trailer companies
- ◆ Loading/unloading time: 1.5 hrs combined (trailer unloads hydrogenated carrier and picks up dehydrogenated carrier)
- ◆ Baseline H2A assumptions include:

H2A Delivery Assumption	Value
Round trip delivery distance	160 km
Delivery labor rate	\$50
Truck capital cost	\$75,000
Fuel cost	0.44 \$(2005)/L

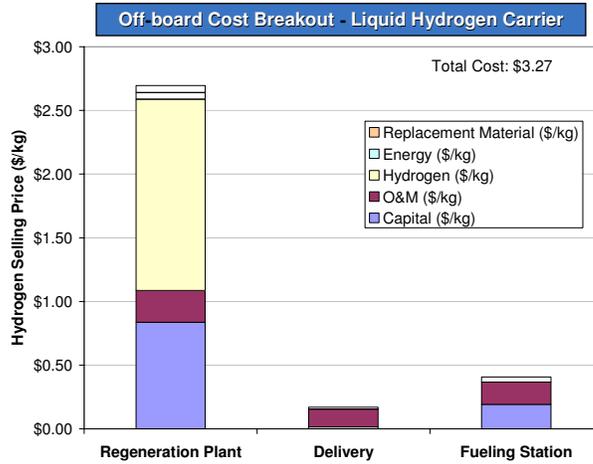


This analysis assumes the fueling station receives the liquid carrier via tanker trucks where the carrier is stored and dispensed to vehicles for on-board dehydrogenation.

- ◆ All components (e.g., storage tanks, pumps, dispensers) are specified according to previously established methods for chemical hydrogen systems
- ◆ On-site storage in each of the hydrogenated and spent carrier tanks is equal to 1.5 truck deliveries
- ◆ Overall cost includes enough carrier material to fill 1/3 of the hydrogenated carrier tank and the full spent carrier tank
- ◆ Electricity consumption due to carrier pumping and other miscellaneous loads are the same as for sodium borohydride (SBH) = 0.50 kWh/kg
- ◆ A range of labor costs were used: \$7.75/hr (minimum wage in CA) - \$15/hr, with the baseline value of \$10/hr



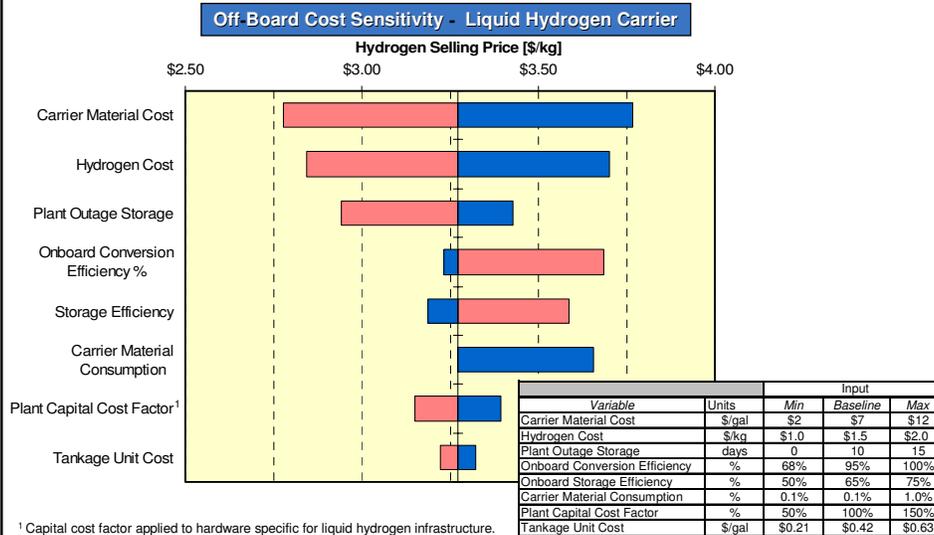
The cost results indicate that the major non-hydrogen cost is the capital cost of the regeneration plant.



If the carrier is used as an off-board transportation media only (i.e., fueling station dehydrogenation), the H₂ selling price would increase to about \$4.14/kg.



Factors effecting the initial and replacement costs of carrier material have the greatest affect on the hydrogen selling price sensitivity.



¹ Capital cost factor applied to hardware specific for liquid hydrogen infrastructure.



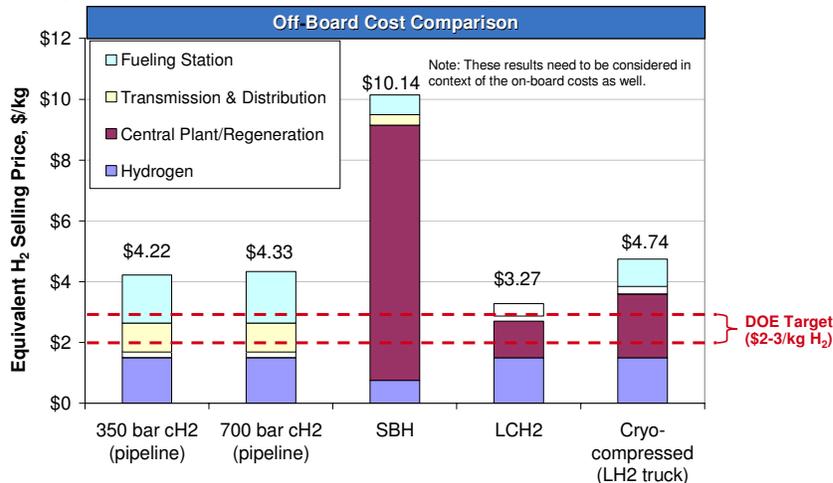
Compared to the preliminary LCH₂ results presented at the 2009 AMR, changes to TIAX's assumptions resulted in a significant decrease in the cost of hydrogen.

- ◆ Decreased the carrier material replacement at the regeneration facility from 2.75% of plant throughput to 0.1%:
 The prior estimate provided by APCI (0.5 to 5%, 2.75% baseline) corresponded to an *annual* replacement rate, given a fixed number of cycles, but was erroneously interpreted as a *per-cycle* replacement rate.
 Feedback from APCI [2010] indicated that this prior estimate was an order of magnitude higher than that seen during real-world testing.
- ◆ Adjusted offboard cost of liquid carrier material from 2008\$ (\$7/gal) to 2005\$ (\$6.35/gal)

2010 Updated Results Compared to 2009 AMR Results	2009 AMR	2010 Update	% Change
Fuel Cost, \$/kg H ₂	\$4.75	\$3.27	-31%



The results of this study project a liquid hydrogen carrier (LCH₂) fuel cost of \$3.27/kg H₂, close to the DOE target of \$2-3/kg H₂.



Note: Production costs assume \$1.50/kg H₂ (H₂A target). Regeneration costs assume 100 TPD H₂ equivalent SBH plant based on hydrogen assisted electrolysis and a 250 TPD H₂ equivalent LCH₂ plant based on N-ethylcarbazole hydrogenation. Delivery and forecourt costs assume 80 km truck delivery from a central plant to the fueling station designed for 1000 kg/day H₂. cH₂ (pipeline) and LH₂ cases assume compressed hydrogen dispensing at 6,250 psi.



“Ownership cost” provides a useful metric for comparing storage technologies on an equal footing, accounting for both on- and off-board (i.e., refueling) costs.

