H2@Scale: Outlook of Hydrogen Carriers at Different Scales

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Department of Energy Hydrogen Carriers Workshop: Novel Pathways for Optimized Hydrogen Transport & Stationary Storage

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H2@Scale: Hydrogen Carriers

Why hydrogen carriers

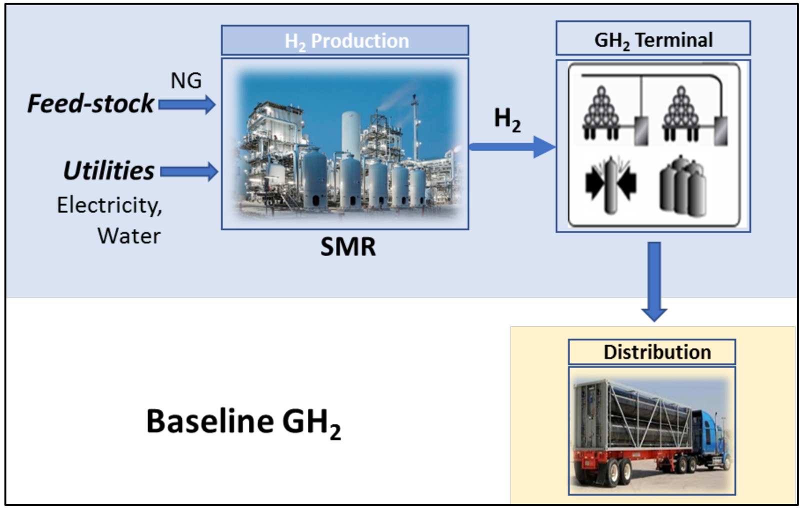
- Transmission over long distances including transoceanic
- Agnostic bulk storage at different scales and duration (daily to seasonal)

Scope of this study

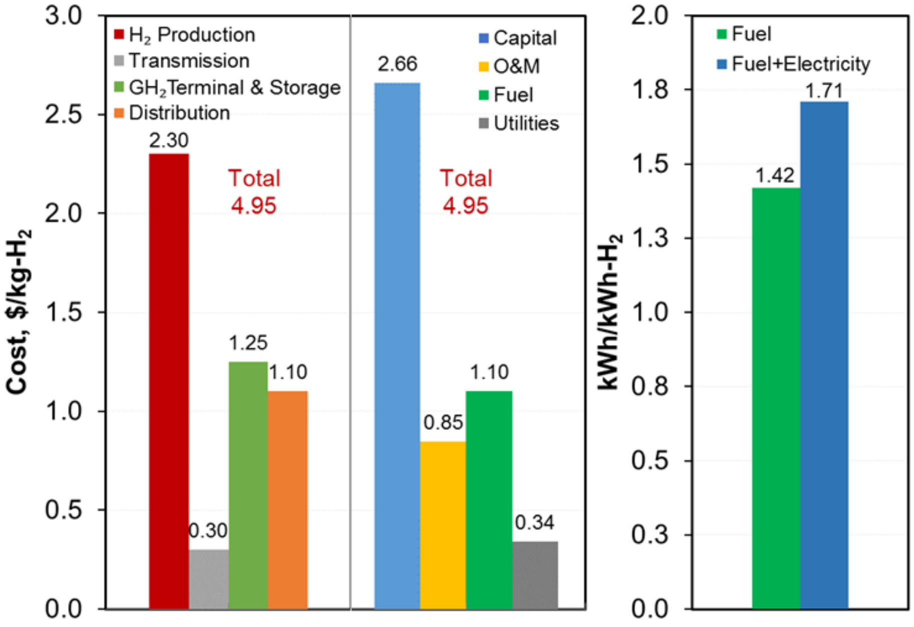
- Representative one-way carriers: methanol and ammonia
- Representative two-way carrier: methyl-cyclohexane/toluene system
- Reference pathway: hydrogen production by steam methane reforming
- Comparative production, transmission and decomposition costs at different demands
- Transmission via trains vs. pipelines
- Storage costs at different scales

	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		

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



- Production site 150 km from city gate
- Distribution includes transmission from production site to city gate



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	12 ¢/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

