

Hydrogen Carriers for Bulk Storage and Transport of Hydrogen

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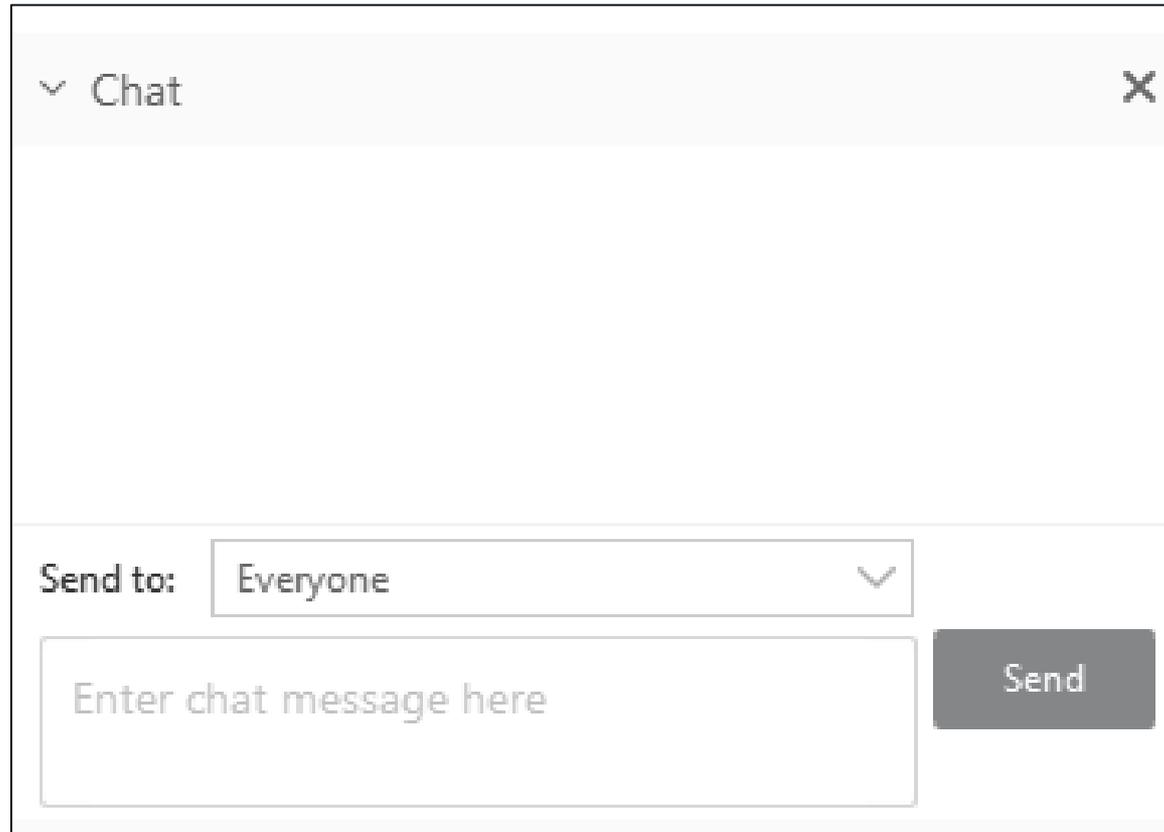
Fuel Cell Technologies Office Webinar

December 6, 2018



Question and Answer

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Outline

- Hydrogen carriers
 - concepts & definitions
 - objectives & goals
- ANL - base lining carriers
 - one-way
 - round trip
 - without H₂
- HyMARC
 - objectives
 - examples
 - identify gaps in knowledge
 - develop scientific tools
 - foundational research to enable rational design
 - summary
- Questions and Answers

Hydrogen Carriers - concepts

- As part of the H2@Scale concept, bulk storage and transport of hydrogen is of critical importance. Storage needs may range from daily to seasonal in duration, and transport distances may exceed hundreds of kilometers.
- The hydrogen carriers research effort is seeking new concepts and materials that have potential to provide advantages over conventional compressed and liquefied hydrogen for bulk storage and transport.

Hydrogen Carriers - definitions

- Hydrogen carriers are hydrogen-rich liquid or solid phase materials from which hydrogen can be liberated on-demand.
- Ideal hydrogen carriers have high hydrogen densities at low pressure and near ambient temperature.
- The formation of the carrier and release of hydrogen from the carrier should be as energy efficient as possible to minimize the energy penalty associated with the use of the hydrogen carrier to store and transport hydrogen.

Hydrogen Carriers: Objectives and Goals

Objectives:

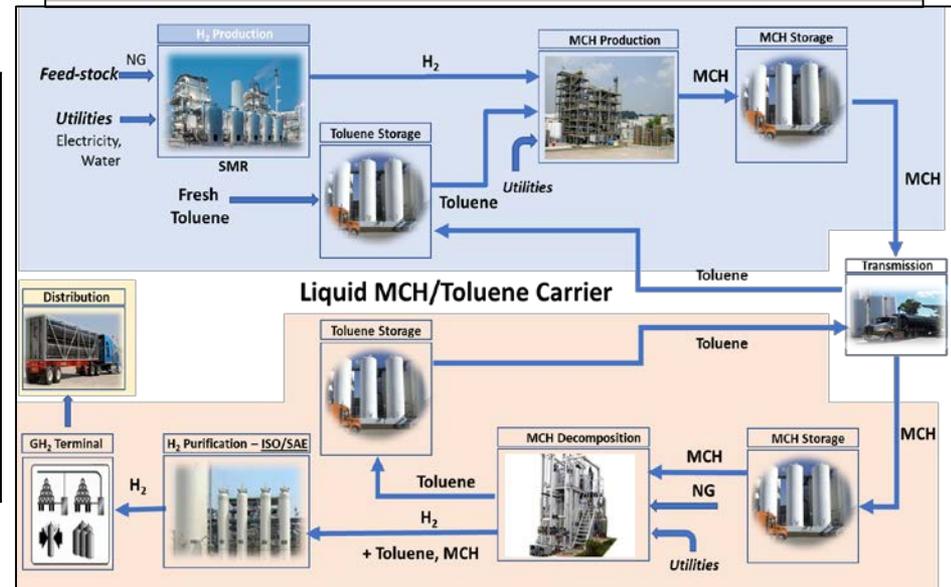
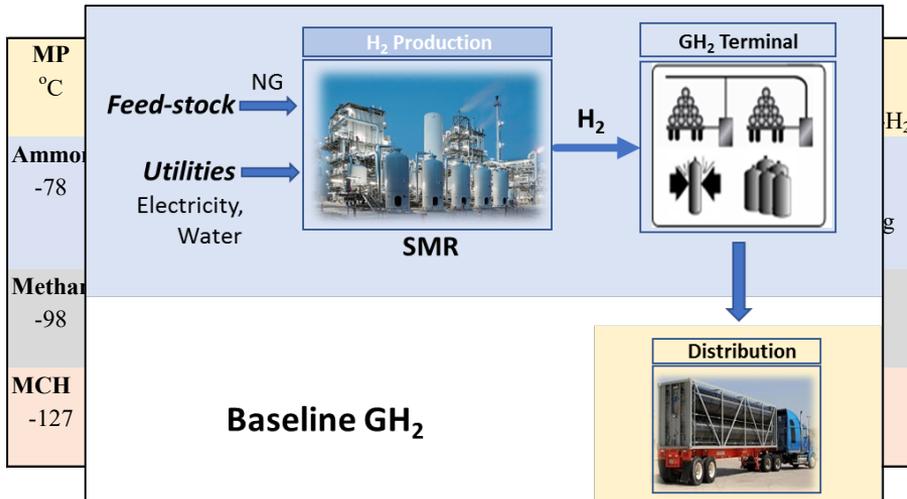
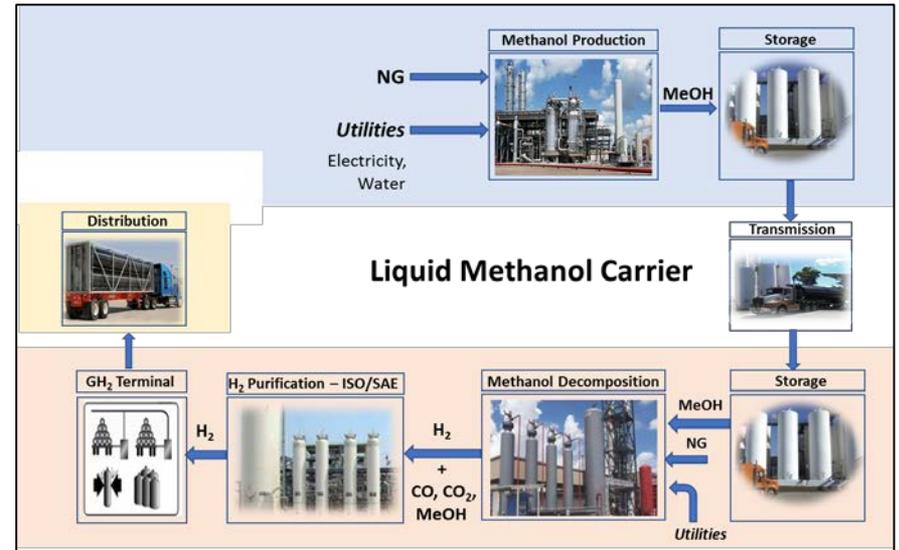
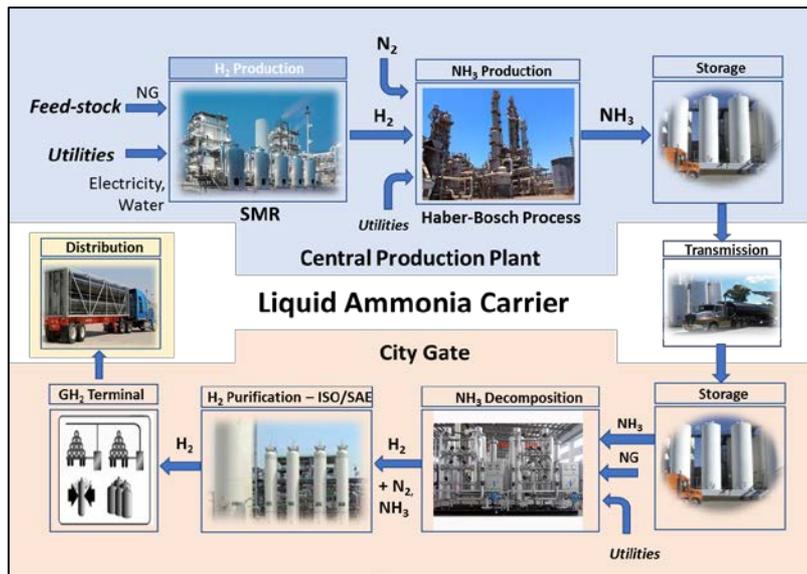
To investigate pathways that will lead to the optimization of hydrogen carriers and to realize the most efficient, safe and economical approaches to:

- (i) transport H₂ from a production facility to the city gate
- (ii) facilitate geographically agnostic H₂ storage.