Simple Ownership Cost (OC) Calculation:

$$OC = \frac{C \times DF \times \text{Markup}}{\text{Annual Mileage}} + \frac{FC}{FE}$$

C = Factory Cost of the On-board Storage System
 DF = Discount Factor (e.g., 15%)
 FC = Fuel Cost of the Off-board Refueling System
 FE = Fuel Economy (e.g., 62 mi/kg)

Ownership Cost Assumptions	Gasoline ICEV	Hydrogen FCV	Basis/Comment
Annual Discount Factor on Capital	15%	15%	Input assumption
Manufacturer + Dealer Markup	1.74	1.74	Assumed mark-up from factory cost estimates ¹
Annual Mileage (mi/yr)	12,000	12,000	H2A Assumption
Vehicle Energy Efficiency Ratio	1.0	2.0	Based on ANL drive-cycle modeling for mid-sized sedan
Fuel Economy (mpgge)	31	62	ICEV: Combined CAFE sales weighted FE estimate for MY 2007 passenger cars ²
H ₂ Storage Requirement (kg H ₂)	NA	5.6	Design assumption based on ANL drive-cycle modeling

¹ Source: DOE, "Effects of a Transition to a Hydrogen Economy on Employment in the United States", Report to Congress, July 2008

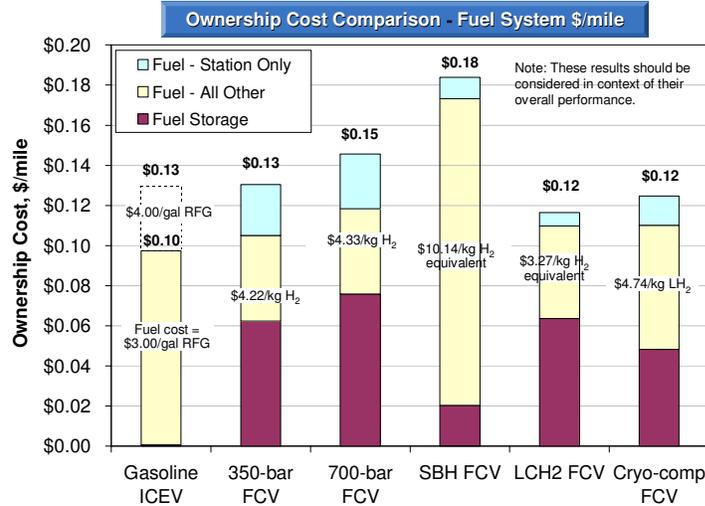
² Source: U.S. Department of Transportation, NHTSA, "Summary of Fuel Economy Performance," Washington, DC, March 2007

This ownership cost assessment implicitly assumes that each fuel system and vehicle has similar maintenance costs and operating lifetime.



Summary Results Ownership Cost Results

When on-board and off-board costs are combined, we see that the LCH₂ system has potential to have roughly the same ownership cost as a gasoline ICEV.



Note: All fuel costs exclude fuel taxes.



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On-board Assessment Background Overview

We evaluated the high-volume manufactured cost of a liquid hydrogen carrier (LCH₂) on-board storage system based on N-ethylcarbazole.

- ◆ We based on cost analysis on ANL's performance assessment² of the Air Products (APCI) regenerable organic liquid carrier, N-ethylcarbazole¹
- ◆ Key features of the LCH₂ system include:
 - Single tank design:** Uses a flexible bladder to separate the spent carrier material from the hydrogenated material. Resistance heat is used to maintain the dehydrogenated carrier above its melting point of 70°C.
 - Dehydrogenation reactor:** An onboard trickle-bed reactor dehydrogenates the carrier at high temperature (270 C) using a thin-film palladium catalyst
 - Balance-of-Plant:** Heats/cool and circulates carrier media. Main cost contributors are the burner and circulation pumps
- ◆ Key advantages of the APCI liquid carrier are its competitive off-board (i.e., refueling) cost and relative ease of transport and dispensing
- ◆ The key disadvantage of this liquid carrier is its low system storage efficiency of 68% (i.e., a large fraction of stored H₂ has to be burned to provide the heat for dehydrogenation)

¹ "Hydrogen Storage by Reversible Hydrogenation of Liquid-Phase Hydrogen Carriers", Cooper, A. and Pez, G., 2007 DOE H₂ Program Review
² "System Level Analysis of Hydrogen Storage Options", Ahluwalia, R.K. et al., 2007 DOE H₂ Program Review, May 2007



The LCH₂ system design incorporates a number of design assumptions that have not been validated with real-world results.

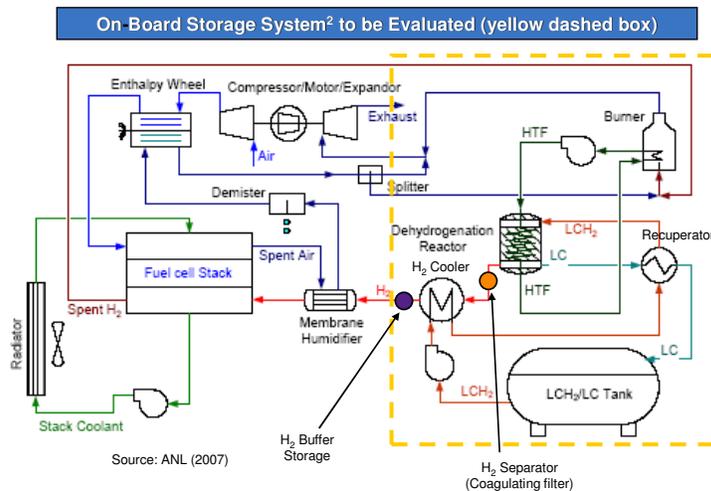
- ◆ **Onboard performance:** Key differences between the APCI demonstrated results and ANL analysis, include:
 - ANL assumes 95% conversion efficiency, whereas APCI has demonstrated 65% (single pass) to 85% (double pass) for a continuous reactor with thin-film catalyst²
 - Trickle bed reactor hydrodynamics on foam has not been demonstrated¹
- ◆ **Tank Design:** The proposed system design uses an unproven single-tank concept with a flexible bladder to separate fresh and spent media. A two tank system may be necessary to ensure the system's technical functionality.
- ◆ **Carrier Media Temperature Management:** The system design uses resistance heaters to maintain the dehydrogenated carrier above its melting point of 70 °C
 - The onboard storage efficiency does not account for the energy needed to operate the resistance heaters, and the tank design does not include insulation that may be necessary to reduce energy losses or prevent solidification of the media.
 - We did not perform a tradeoff analysis to compare the additional operating cost associated with maintaining the tank's temperature against the additional capital expense, size, and weight of adding insulation to the storage tank
 - A lower melting-point carrier may need to be engineered to avoid this efficiency penalty.

¹ "System Level Analysis of Hydrogen Storage Options", Ahluwalia, R.K. et al., 2007 DOE H₂ Program Review, May 2007

² "Reversible Liquid Carriers for an Integrated Production, Storage and Delivery of Hydrogen", Toseland, B. and Pez, G., 2008 DOE H₂ Program Review



We used the onboard system definition and design developed by APCI¹ and ANL² as the basis of our cost assessment.



¹ "Hydrogen Storage by Reversible Hydrogenation of Liquid-Phase Hydrogen Carriers", Cooper, A. and Pez, G., 2007 DOE H₂ Program Review

² "System Level Analysis of Hydrogen Storage Options", Ahluwalia, R.K. et al., 2007 DOE H₂ Program Review, May 2007



The high volume (500,000 units/year) manufactured cost for the LCH₂ system was estimated from raw material prices, capital equipment, labor, and other operating costs.