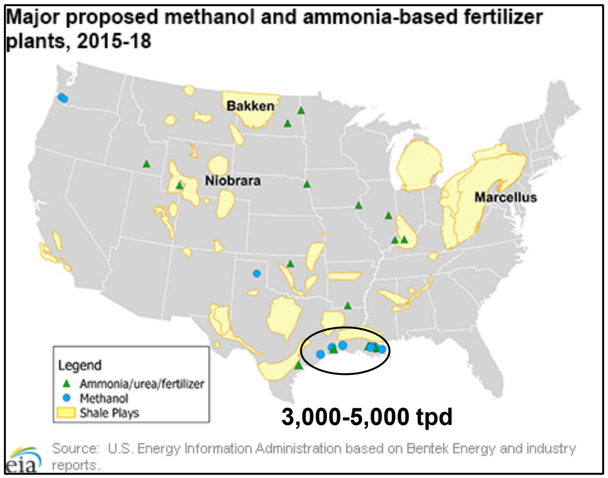
tpd: ton/day
t: ton = 1000 kg

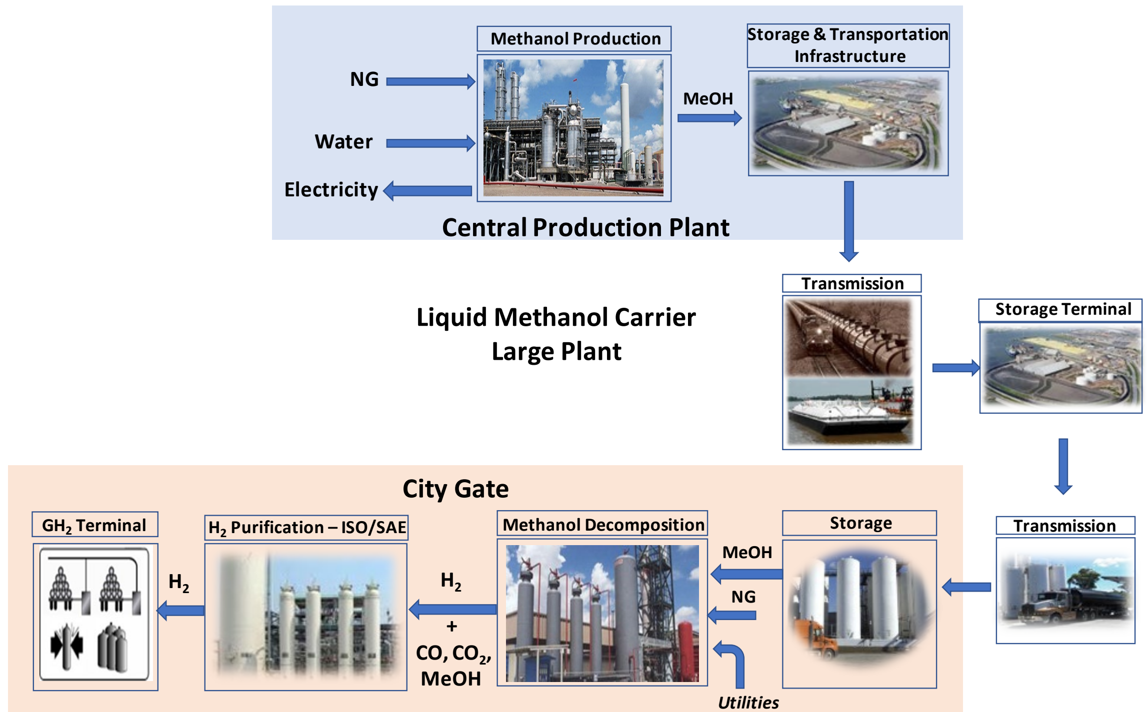
Baseline GH_2 scenario: Central SMR; GH_2 terminal: H_2 compression & storage; truck distribution;

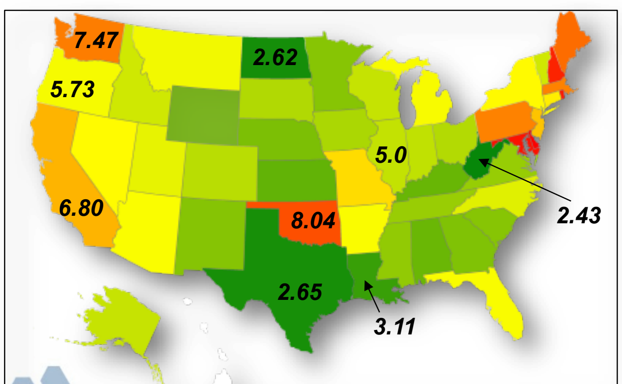
Hydrogen Carrier Pathways – Large Production Plants

