System Level Analysis of Hydrogen Storage Options

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U.S. DOE Hydrogen and Fuel Cells Program

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Project ID: ST001

Overview

Timeline

- Project start date: Oct 2009
- Project end date: N/A
- Project continuation and direction determined annually by DOE

Barriers

- H_2 Storage Barriers Addressed:
  - A: System Weight and Volume
  - B: System Cost
  - C: Efficiency
  - E: Charging/Discharging Rates
  - J: Thermal Management
  - K: Life-Cycle Assessments

Budget

- FY18 DOE Funding: $500 K
- FY19 DOE Funding: $500 K

Partners/Interactions

- HyMARC: PNNL, NREL, LBNL
- Delivery Team, Hydrogen Interface Taskforce (H2IT), ANL-H2A, ANL-HDSAM
- HMAT, TARDEC, BMW, LLNL
- Ford, ORNL, UM
- Strategic Analysis, PNNL, Ford

Relevance and Impact

Develop and use models to analyze the on-board and off-board performance of physical and material-based automotive hydrogen storage systems

- Conduct independent systems analysis for DOE to gauge the performance of H_2 storage systems
- Provide results to material developers for assessment against system performance targets and goals and help them focus on areas requiring improvements
- Provide inputs for independent analysis of costs of on-board systems.
- Identify interface issues and opportunities, and data needs for technology development
- Perform reverse engineering to define material properties needed to meet the system level targets

Impact of FY2019 work

- Determined the scenario for which methanol as hydrogen carrier can be cost competitive with the incumbent technology
- Proposed initial targets for production, transmission and decomposition of hydrogen carriers for overall \$2/kg H_2 production cost
- Established the cost of storing 1-3000 tonnes of H_2 in underground tubes, lined rock caverns, and salt caverns
- Determined carbon fiber requirements, gravimetric capacities, volumetric capacities and dormancy for 350-bar, 700-bar and cryo-compressed hydrogen storage on-board medium-duty and heavy-duty trucks

Approach

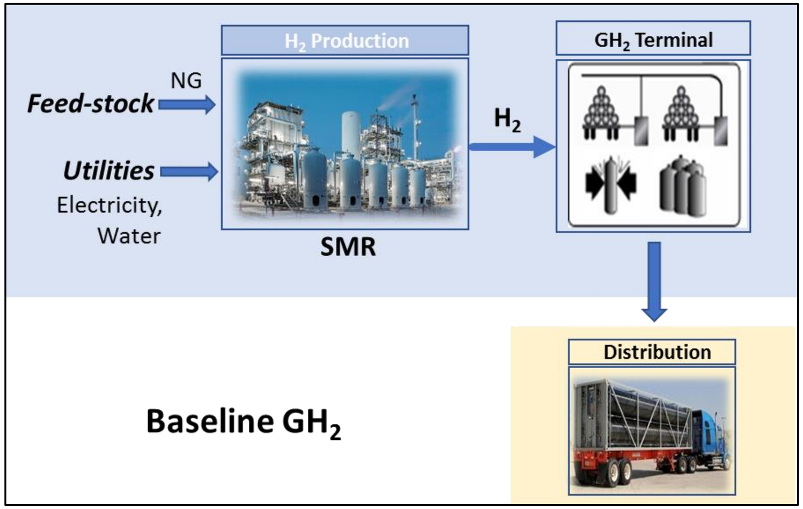
- Develop thermodynamic and kinetic models of processes in physical, complex metal hydride, sorbent, and chemical H_2 storage systems
  - Address all aspects of on-board and off-board storage targets, including capacity, charge/discharge rates, emissions, and efficiencies
  - Perform finite-element analysis of compressed hydrogen storage tanks
  - Assess improvements needed in materials properties and system configurations to achieve storage targets
- Select model fidelity to resolve system-level issues
  - On-board system, off-board spent fuel regeneration, reverse engineering
  - Conduct trade-off analyses, and provide fundamental understanding of system/material behavior
  - Calibrate, validate, and evaluate models
- Work closely with DOE technology developers, national labs and others in obtaining data, and provide feedback
- Participate in meetings and communicate approach and results to foster consistency among DOE-sponsored analysis activities

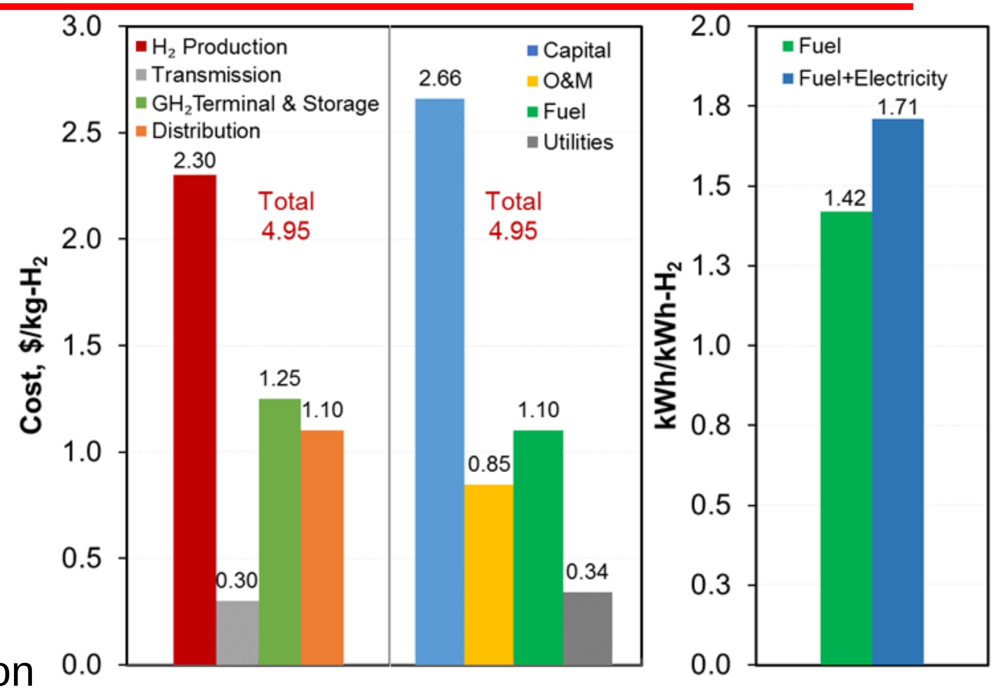
FY2019 Tasks and Progress

1. Hydrogen Carriers (FY2019 Q1 and Q4)
   – Completed initial analysis of three hydrogen carriers. Identified a carrier and scenario that is cost competitive with the baseline gaseous hydrogen scenario
2. Bulk Storage (FY2019 Q2)
   – Determined levelized cost of 500 t-H_2 bulk storage in underground pipes, lined rock caverns, and salt caverns
3. Hydrogen Storage for Medium and Heavy Duty Trucks (FY2019 Q3)
   – Completed preliminary analysis of 10-150 kg hydrogen storage for medium and heavy-duty trucks.

			Date Completed	% Complete
1	Complete initial analysis of at least three one-way and two-way hydrogen carriers relative to the 2020 targets of $2/kg hydrogen production and $2/kg delivery cost	12/18	12/18	100
2	Prepare a report on technology and economics of bulk storage of hydrogen in different quantities (equivalent to 10-30 days storage), solicit feedback from area experts, and make the report publically available	03/19	03/31	75
3	Prepare a report on hydrogen storage for medium and heavy-duty trucks and invite feedback from stakeholders	06/19		50
4	Prepare case studies on hydrogen carriers for specific hydrogen supply and demand scenarios. Document results of reverse engineering analysis for carrier and process requirements to meet efficiency and cost targets ($4/kg hydrogen)	09/19		25

Baseline Gaseous Hydrogen (GH_2) Pathway: 50 tpd-H_2





Why hydrogen carriers

- Transmission over long distances
- Bulk storage at different scales and duration

Financial Assumptions	City annual average daily use = 50 tpd-H_2; Operating capacity factor = 90%; Internal rate of return (IRR) = 10%; Depreciation (MACRS)=15 yrs; Plant life=30 yrs; Construction period=3 yrs		
	NG	**Electricity**	**Water**
Feedstock and Utilities	6.80 $/MBtu	5.74 ¢/kWh	0.54 ¢/gal
SMR Consumption, /kg-H_2	0.156 MBtu	0.569 kWh	3.35 gal
GH_2 Terminal	HDSAM v 3.1, Compressed Gas H_2 Terminal		
H_2 Storage	10-days geologic storage of H_2 for plant outages		
H_2 Distribution	400 kg/day H_2 dispensing rate at refueling station		
Tube Trailers	**Payload**	**Volume**	
	1042 kg	36 m^3	

DOE record: 13-16 $/kg-$H_2$ dispensed for very low production volume

- GH_2 scenario includes 10-d (500 t-H_2) geologic storage which is not available at all sites
- Future liquid carrier scenarios will consider options to circumvent geologic storage

tpd: tonnes/day
t: tonne = 1000 kg;

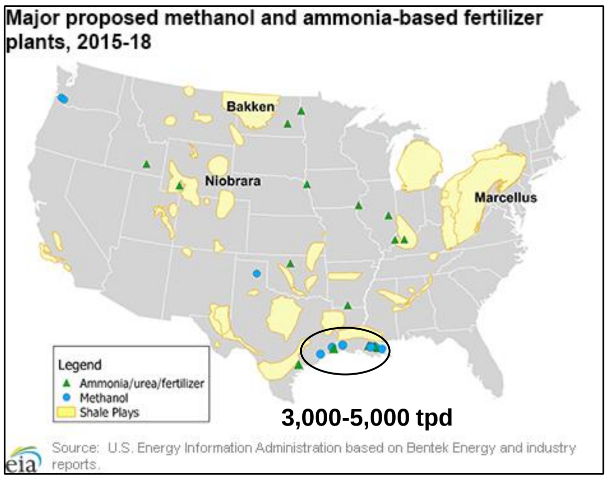
Baseline GH_2 scenario: Central SMR; GH_2 terminal: H_2 compression & storage; truck distribution;

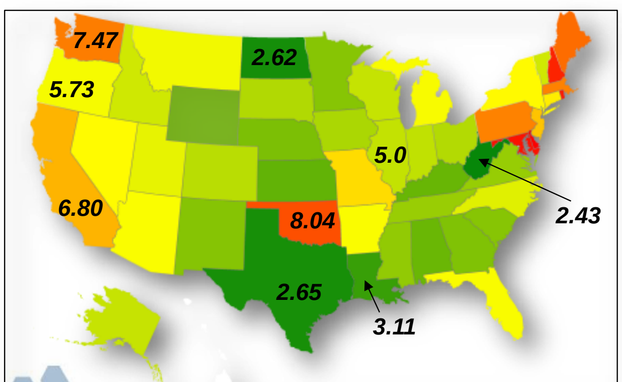
Accomplishment

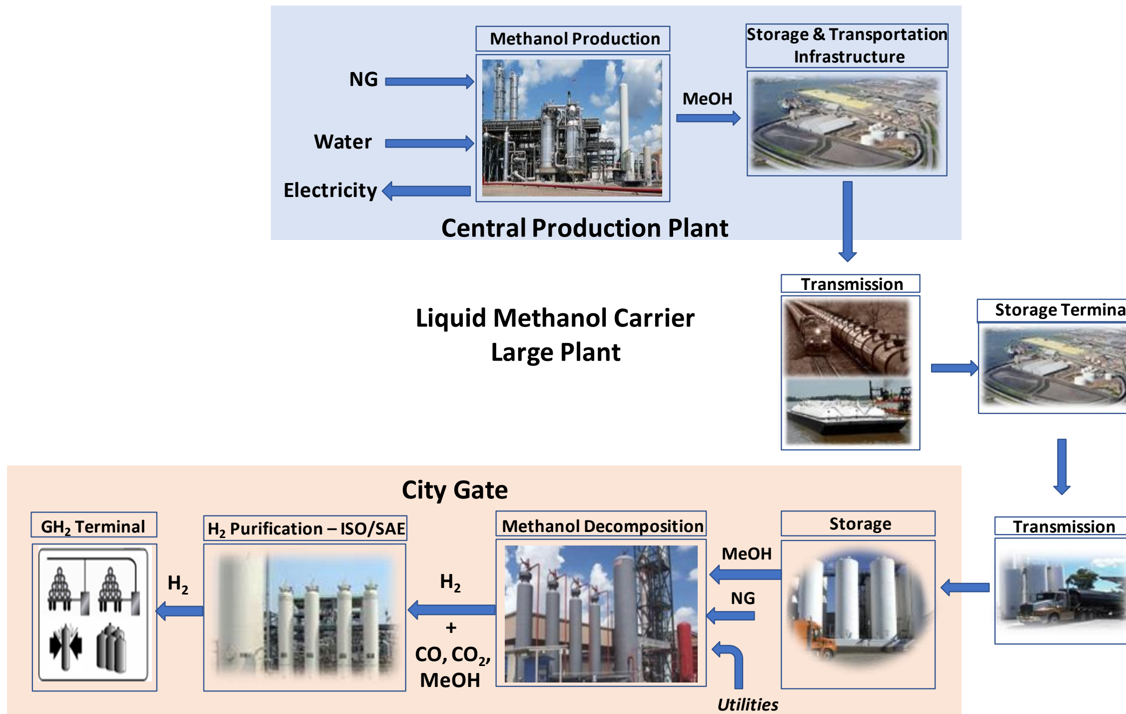
Hydrogen Carrier Pathways – Large Production Plants

Scenario: Large hydrogenation plant for economy of scale

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







- Similar pathway for ammonia
- MCH pathway includes a transmission leg for return of toluene to the production plant

EIA: Industrial NG $/MBtu (2017 average), See slide 30 for references

Accomplishment

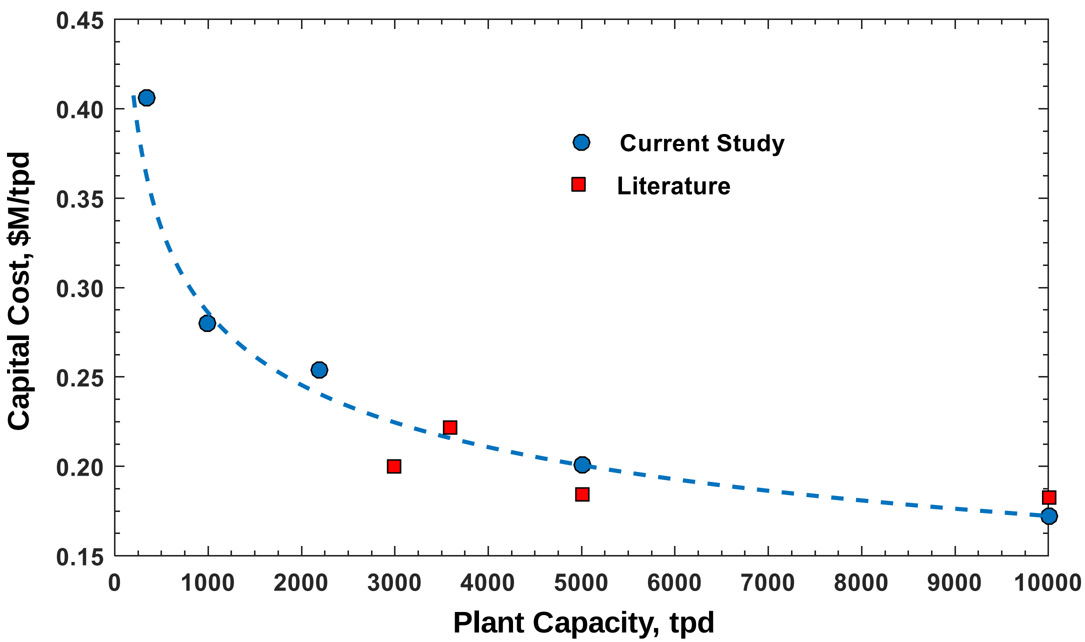
Capital Cost of Methanol Plants

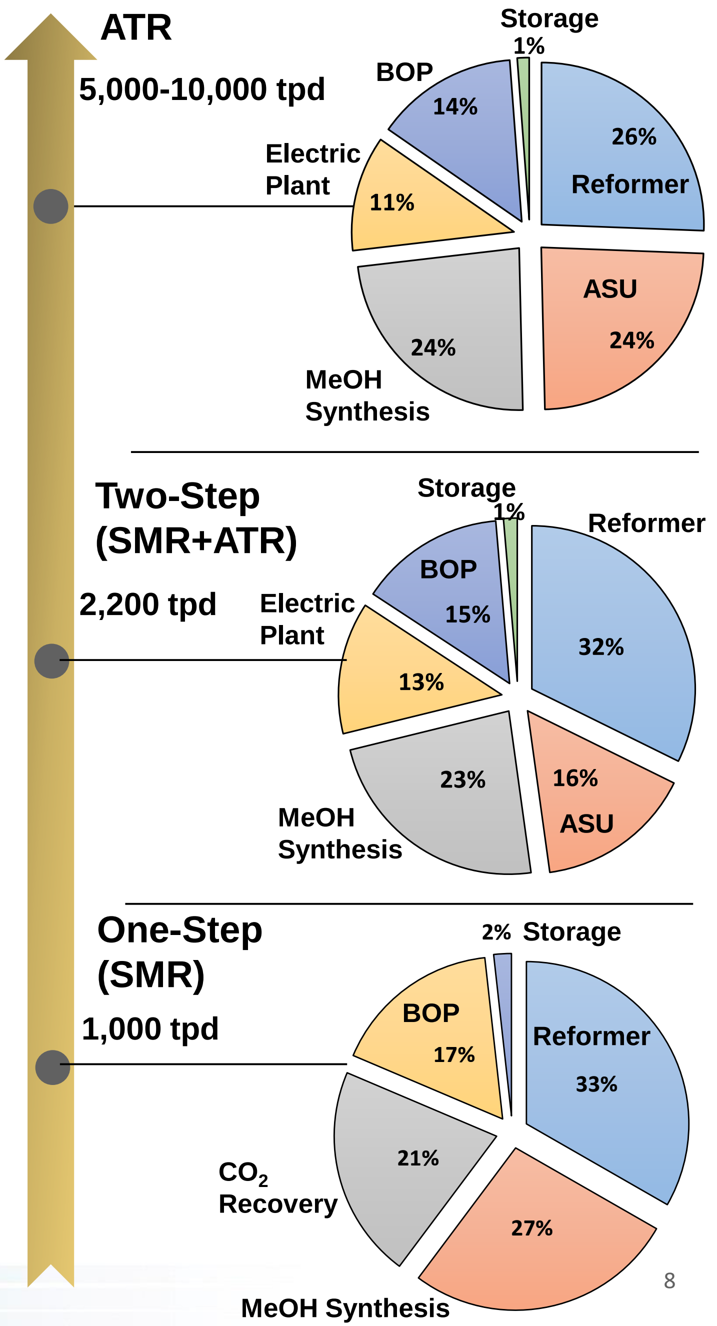
Capital cost minimized depending on scale