LCH ₂ Storage System – Major Components	BOP Bottom-up Costing Methodology
<ul style="list-style-type: none"> Dehydrogenation Reactor Liquid Carrier Storage Tank HEX Burner H₂ Cooler H₂ Separator Recuperator H₂ Buffer Storage 	<ul style="list-style-type: none"> Develop Bill of Materials (BOM) Obtain raw material prices from potential suppliers Develop production process flow chart for key subsystems and components Estimate manufacturing costs using TIAX cost models (capital equipment, raw material price, labor rates)

- ◆ We used a bottom-up approach to determine manufactured cost for the dehydrogenation reactor and LCH₂/LC storage tank.
- ◆ We costed the microchannel heat exchangers for the HEX burner, H₂ cooler and recuperator based on direct materials and 1.5X bottom-up process costs for tube-fin heat exchangers.
- ◆ We costed the H₂ buffer storage tank based on direct materials.
- ◆ We based the cost of purchased components (i.e. Heat Transfer Fluid (HTF) pump, Liquid Carrier (LCH₂) pump, H₂ burner, H₂ blower, coagulating filter, LCH₂ tank heater, piping, sensors, controls, valves and regulators) on vendor quotes/catalog prices, adjusted for high-volume production.



We based our media and storage tank assumptions and specifications on discussions with APCI and ANL and their 2007 Merit Review presentations^{1,2}.

System Element	Design Parameter	Value	Basis/Comment
Media/System	Media/Material	N-ethylcarbazole	ANL ² , APCI ¹
	Material H ₂ storage capacity	5.8 wt%	ANL ² , APCI ¹
	Storage system efficiency	67.7%	ANL ² ; includes H ₂ utilized to fire burner only (does not include 95% reactor conversion efficiency)
	LCH ₂ solution density	1200 kg/m ³	ANL ²
	LC solution density	950 kg/m ³	ANL ²
LCH ₂ /LC Storage Tank	Tank material of construction	HDPE	ANL ²
	% excess tank volume	10%	Over fuel volume, to account for sloshing
	Usable H ₂ capacity	5.6 kg	Design basis; note: ANL ² analysis done for 6.4 kg usable H ₂
	Stored H ₂ capacity	8.7 kg	Calculated based on 95% conversion efficiency and 67.7% storage efficiency; note: ANL ² analysis done for 10 kg stored H ₂
	Bladder/separator?	Yes	Single tank design; needed to separate LCH ₂ from LC
	Temperature	70 °C	Needed to prevent solidification

¹ "Hydrogen Storage by Reversible Hydrogenation of Liquid-Phase Hydrogen Carriers", Cooper, A. and Pez, G., 2007 DOE Hydrogen Program Review

² "System Level Analysis of Hydrogen Storage Options", Ahluwalia, R.K. et al., 2007 DOE Hydrogen Program Review, May 2007



The dehydrogenation reactor design was also based on information from APCI and ANL.

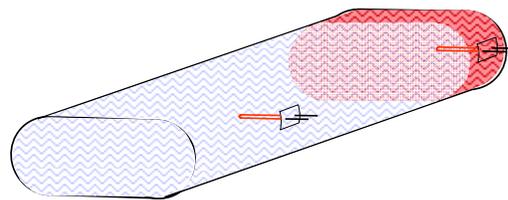
System Element	Design Parameter	Value	Basis/Comment
Dehydrogenation Reactor	Type	Vertical, tubular trickle bed reactor	ANL ²
	Heat of dehydrogenation	+51 kJ/mol H ₂	APCI ¹ , ANL ² ; =25 MJ/kg H ₂
	Catalyst	Pd on Li Aluminate	Dispersed wash-coat (thin-film) catalyst, 50 micron, 363 mm active length
	Catalyst concentration	4% wt. of substrate	
	Catalyst substrate	40-ppi Al-6101 foam	92% porosity, 224 kg/m ³ bulk density
	Conversion efficiency	95%	ANL ²
	Liquid Hourly Space Velocity (LHSV)	20 h ⁻¹	ANL ² ; H ₂ volumetric flow rate/liter reactor volume
	Peak operating temp.	240-270 °C	ANL ²
	Max. operating pressure	8 bar (116 psi)	ANL ²
	HX tube material	Al-2219-T81	ANL ² ; 40 tubes (11.1 mm OD, 0.8 mm wall, 400 mm length)
	Reactor vessel material	Al-2219-T81	ANL ² ; 182 mm OD, 0.8 mm wall, 460 mm total length, 2.25 safety factor

¹ "Hydrogen Storage by Reversible Hydrogenation of Liquid-Phase Hydrogen Carriers", Cooper, A and Pez, G., 2007 DOE Hydrogen Program Review
² "System Level Analysis of Hydrogen Storage Options", Ahluwalia, R.K. et al., 2007 DOE Hydrogen Program Review, May 2007

Other component design assumptions are presented in the Appendix.

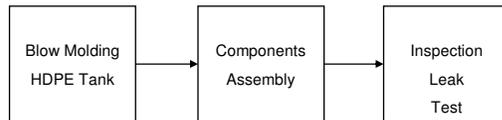


A single high-density polyethylene (HDPE) tank holds the LCH₂ and spent carrier (LC), separated by a moving bladder¹. Resistance heaters maintain the solutions above 70 °C².



Storage Tank Bill-of-Materials

1. HDPE tank
2. Bladder
3. LCH₂ inlet with O-ring (fill in)
4. LCH₂ outlet with O-ring (delivery)
5. LC inlet with O-ring (return from reactor)
6. LC outlet with O-ring (drain out)
7. LCH₂ side resistance heater
8. LC side resistance heater
9. LCH₂ side level sensor
10. LCH₂ side drain
11. LC side drain
12. LCH₂ side pressure release valve
13. LC side pressure release valve
14. Mounting steel brackets (2)
15. Bolts (4)
16. Nuts (4)
17. Washers (4)



LCH₂/LC Storage Tank Manufacturing Flow Chart

¹ LCH₂/LC storage tank design based on sodium borohydride (SBH) storage tank. Single tank/bladder design may be easier than for SBH tank since SBH is highly caustic and also tends to precipitate out of the solution.
² ANL system efficiency calculations of 67.7% do not include heater parasitics. A lower melting-point liquid carrier may need to be engineered to avoid efficiency penalty.



We used Year 2008 prices for the key raw materials, which are listed below. Subsequently, we deflated all material prices by 9.27% to Year 2005 USD.

System Element	Raw Material	Price (2005\$)	Basis/Comment
Media	N-ethylcarbazole	\$6.35/gal	APCI; \$2-12/gal range (2008\$), deflated to 2005\$; consistent with TIAX off-board LCH ₂ storage system assessment
LCH ₂ /LC Storage Tank	HDPE	\$1.6/kg	Plastics Technology, May 2008, pg. 95, deflated to 2005\$
Dehydrogenation Reactor	Pd catalyst	\$12.7/g (\$395/tr.oz.)	www.metalprices.com; June, 2008, deflated to 2005\$
	Li Aluminate	\$43.8/kg	Sigma-Aldrich ¹ , deflated to 2005\$
	Al-6101	\$9.6/kg	Bulk price from Alcoa (2009), deflated to 2005\$
	Al-2219-T81	\$12.7/kg	Assumed 30% higher price than AL-6101, based on spread in price between Al-6101 and Al-2219 from 2008
	HTF (XCellTherm® 600)	\$7.26/gal	RadCo Industries, Inc., June 2008, deflated to 2005\$
HEX Burner	Inconel 600	\$15.0/kg	www.metalprices.com; June, 2008, deflated to 2005\$
H ₂ Cooler, Recuperator	SS316	\$7.26/kg	www.metalprices.com; June, 2008, 1-year avg, deflated to 2005\$.

¹ <https://www.sigmaaldrich.com/catalog/search/ProductDetail?ProdNo=336637&Brand=ALDRICH>



We based the cost of purchased components on vendor quotes/catalog prices, using our judgment to adjust for high-volume production.