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







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

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

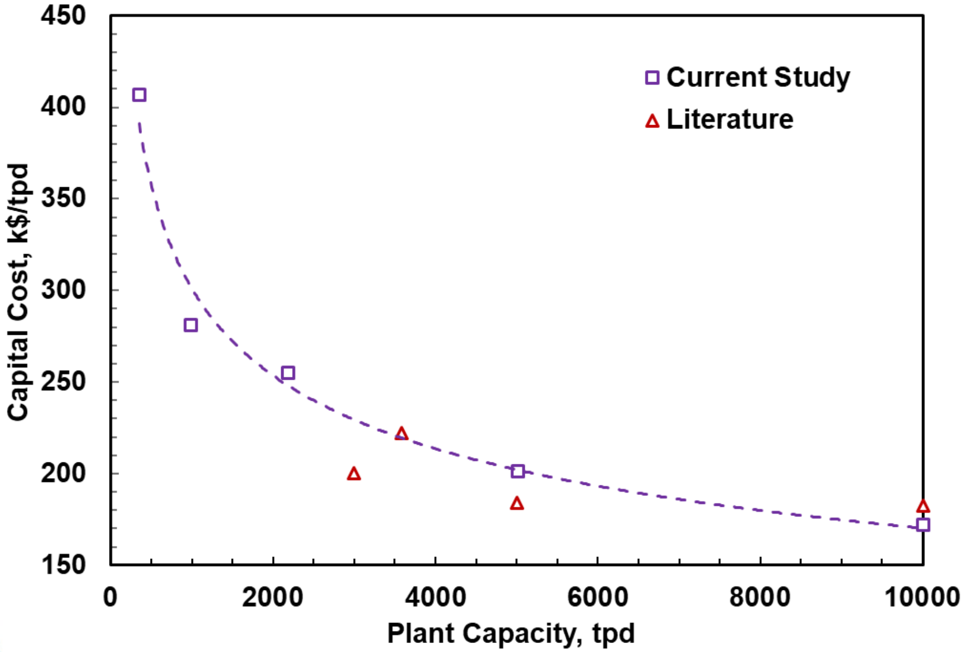
Capital Cost of Methanol Plants

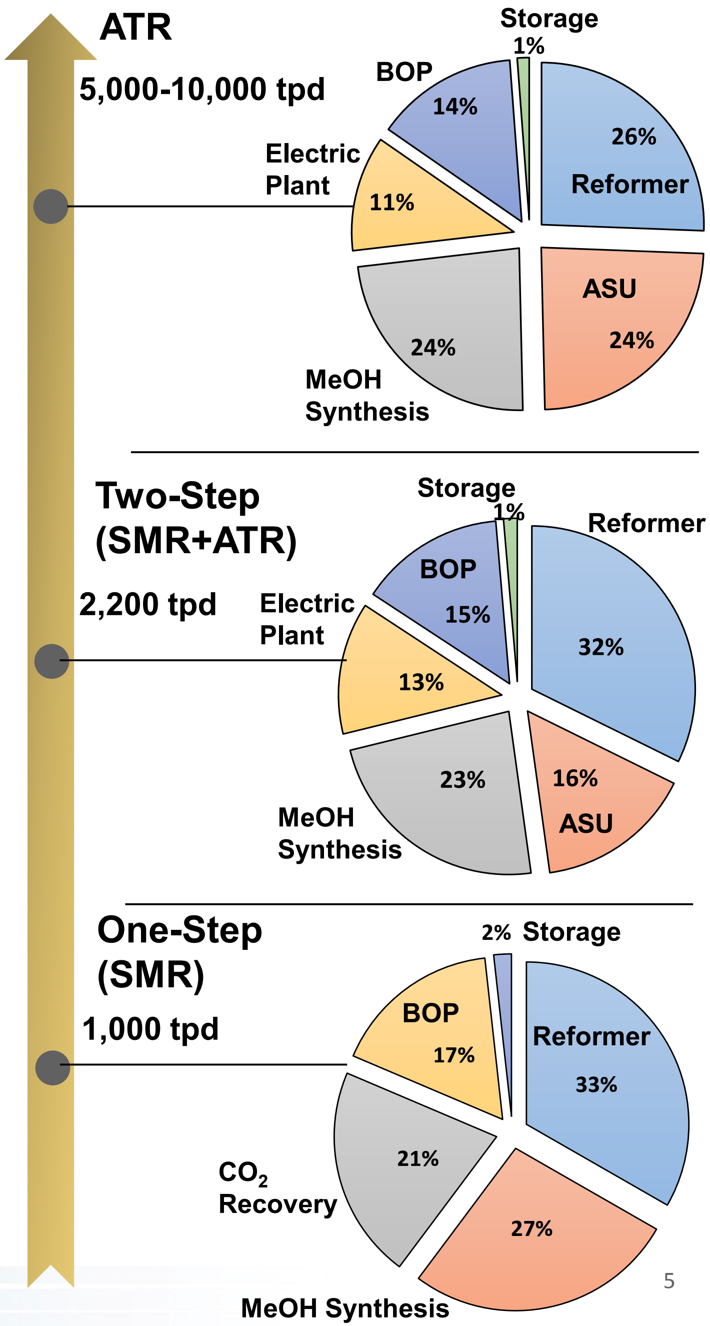
Capital cost minimized depending on scale

- 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

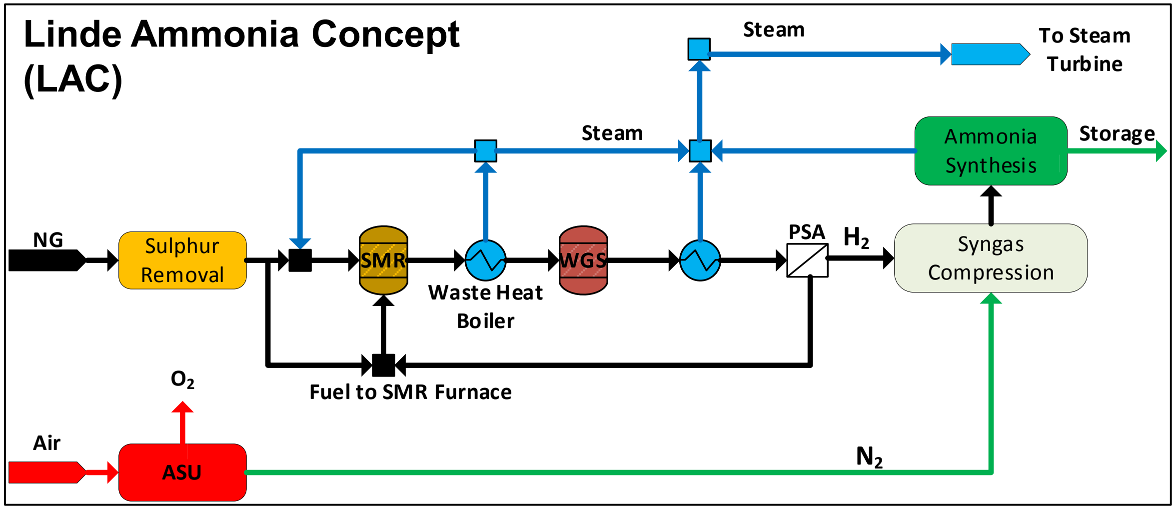
- Storage (30 days) of methanol accounts for a small fraction of total capital costs
- Capital cost: 202k$/tpd at 5,000 tpd, 172k$/tpd at 10,000 tpd