- ATR (auto-thermal reforming) for capacity >3000 tpd
- Two-step reforming for capacity >1800 tpd
- SMR (steam methane reforming) below 1500 tpd

Reformer, ASU and/or CO_2 removal account for ~50% of total capital costs

- Storage (30 days) of methanol accounts for a small fraction of total capital costs



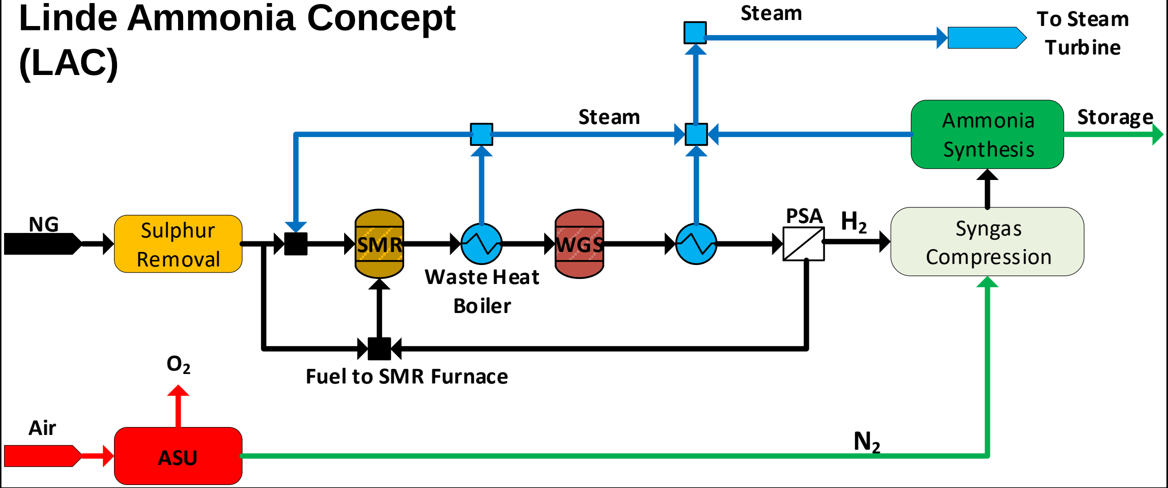


Literature: ADI Analytics, Sojitz Corp., Foster & Wheeler

Accomplishment

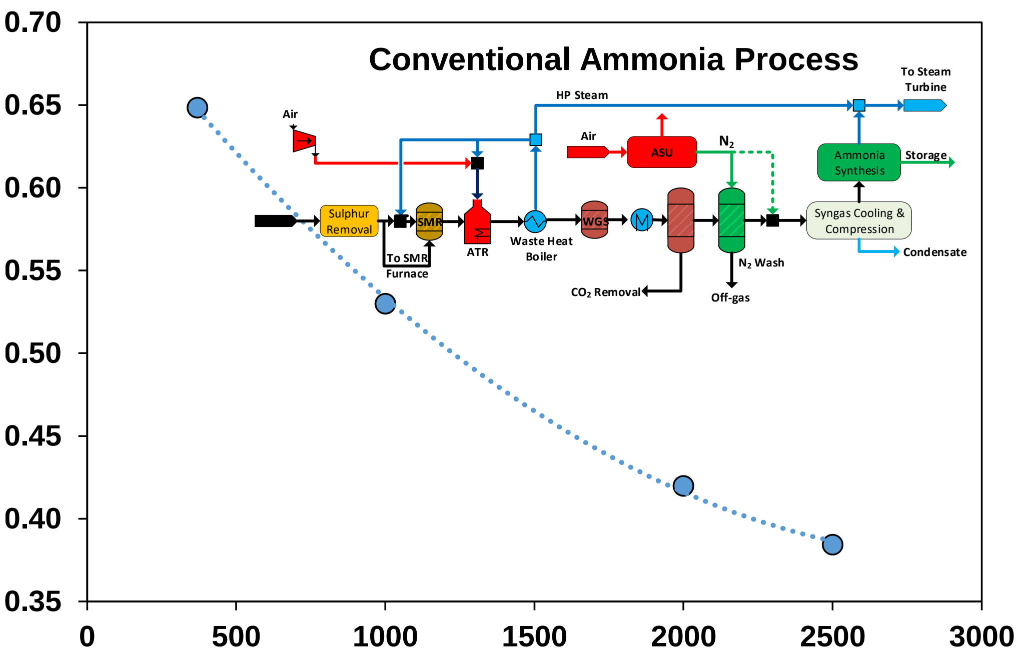
Capital Cost of Ammonia Plants

Linde Ammonia Concept (LAC)

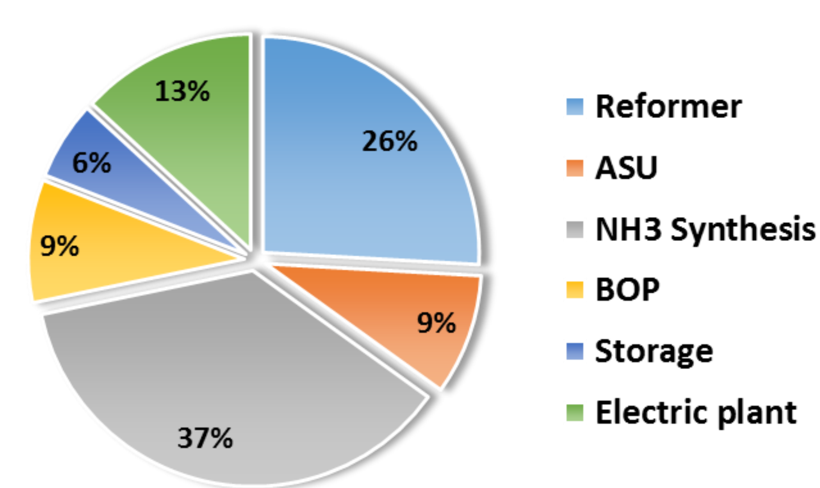


1000-2500 tpd scale

- $H_2O/C=2.8$
- Ultrapure syngas, minimal purge
- Ammonia converter: Three-bed radial flow, internal heat-exchangers
- NG demand: 0.029 MBtu/kg-NH_3
- Electricity demand: 0.9 kWh$_e$/kg-NH_3
- Steam Turbine: 0.98 kWh$_e$/kg-NH_3



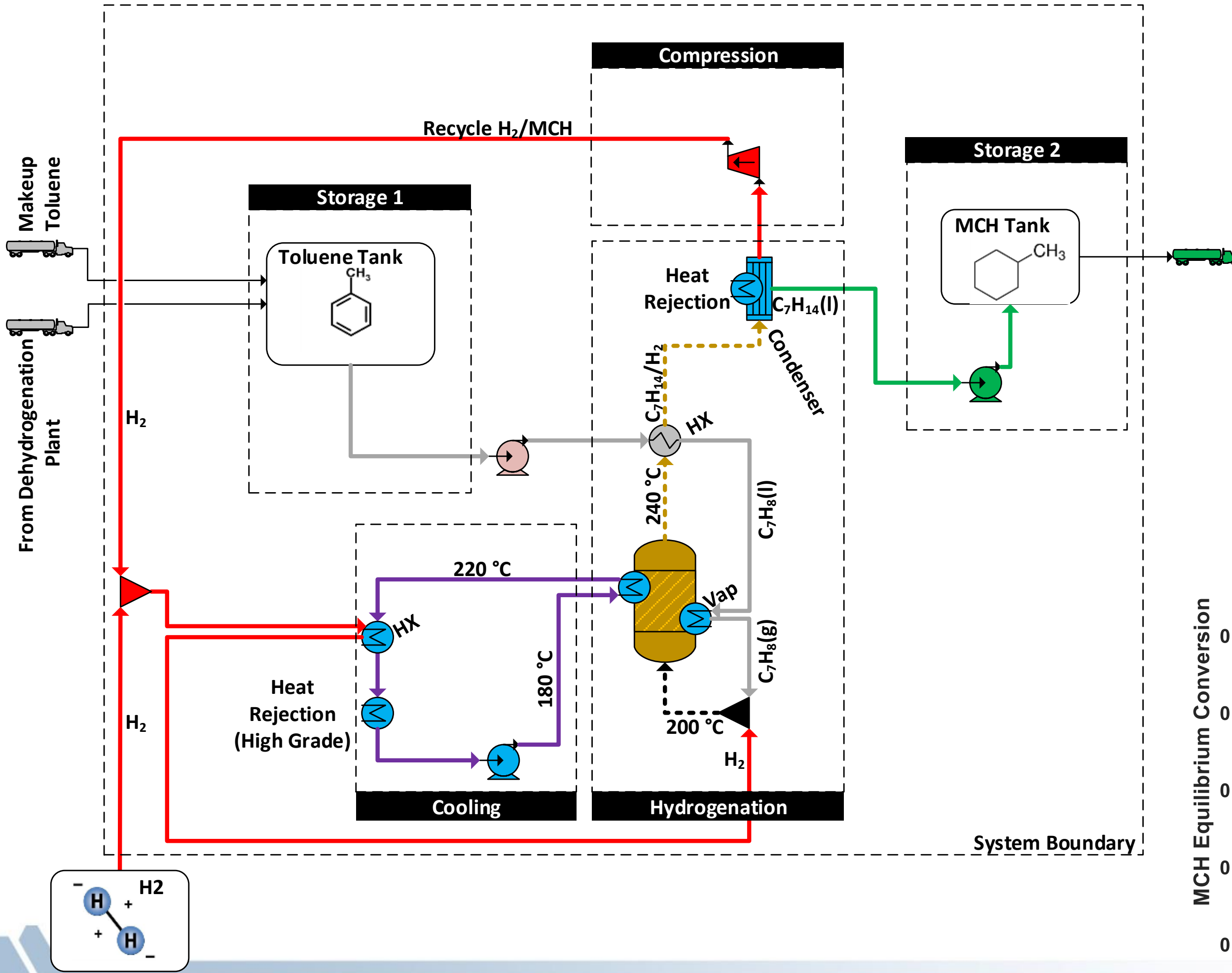
Breakdown of Capital Costs (2,500 tpd)



Capital cost shown for LAC but are similar for the conventional ammonia process

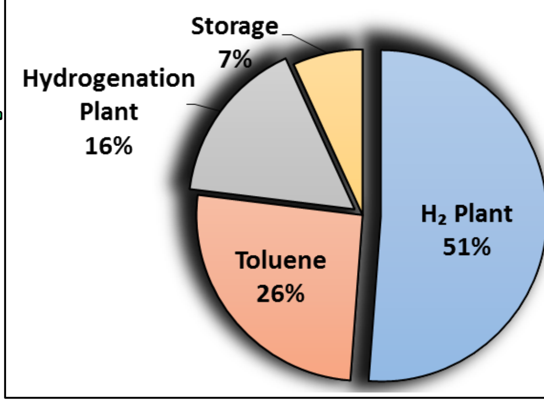
Capital Cost of Toluene Hydrogenation Plant

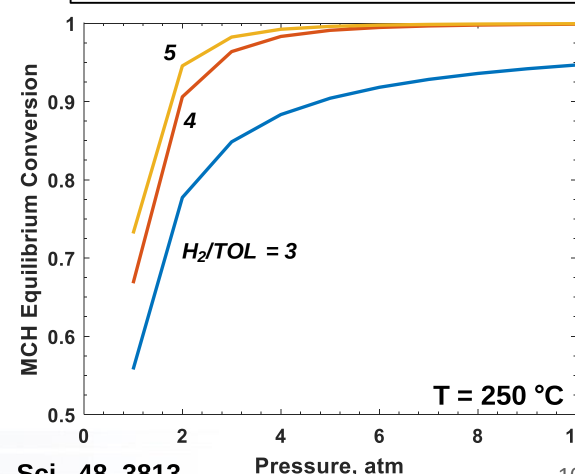
- Reactor operated at 240°C and 10 atm for nearly complete conversion. Conversion is kinetically limited. No side-reactions are considered.
- Allowing for 0.5 atm pressure drop, 98.5% of MCH condenses at 9.5 atm and 45°C
- Excess H_2 and MCH vapor recycled (H_2/Toluene ratio = 4/1)
- Toluene makeup = 0.84% (due to dehydrogenation losses)



Plant Sizes
- H_2: 350 tpd
- MCH: 6,764 tpd

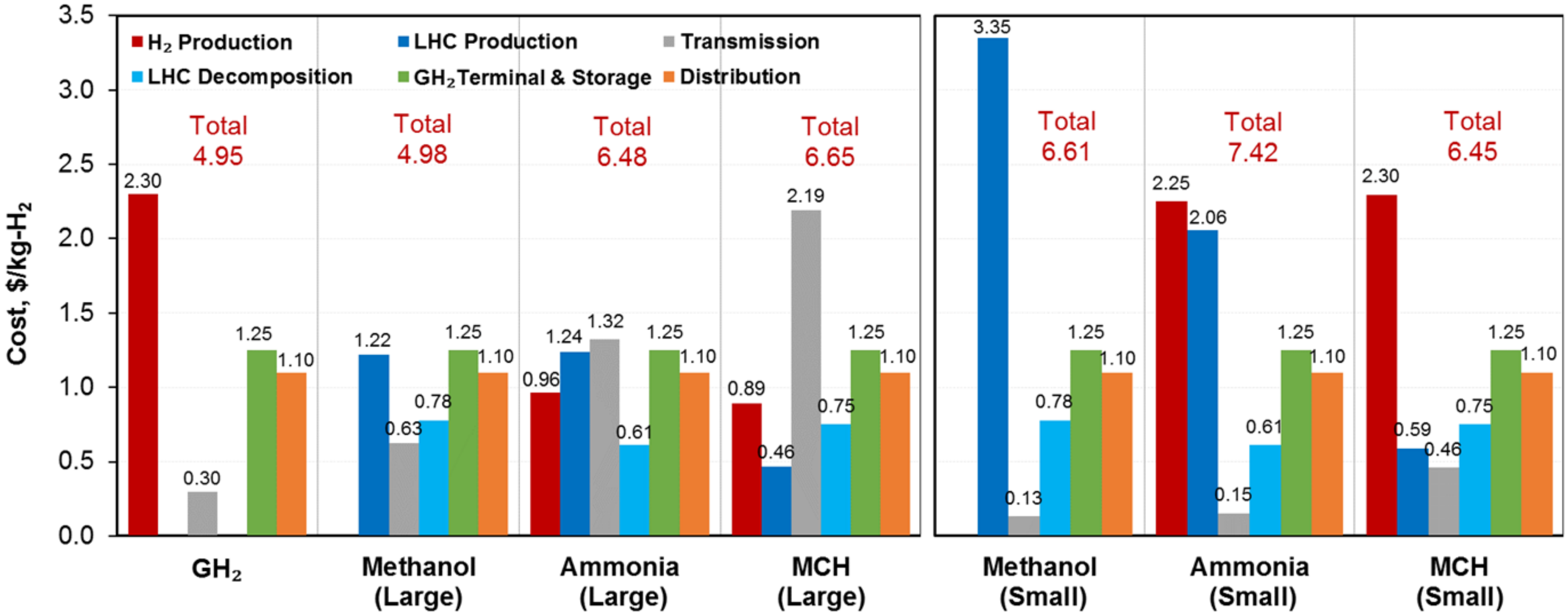
Capital Cost ($M 0.067/tpd-MCH





Lindfors, L.P. et. al. (1993). Kinetics of Toluene Hydrogenation on Ni/Al_2O_3 Catalyst. Chem. Eng. Sci., 48, 3813

Hydrogen Carriers
Levelized Cost of H_2 Distributed to Stations (50 tpd-H_2)



Large methanol scenario is competitive with the baseline GH_2 scenario

- Compared to 350-tpd small plant scenario, \$2.13 \$/kg-H_2 lower production cost, offset by 0.50 \$/kg-H_2 higher transmission cost

As a carrier, ammonia is more expensive than methanol

- Advantage of economy of scale partially offset by higher transmission cost

Centralized MCH production scenario (6,700 tpd) does not scale well

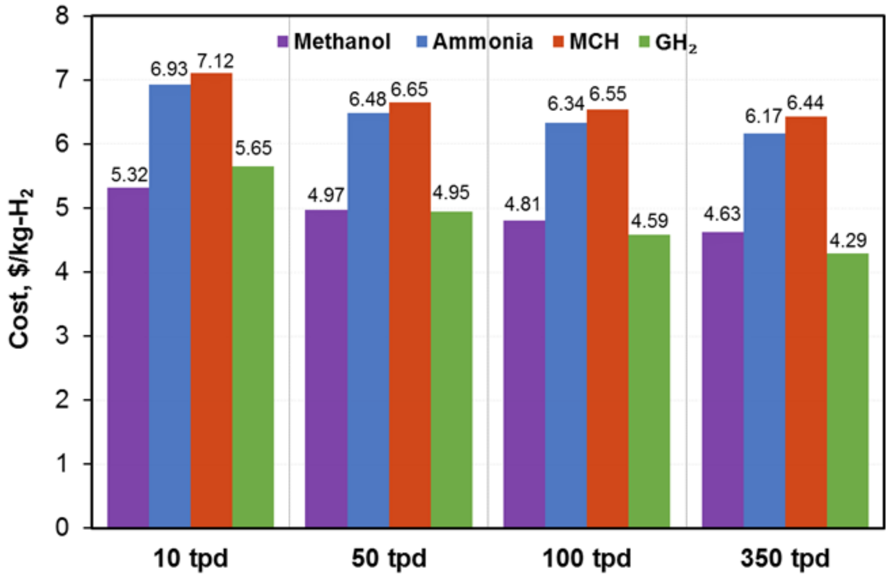
- 1.54 \$/kg-H_2 saving in H_2 and LCH production cost < 1.73 \$/kg-H_2 added transmission cost

LHC production rates in small plant scenarios: 350 tpd methanol, 370 tpd ammonia, 890 tpd MCH