Purchased Component	Weight (kg)	Volume (L)	Cost (\$)	Basis/Comment
HTF Pump	40	30	\$400	0.4X McMaster-Carr catalog price; ANL ¹ : XCellTherm® 600, 458 L/min, 320 °C, ΔP=1 bar
LCH ₂ Pump	20	10	\$200	0.4X McMaster-Carr catalog price; ANL ¹ : LCH ₂ , 2.65 L/min, 70 °C, ΔP=8 bar
H ₂ /air Non-catalytic Burner	2	1	\$400	0.4X McMaster-Carr catalog price \$1,000 for NG burner, 180,000 Btu/h; ANL ¹ : 82 kW, 5% excess O ₂ , Inconel
H ₂ Blower	2.0	5	\$18	0.5X Modine OEM \$37 not including tooling and capital cost markup 1.2
Coagulating filter	1.8	0.8	\$43	0.4X McMaster-Carr retail price of \$105
LCH ₂ Tank Heater	0.1	0.0	\$4	Bottom-up costing using Boothroyd-Dewhurst DFMA® software, with 1.5X markup for component supplier overhead and profit
Piping & Fittings	7	3	\$72	
Sensors & Controls	0.0	0.0	\$30	
Valves & Connectors	3	2	\$105	
Pressure Regulators	1	1	\$44	

¹ "System Level Analysis of Hydrogen Storage Options", Ahluwalia, R.K. et al., 2007 DOE Hydrogen Program Review, May 2007
 Note: A complete bill of materials is included in the appendix

We performed bottom-up costing (i.e., raw materials, process flow charts) on all other components.



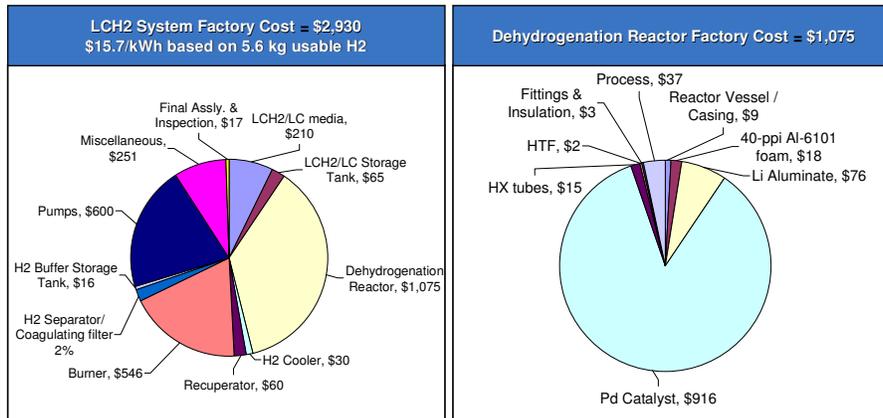
Processing cost makes up just ~5% of the total system cost due to the high production volume assumption and large fraction of purchased components.

On-board System Cost Breakout Liquid Hydrogen Carrier – 5.6 kg H ₂	Material, \$	Processing, \$	Processing Fraction
LCH ₂ /LC Media ¹	210	(purchased)	0%
LCH ₂ /LC Storage Tank	55	10	15.4%
Dehydrogenation Reactor	1,038	37	3.4%
- Pd Catalyst	916	(purchased)	0%
- Li Aluminate	76	(purchased)	0%
- Al-6101 foam substrate	18	19	51.8%
- Reactor Vessel (Al-2219-T81)	9	2	18.1%
- HX tubes (Al-2219-T81)	15	16	51.7%
- Other (HTF, insulation, fittings)	5	(purchased)	0%
H ₂ Cooler	6	24	80%
Recuperator	36	24	40%
Burner	510	36	6.6%
- Microchannel HX	92	36	28.2%
- H ₂ /air non-catalytic burner	400	(purchased)	0%
- H ₂ blower	18	(purchased)	0%
H ₂ Separator/Coagulating filter	52	7	11.8%
H ₂ Buffer Storage Tank	16	0.5	3.1%
Pumps	600	(purchased)	0%
- HTF pump	400	(purchased)	0%
- LCH ₂ pump	200	(purchased)	0%
Miscellaneous	251	(purchased)	0%
Final Assembly & Inspection	0	17	100.0%
Total Factory Cost	2,774	156	5.3%

¹ Cost is based on \$7/gal LCH₂, consistent with TIAX off-board LCH₂ storage system assessment, which is based on input from APCI.



We estimate the high-volume factory cost¹ of the system to be about \$2,930, or \$15.7/kWh, of which ~31% is due to the cost of the Pd catalyst.



Note: A trade-off study was not performed on the size/cost of the pumps versus size/cost of the reactor sub-system and burner.
¹ Cost includes deflation by 9.27% to Year 2005 USD.



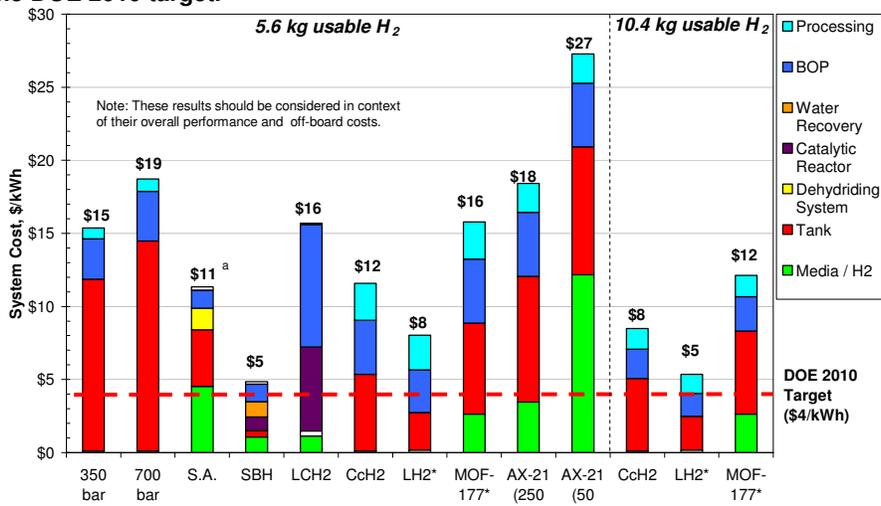
Compared to the preliminary LCH₂ results presented at the 2009 AMR, changes to TIAX's assumptions and calculations resulted in a minor adjustment in the onboard cost estimate.

- ◆ Corrected the volume, weight, and cost of the LCH₂/LC Media and LCH₂ Tank such that they are calculated based on the amount of LCH₂, not LC.
- ◆ Increased the cost of the coagulator filter cost from \$21 to \$43. The new cost is based on a 60% discount from low volume catalog list price (consistent with other BOP components); the previous cost was based on an 80% discount.
- ◆ Increased the price of aluminum from \$2.5/kg to \$9.6/kg for AL-6101, and \$3.7/kg to \$12.7/kg for AL-2219

2010 Updated Results Compared to 2009 AMR Results	2009 AMR	2010 Update	% Change
System Cost, \$/kWh	15.4	15.7	+2%



The LCH₂ on-board storage system cost is projected to be 4 times higher than the DOE 2010 target.



^aDenotes preliminary estimate, to be reviewed prior to completion of TIAX's cost analysis.

^aThe sodium alanate system requires high temp. waste heat for hydrogen desorption, otherwise the usable hydrogen capacity would be reduced.