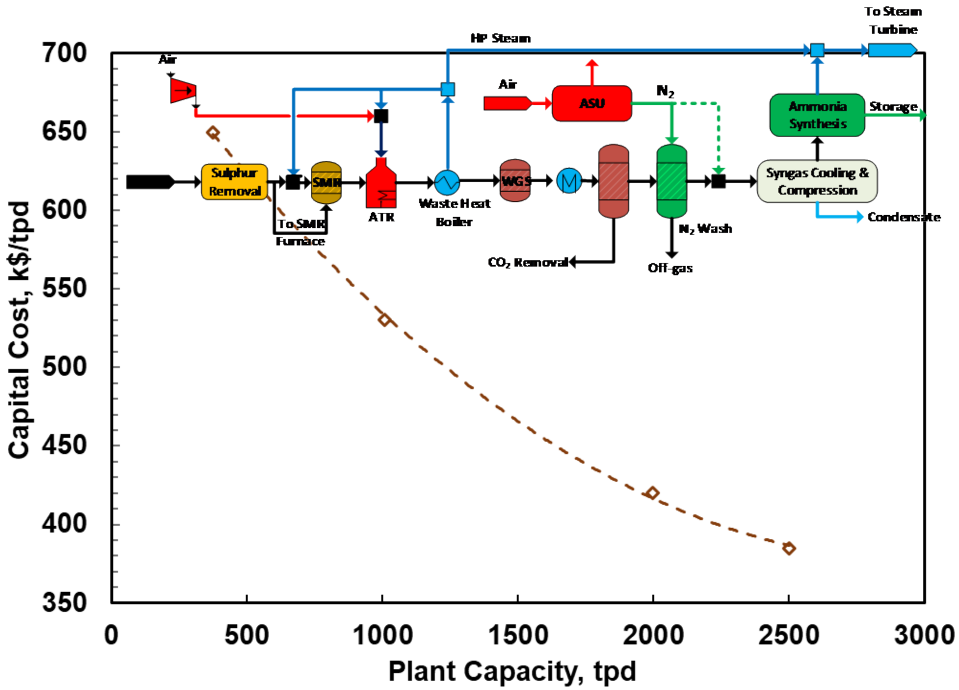
Literature: ADI Analytics, Sojitz Corp., Foster & Wheeler

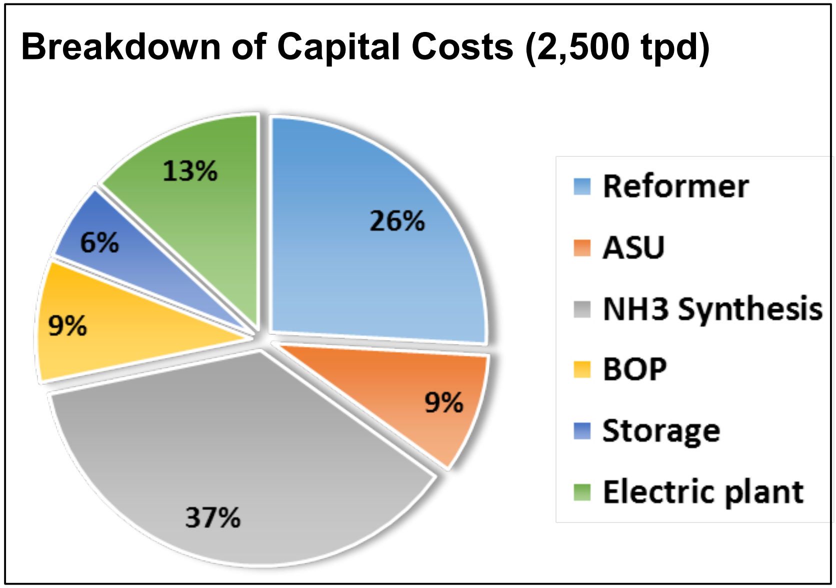
Capital Cost of Ammonia Plants



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
- Capital cost: 385k$/tpd at 2500 tpd