Hydrogen Carriers: Outlook

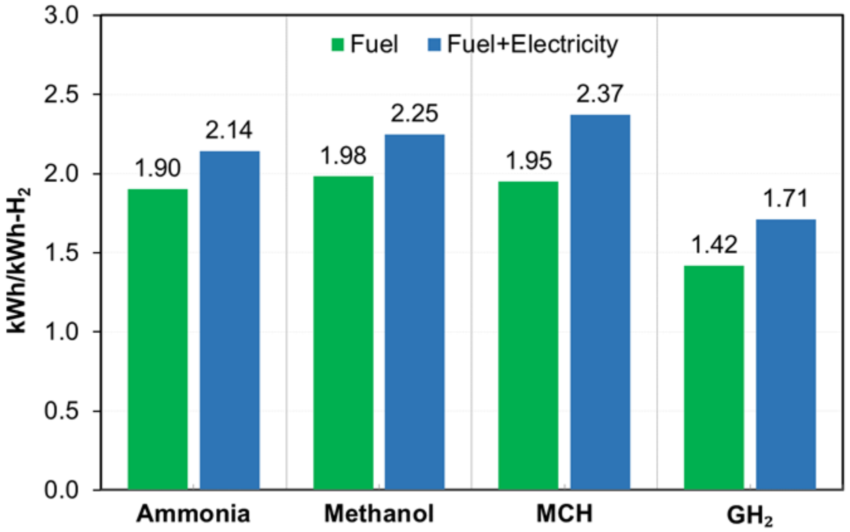
H_2 Production Cost at Different Demands

- Methanol as hydrogen carrier may be attractive in the transition phase, <50-tpd H_2 demand



Energy Efficiency (50 tpd-H_2)

- Fuel plus electricity data assume 33% efficiency in generating electrical power



Proposed LHC Targets for \$2/kg H_2 Production Cost

- \$1/kg-H_2 LHC production: compare with \$1.22 for methanol and \$0.89 for fuel cell quality H_2
- \$0.50/kg-H_2 LHC transmission: compare with \$0.63 for methanol
- \$0.50/kg-H_2 LHC decomposition and H_2 purification: compare with \$0.61 for methanol

Current Status: \$2.63 for methanol, \$4.13 for ammonia, \$4.29 for MCH/toluene

Next Step: Translate LHC cost targets to LHC material property targets

Bulk H_2 Storage Methods

NG Spherical Pressure Vessel, Germany

NG Pipe Storage, Erdgas, Switzerland

LH_2 Cryogenic Storage, NASA

FY 2019 Work

- Pipe storage, salt cavern, lined rock cavern

Future Work

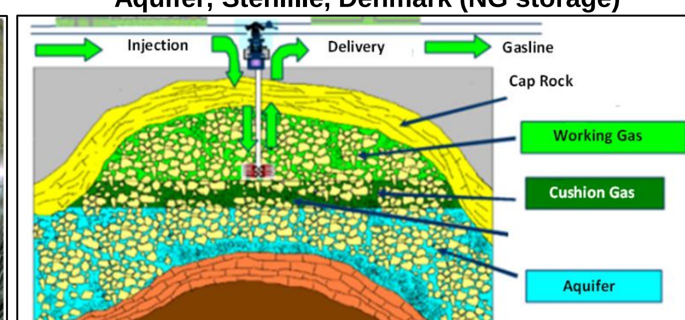
- Forecourt, cryogenic

	Pressure Vessels				Cryogenic	Geologic Storage		
	Spherical Vessels	Pipe Storage	Pre-stressed Concrete	WireTough		Aquifer	Salt Cavern	Lined Rock Cavern
Pressure, bara	1-10.4	7-100	7-875	7-875	20	150-170	55-152	10-230
Diameter, m	39.5	1.4	2.2	0.43	20			35
Wall Thickness, mm	34		110					6-12
Length, m		200 (13x15)		9.2				
Depth, m						1,500	1,200	115
Height, m			5.3					52
Water Volume, m^3	32,000	6,100	22	0.77	3400	4,141,000	566,000	40,000
Net Volume (STP), m^3	273,664	500,556	10,979	428	2,558,399	211,346,012	41,379,324	7,119,024
H_2 Stored, t	27	50	1	0.0389		54,000	6,000	672
Working Capacity, t	24.6	45	0.987	0.0385	230	19,000	3,720	640
Application		City Gate	Forecourt	Forecourt	City Gate Forecourt		City Gate	City Gate

Salt Cavern, H_2 Storage, Praxair, Texas

Rock excavation (dome), Skallen,

Aquifer, Stenlille, Denmark (NG storage)

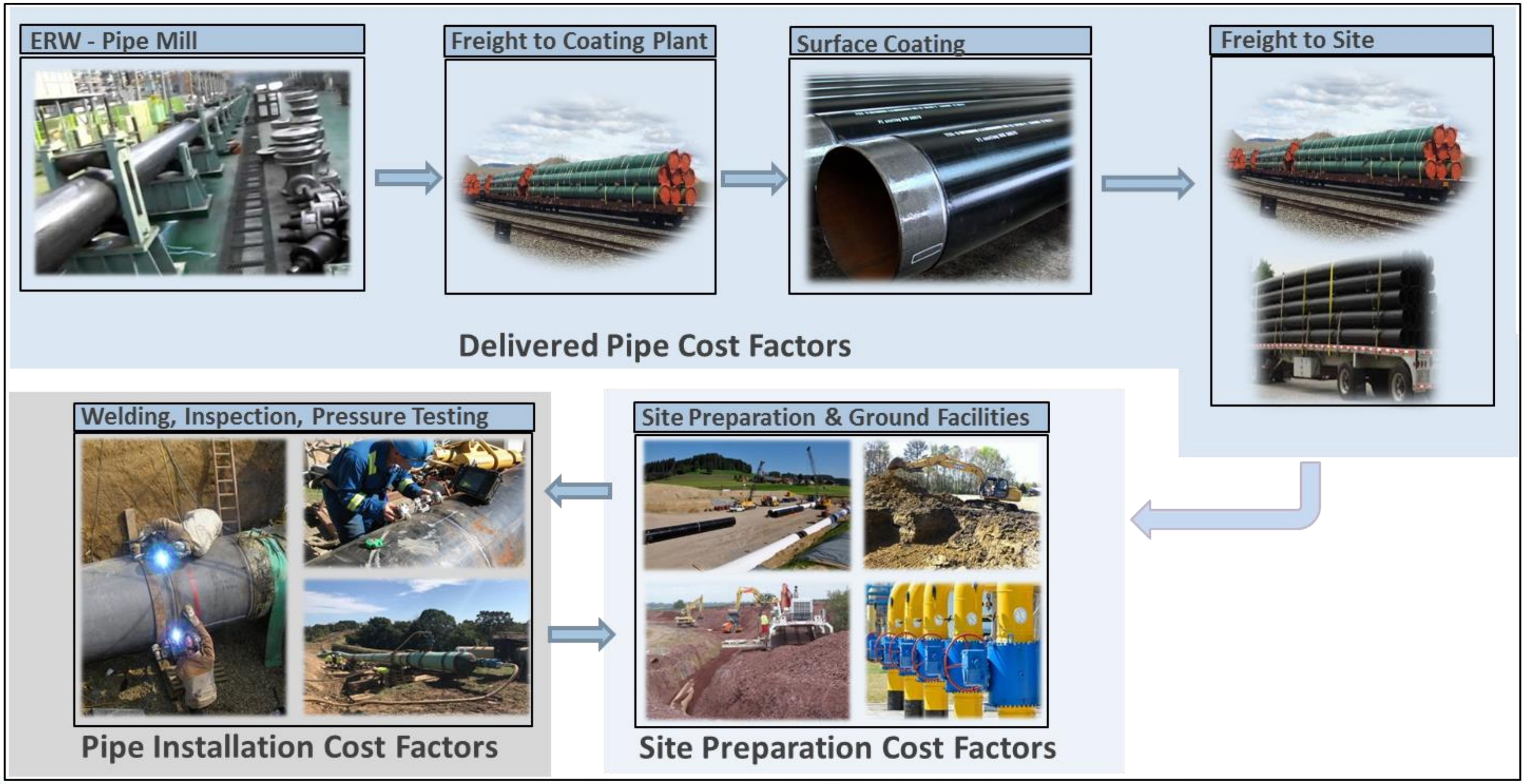


See slide 30 for references

Bulk H_2 Storage in Underground Pipes

500 t-H_2 storage needed for 10-d outages of 50 tpd-H_2 capacity H_2 plants

- **Delivered pipe costs**: API 5L Grade X52 tubes (18”-36” O.D. variable schedule, 40 ft.); 3 layer polyethylene coating; shipping (1000 miles by rail, local - 100 miles by trailer to site)
- **Site preparation costs**: Excavation and backfilling (pipes covered by 1.2 m of soil, 80 cm clearance between pipe strings)**;** Above ground facilities (pipes, valves, compressor)
- **Pipe installation costs**: Shielded metal arc welding, radiographic weld inspection & joint coating; Hydrostatic pressure test and drying.



ERW: Electric Resistance Welding

See slide 30 for references

Cost of 500 t-H_2 Underground Pipe Storage Facility

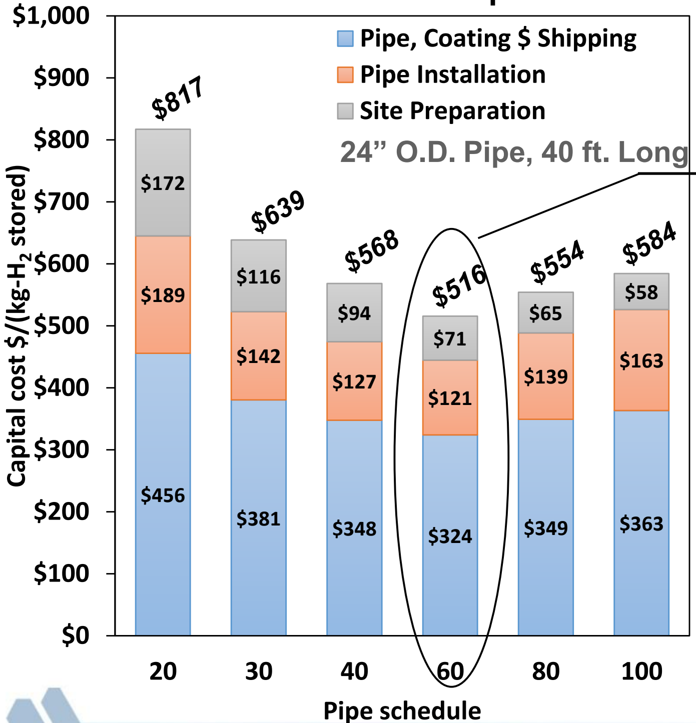
Underground storage facility using 24” O.D. schedule 60 (0.968” wall thickness) pipe incurs lowest overall capital cost ($516/kg-$H_2$ stored). 50% of cost due to pipe manufacturing.

- <Sch. 60**:** Cost increase: Number of pipes, surface coating, pressure test, excavation site
- >Sch. 60: Cost increase: Pipe mass, welding costs, shipping costs
- Sch. 60: Working pressure (8-100 bara); 300 parallel pipe strings, 3150 ft. total length (180-miles equivalent length); 110 acres of land requirement

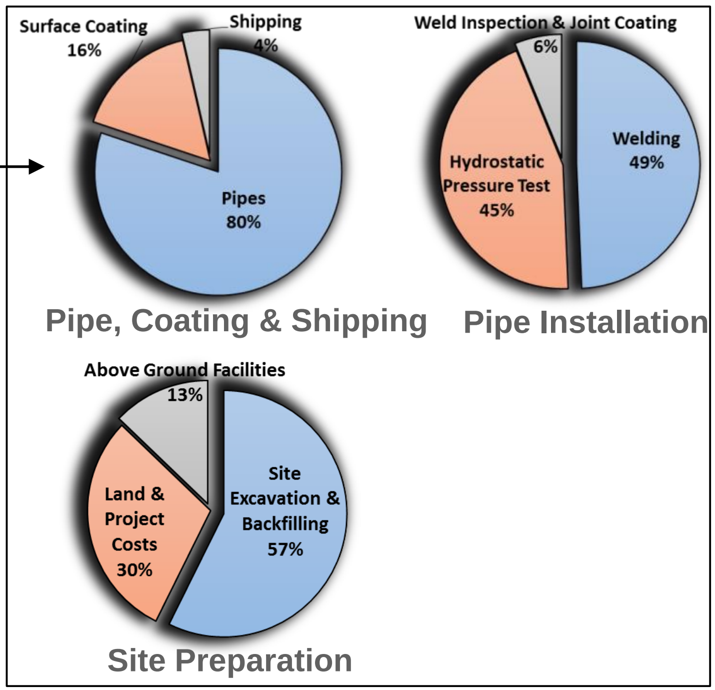
Levelized cost of hydrogen storage (50 tpd basis): $2.17/kg-$H_2$ (95% CAPEX)

- Cost sensitivity: 1.87-2.39 $/kg-$H_2$ based on historic swings in line prices (Δ$359/t)

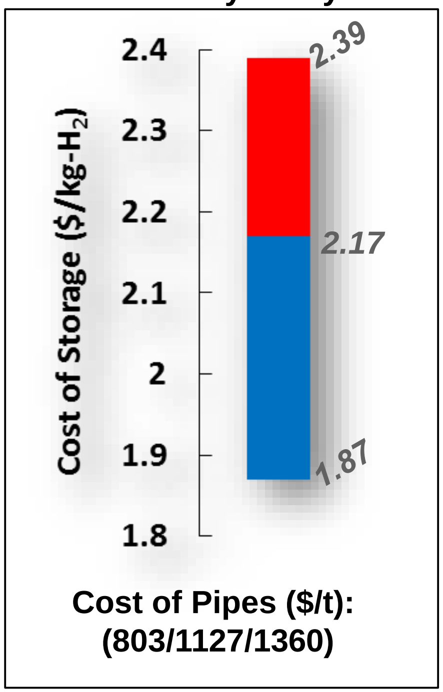
Breakdown of Main Capital Costs



Breakdown of Capital Costs, (24” O.D., sch. 60)



Single Variable Sensitivity Study



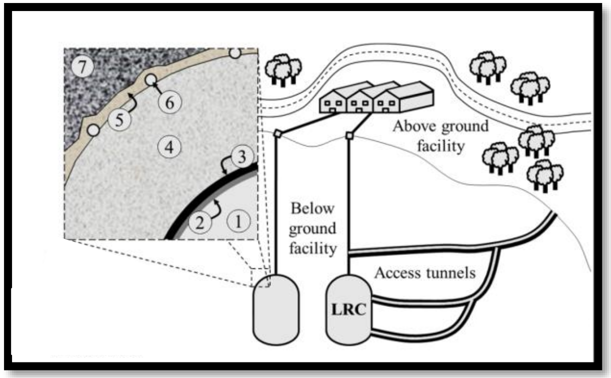
Accomplishment

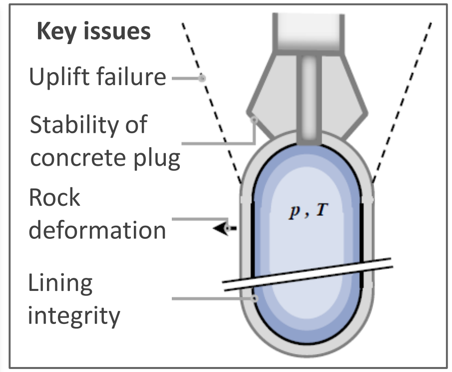
Bulk H_2 Storage in Underground Lined Rock Caverns (LRC)

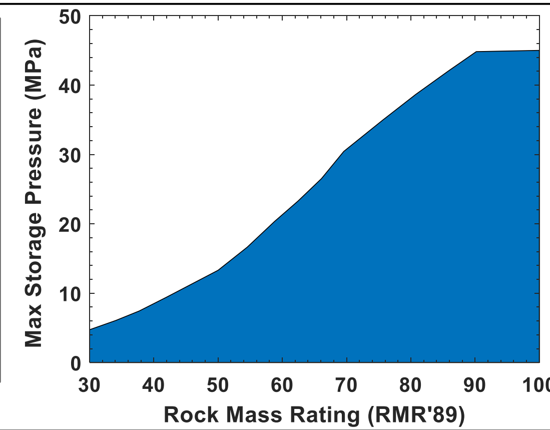
H_2 plant capacity: 50 tpd-H_2, 10 days of H_2 storage for plant outages (500 t-H_2 storage)

- **Design Case:** Base case design adapted from demonstration plant for natural gas storage at Skallen (south-west of Sweden)[1]. Surrounding rock absorbs forces; concrete layer acts as load transfer medium; thin liner encloses cavern for gas tightness
- **Base Parameters**: 150 m rock cover, 150 atm storage pressure, 90% working gas, 800 m access tunnels, 15 mm thick liner (mild steel), 2 m thick concrete layer, 1 mile of pipeline to outcrops
- **Main costs**: Cavern excavation > Tunnel excavation > concrete layer ≈ liner

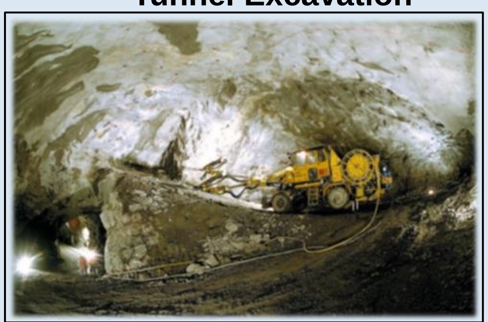
1. Cavern
2. Steel Lining
3. Sliding Layer
4. Concrete
5. Shotcrete
6. Drainage
7. Rock Mass