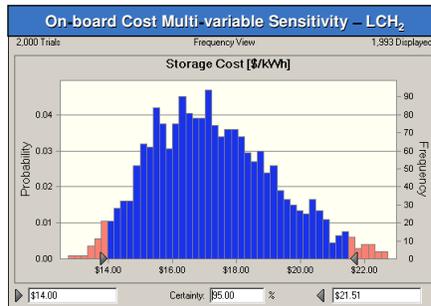
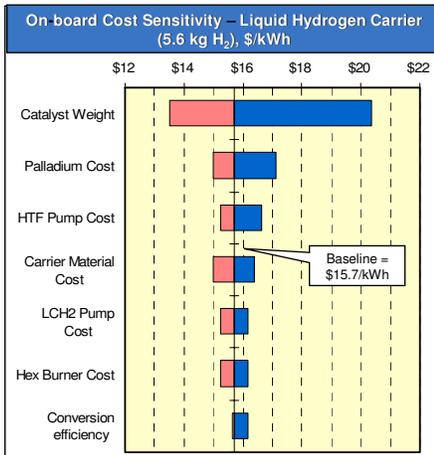
To account for the uncertainty in the onboard cost projections, we developed “low” and “high” cost estimates as inputs to the sensitivity analysis.

Key Sensitivity Parameters	On-board Cost Sensitivity – LCH ₂			
	Baseline	Min	Max	Basis/Comment
Conversion Efficiency	95%	65%	100%	◆ Baseline from ANL 2007 DOE AMR ¹ , min from APCI 2008 DOE AMR ²
Catalyst Weight (kg)	1.8	0.9	3.6	◆ Min and Max are one half and two times the baseline
Palladium Cost (2008\$/troy oz.)	436	360	580	◆ Baseline from metalprices.com annual average ◆ Min and Max estimates from min and max LME values in 2008
HTF Pump Cost	\$400	\$300	\$600	◆ Baseline from catalog prices discounted by ~60%
LCH ₂ Media Cost (2008\$ per gal)	\$7	\$2	\$12	◆ Discussion with APCI
LCH ₂ Pump Cost	\$200	\$100	\$300	◆ Baseline from catalog prices discounted by ~60%
Aluminum T6101 Cost (\$/kg)	9.6	4.8	19.2	◆ Min and Max are one half and two times the baseline
Aluminum T6101 Cost (\$/kg)	12.7	6.4	25.4	◆ Min and Max are one half and two times the baseline
HEX Burner Cost	\$400	\$300	\$500	◆ Baseline from catalog prices for natural gas burners discounted by ~60%.

¹ “System Level Analysis of Hydrogen Storage Options”, Ahluwalia, R.K. et al., 2007 DOE Hydrogen Program Review, May 2007
² “Reversible Liquid Carriers for an Integrated Production, Storage and Delivery of Hydrogen”, Toseland, B. and Pez, G., 2008 DOE H₂ Program Review



The overall cost of the onboard liquid carrier system is most sensitive to the amount of catalyst, the catalyst cost, and purchased component prices



System Cost	\$/kWh
Base Case	15.7
Mean	17.3
Standard Deviation	1.94
“Low” Case	14.0
“High” Case	21.5



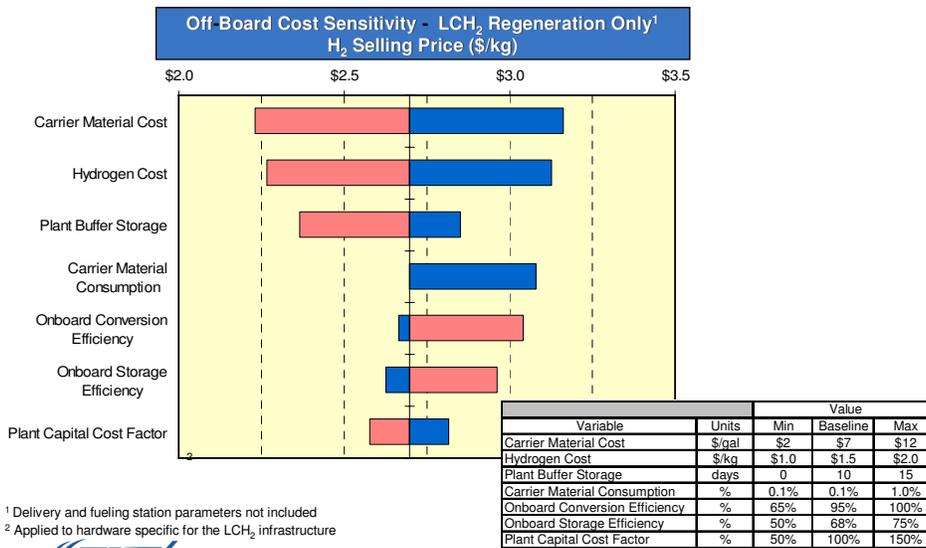
Sections

- 1 Summary Results
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Appendix Off-board Assessment *Regeneration Plant Sensitivity Analysis*

The sensitivity analysis shows the large affect that carrier cost and process efficiency assumptions have on the regeneration cost.

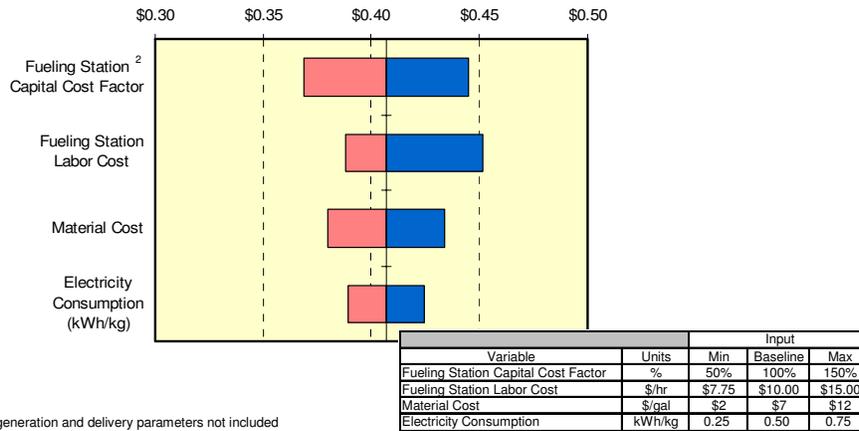


¹ Delivery and fueling station parameters not included
² Applied to hardware specific for the LCH₂ infrastructure



Major LCH₂ fueling station cost drivers include capital, labor, carrier cost, and utilities.

Off-Board Cost Sensitivity - LCH₂ Fueling Station Only¹
H₂ Selling Price (\$/kg)



¹ Regeneration and delivery parameters not included
² Applied to hardware specific for the LCH₂ infrastructure



We based our system assumptions and component specifications on APCI¹ and ANL² 2007 DOE Merit Review presentations.

System Element	Design Parameter	Value	Basis/Comment
H ₂ Buffer Storage Tank	Material	Al-2219-T81	ANL ² ; (249 mm OD, 0.5 mm wall, 744 mm total length, 2.25 safety factor)
	Peak Operating Temp	80 °C	ANL ²
	Max. Operating Pressure	8 bar (116 psi)	ANL ²
	Tank capacity	20 g H ₂	ANL ²
HEX Burner	Burner type	H ₂ /air (non-catalytic)	ANL ² ; 5% excess O ₂ , 1100 °C combustion products' exit temperature
	Burner fuel	32.3% by weight of stored H ₂	
	Burner firing rate	82 kW (280,000 Btu/h)	
	HX Type	Counterflow Microchannel	ANL ² ; HTF=XCeItherm® 600, 100 °C approach temp., 310 microchannels (14.1 mm x 0.9 mm x 363 mm)
	HX Material	Inconel 600	
H ₂ Cooler	HX Type	Counterflow Microchannel	ANL ² ; T _{outlet} = 80 °C, 90 microchannels (10.6 mm x 1.4 mm x 165 mm)
	HX Material	SS316	
Recuperator	HX Type	Counterflow Microchannel	ANL ² ; T _{LCH₂} = T _R -10 °C, 610 microchannels (10.1 mm x 0.6 mm x 263 mm)
	HX Material	SS316	