Goals:

- (i) Development of novel hydrogen carriers (new concepts in liquids and solids).
- (ii) Development of alternate approaches to prepare and release hydrogen from hydrogen carriers.

Hydrogen Carrier Pathways – Small Plants



H₂ Carrier Study: Tools and Parameters

Financial Assumptions	City H ₂ annual average daily use = 50,000 kg-H ₂ /day; Operating capacity factor = 90%; Internal rate of return (IRR) = 10%; Depreciation (MACRS)=20 yrs; Plant life=40 yrs; Construction period=3 yrs			
	NG	Electricity	Water	Toluene
Feedstock and Utilities	6.00 \$/MBtu	5.74 ¢/kWh	0.54 ¢/gal	0.768 \$/kg
H₂ Production by SMR, /kg-H₂	0.156 MBtu	0.569 kWh	3.35 gal	
Hydrogenation				
Ammonia	Haber-Bosch process and cryogenic air separation unit; 370 tpd ;			
Methanol	Steam reforming of CH ₄ /CO ₂ to synthesis gas (H ₂ -CO)/(CO+CO ₂)=2.05; Conversion to methanol; methanol purification; 350 tpd ;			
Toluene	>99% conversion of toluene to MCH over non-PGM catalyst, 890 tpd MCH			
Dehydrogenation				
Ammonia	Catalytic decomposition of ammonia at high temperatures; H ₂ purification by PSA at 20 atm (85% recovery)			
Methanol	Catalytic steam reforming, H ₂ purification by PSA at 20 atm (85% recovery)			
MCH	95% conversion of MCH to toluene; 2.5% make-up toluene H ₂ purification by PSA at 20 atm (90% recovery)			
Storage	LHC: 30 days at central production plant, 2 days at dehydrogenation plant H ₂ : 10 days geologic storage for plant outages			
Transmission	HDSAM v 3.1, Truck Liquid Delivery			
	Ammonia	Methanol	MCH	GH₂
Payload (kg)	22,500	22,500	22,500	1,042
Volume (m³)	37	28	29	36
H₂ (kg)	3398	3465	1112	1042
GH₂ Terminal	HDSAM v 3.1, Compressed Gas H ₂ Terminal			
H₂ Distribution	400 kg/day H ₂ dispensing rate at refueling station			

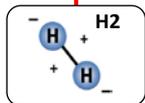
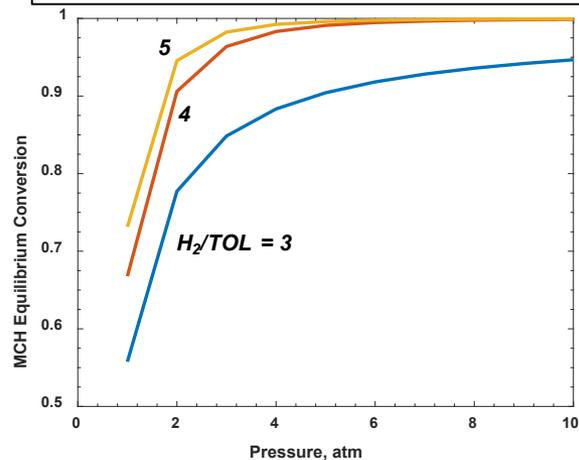
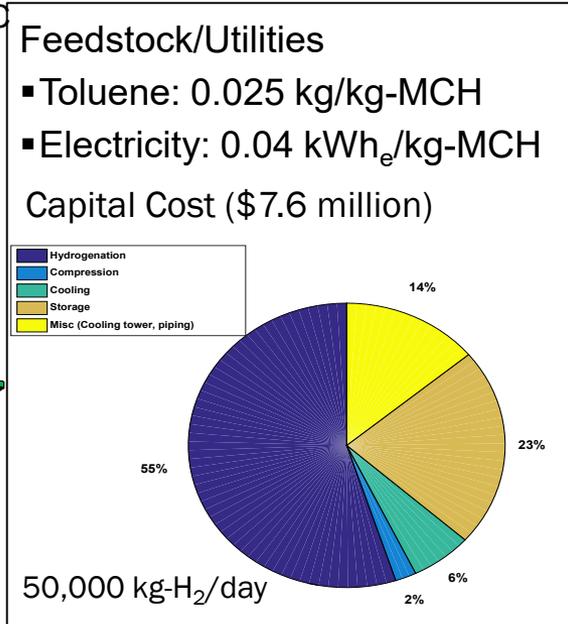
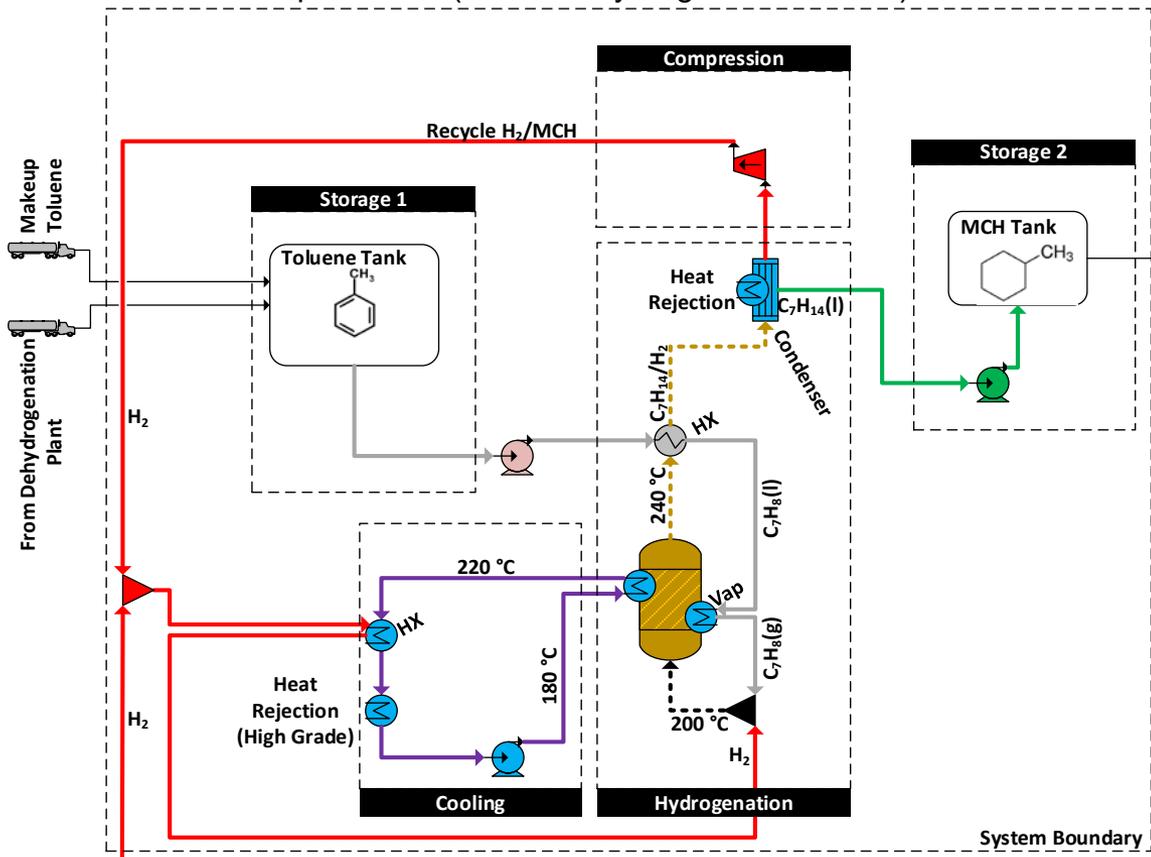
Rath, L. (2011). Cost and performance baseline for fossil energy plants: Coal to synthetic natural gas and ammonia. DOE/NETL-2010/1402.

Tan, E. et al. (2015). Process design and economics for the conversion of lignocellulosic biomass to hydrocarbons via indirect liquefaction. NREL/TP-5100-62402.