Tunnel Excavation



Cavern Excavation + Drainage

Liner installation

Concrete filling of cavern

LRC Main Cost Factors

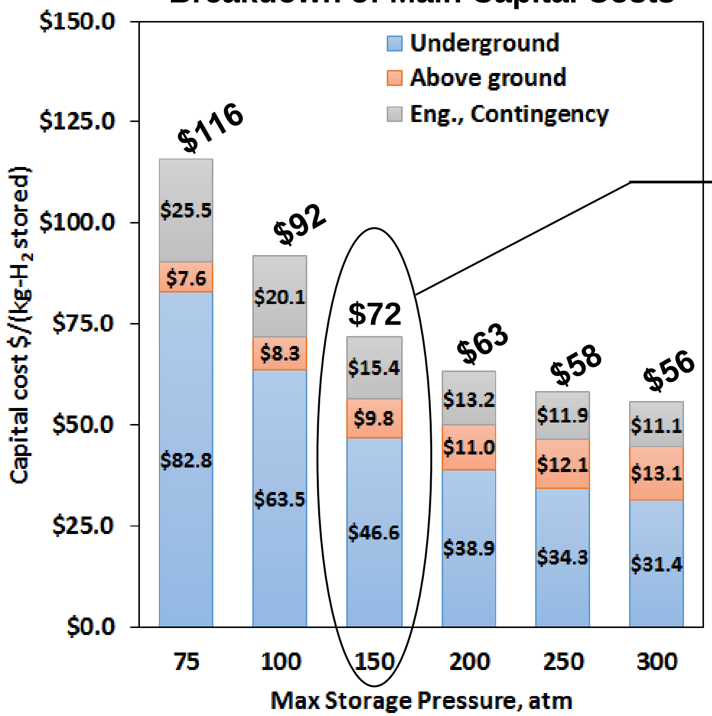
1) Sofregaz US Inc.,(1999), Commercial Potential of Natural Gas Storage in Lined Rock, Report SZUS-0005 DE-AC26-97FT34348-01

Cost of 500 t-H_2 Underground Lined Rock Cavern Facility

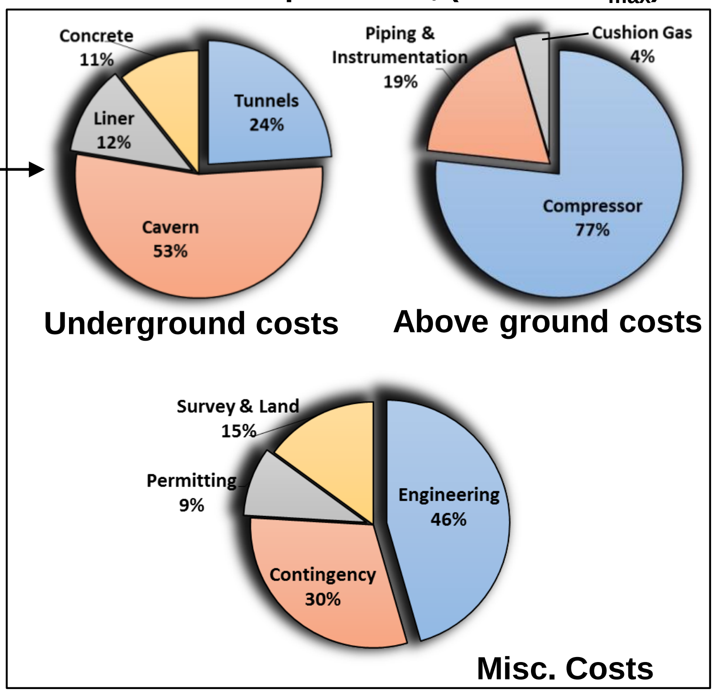
Overall capital cost of underground LRC facility decreases as the storage pressure (P_{max}) increases. Minimum pressure is kept constant at 20 atm.

- **P_{max}<150 atm:** Significant cost increase due to cavern excavation, liner and concrete
- **P_{max}>150**: Modest cost decrease: Underground tunnel, survey and land costs remain fixed; Increase in costs for above ground facility (compressor and piping)
- **Levelized cost of hydrogen storage (50 tpd basis):** \$0.36/kg-H_2 (85% CAPEX)
  - Cost sensitivity: 0.31-0.43 \$/kg-H_2 based on 100-250 atm P_{max}

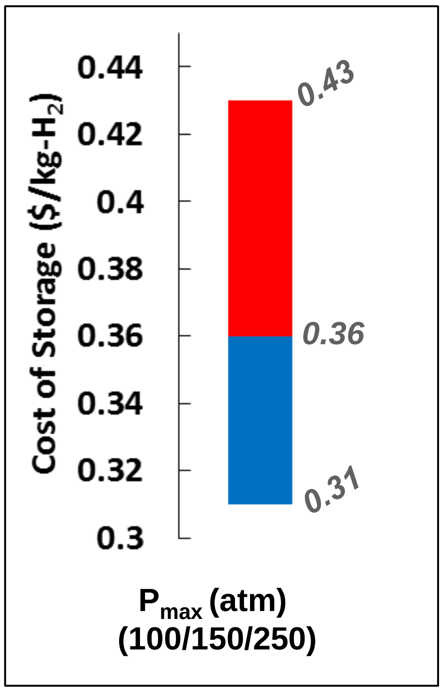
Breakdown of Main Capital Costs



Breakdown of Capital Cost, (150 atm P_{max})



Single Variable Sensitivity Study

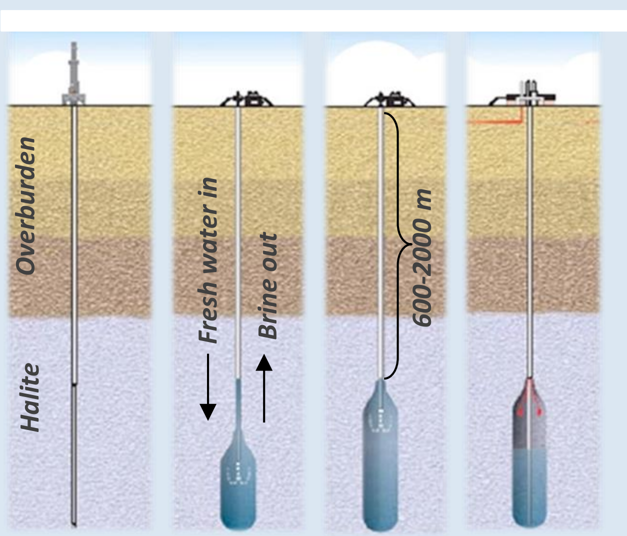


Bulk H_2 Storage in Underground Salt Cavern

H_2 plant capacity: 50 tpd-H_2, 10 days of H_2 storage for plant outages (500 t-H_2 storage)

- **Cavern construction :** Geological survey -> bore and install production tubing -> solution mining -> de-brine and mechanical integrity test (MIT)
- **Associated costs**: Brine transport (10 miles) and disposal (Class II wells), Gas drying
- **Base Parameters**: 800 m cavern roof depth, 120 atm storage pressure, 30% cushion gas, 80,000 m^3 cavern water volume, 1 mile of pipeline to facility
- **Main costs**: Cavern construction> Brine disposal ~ Above ground facility
- **Sensitivity:** Cavern roof depth 500-1200 m (70-190 atm storage pressure)

Cavern construction



Bore hole, + casing

Solution mining

Solution mining completed

Gas injection for brine removal

Above ground facilities

Compressor, pipes

Gas drying

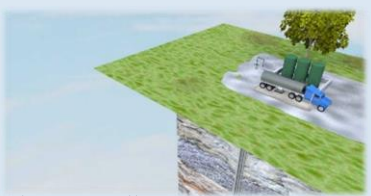
Brine transportation

Pipeline

4,000 gallon truck

Brine disposal

Waste treatment plant



Class II well

Salt production

Chlor-alkali

Underground salt cavern main costs

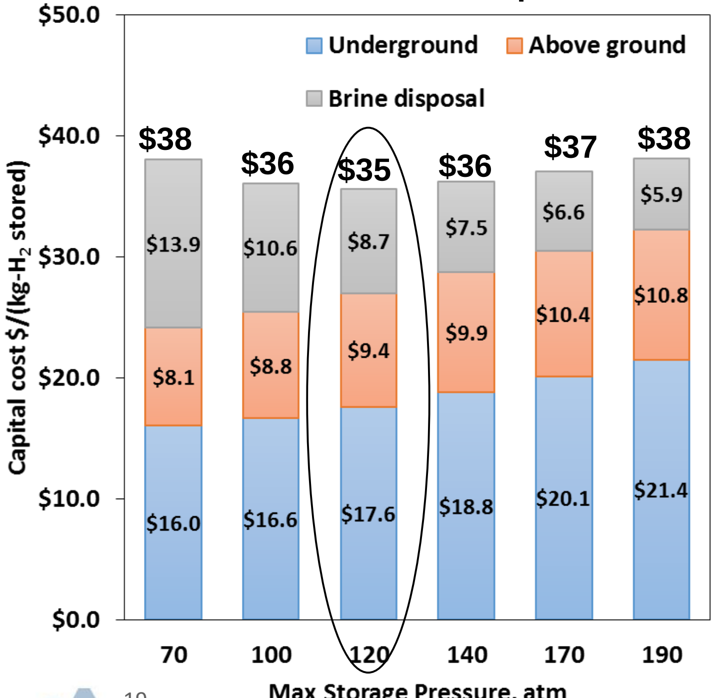
See slide 30 for references

Cost of 500 t-H_2 Underground Salt Cavern Facility

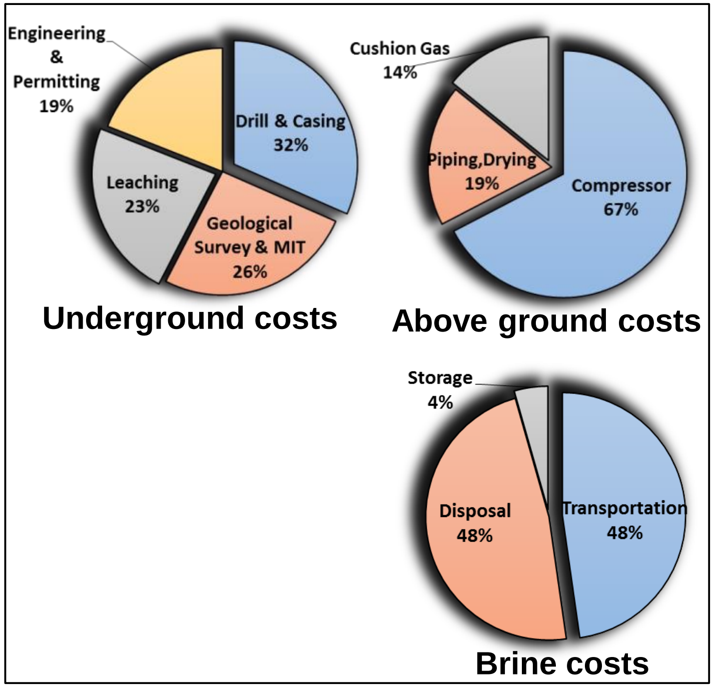
Overall capital cost of underground salt cavern facility remains constant as the storage pressure (P_{max}) increases. Minimum cushion gas[1] is kept constant at 30% of storage capacity.

- **P_{max}>70 atm:** Cost increases due to compressor size, bore and production tubing installation (increase in depth)
- **P_{max}>70 atm**: Cost decreases due to brine disposal and leaching (smaller cavern volume)
- **Levelized cost of hydrogen storage (50 tpd basis):** \$0.21/kg-H_2 (75% CAPEX)
  - Cost sensitivity: 0.19-0.27 \$/kg-H_2 based on brine disposal cost 0-2 \$/bbl

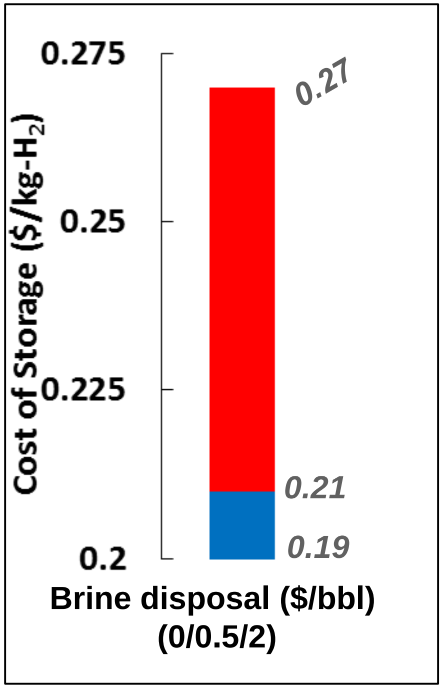
Breakdown of Main Capital Costs



Breakdown of Capital Cost, (150 atm P_{max})



Single Variable Sensitivity Analysis



MIT=Mechanical Integrity Testing

[1]Cushion gas = \$2.50/kg-H_2

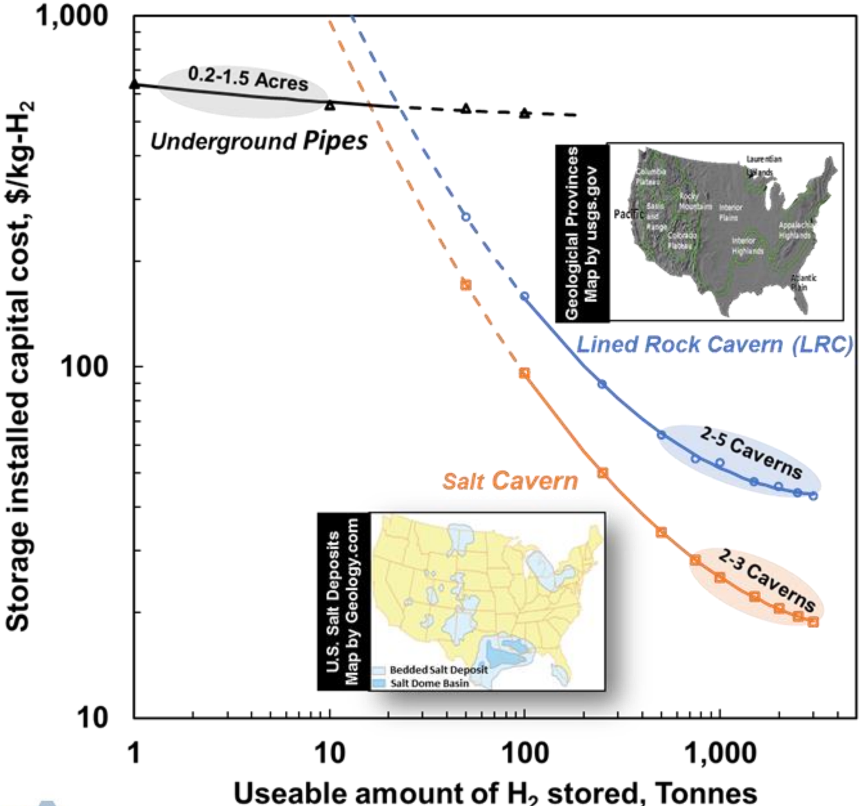
Accomplishment

Bulk H_2 Storage: Outlook

- Underground pipes more economical than geological storage for <20-t usable stored H_2
- At large scale, salt caverns generally more economical than lined rock caverns
- Storing >750-t usable H_2 may require multiple caverns

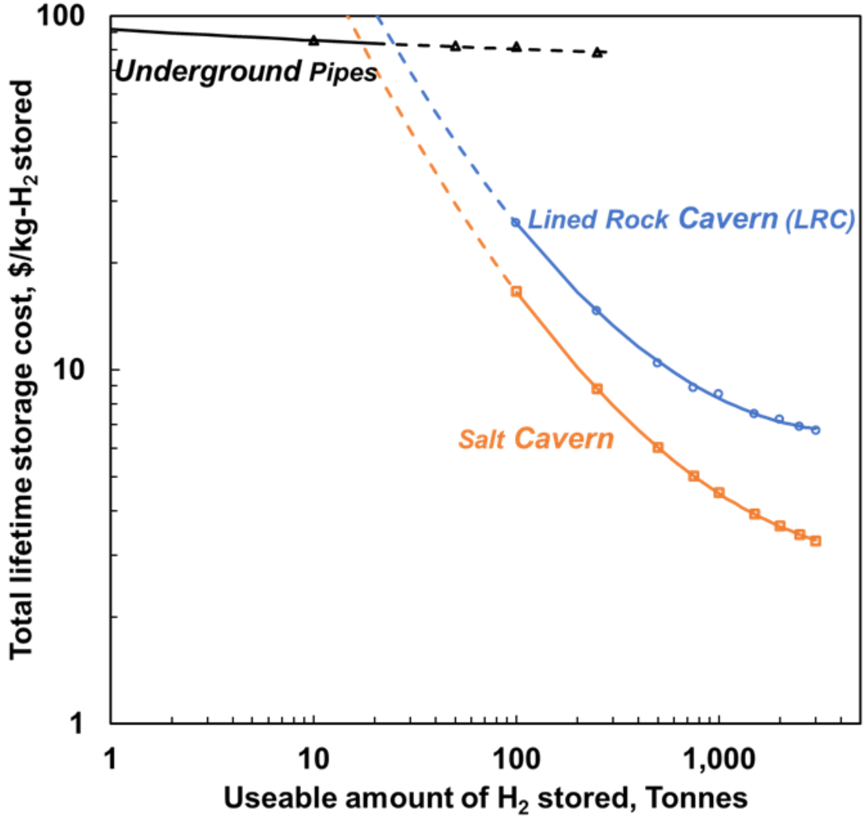
Installed Capital Cost

- Underground pipes: 100 bar
- LRC and salt caverns: 150 bar



Yearly Storage Cost

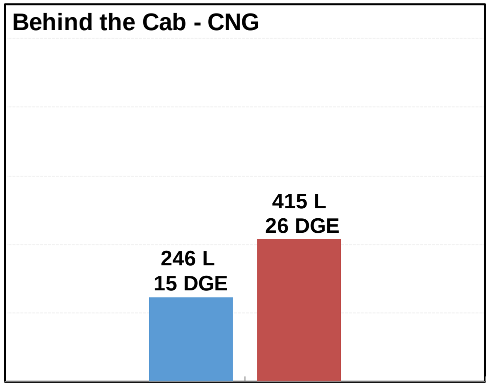
- Inclusive of CAPEX and operating & maintenance cost

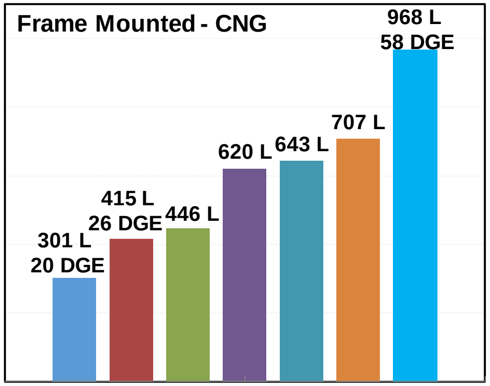


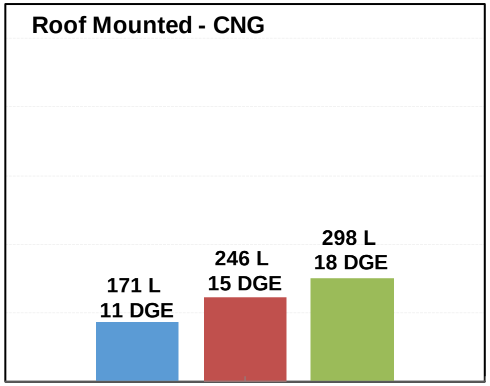
Hydrogen Storage for Medium and Heavy-Duty Trucks