¹ "Hydrogen Storage by Reversible Hydrogenation of Liquid-Phase Hydrogen Carriers", Cooper, A. and Pez., G. 2007 DOE Hydrogen Program Review
² "System Level Analysis of Hydrogen Storage Options", Ahluwalia, R.K. et al., 2007 DOE Hydrogen Program Review, May 2007



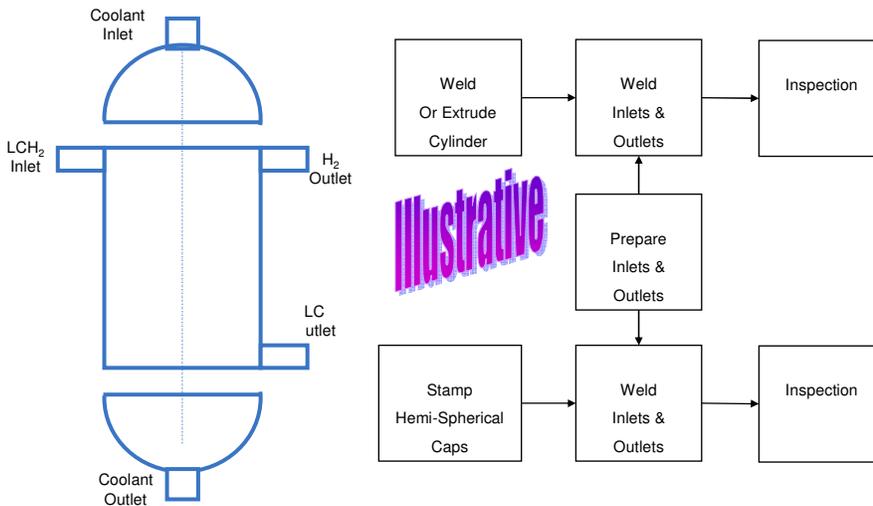
We based our system assumptions and component specifications on APCI¹ and ANL² 2007 DOE Merit Review presentations.

System Element	Design Parameter	Value	Basis
HTF Pump	Working fluid	XCelTherm® 600	ANL ²
	Operating Temp	320 °C	
	Pressure Head	1 bar (15 psi)	
	Density	850 kg/m ³	
	Flow rate	458 Liter/min (6.5 kg/s)	
LCH ₂ Pump	Working fluid	LCH ₂	ANL ²
	Operating Temp	70 °C	
	Pressure Head	8 bar (116 psi)	
	Density	1200 kg/m ³	
	Flow rate	2.65 Liter/min (0.053 kg/s)	

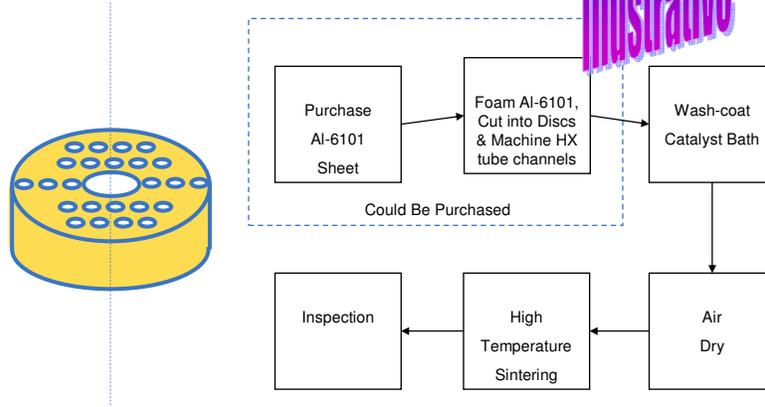
¹ "Hydrogen Storage by Reversible Hydrogenation of Liquid-Phase Hydrogen Carriers", Cooper, A. and Pez., G. 2007 DOE Hydrogen Program Review
² "System Level Analysis of Hydrogen Storage Options", Ahluwalia, R.K. et al., 2007 DOE Hydrogen Program Review, May 2007



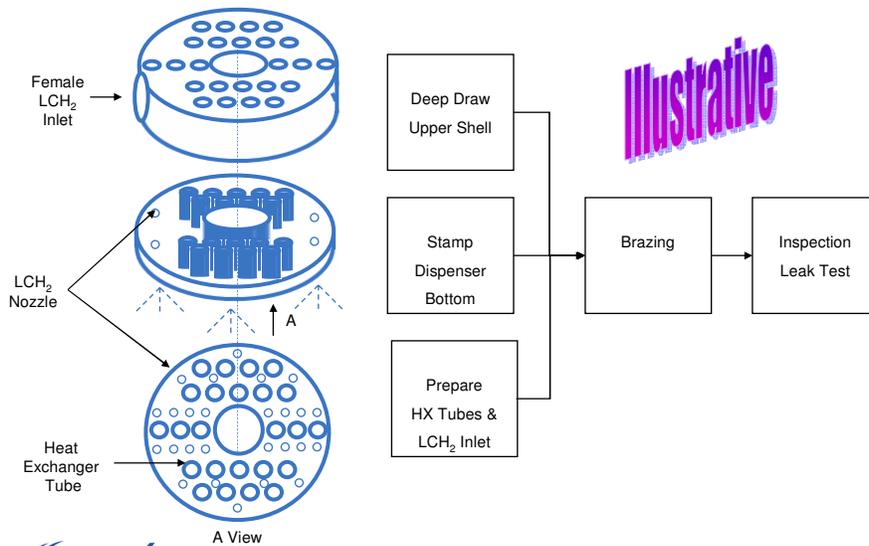
The reactor vessel is assumed to be made of Al-2219-T81 alloy which can be welded or extruded into a cylindrical shape. The inlets and outlets as well as headers are stamped into shape.



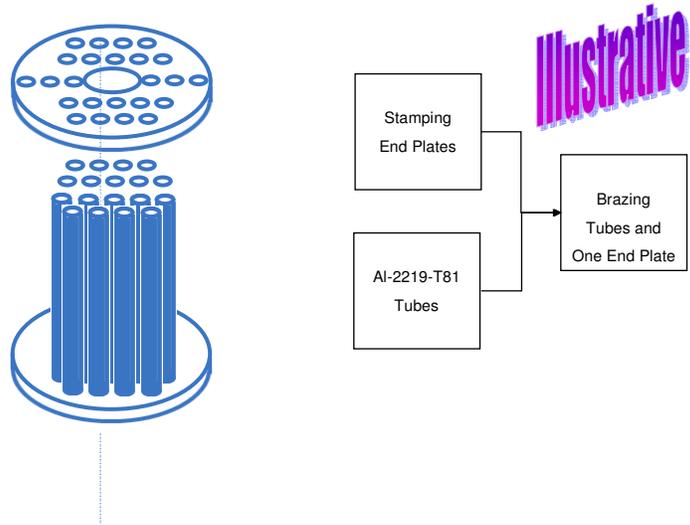
40-ppi Al-6101 foam (92% porosity) was picked as the catalyst substrate. The catalyst metals Pd and Li Aluminate are wash-coated onto the aluminum foam.