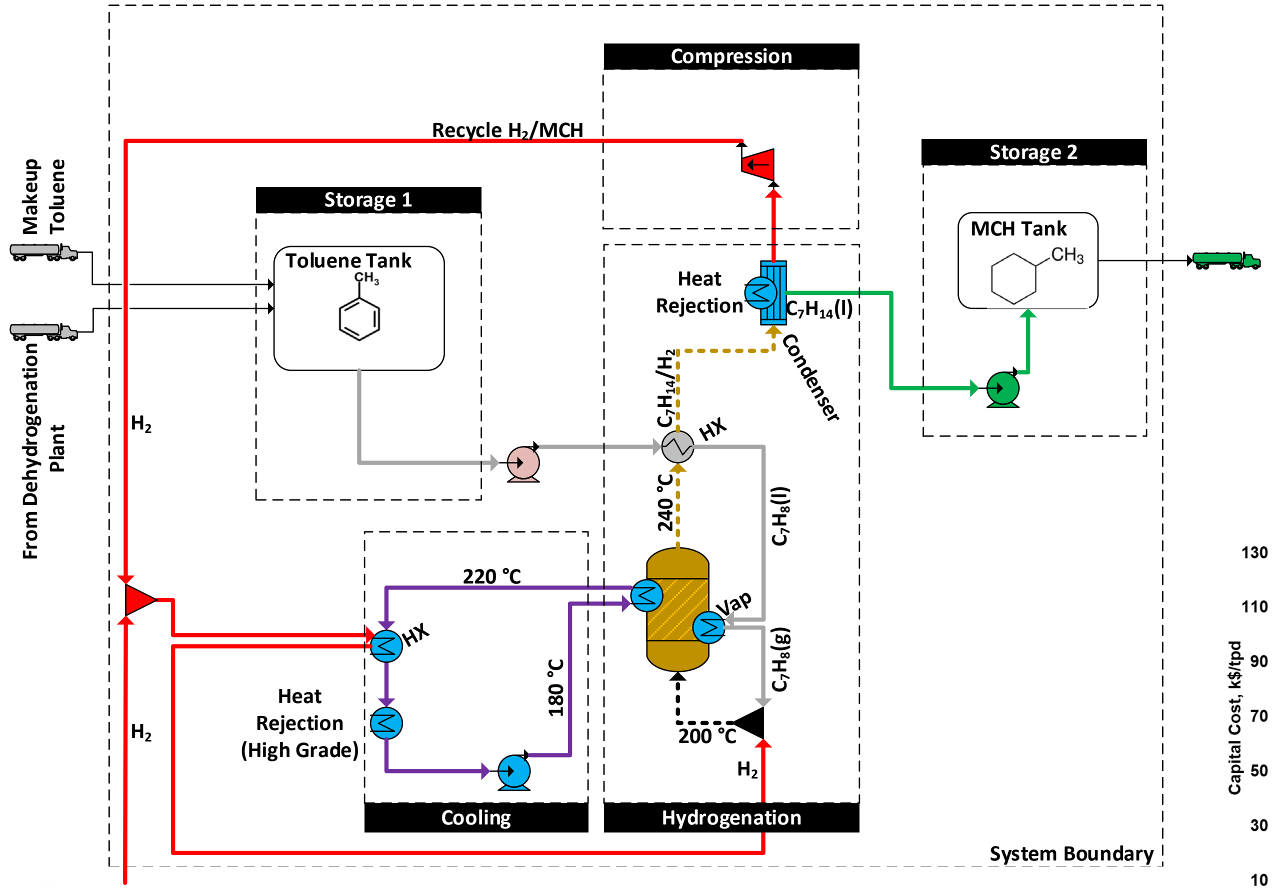




Capital cost shown for LAC but are similar for the conventional ammonia process

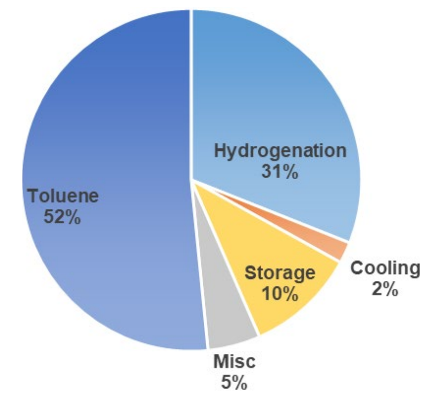
Capital Cost of Toluene Hydrogenation Plant

- Reactor operated at 240°C and 10 atm for nearly complete conversion. Excess H_2 and MCH vapor recycled (H_2/Toluene ratio = 4/1)
- Condenser included for 98.5% MCH recovery at 9.5 atm and 45°C
- Toluene makeup = 0.84% (due to dehydrogenation losses)
- Capital cost of 6,180-tpd MCH and SMR plants: (16+27)k$/tpd-MCH