Packaging Options[1,2,3]

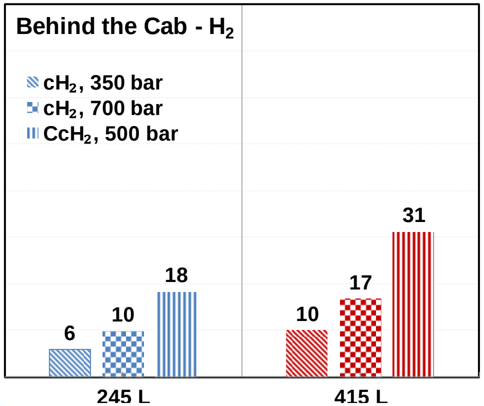
Internal Volume, L/tank

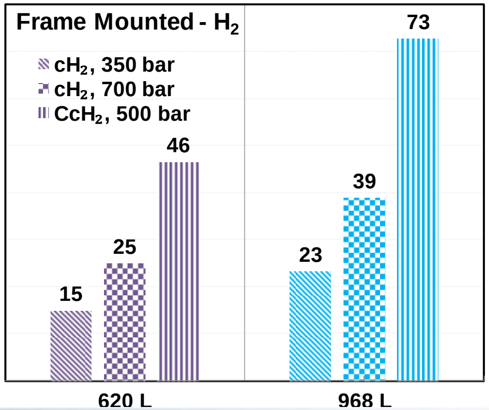


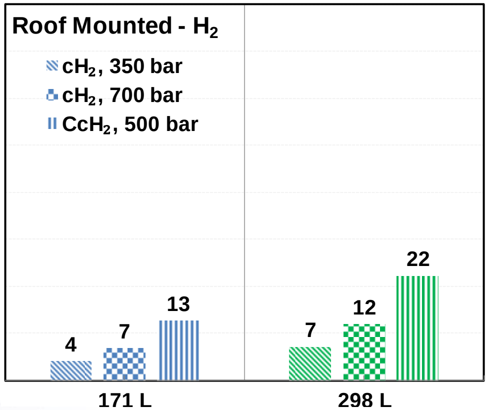




H_2 Stored, kg/tank







[1]Gangloff, Kast, Morrison, and Marcinkoski, JEECS 2017 (14) 021001-1 ; [2]http://www.a1autoelectric.com/; [3]Strategic Analysis

H_2 Storage for MD and HD Trucks: Carbon Fiber Requirement

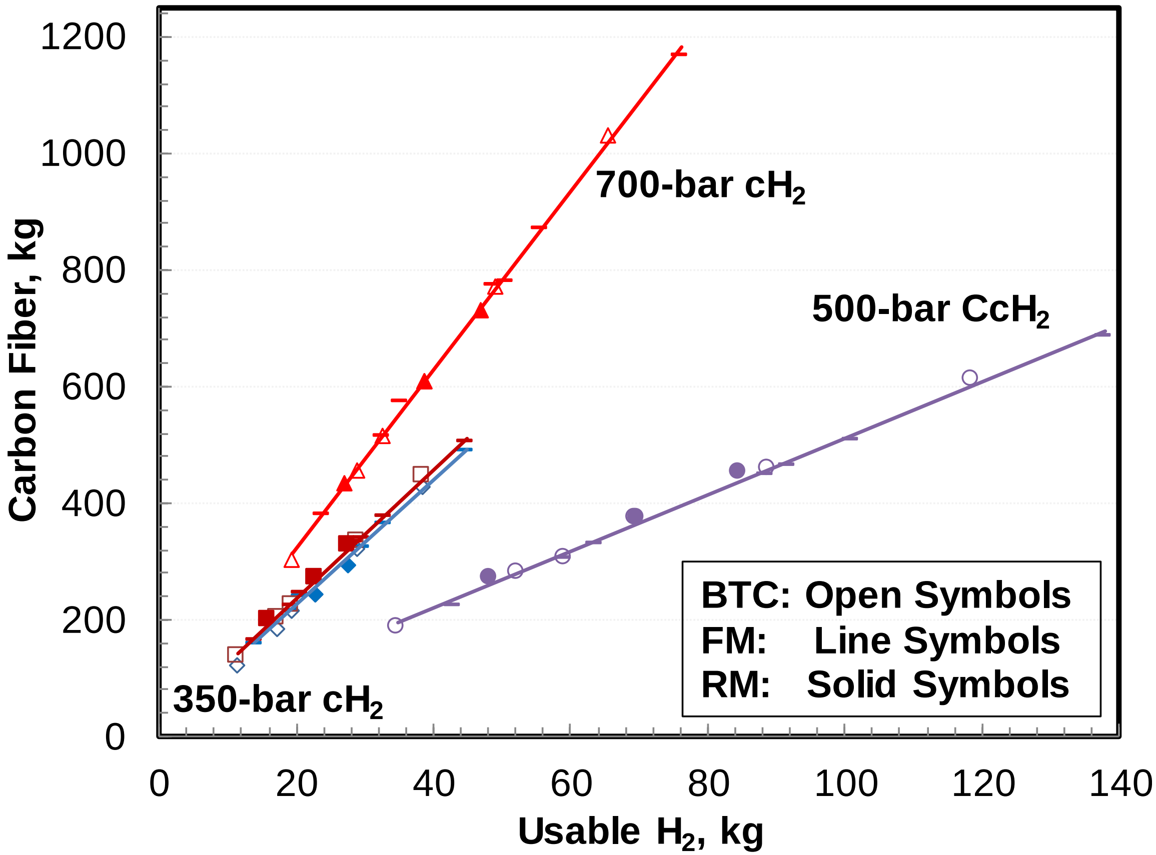
Layout	Tank Volume (L)	Number of Tanks	Carbon Fiber Composite (kg): cH_2 350-bar Type 3	cH_2 350-bar Type 4	cH_2 700-bar Type 4	CcH_2 500 bar
BTC	246 - 415	2, 3, 4	122 - 429	136 - 447	314 - 1030	188 - 611
FM	301 - 968	2	159 - 489	165 - 506	382 - 1168	225 - 687
RM	172 - 298	4	200 - 294	201 - 327	434 - 731	272 - 453

Carbon fiber composite requirement for same usable H_2

- ABAQUS/WCM FEA and FE-SAFE simulations
- 2.25 burst safety factor
- 15,000 pressure cycles
- CcH_2 << 350 bar Type-3 cH_2 ~ 350 bar Type-4 cH_2 << 700 bar Type-4 cH_2

Future work

- In collaboration with HMAT, verify fatigue life of SS 316 liner in CcH_2
- In collaboration with HMAT, verify fatigue life of Al 6061-T6 alloy liner in cH_2



H_2 Storage for MD and HD Trucks: Gravimetric Capacity

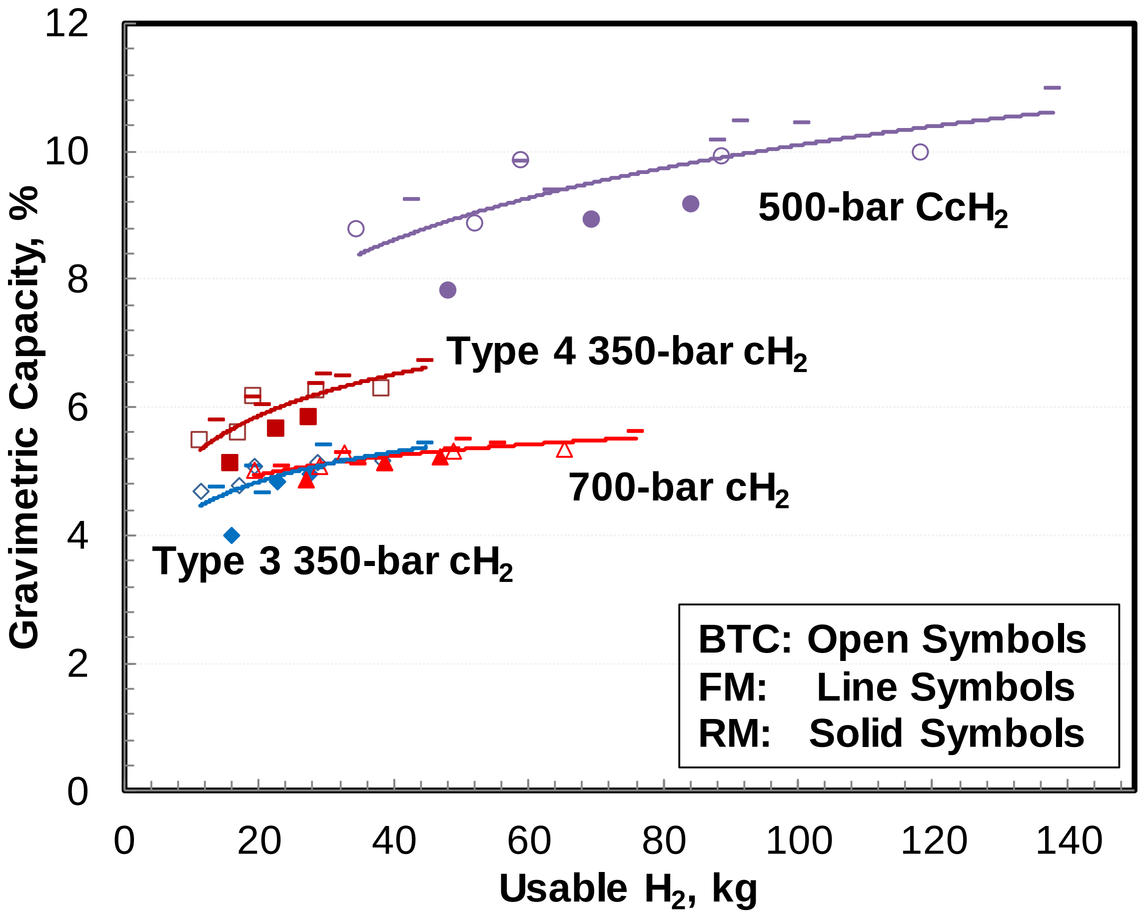
Layout	Tank Volume (L)	Number of Tanks	Gravimetric Capacity (%) cH2 350-bar Type 3	Gravimetric Capacity (%) cH2 350-bar Type 4	Gravimetric Capacity (%) cH2 700-bar Type 4	Gravimetric Capacity (%) CcH2 500 bar
BTC	246 - 415	2, 3, 4	4.7 - 5.2	5.5 - 6.3	5.0- 5.3	8.8 - 10.0
FM	301 - 968	2	4.7 - 5.4	5.8 - 6.7	5.1 - 5.6	9.2 - 11.0
RM	172 - 298	4	4.0 - 5.0	5.1 - 5.8	4.9 - 5.2	7.8 - 9.2

Gravimetric capacity for same usable H_2

- CcH_2 >> 350 bar Type-4 cH_2 > 700 bar Type-4 cH_2 > 350 bar Type-3 cH_2

Future work

- Mounting of BTC, FM and RM tanks, structural reinforcement, safety
- Update BOP components and systems for trucks



Accomplishment

H_2 Storage for MD and HD Trucks: Volumetric Capacity

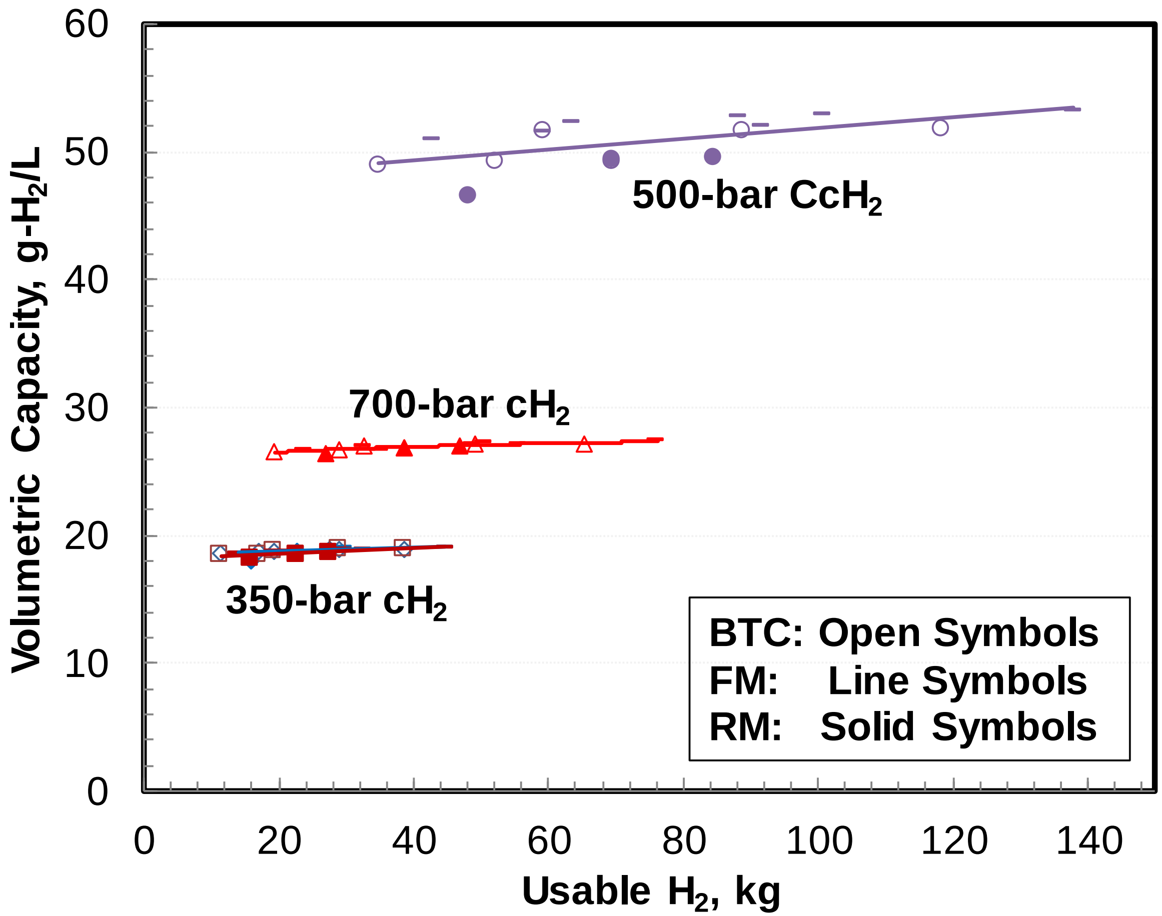
Layout	Tank Volume (L)	Number of Tanks	Volumetric Capacity (g-H_2/L) cH$_2$ 350-bar Type 3	cH$_2$ 350-bar Type 4	cH$_2$ 700-bar Type 4	CcH$_2$ 500 bar
BTC	246 - 415	2, 3, 4	18.6 - 18.9	18.4 - 18.9	26.6 - 27.1	49.0 - 51.7
FM	301 - 968	2	18.6 - 19.0	18.6 - 19.1	26.7 - 27.4	51.0 - 53.2
RM	172 - 298	4	18.1 - 18.8	18.2 - 18.6	26.4 - 26.9	46.5 - 49.5

Volumetric capacity for same usable H_2

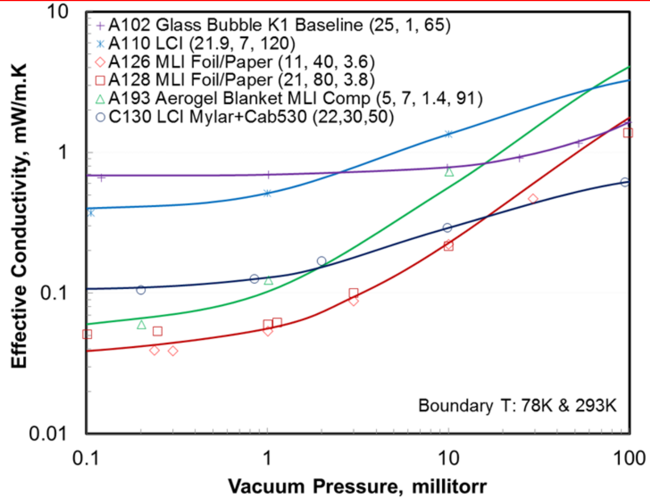
- CcH$_2$ >> 700 bar Type-4 cH$_2$ > 350 bar Type-4 cH$_2$ ~ 350 bar Type-3 cH$_2$
- Usable H_2 (10 bar min. pressure)
  - 98% 700 bar
  - 97% 350 bar
  - 95% CcH$_2$

Future work

- Assess CcH$_2$ at lower pressures (275-350 bar) for truck-specific duty cycles

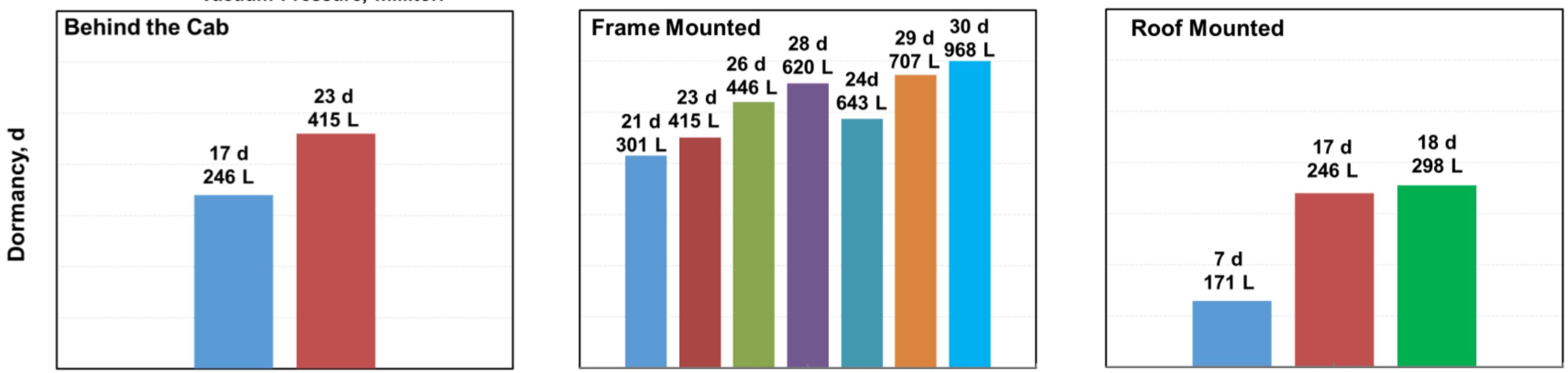


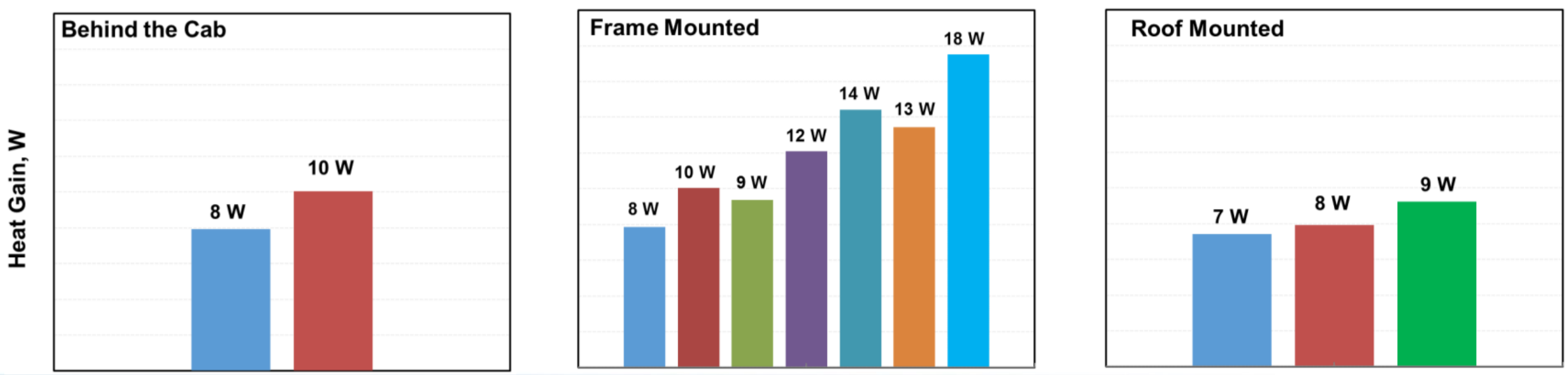
Cryo-compressed Tanks – Dormancy and Heat Gain



> 7-d dormancy for 95% initially-full tank with 40 layers of MLVSI and 3-millitorr vacuum pressure

- Effective conductivity[1] modeled using Hastings correlations (NASA/TM-2004-213175) for gas radiation, solid conduction and gas conduction
- Dormancy scales with the amount of hydrogen stored and depends on para-to-ortho conversion





[1]Data from DE-EE0007649 - Integrated Insulation System for Cryogenic Automotive Tanks (iCAT), Vencore Services and Solutions, Inc.