Campbell, C. (2014). Hydrogen storage and fuel processing strategies. PhD Thesis, Newcastle University

Hydrogenation of Toluene

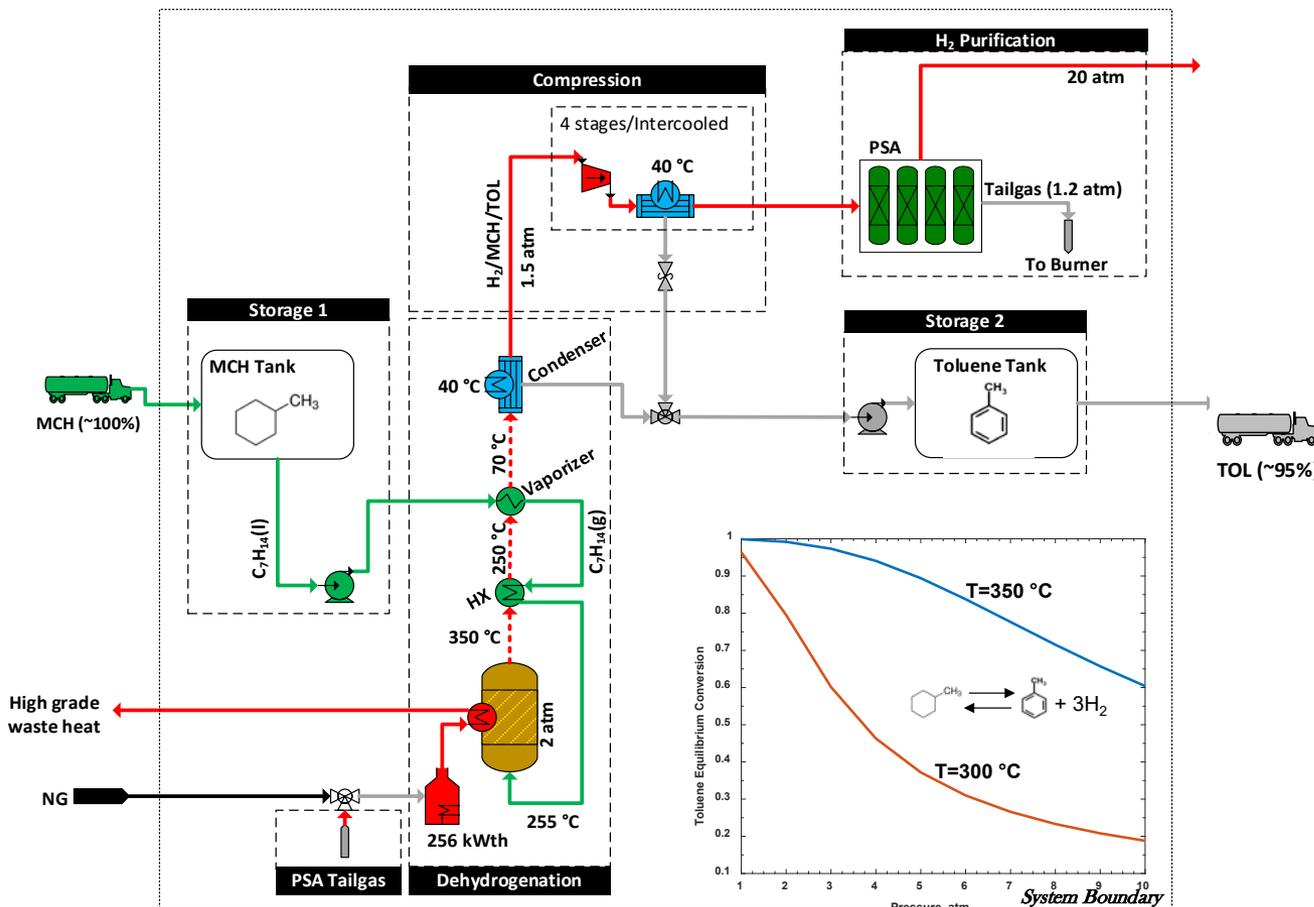
- Reactor operated at 240°C and 10 atm for nearly complete conversion. Conversion is kinetically limited. No side-reactions are considered.
- Allowing for 0.5 atm pressure drop, 98.5% of MCH condenses at 9.5 atm and 45°C
- Excess H₂ and MCH vapor recycled (H₂/Toluene ratio = 4/1)
- Toluene makeup = 2.52% (due to dehydrogenation losses)



Lindfors, L.P. et. al. (1993). Kinetics of Toluene Hydrogenation on Ni/Al₂O₃ Catalyst. Chem. Eng. Sci., 48, 3813

Dehydrogenation of Methylcyclohexane

- Reactor operated at 350°C and 2 atm. Conversion is 95% with 99.9% toluene selectivity. No side-reactions considered.
- Allowing for 0.5 atm pressure, 80% of toluene condenses at 1.5 atm and 40°C
- Remaining toluene condenses during the compression cycle (4 stages)
- H₂ separation by PSA at 20 atm, 90% recovery (ISO/SAE H₂ quality)



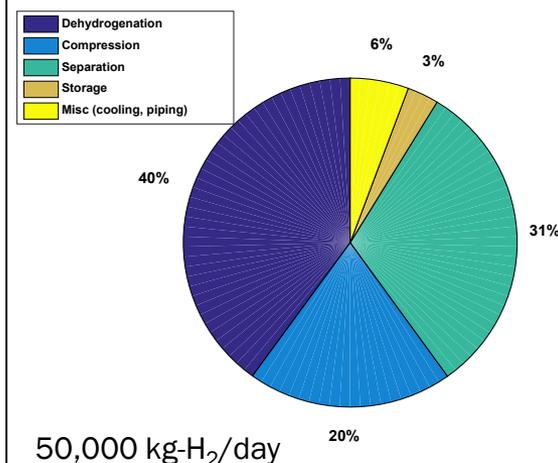
Losses

- Toluene+MCH: 2.52%
- Hydrogen: 11%
- Heat: 0.36 kWh_{th}/kWh_{th}-H₂

Feedstock/Utilities

- NG: 0.22 kWh_{th}/kWh_{th}-H₂
- Electricity: 0.04 kWh_e/kWh_{th}-H₂

Capital Cost (\$26.2 million)

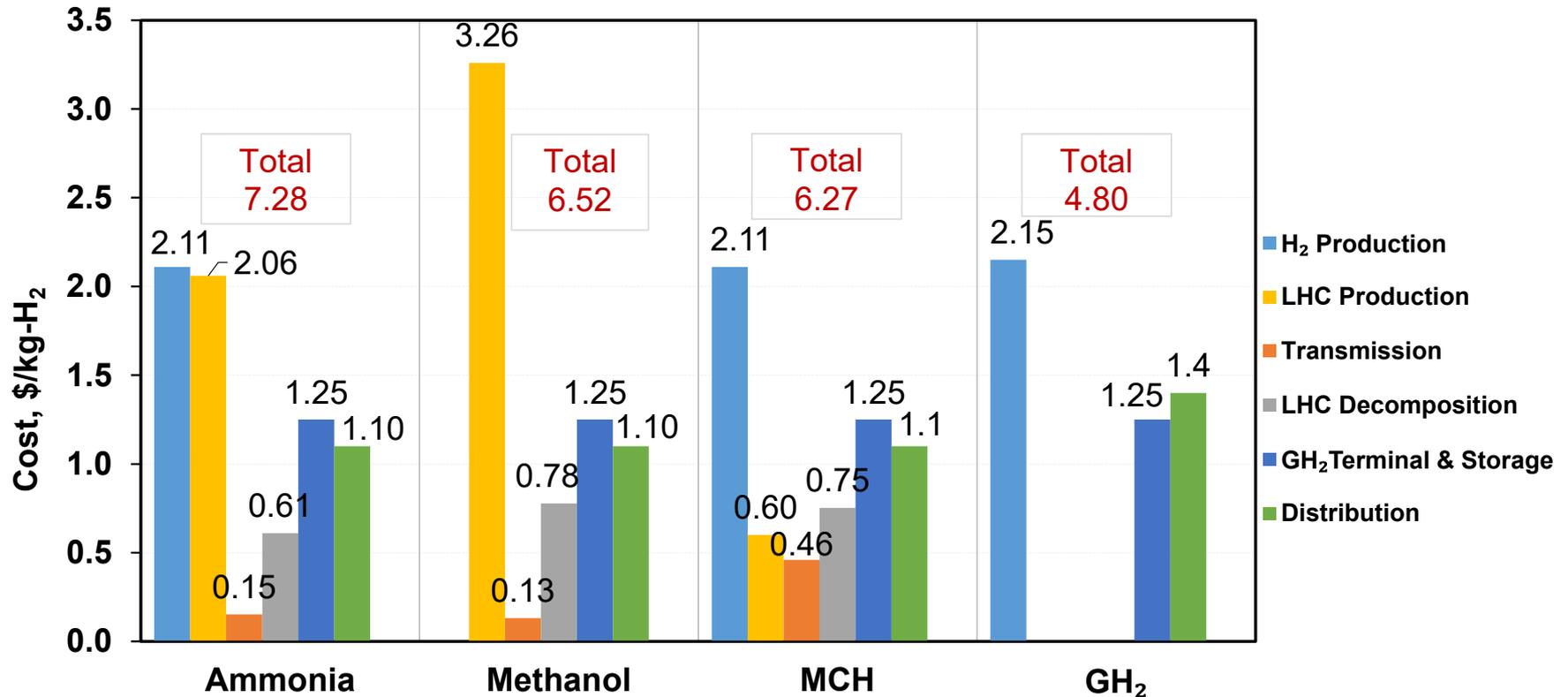


Okada, Y. et. al. (2006). Development of Dehydrogenation Catalyst for Hydrogen Generation in Organic Chemical Hydride Method. Int. J. Hydrogen Energy, 31, 1348.