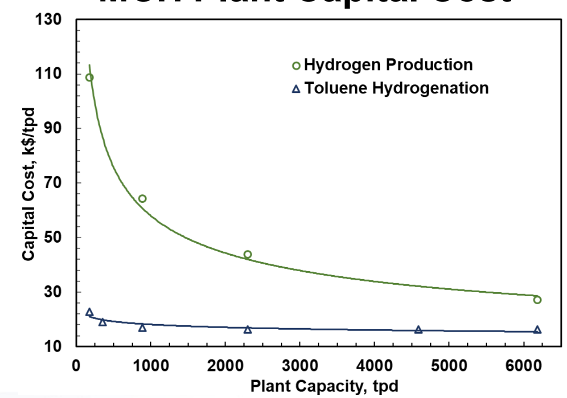


Capital Cost Factors

- MCH: 6,180 tpd
- H_2: 350 tpd



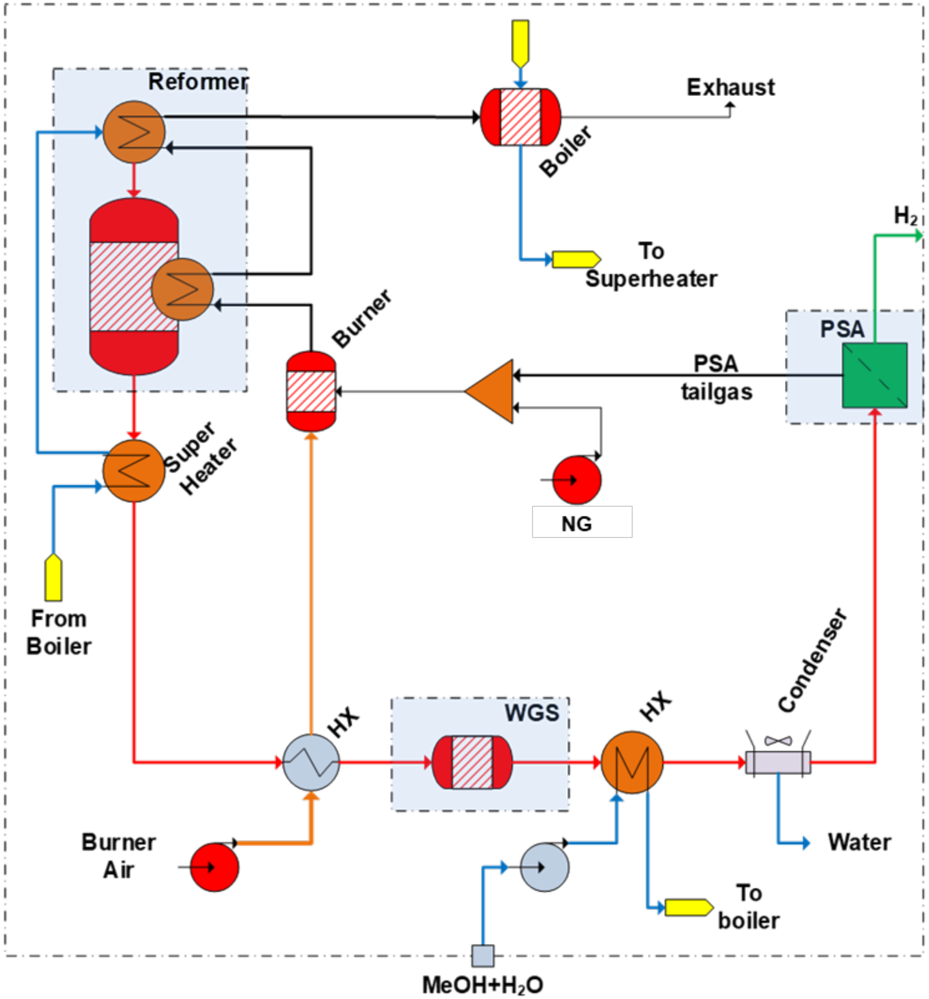
MCH Plant Capital Cost



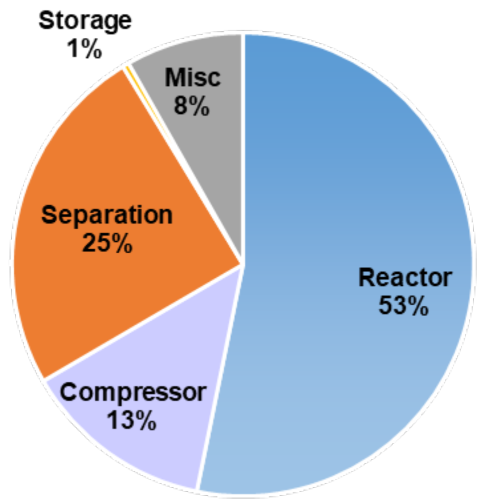
Lindfors, L.P. et. al. (1993). Kinetics of Toluene Hydrogenation on Ni/Al_2O_3 Catalyst. Chem. Eng. Sci., 48, 3813