FY2019 Collaborations

Hydrogen Carriers	HyMARC: PNNL, NREL, LBNL
Bulk Storage	ANL (H2A Group), ANL (HDSAM), H2IT Taskforce
Compressed Hydrogen Storage for Trucks	SA Team: SA, ANL, PNNL Ford
Cryo-Compressed Hydrogen Storage for Trucks	HMAT: PNNL, SNL TARDEC LLNL, BMW
Off-Board Cost	ANL (H2A Group), ANL (HDSAM), H2IT Taskforce
On-Board Cost	Strategic Analysis Inc (SA)

- Argonne develops the storage system configuration, determines performance, identifies and sizes components, and provides this information to SA for manufacturing cost studies

Future Work

1. Hydrogen Carriers
   - Scenarios that favor hydrogen carriers such as by-product H_2
   - Case studies with different demand and supply scenarios
   - Carriers that are particularly suitable for renewable hydrogen production and energy storage
   - Reverse engineering to determine desirable properties of liquid carriers including ease of dehydrogenation and H_2 purification
   - Coordination with HyMARC consortium to analyze emerging materials

2. Bulk Storage of Hydrogen
   - Complete analyses of different storage methods (geological and non-geological), storage capacities (1-10 days), and storage locations (city gate vs. forecourt)

3. Hydrogen Storage for Medium and Heavy-Duty Trucks
   - Continue to conduct finite element simulations to verify cycle life and carbon fiber requirements
   - Mounting of BTC, FM and RM tanks, structural reinforcement, safety

Project Summary

Relevance:	Independent analysis to evaluate on-board and off-board performance of materials and systems
Approach:	Develop and validate physical, thermodynamic and kinetic models of processes in physical and material-based systems Address all aspects of on-board and off-board targets including capacities, rates and efficiencies
Progress:	Determined the scenario for which methanol as hydrogen carrier can be cost competitive with the incumbent technology Proposed initial targets for production, transmission and decomposition of hydrogen carriers for overall \$2/kg H_2 production cost Established the cost of storing 1-3000 tonnes of H_2 in underground tubes, lined rock caverns, and salt caverns Determined carbon fiber requirements, gravimetric capacities, volumetric capacities and dormancy for 350-bar, 700-bar and cryo-compressed hydrogen storage on-board medium-duty and heavy-duty trucks
Collaborations:	Ford, HyMARC, LLNL, PNNL, SA, Delivery Team
Proposed Future Work:	Determine desirable material properties and analyze scenarios that favor hydrogen carriers Complete analysis of stationary hydrogen storage for different scales, duration and applications Validate results for hydrogen storage on-board HDVs and MDVs

Reviewer Comments

Generally favorable reviews with the following comments/recommendations

- The approach is straightforward and rational. This project continues to serve a valuable role
- Excellent progress was achieved in FY 2017 and 2018 in all four focus areas
- Excellent interactions and collaborations
- Essential to augment collaborations with HyMARC
- Add specific activities on carriers that favor transition to large-scale renewable resources

FY19 work scope consistent with above recommendations

√ Fostered closer interactions with HyMARC on hydrogen carriers. Presented work at HyMARC meeting and jointly with PNNL at FCTO webinar. Collaborating to define targets and needs for material development and characterization.

√ Started a new interaction with TARDEC to promote work on cryo-compressed storage for heavy-duty vehicles

√ Closely coordinating the task on on-board storage for medium-duty and heavy-duty vehicles with Strategic Analysis

√ Extended expertise and knowledge to bulk hydrogen storage at different scales and for different applications

√ Transitioning work to maintain relevance and address critical issues as DOE focus shifts to H2@Scale

Excerpt of References

Slide 7-10, Hydrogen Carriers

Aasberg-Petersen, K et al. Large Scale Methanol Production from Natural Gas. www. Topsoe.com

Pattabathula, V and Richardson, J. (2016). Introduction to Ammonia Production. www.aiche.org/cep

Okada et al. (2006). Development of dehydrogenation catalyst for hydrogen generation in organic chemical hydride method. Int. J. Hydrogen Energ., 31, 11348-1356.

Surface Transportation Board. Carload waybills for all U.S. rail traffic submitted by those rail carriers terminating 4,500 or more revenue carloads annually. https://www.stb.gov/stb/industry/econ_waybill.html

Slide 13, Bulk H_2 Storage Methods

Tietze, V., Luhr, S. and Stolten, D. (2016). Bulk Storage Vessels for Compressed and Liquid Hydrogen. Hydrogen Science and Engineering : Materials, Processes, Systems and Technology, Wiley-VCH Verlag.

Energy Technology Institute. (2018). Salt Cavern Appraisal for Hydrogen and Gas Storage. Stage 2 Report, 5149533-MD-REP-005

Olaf, K., Prelicz, R. and Rudolph T. (2013). Assessment of the potential, the actors and relevant business cases for large scale and seasonal storage of renewable electricity by hydrogen underground storage in Europe. HyUnder Grant agreement no.: 303417

Sofregaz and LRC (1999). Commercial Potential of Natural Gas Storage in Lined Rock Caverns. Topical Report SZUS-0005 DE-AC26-97FT34348-01

Slide 14, Bulk H_2 Storage in Underground Pipes

Fekete R. at. al (2015), Economic impact of applying high strength steels in hydrogen gas pipelines. Int. J. Hydrogen Energ., 40, 10547-10558.

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USDA Forest Service Northern Region Engineering, (2017). Cost Estimating Guide for Road Construction

Slide 16, Bulk H_2 Storage in Underground Lined Rock Caverns (LRC)

Brandshaug, T. et. al (2001). Technical Review of the Lined Rock Cavern (LRC) Concept and Design Methodology: Mechanical Response of Rock Mass. DE-AM26-99FT40463.

Glamheden, R. and Curtis, P. (2006). Excavation of a cavern for high-pressure storage of natural gas. Tunneling and Underground Space Technology 21 (2006) 56–67.

Robb, A. (2007). Review of cost and excavation time of the very large water Cerenkov detector chamber. Topical Report, RSI-1919

Slide 18, Bulk H_2 Storage in Underground Salt Cavern

Barron. T.F. (1994). Regulatory, Technical Pressures Prompt More U.S. Salt-Cavern Gas Storage. Oil and Gas Journal.

EPA. (2018). Detailed Study of the Centralized Waste Treatment Point Source Category. EPA-821-R-18-004

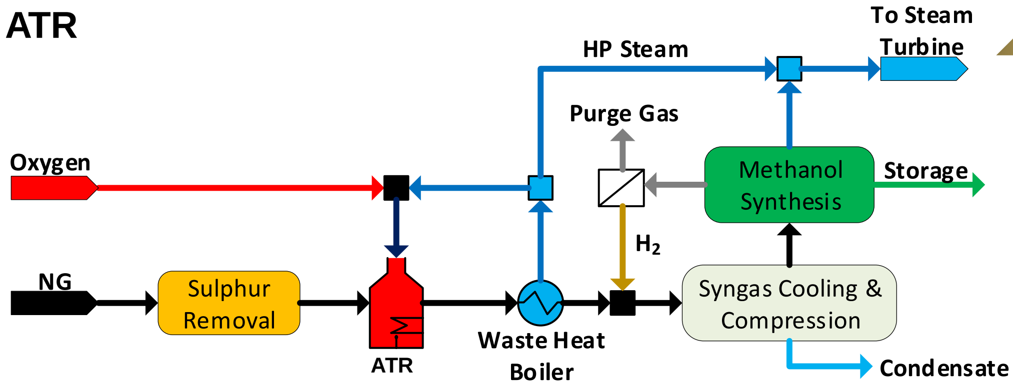
Veil, J. (2015), Class II Injection Wells Are an Integral Part of U.S. Oil and Gas Production. GWPC UIC Meeting, Austin, TX

Lord, A.S. (2014). Geologic storage of hydrogen: Scaling up to meet city transportation demands. Int. J. Hydrogen Energ., 39, 15570-15582.

Technical Back-Up Slides

Methanol Production Plant Configurations

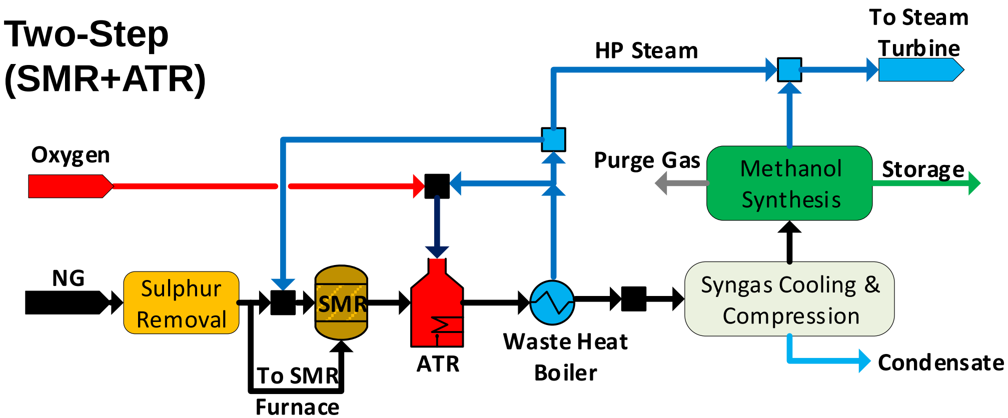
ATR



5,000-10,000 tpd 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 kWh_e/kg-MeOH
- Steam Turbine: 0.5 kWh_e/kg-MeOH

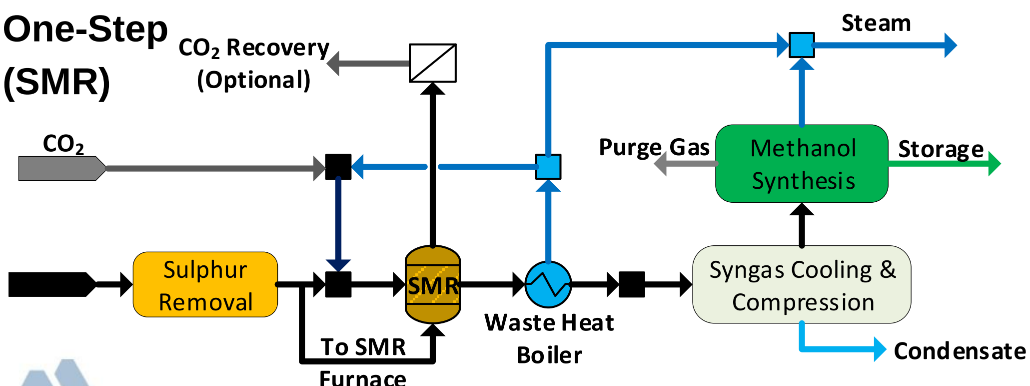
Two-Step (SMR+ATR)



2,000-4,000 tpd 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 kWh_e/kg-MeOH
- Steam Turbine: 0.48 kWh_e/kg-MeOH

One-Step (SMR)



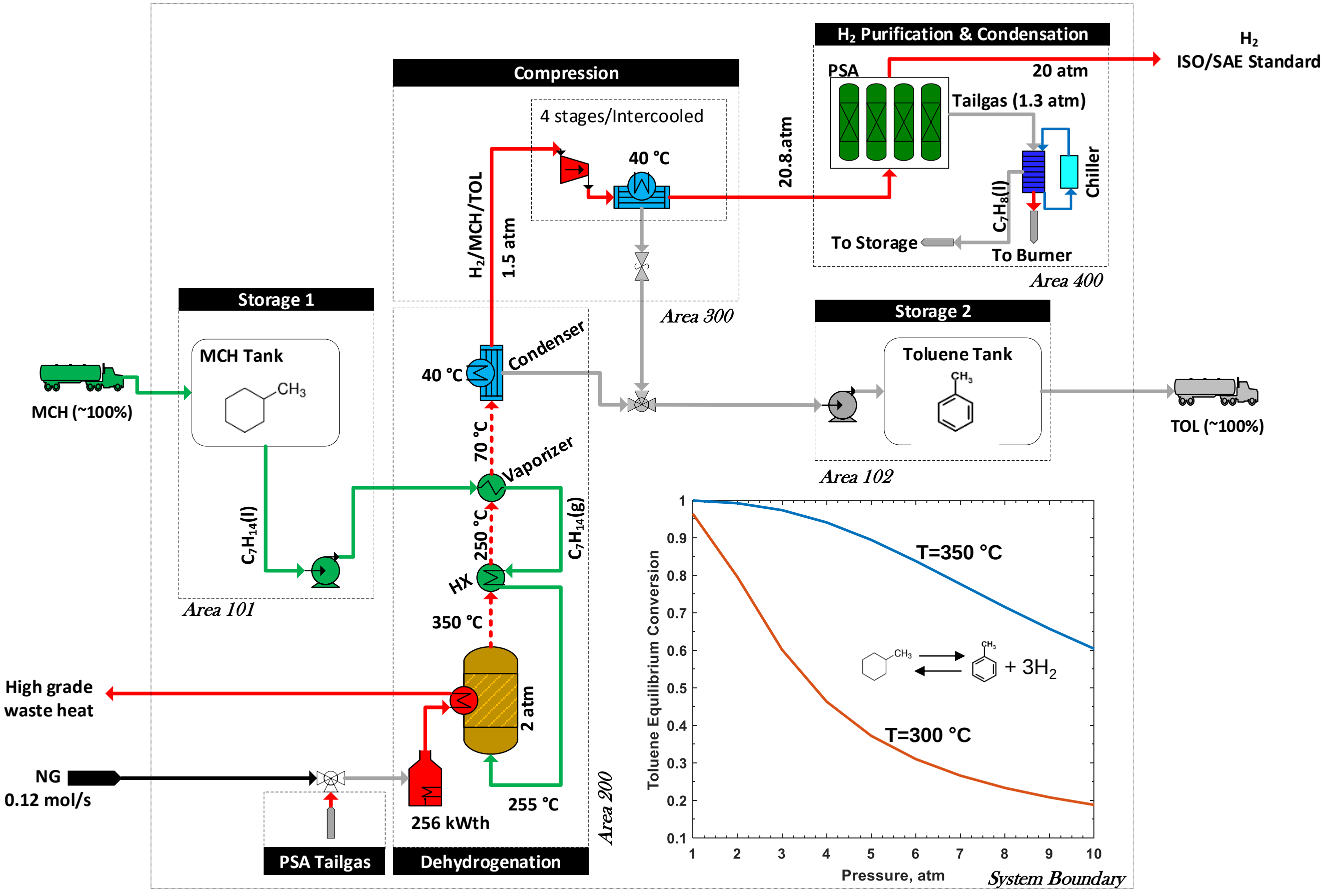
<1,700 tpd scale

- $CO_2/C=0.3$, $H_2O/C=3.5$
- M (reformer): 2.05
- 1 BWR or Quench reactor
- Electricity demand: 0.14 kWh_e/kg-MeOH
- Steam Turbine: <u>*Not economical*</u>

BWR = Boling Water Reactor *ASU= Air Separation Unit* *Syngas stoichiometric molar ratio (M)= (H_2-CO_2)/(CO+CO_2)*

Capital Cost of Methylcyclohexane Dehydrogenation Plant

- Reactor operated at 350°C and 2 atm. Conversion is 98% 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 during the compression cycle (4 stages) and chiller
- H_2 separation by PSA at 20 atm, 90% recovery (ISO/SAE H_2 quality)