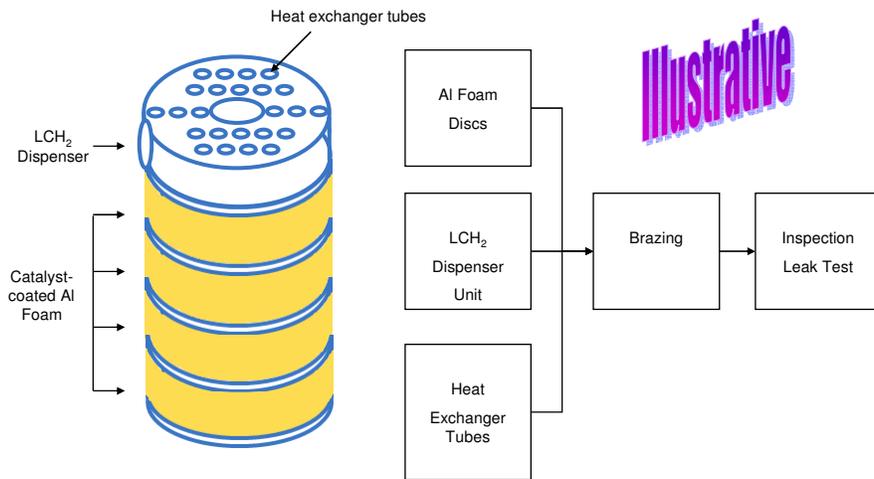
The LCH₂ dispenser was designed to evenly distribute the LCH₂ solution through the catalyst.



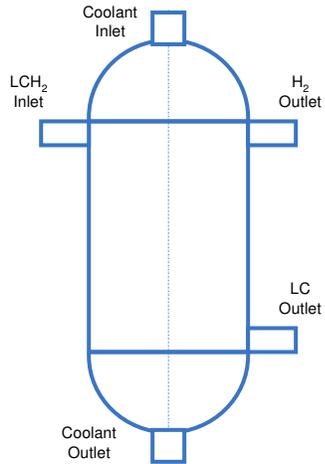
The heat exchanger tubes in the reactor are made of Al-2219-T81 alloy. They were assumed to be vacuum brazed.



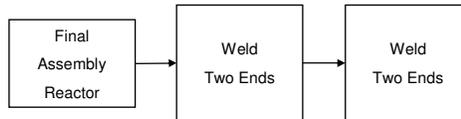
The LCH₂ solution dispenser and catalyst-coated Al foam discs were inserted into the tubular heat exchanger. A brazing process was used to firmly assemble them together.



The heat exchanger/LCH₂ solution dispenser/Al foam sub-assembly would be inserted into the reactor shell. The two reactor headers are assumed to be welded onto the cylindrical reactor shell.

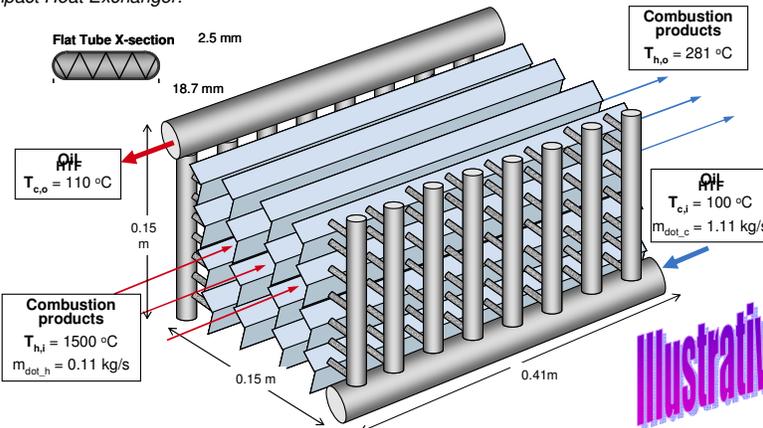


Illustrative



A non-catalytic H₂/air burner is assumed to supply the required heat of dehydrogenation by heating up the HTF¹ via a microchannel heat exchanger.

Compact Heat Exchanger:



Illustrative

Thermal integration with the stack was not considered at this time.



¹ HTF = Heat Transfer Fluid, assumed to be XCellTherm® 600

Appendix On-board Assessment *Weight, Volume, Cost Breakout*

On-board system detailed breakout – Weight (kg), Volume (L), Cost¹ (\$)

Component	System Weight (kg)	System Volume (L)	System Cost (\$)
LCH2/LC media	150.1	125.1	\$209.9
LCH2/LC Storage Tank	10.4	46.1	\$64.6
Dehydrogenation Reactor	7.4	19.1	\$1,075.2
H2 Cooler	0.8	0.3	\$30.3
Recuperator	5.0	1.6	\$60.1
Burner	10.1	8.0	\$546.4
H2 Separator/Coagulating filter	3.1	0.8	\$59.6
H2 Buffer Storage Tank	1.3	36.3	\$15.9
Pumps	60.0	40.0	\$600.0
Miscellaneous	7.9	5.5	\$250.8
Final Assly. & Inspection	0.0	0.0	\$17.0
Total	256	283	\$2,930

¹ Cost includes deflation by 9.27% to Year 2005 USD.



Appendix Onboard System *Detailed Bill of Materials (1)*

Onboard System BOM: Storage Tank & Dehydrogenation Reactor

Description	Qty	Material	Volume (cm3)	Weight (kg)	Cost (USD)
LCH2/LC Storage Tank	1		171,189	160.54	\$264.26
LCH2/LC Fuel Tank	1		171,189	0.00	\$0.00
Fuel Tank Body	1	HDPE	7,056	6.70	\$11.13
Solution Outlet Fitting	1	SS316	9	0.07	\$1.00
Solution Inlet Fitting	1	SS316	9	0.07	\$1.00
Solution Drain Fitting	1	SS316	9	0.07	\$1.00
Drain Plug	1	SS316	5	0.05	\$0.50
Mounting Bolt	6	Misc	5	0.05	\$0.10
Nut	6	Misc	5	0.05	\$0.05
Washer	6	Misc	5	0.05	\$0.05
Level Transmitter	1	Misc	5	0.05	\$5.00
Temperature Transmitter	1	Misc	5	0.05	\$4.00
LCH2 Solution	1	LCH2	125,103	150.12	\$209.91
Heater	2	Misc	10	0.10	\$8.00
Separator Assembly	1	SS316	388	3.10	\$22.52
Dehydrogenation Reactor	1		19,116	7.36	\$1,038.31
Reactor Vessel / Casing	1	Al-2219-T81 alloy	12,008	0.71	\$9.03
40-ppi Al-6101 foam	1	Al-6101 alloy	8,209	1.84	\$17.65
Li Aluminate	1	Li Aluminate	665	1.73	\$75.72
Pd Catalyst	1	Pd	6	0.07	\$915.77
LCH2 Solution Inlet Fitting	1	SS316	9	0.30	\$1.00
LC Solution Outlet Fitting	1	SS316	9	0.30	\$1.00
HX tubes	1	Al-2219-T81 alloy	414	1.18	\$14.94
HTF		XCEL THERM 600	1,134	0.96	\$2.17
Insulation		GF	7,108	0.27	\$1.01



Onboard System BOM: Support Systems

Description	Qty	Material	Volume (cm3)	Weight (kg)	Cost (USD)
H2 Cooler	1	Misc	326	0.85	\$6.13
Microchannel HX	1	SS316	326	0.85	\$6.13
Recuperator	1	SS316	1,592	4.96	\$36.00
Microchannel HX	1	SS316	1,592	4.96	\$36.00
Burner	1	Misc	7,953	10.12	\$510.26
Microchannel HX	1	Inconel	2,153	6.12	\$91.76
H2/air non-catalytic 82 kW burner	1	Misc	1,000	2.00	\$400.00
H2 Blower	1	Misc	4,800	2.00	\$18.50
H2 Separator/Coagulating filter			784	3.08	\$52.40
Coagulation filter	1	Misc	783	1.80	\$43.09
Separator	1	SS316	1	1.28	\$9.31
Flow Components	1	Misc	1,826	2.45	\$59.50
3-Way Valve	1	Misc	262	0.45	\$40.00
Piping System	1	SS316	1,564	0.00	\$15.00
Fitting	10	SS316	0	2.00	\$4.50
H2 Buffer Storage Tank	1	Misc	36,271	1.33	\$15.87
Buffer Storage Tank Body	1	Al-2219-T81 alloy	36,229	0.96	\$12.22
Outlet Fitting	1	SS316	9	0.07	\$1.00
Inlet Fitting	1	SS316	9	0.07	\$1.00
Drain Fitting	1	SS316	9	0.07	\$1.00
Drain Plug	1	SS316	5	0.05	\$0.50
Mounting Bolt	6	Misc	5	0.05	\$0.10
Nut	6	Misc	5	0.05	\$0.05