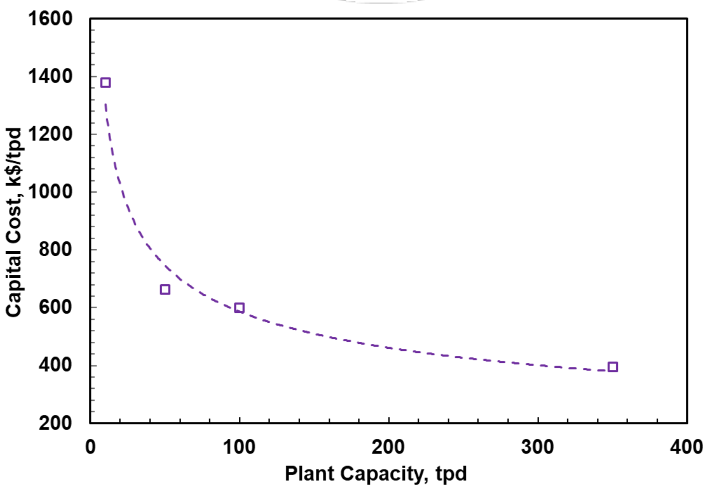
Capital Cost of Methanol Decomposition Plant

- Methanol steam-reformed at 3 bar, 290°C
- Capital cost decreases from 662k$/tpd at 50 tpd-$H_2$ to 396k$/tpd at 350 tpd-$H_2$



Methanol Steam Reforming Plant with PSA for H_2 Purification



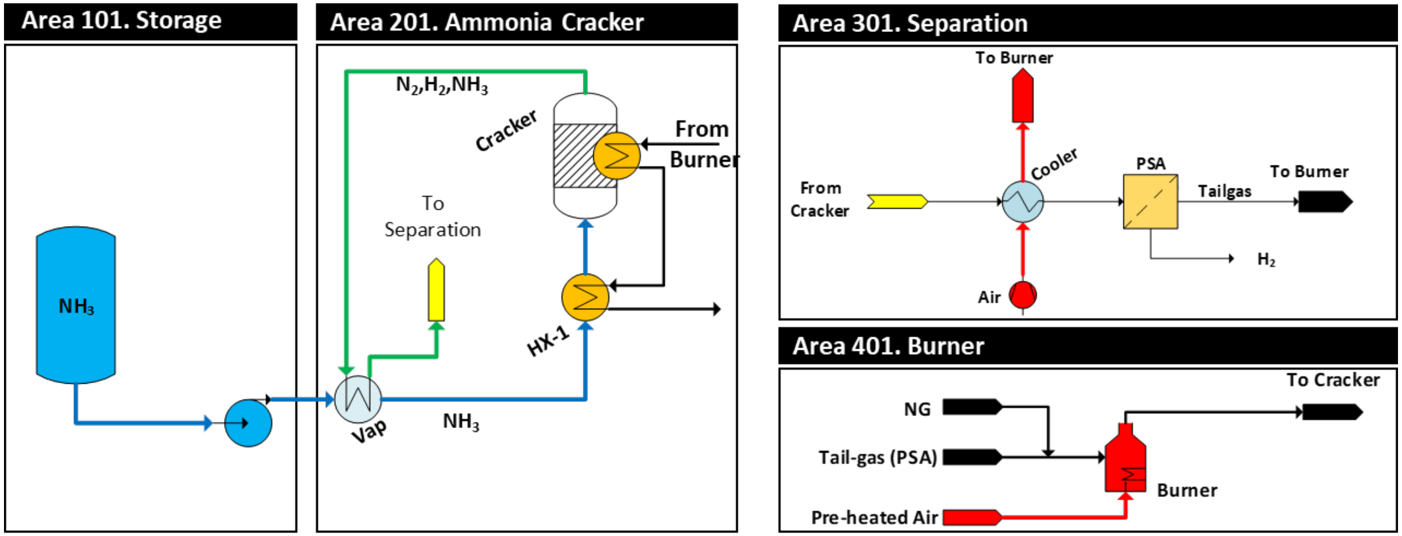


Methanol Dehydrogenation Plant Capital Cost

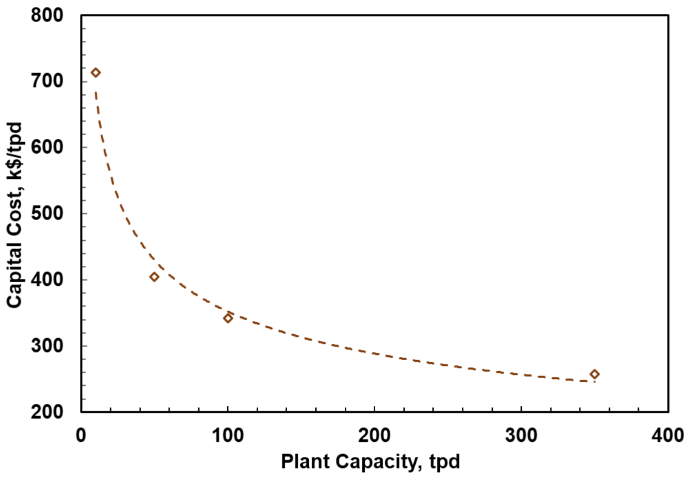
Capital Cost of Ammonia Decomposition Plant