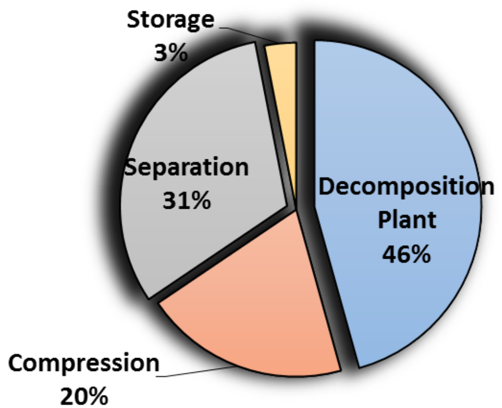
Losses

- Toluene+MCH: 0.84%
- Hydrogen: 10%
- Heat: 0.36 $kWh_{th}/kWh_{th}\text{-}H_2$

Feedstock/Utilities

- NG: 0.22 $kWh_{th}/KWh_{th}\text{-}H_2$
- Electricity: 0.04 $kWh_e/KW_{th}\text{-}H_2$

Capital Cost ($M 0.72/tpd-$H_2$)



50 tpd-H_2

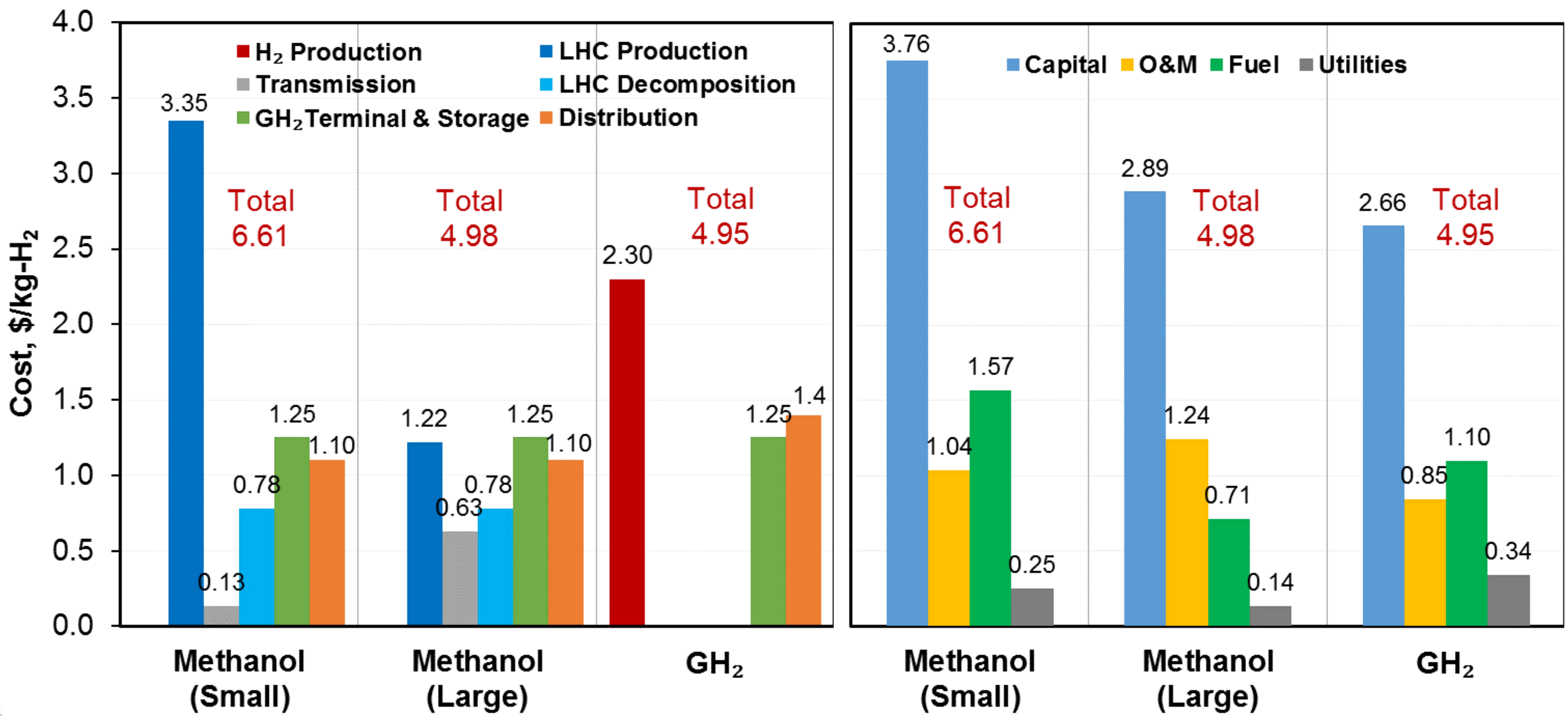
Okada, Y. et. al. (2006). Development of Dehydrogenation Catalyst for Hydrogen Generation in Organic Chemical Hydride Method. Int. J. Hydrogen Energy, 31, 1348.

MeOH Pathway
Levelized Cost of H_2 Distributed to Stations (50 tpd-H_2)

Liquid carrier option can be competitive with the baseline GH_2 scenario.

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

- 2.13 \$/kg-H_2 lower LHC production cost
  - 0.97 \$/kg-H_2 lower fuel (\$2.65/MBtu vs. \$6.80/MBtu NG cost) + utilities cost
- 0.50 \$/kg-H_2 higher transmission cost



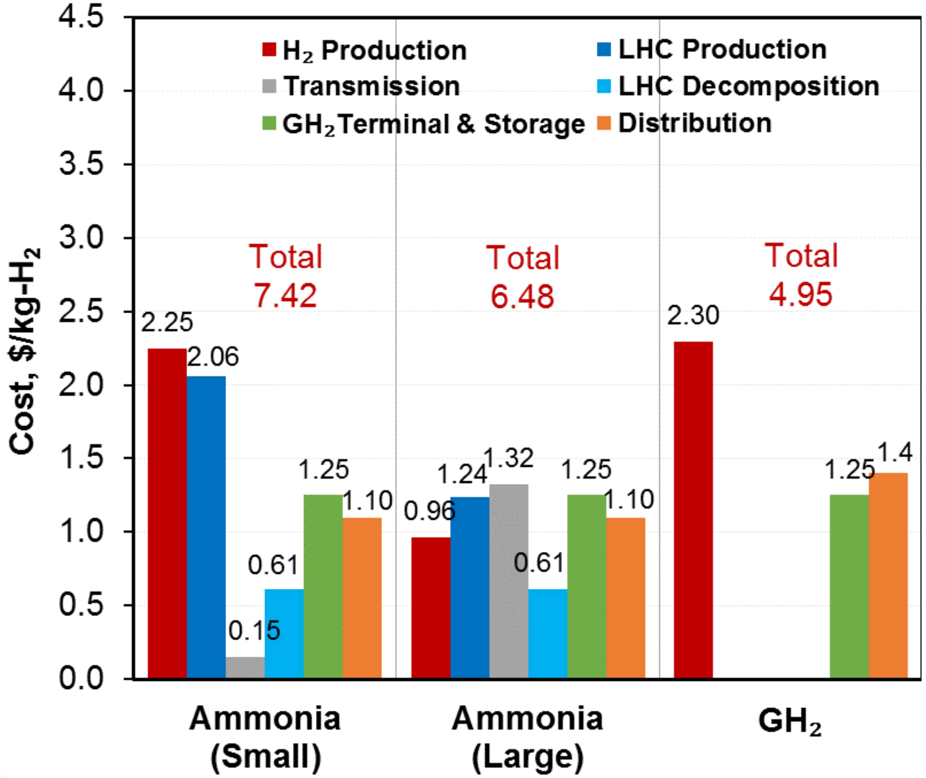
Ammonia Pathway
Levelized Cost of H_2 Distributed to Stations (50 tpd-H_2)

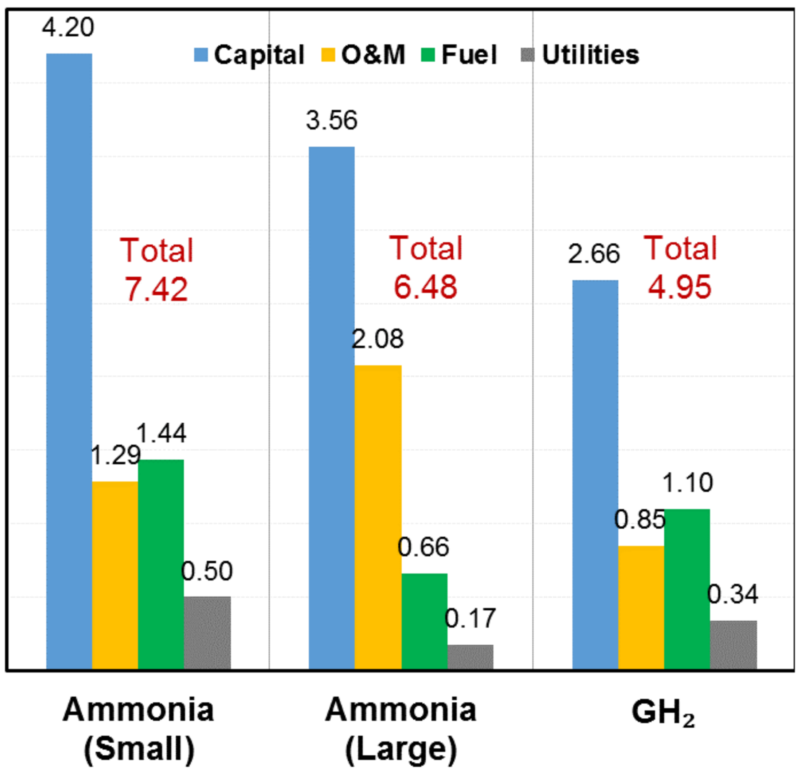
As a carrier, ammonia is a more expensive option than methanol

- Advantage of economy of scale partially offset by higher transmission cost

Large (2,500 tpd) vs. small (370 tpd) ammonia production plants

- 1.29 \$/kg-H_2 lower H_2 production cost (\$2.65/MBtu vs. \$6.80/MBtu NG cost)
- 0.82 \$/kg-H_2 lower LHC production cost
- 1.17 \$/kg-H_2 higher transmission costs





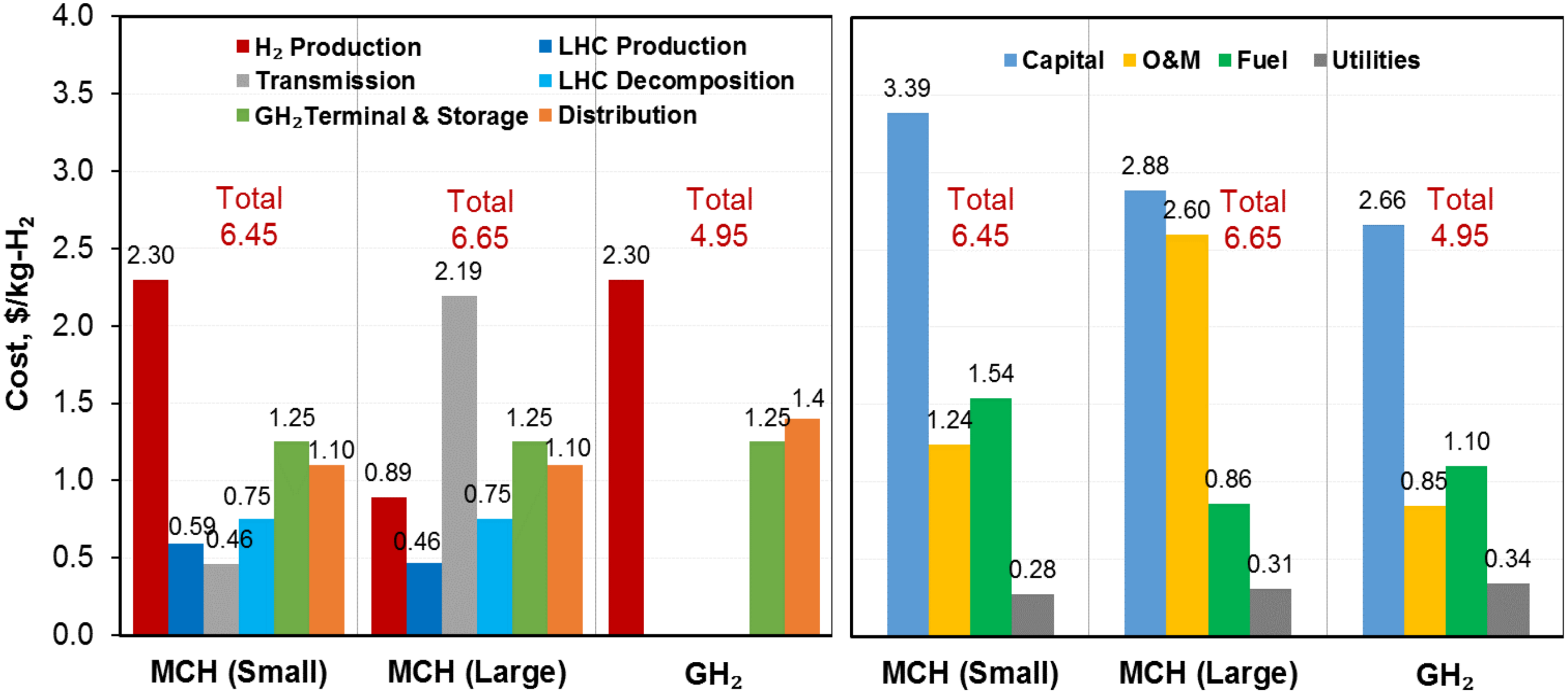
MCH/Toluene Pathway
Levelized Cost of H_2 Distributed to Stations (50 tpd-H_2)

Advantage of producing MCH at large scale more than completely offset by higher transmission cost

- Investigate alternate transmission modes: barges, tankers, train ownership

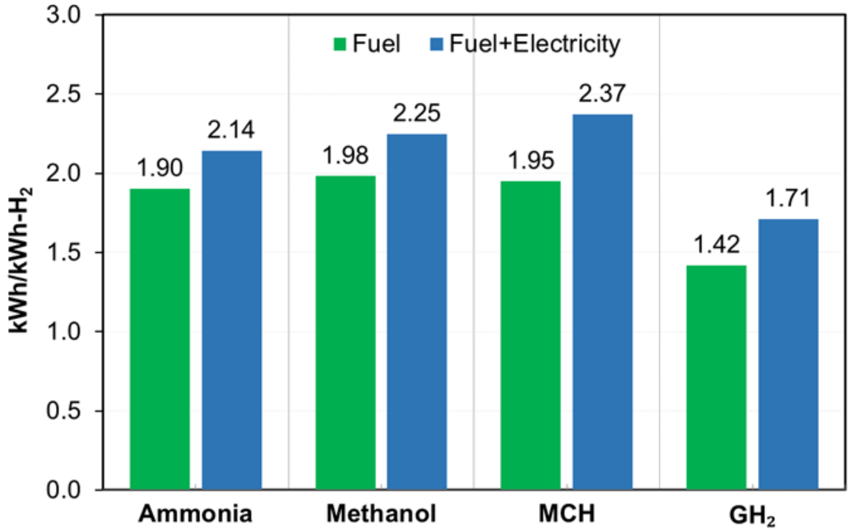
Large (6,700 tpd) vs. small (890 tpd) MCH production plants

- 1.41 \$/kg-H_2 lower H_2 production cost (\$2.65/MBtu vs. \$6.80/MBtu NG cost)
- 0.13 \$/kg-H_2 lower LHC production cost
- 1.73 \$/kg-H_2 higher transmission cost



Hydrogen Carriers: Summary

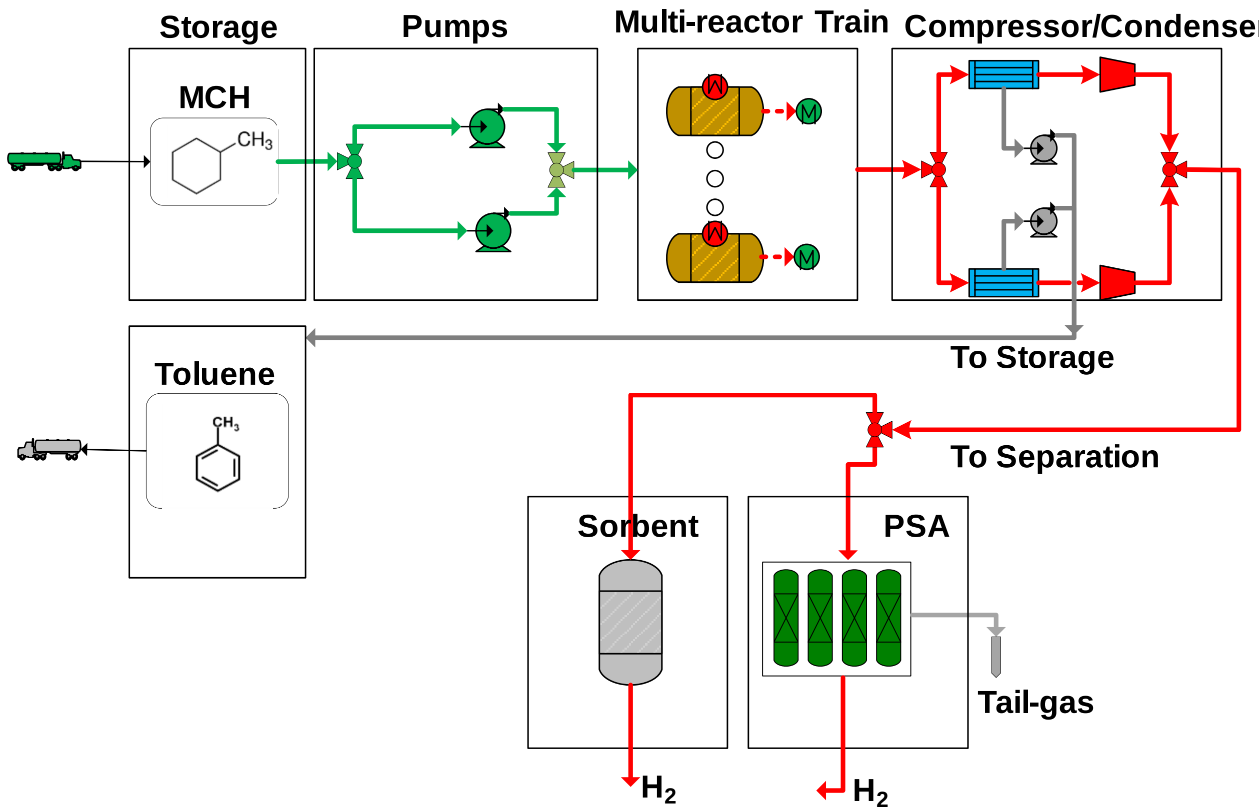
MP	BP	H_2 Capacity		Production		Decomposition		
°C	°C	wt%	g/L	P, bar	T, °C	P, bar	T, °C	ΔH kJ/mol-H_2
Ammonia								
-78	-33.4	17.6	121	150	375	20	800	30.6
				Haber-Bosch Process Fe Based Catalyst		High-Temperature Cracking Ni Catalyst		
Methanol								
-98	64.7	18.75	149	51	250	3	290	16.6
				$Cu/ZnO/Al_2O_3$ Catalyst		Steam Reforming		
MCH								
-127	101	6.1	47	10	240	2	350	68.3
				Non-PGM Catalyst		Pt/Al_2O_3 Catalyst		