Levelized Cost of H₂ Distributed to Stations (50,000 kg-H₂/d)

Liquid carrier options incur incremental costs of 1.44-2.23 \$/kg-H₂ (33 - 47%)

- LHC production costs (\$/kg-H₂): ammonia (2.06) > methanol (1.11) > MCH (0.60)
- LHC decomposition costs (\$/kg-H₂): methanol (0.78) \approx MCH (0.75) > ammonia (0.61)
- Transmission & distribution (\$/kg-H₂): MCH (1.56) > GH₂ (1.40) > ammonia \approx methanol (1.24)



DOE record: 13-16 \$/kg-H₂ dispensed for very low production volume

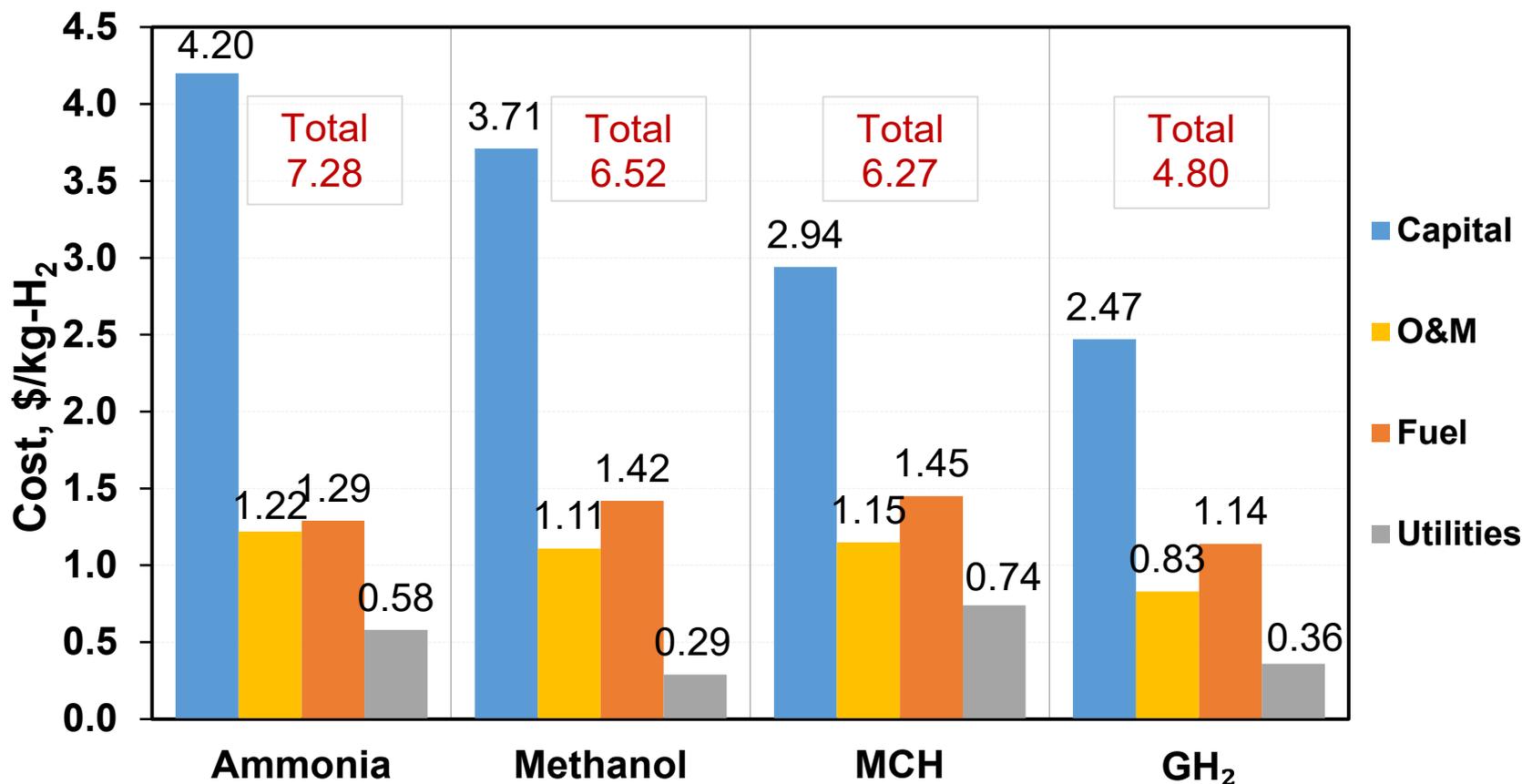
- All four scenarios include 10-d (500,000 kg-H₂) geologic storage which is not available at all sites. Future liquid carrier scenarios will consider options to circumvent geologic storage.

Baseline GH₂ scenario: Central SMR, H₂ compression & storage; truck transmission; GH₂ terminal

Breakdown of Levelized Cost of H₂ Distributed to Stations

Sources of increases in levelized costs compared to GH₂ scenario

- Ammonia: 70% capital; remaining equally between O&M, fuel and utilities
- Methanol: 73% capital; comparable O&M and fuel; small for utilities
- MCH: 32% capital; remaining equally between O&M, fuel and utilities

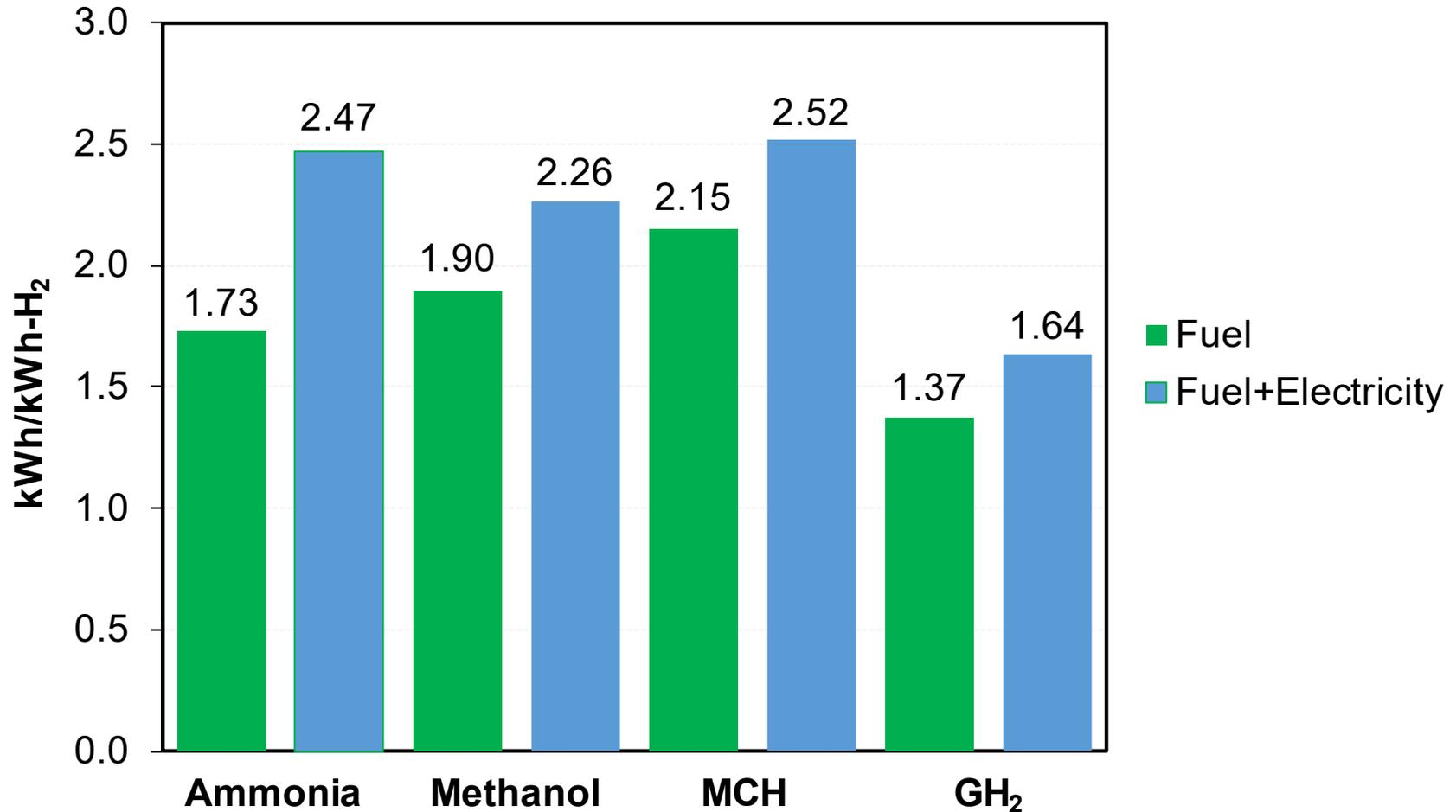


For cost breakdown, fuel refers to natural gas (NG); utilities include electricity, water & make-up toluene

Energy Efficiency

Endothermic dehydrogenation step including PSA at city gate is the largest contributor to the increase in energy consumption

- Total energy includes fuel plus electrical energy, assuming 33% efficiency in generating electrical power
- Energy consumption (kWh/kWh-H₂): MCH \cong ammonia (2.52) > methanol (2.26) > GH₂ (1.64)