Onboard System BOM: Support Systems

Description	Qty	Material	Volume (cm3)	Weight (kg)	Cost (USD)
Pumps	1		40,000	60.00	\$600.00
HTF pressure head: 1 bar	1		30,000	40.00	\$400.00
LCH2 pressure head: 8 bar	1		10,000	20.00	\$200.00
Fill port	1	Misc	524	0.91	\$28.00
Inlet Quick Connector	1	Misc	262	0.45	\$14.00
Outlet Quick Connector	1	Misc	262	0.45	\$14.00
Valves	1	Misc	1,311	2.50	\$77.00
Solenoid Valve	1	Misc	262	0.50	\$25.00
Ball Valve	1	Misc	262	0.50	\$13.00
Check Valve	1	Misc	262	0.50	\$14.00
Pressure Relief Device	1	Misc	262	0.50	\$5.00
Pressure Relief Valve	1	Misc	262	0.50	\$20.00
Sensors	1	Misc			\$30.00
Temperature Transducer	1	Misc			\$10.00
Pressure Transducer	1	Misc			\$20.00
Pipe & Fitting	1	Misc	1,042	1.00	\$12.25
Piping	1	SS316	1,042	0.00	\$10.00
Fitting	5	SS316		1.00	\$2.25
Primary Pressure Regulator	1		787	1	\$44.00

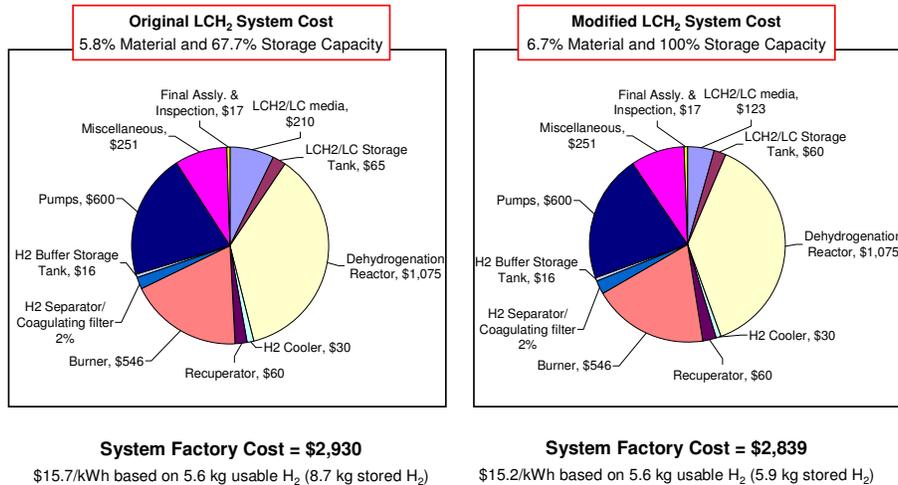


We conducted a “rough estimate” analysis of an autothermal liquid carrier by making simple modifications to our existing liquid hydrocarbon (LCH₂) model.

- ◆ We modified the original (i.e., N-ethylcarbazole) LCH₂ material assumptions based on input from APCI assuming a hypothetical autothermal carrier
 - Original System: 5.8% material capacity and 67.7% storage capacity (i.e., 32.3% of the stored hydrogen has to be burned to generate heat for dehydrogenation)
 - Modified System: 6.7% material capacity and 100% storage capacity (i.e., assume no hydrogen has to be burned)
- ◆ We maintained the 95% dehydrogenation reactor conversion efficiency
- ◆ The modified system would require an oxidation reactor, but would not require a HEX burner
 - The oxidation reactor would use a V₂O₅ catalyst
 - We roughly assumed there would be no net change in cost, weight, and volume from swapping the HEX burner with the oxidation reactor
- ◆ All other BOP components were assumed to be the same



Although the system weight and volume are reduced by 25%, the improved material and storage capacities reduces the system cost by less than 5%.



Note: a trade-off study was not performed on the size/cost of the pumps versus size/cost of the reactor sub-system.



Our “rough estimate” for an autothermal liquid carrier shows a 25% reduction in system weight and volume is possible, but cost savings are minimal.

- ◆ With improved material (5.8% → 6.7%) and storage (67.7% → 100%) capacities, the modified on-board system shows significant weight and volume reductions

However, additional material and BOP improvements would be required to meet the 2010 DOE weight and volume targets

Modified LCH ₂ System Versus DOE Targets	Weight (kg)	Volume (L)
LCH ₂ Material Only	88	73
-including tank	96	99
2010 DOE target for 5.6 kg usable H ₂	124	200
Net available for BOP	28	101
Current estimate for BOP	95	112

- ◆ Improvements to the material and storage capacities do little to decrease the system cost because the dehydrogenation reactor and BOP account for over 90% of the system cost
 The dehydrogenation reactor accounts for ~40% of the system cost (Pd catalyst accounts for 85% of the reactor cost)
 The system pumps and HEX burner/oxidation reactor account for another ~40% of the system cost



Vehicle cost estimates assume that all FCV components, except the fuel storage system, meet DOE’s cost goals for 2015 and beyond¹.

Vehicle Cost Assumptions ¹ (\$/vehicle)	Gasoline ICEV	cH ₂ FCV ²	SBH FCV	LCH ₂ FCV	Basis/Comment
Glider	\$7,148	\$7,148	\$7,148	\$7,148	Group of components (e.g., body, chassis, suspension) that will not undergo radical change
IC Engine/Fuel Cell Subsystem	\$2,107	\$2,549	\$2,549	\$2,549	Includes engine cooling radiator
Transmission, Traction Motor, PE	\$1,085	\$1,264	\$1,264	\$1,264	Includes electronics cooling radiator
Exhaust, Accessories	\$500	\$500	\$500	\$500	Assumes exhaust and accessories are \$250 each
Energy Storage	\$110	\$1,755	\$1,755	\$1,755	Includes battery hardware, acc battery and energy storage cooling radiator
Fuel Storage	\$51	\$5,548	\$1,632	\$5,026	H ₂ storage cost from On-board Cost Assessment
Manufacturing/ Assembly Markup	\$5,500	\$7,045	\$7,045	\$7,045	OEM manufacturing cost is marked up by a factor of 1.5 and a dealer mark-up of 1.16
Dealer Markup	\$2,690	\$3,445	\$3,445	\$3,445	
Total Retail Price	\$19,191	\$29,222	\$25,328	\$28,703	

¹ Source: DOE, "Effects of a Transition to a Hydrogen Economy on Employment in the United States", Report to Congress, July 2008. All costs, except for the FCV Fuel Storage costs, are based on estimates for the Mid-sized Passenger Car case. See report for details.

² cH₂ FCV option assumes 6,250 psi dispensing and 5,000 psi on-board storage system.



When the whole vehicle, including the powertrain purchased price, is included, the conventional gasoline ICEV will likely be noticeably cheaper than the FCV options.