	Levelized Cost at Station ($/kg-$H_2$)				
	Methanol	Ammonia	MCH / Toluene	GH_2	Comments
H_2 Production		0.96	0.89	2.30	Ammonia more expensive to produce than MCH from toulene
LHC Production	1.22	1.24	0.46		Methanol produced directly from NG under mild conditions
LHC Transmission	0.63	1.32	2.19		Refrigerated rail cars needed for ammonia
LHC Decomposition	0.78	0.61	0.75		H-capacity of MHC is only 47 g/L
GH_2 Terminal & Storage	1.25	1.25	1.25	1.25	Ideally, LCH should decompose at PSA operating pressure
Distribution	1.10	1.10	1.10	1.40	GH_2 distributed from production site to refueling station
Total	4.98	6.48	6.65	4.95	

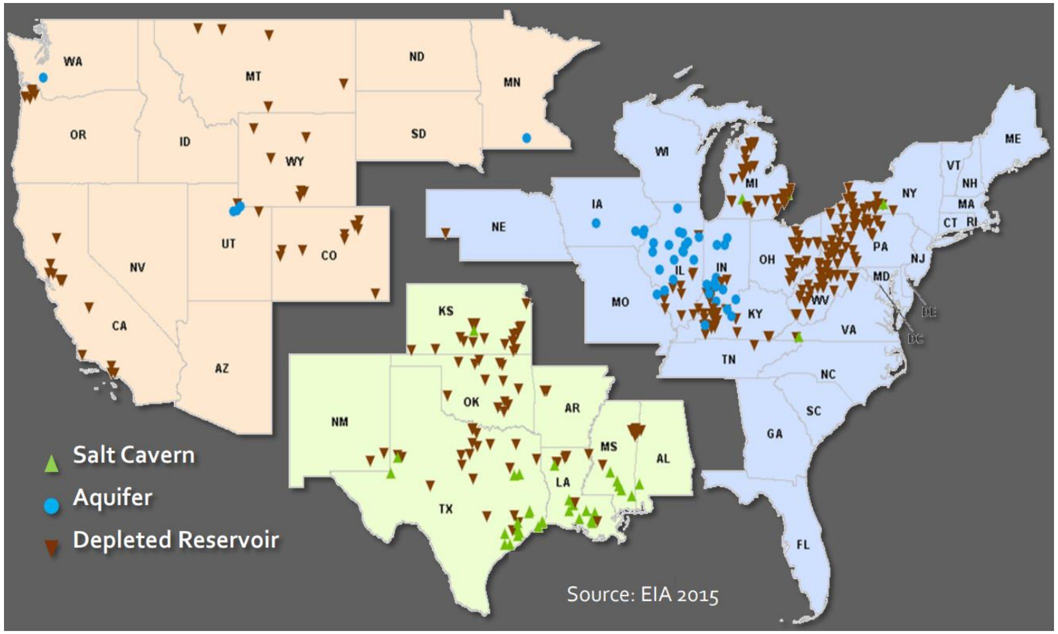
Next Step
Reducing H_2 Bulk Storage Requirement with Liquid Carriers

Parallel dehydrogenation steps

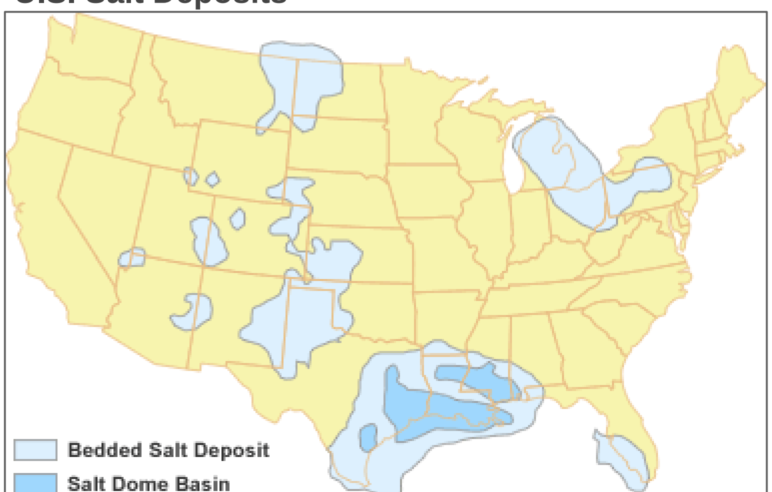


- Desirable to have a carrier (low ΔG and ΔH) that can be dehydrogenated under mild operating conditions
- Liquid phase decomposition at high pressures to ease compression requirements
- Minimal or no side products, simple purification steps

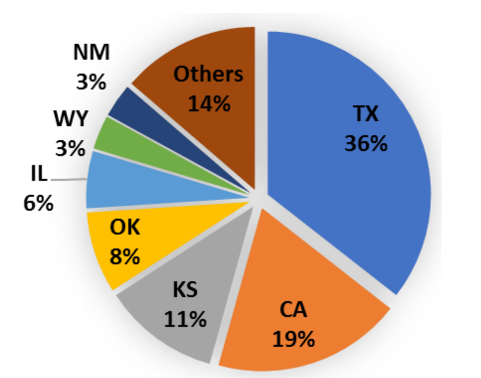
Underground Storage



U.S. Salt Deposits

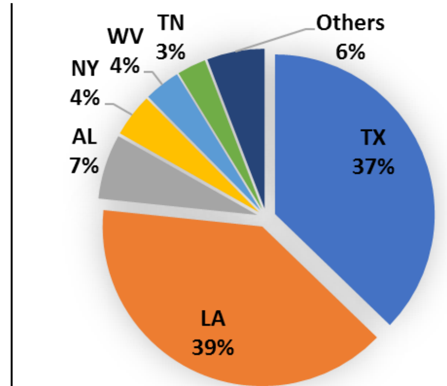


Source: Geology.com



U.S. Class II wells in operation (180,000)

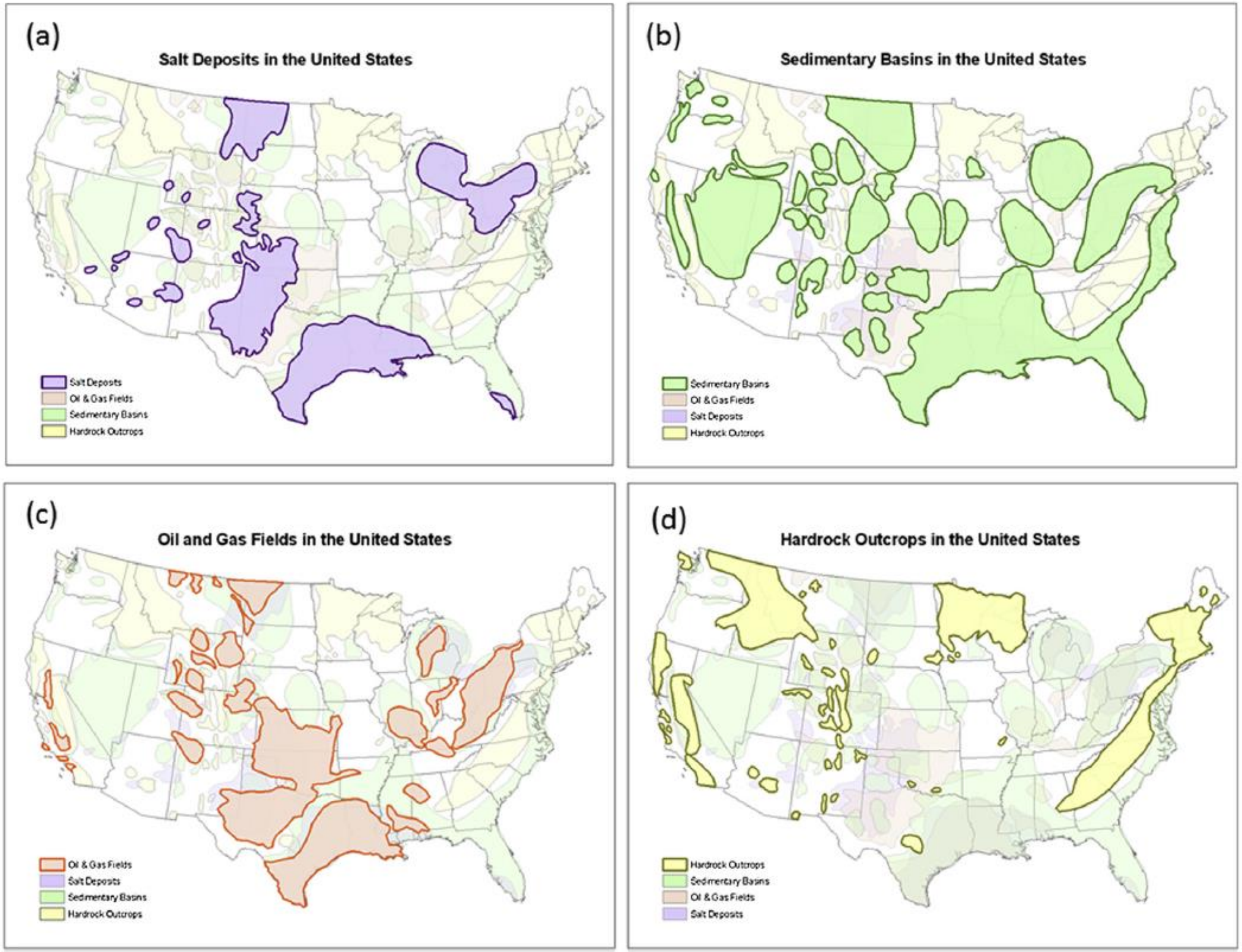
Source: EPA



U.S. Chlorine Production Capacity (14 million tonne/year)

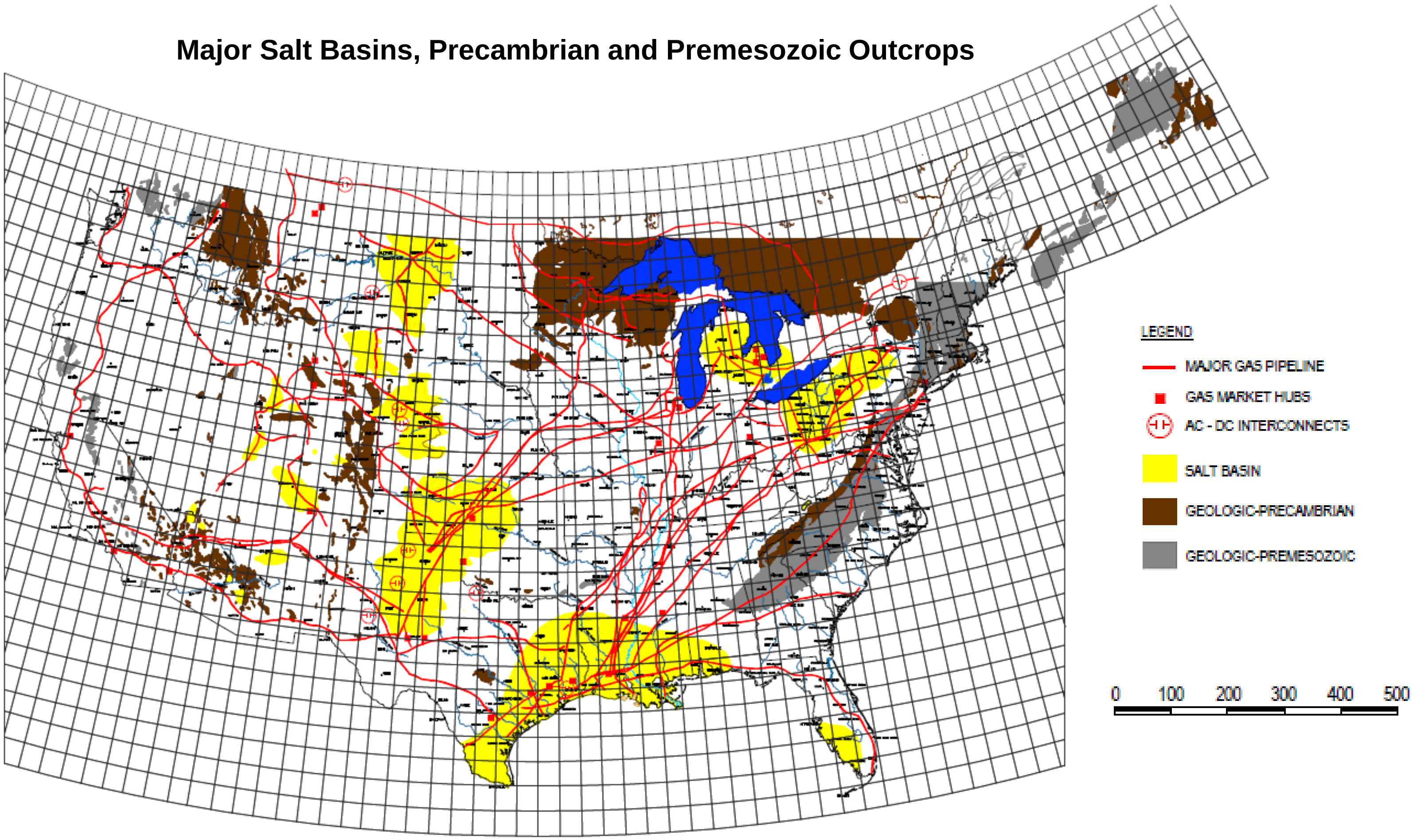
Source: Applied Energy, 217 (2008)

Underground Geological Storage Potential[1]



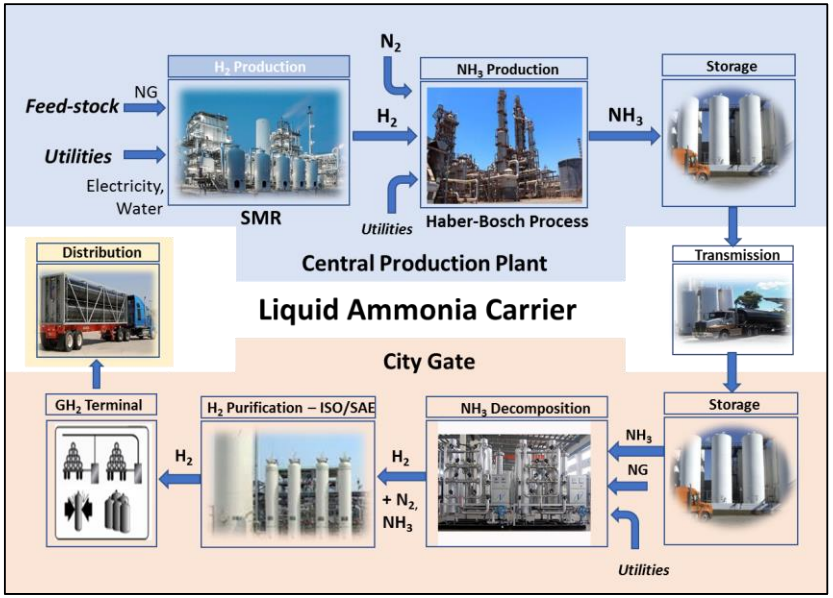
[1]Lord et al. (2014). Geologic storage of hydrogen: Scaling up to meet city transportation demands. Int. J. Hydrogen Energy, 39, 15570-15582

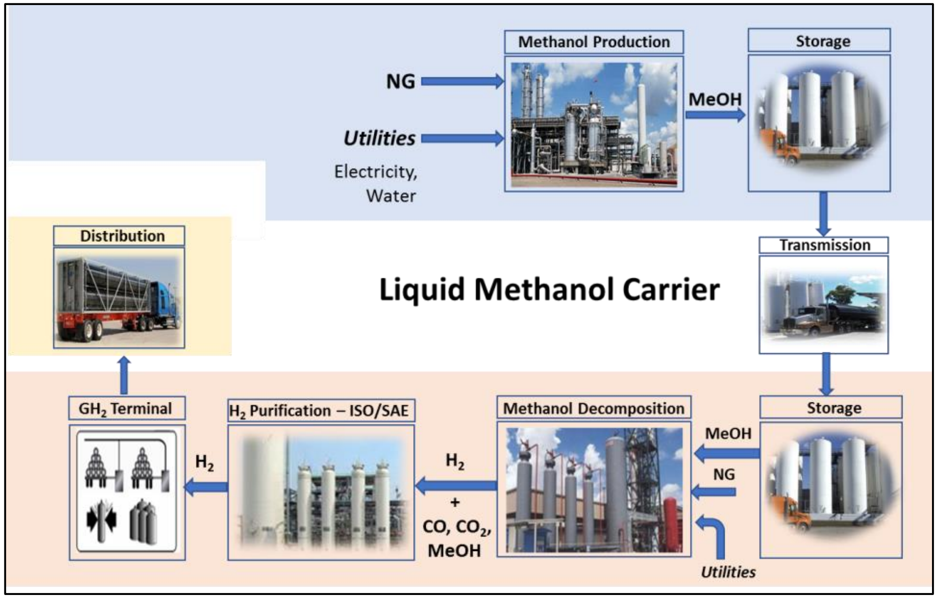
Underground Geological Storage Potential[2]



[2]Sofregaz US Inc. and LRC (1999). Commercial potential of natural gas storage in lined rock caverns (LRC). Topical report SZUS-0005-DE-AC26-97FT34348-01

Hydrogen Carrier Pathways – Small Plants





MP	BP	H_2 Capacity		Production		Decomposition		
°C	°C	wt%	g/L	P, bar	T, °C	P, bar	T, °C	ΔH kJ/mol-H_2
Ammonia								
-78	-33.4	17.6	121	150	375	20	800	30.6
				Haber-Bosch Process		High-Temperature Cracking		
				Fe Based Catalyst		Ni Catalyst		
Methanol								
-98	64.7	18.75	149	51	250	3	290	16.6
				$Cu/ZnO/Al_2O_3$ Catalyst		Steam Reforming		
MCH								
-127	101	6.1	47	10	240	2	350	68.3
				Non-PGM Catalyst		Pt/Al_2O_3 Catalyst