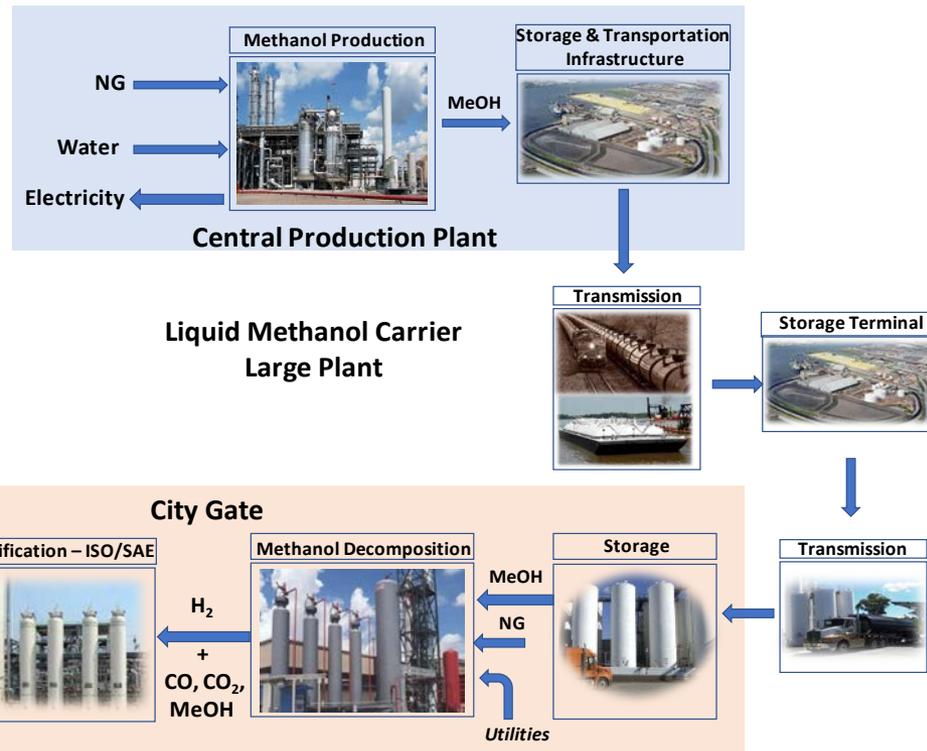
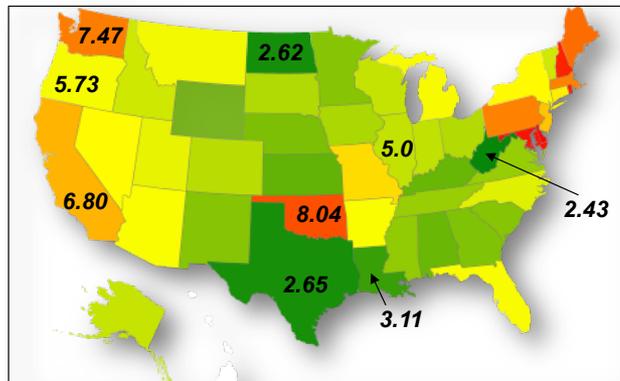
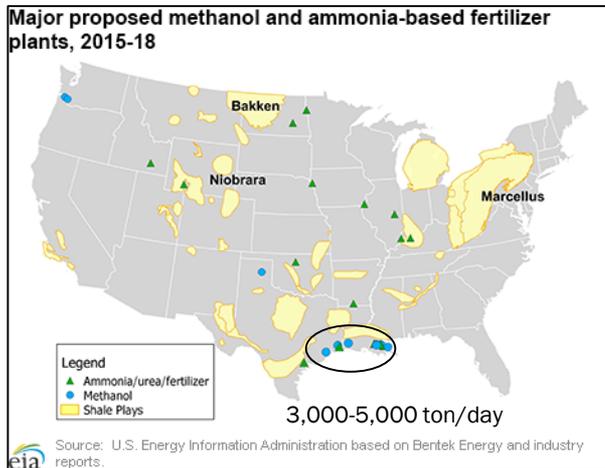


For calculating energy efficiency, make-up toluene is included with fuel

Hydrogen Carrier Pathways – Large Plants

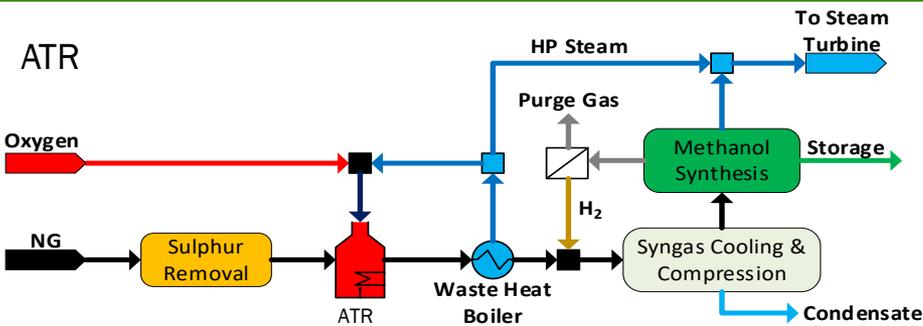
Scenario: Large hydrogenation plant for economy of scale

- Methanol Production: 10,000 tons per day; syngas production by ATR
- Location: Gulf of Mexico; low NG price outlook; diverse sources; plethora of critical energy infrastructure
- Transmission: Unit train (once a week) to storage terminal in California (3250 km); local transmission by truck (150 km) to city gate



EIA: Industrial NG \$/MBtu (2017 average)

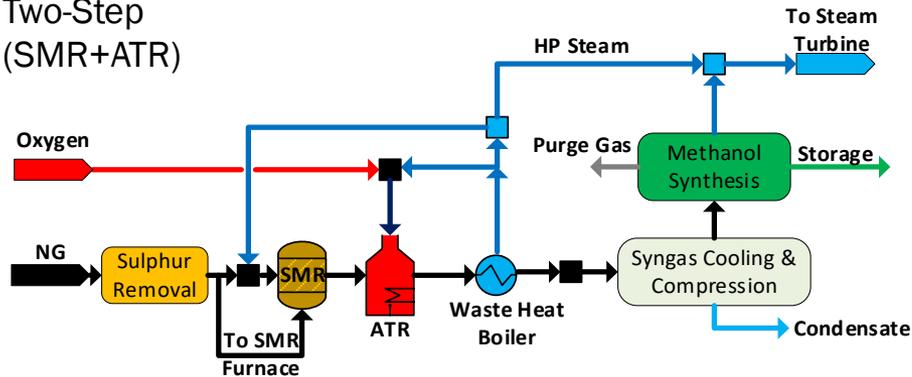
Scaling of Methanol Plants



5,000-10,000 tons/day scale

- $O_2/C=0.6$, $H_2O/C=0.6$
- M (reformer): 1.84
- 1-2 ASU's in parallel
- 2-4 BWR's in parallel
- Electricity demand: $0.4 \text{ kWh}_e/\text{kg-MeOH}$
- Steam Turbine: $0.5 \text{ kWh}_e/\text{kg-MeOH}$

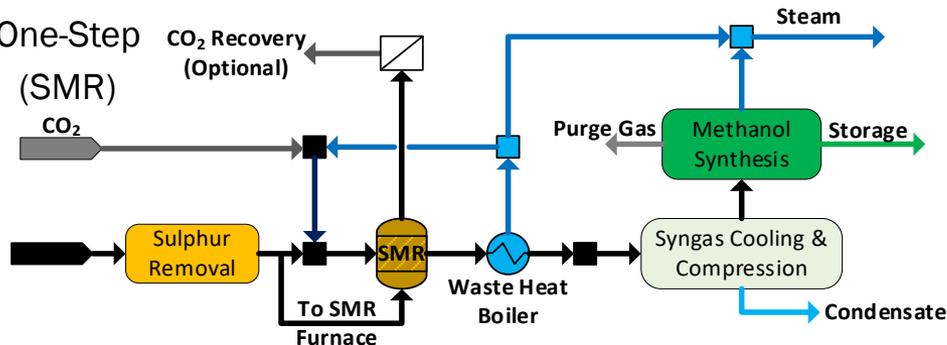
Two-Step
(SMR+ATR)



2,000-4,000 tons/day scale

- $O_2/C=0.48$, $H_2O/C=1.8$
- M (reformer): 2.05
- 1 ASU
- 1-2 BWR's in parallel
- Electricity demand: $0.33 \text{ kWh}_e/\text{kg-MeOH}$
- Steam Turbine: $0.48 \text{ kWh}_e/\text{kg-MeOH}$

One-Step
(SMR)



<1,700 tons/day scale

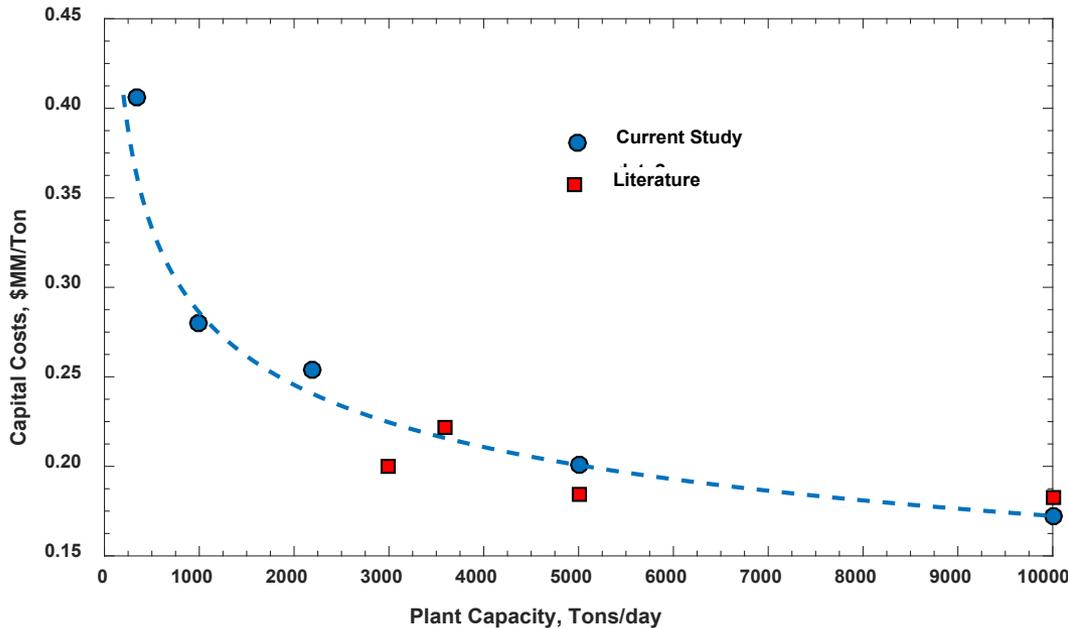
- $CO_2/C=0.3$, $H_2O/C=3.5$
- M (reformer): 2.05
- 1 BWR or Quench reactor
- Electricity demand: $0.14 \text{ kWh}_e/\text{kg-MeOH}$
- Steam Turbine: Not economical

BWR = Boiling Water Reactor ASU= Air Separation Unit

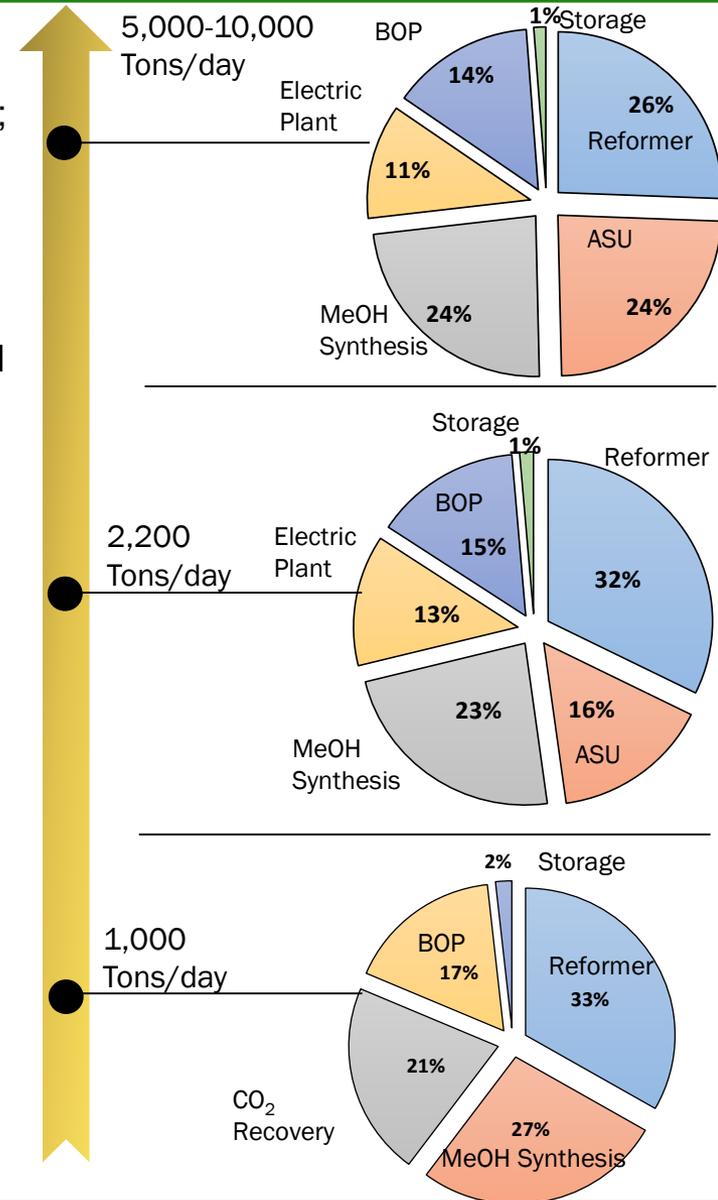
Syngas stoichiometric molar ratio $(M) = (H_2 - CO_2)/(CO + CO_2)$

Scaling of Methanol Plants – Total Capital Costs

- Capital costs minimized depending on scale: ATR for capacities >3000 tons/day; two-stage reforming at capacities >1800 tons/day; SMR below 1500 tons/day
- Low cost CO₂ from other sources assumed unavailable
- Reformer, ASU and/or CO₂ removal account for ~50% of total capital costs
- Storage (30 days) of methanol accounts for a small fraction of total capital costs



Literature: ADI Analytics, Sojitz Corp., Foster & Wheeler

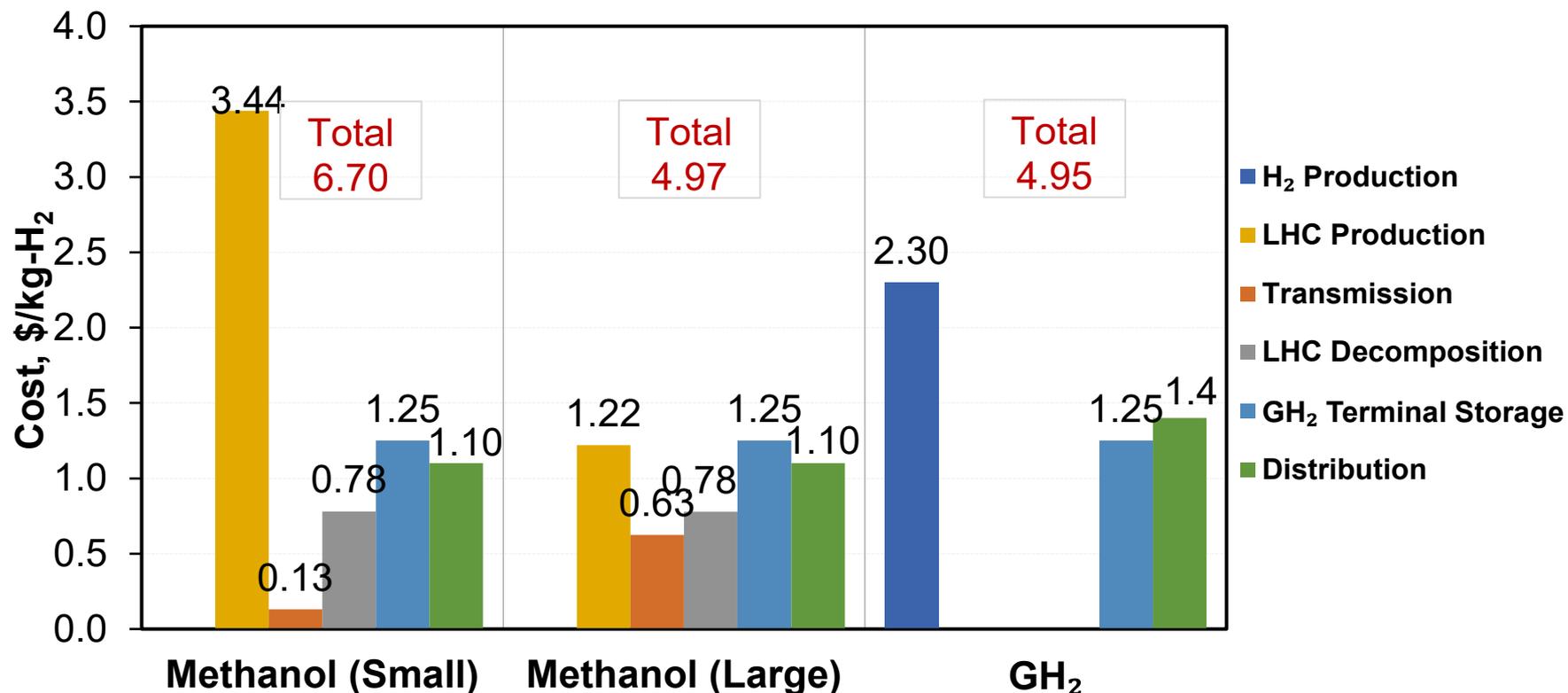


Levelized Cost of H₂ Distributed to Stations (50,000 kg-H₂/d)

Liquid carrier can be competitive with the baseline GH₂ scenario.

Large (10,000 tpd) vs. small (350 tpd) methanol production plants

- 0.92 \$/kg-H₂ lower LHC production capital cost
- 0.88 \$/kg-H₂ lower feedstock cost (\$2.65/MBtu vs. \$6.80/MBtu NG cost)



Next Steps

1. Calibrate initial results
 - Field data for ammonia and methanol plants of different capacities
 - MCH production and dehydrogenation
2. Analyze scenarios that favor hydrogen carriers
 - Case studies with different demand and supply scenarios
3. Investigate carriers that are particularly suitable for renewable hydrogen production and energy storage
4. Conduct reverse engineering to determine desirable properties of liquid carriers
5. Coordinate with HyMARC consortium to analyze emerging materials
 - Formic acid (H_2CO_2), solid formates (M^+CO_2^-), aqueous mixtures of $\text{PhOH}/\text{M}^+\text{PhO}^-$)

HyMARC Objectives in Hydrogen Carriers

- Defining the important properties of hydrogen storage materials beyond onboard vehicular.
- Determining the advantages and limitations for materials and approaches to hydrogen carriers for transport and long term storage.
- Investigating novel approaches to release or 'adsorb' hydrogen onto carriers.
- Characterizing novel approaches to preparing hydrogen carriers that do not require a discreet step of making gaseous hydrogen.
- Comparing approaches that can be used to prevent phase changes
- Optimizing the balance of catalyst properties: Stability (TON), rates (TOF), \$'s, selectivity, heterolytic vs homolytic hydrogen activation.
- Validating concepts for rational design.

Leveraging capability and expertise in HyMARC consortium for accelerating progress in hydrogen carriers

Examples

Electrocatalysis. Approaches to produce hydrogen carriers without direct production of hydrogen .

Investigation of approaches for formation of hydrogen carriers that do not utilize molecular H_2 as a reagent, for example, electrochemical approaches to produce hydrogen carriers.

- N_2 : to (a) ammonia and (b) hydrazine hydrate
- CO_2 to: (a) HCO_2H , (b) HCO_2^- and/or (c) $MeOH$
- C_6H_5OH to $C_6H_{11}OH$

Examples Cont.

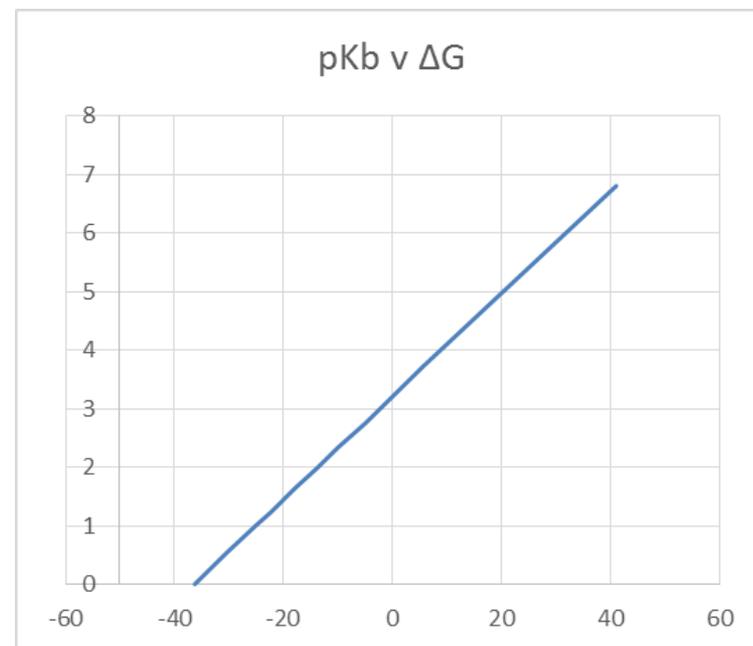
Aqueous organic carriers

Aqueous alcohol mixtures provide opportunities for enhancing the properties of hydrogen carriers. The first equivalent of H_2 is released from the alcohol forming an aldehyde. The subsequent reaction of the aldehyde with H_2O to form the vicinal diol, and subsequent dehydrogenation, provides a 2nd equivalent of H_2 essentially from the water.

- $RCH_2OH \rightleftharpoons RCHO + H_2$
- $RCHO + H_2O \rightleftharpoons RCH(OH)_2$
- $RCH(OH)_2 \rightleftharpoons RCOOH + H_2$

How can you vary the strength of an exogenous base, $B:$, to tune the overall thermodynamics of the reaction?

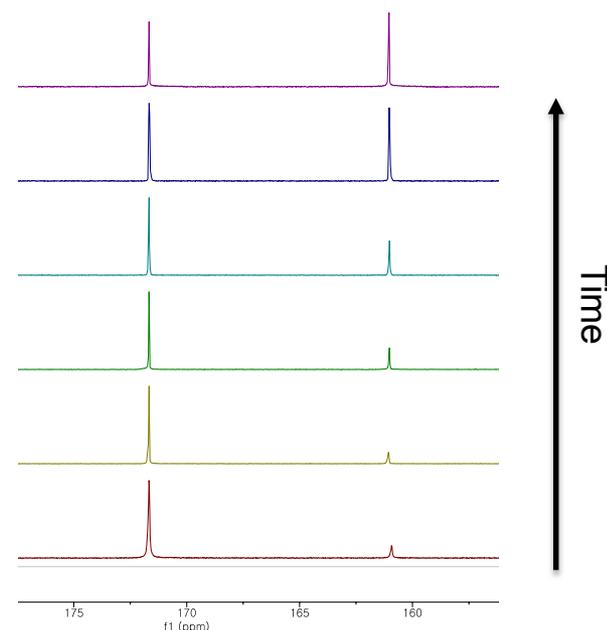
- $RCOOH + B: \rightleftharpoons [RCO^{2-}][BH^+]$



Examples Cont.

Formate/Bicarbonate cycle

The reaction is reversible under mild conditions. Given the stability, low cost, and benign nature of bicarbonate and formate this reversible reaction could be optimal for large scale bulk storage of hydrogen. What are catalysts that are optimized for OH and CH bond activation (one H comes from HO-H and the other H from H-CO₂⁻ .)



Solution phase ¹³C NMR showing approach to equilibrium at 20 °C

Examples Cont.

Formic acid provides 'chemical compression'

Hydrogen release from formic acid is entropy controlled. ΔG is negative and ΔH is positive. Can generate 1000 bar pressure.

- $\text{H}_2\text{CO}_2 \rightleftharpoons \text{H}_2 + \text{CO}_2$
- What are approaches for separation of CO_2 and H_2 ?
- Controlling selectivity (CO_2 vs CO)?
- What are best approaches to make Formic Acid?



Addressing Gaps in Knowledge

Chemical compression. Develop high pressure measurement capabilities for liquid carriers to validate the ability to generate high pressure H₂ from catalytic release of H₂ from solutions of formic acid to test catalyst.

- What is the best design for a test reactor to measure high pressure H₂ and stability of catalyst under acidic conditions?
- Can single site heterogeneous, e.g., metal ions in MOFs or molecular catalysts activate H₂ and the unsaturated carrier simultaneously?
- Are nanoparticles the best approach to catalyze H₂ activation?
- How can catalysts be stabilized under high reducing conditions, e.g., high pressure H₂, concentrated carriers, acidic conditions, e.g., >10 M formic acid?
- Do we need a metal catalyst that is meta-stable as a hydride during hydrogenation and destabilized during hydrogen release or can one catalyst perform both release and uptake?
- Do we need to use a different catalyst for uptake and for release?

Liquid phase PCT (modeling isotherms from thermodynamics and measuring PCT curves to obtain thermodynamic parameters in liquid phase carriers.

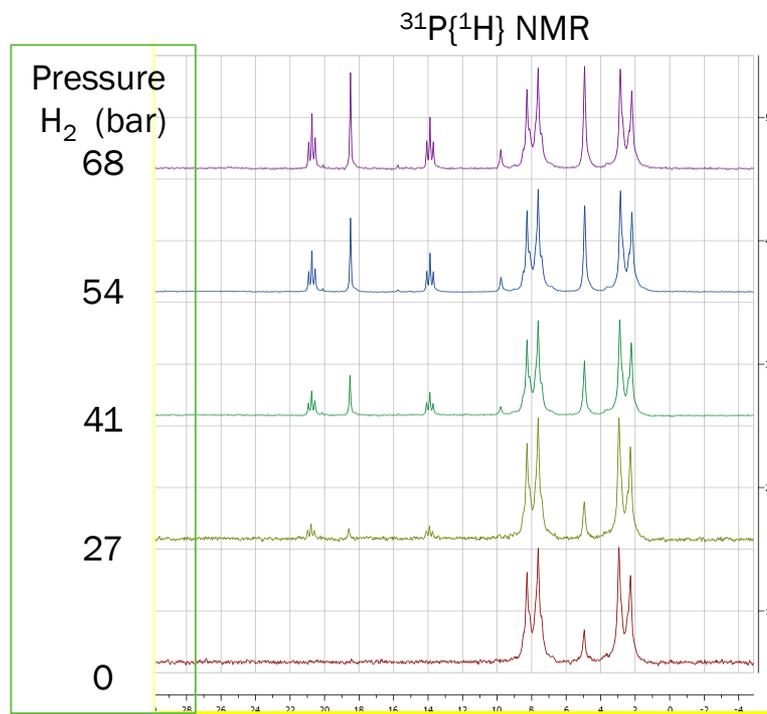
- Can PCT be adapted for measuring van't Hoff curves for liquid carriers?
- What are the shapes of PCT curves for liquids as a function of temperature and pressure? Can we use fuel blends to lower melting point of hydride materials to maintain a low vapor pressure of carrier?
- Can we use fuel blends to lower melting point of hydride materials to maintain a low vapor pressure of carrier?

Research Tools

Variable P, T liquid NMR to measure K_{eq} in liquid carriers

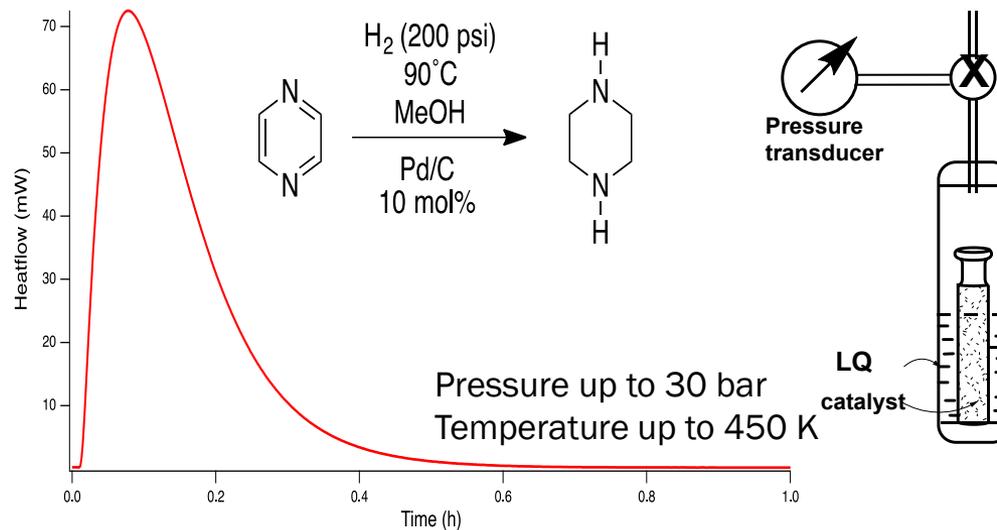


- ▶ Machined in-house, bottom is virgin PEEK, top is carbon-filled PEEK
- ▶ pressure tested to 1,000 bar
- ▶ temperature range : 170 to 370 K



Research Tools

Reaction calorimetry to measure kinetics and thermodynamics of H₂ uptake in hydrogen carriers



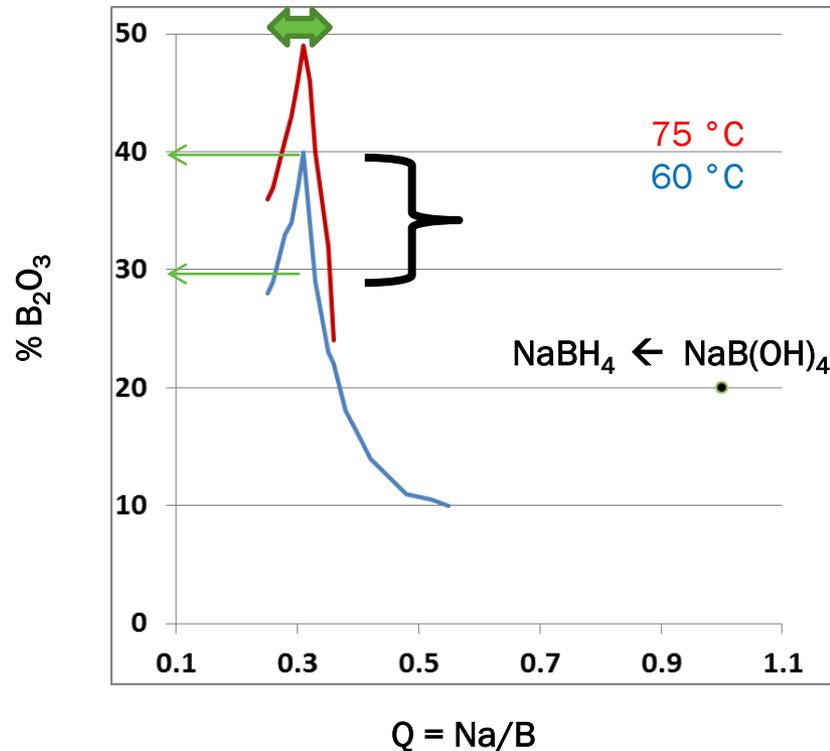
$$\Delta H_{exp} = -64(4) \text{ kJ/mol H}_2 \text{ (this work)}$$

$$\Delta H_{calc} = -56 \text{ to } -63 \text{ kJ/mol H}_2$$

Note heat is measured as function of time so we can compare rates of different catalysts

Rational Design

Maintaining a single phase (liquid)



Steep slope for solubility as function of Q range 0.25 ($Na/4B$) to 0.33 ($Na/3B$).

What families of 'borohydrides' have Q in this range?

$Na[B_4H_9]$ & $Na[B_3H_8]$

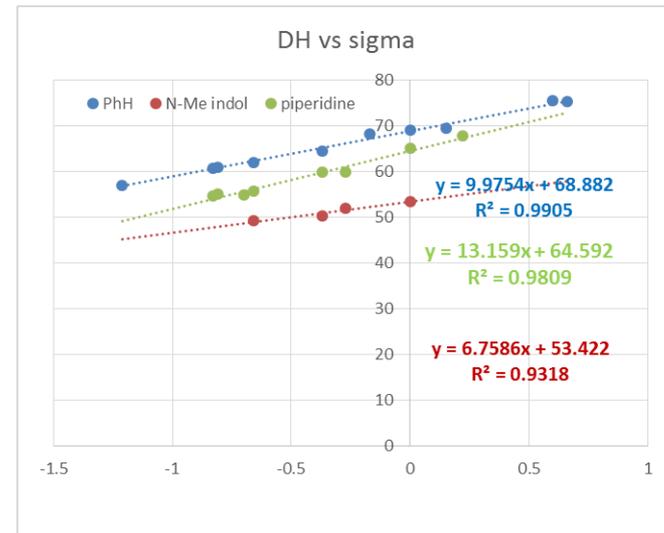
Are there similar 'prediction rules' for reversible carriers?

Data from solubility tables US Borax

Rational Design Cont.

Liquid carriers (tuning and predicting thermodynamics)

- Decrease ΔH_{H_2} - adding negative charge to arene ring results in a lower enthalpy of H_2 adsorption in a predictable way.
- Developing methods to predict enthalpy of hydrogenation for families of hydrogen carriers
 - Want both small intercept and larger slope



Comparison of 'families'
of hydrogen carriers.
* ΔH vs Hammett σ

*New J. Chem., 2008, 32, 1027

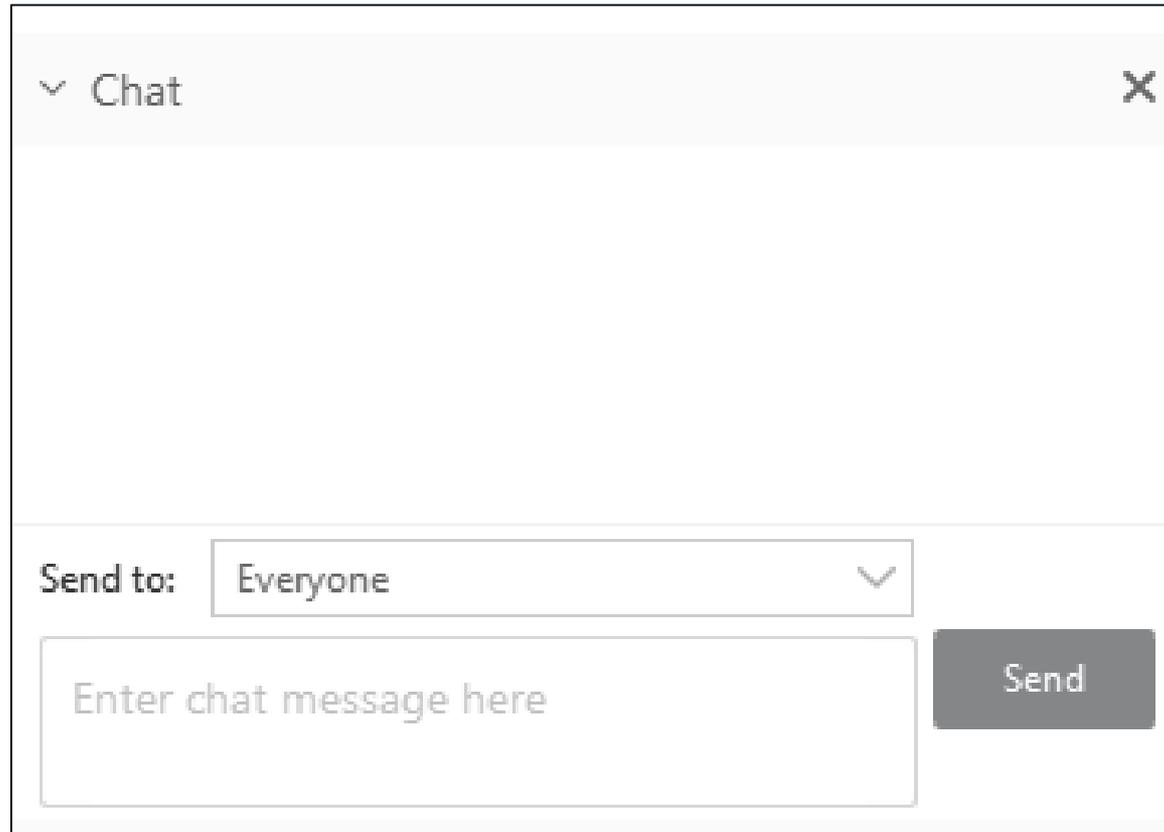
Summary

Summary of HyMARC role – analysis of alternate concepts

- Making H₂ carriers without H₂ (electrochemical)
- H₂O as a reactant to form H₂ (ROH and HCO₂⁻)
- Chemical compression (entropy controlled release of H₂)
- Controlling selectivity (CO₂ vs CO)
- Integrated separation technologies (H₂ from CO₂, CO)
- Preserving liquid phase throughout H₂ release and uptake
- Integrating electro and thermal catalysis processes
- Bio-inspired processes/catalysis
- Hydride eutectic systems
- Framework materials (COFs, MOFs, etc.)
- Heterolytic sorption of H₂
- Dynamic materials

Question and Answer

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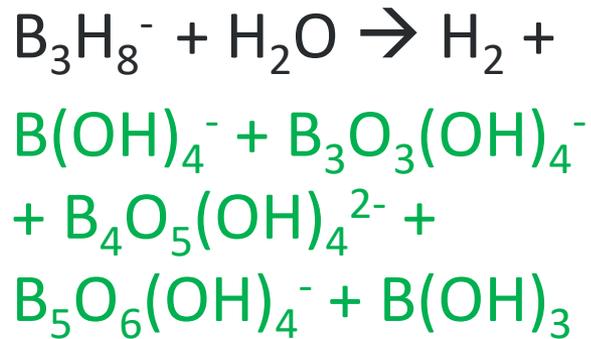
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Backup Slides

Why Does this Work?

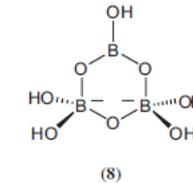
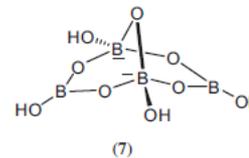
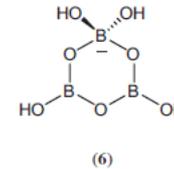
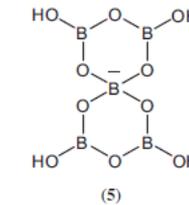
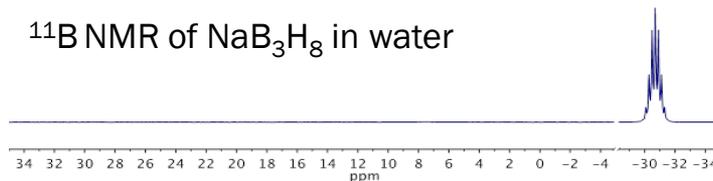
Hydrolysis of BH_4^- leads to mixture of products.



^{11}B NMR of polyborate mixture



^{11}B NMR of NaB_3H_8 in water



Solution of 'solids' is meta-stable. Mixture of products makes it difficult to crystallize