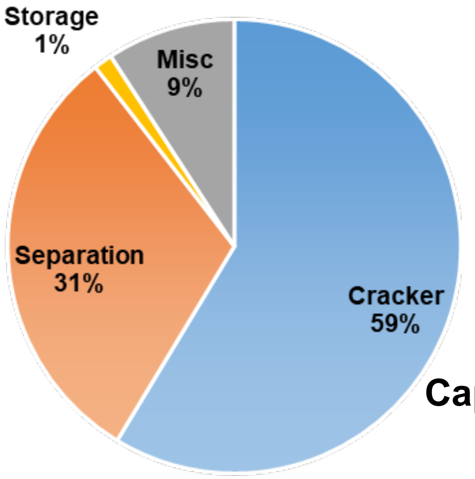
- Ammonia cracked at 20 bar, 800°C on a Ni catalyst
- Capital cost decreases from 405k$/tpd at 50 tpd-$H_2$ to 257k$/tpd at 350 tpd-$H_2$

Ammonia Cracker with PSA for H_2 Purification



Capital Costs of Ammonia Decomposition Plant

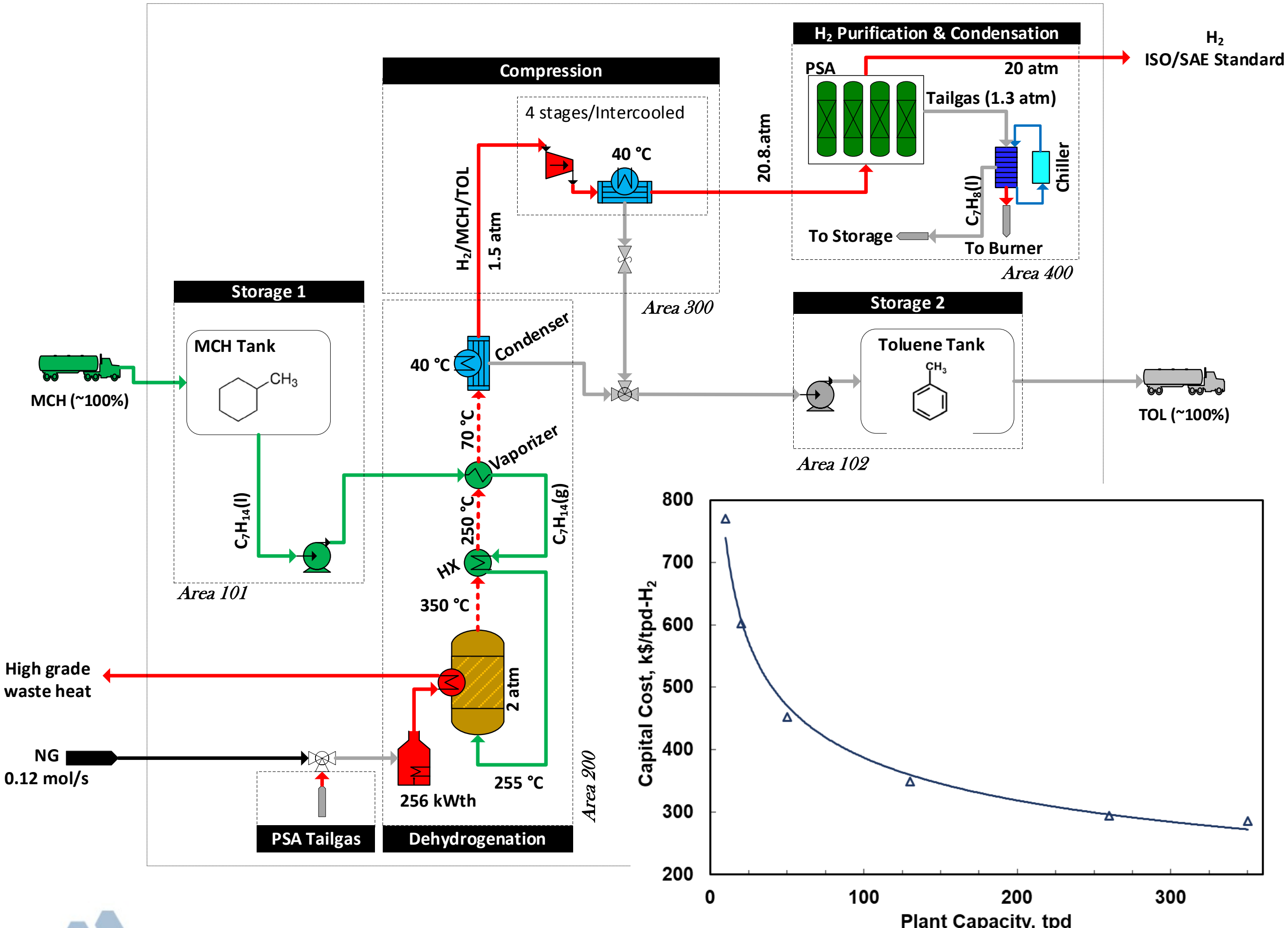




Capital Cost Factors 50-tpd H_2

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.
- Condenser included for 80% toluene recovery at 1.5 atm and 40°C, remaining during the compression cycle (4 stages) and chiller
- Capital cost decreases from 452k\$/tpd at 50 tpd-H_2 to 286k\$/tpd at 350 tpd-H_2



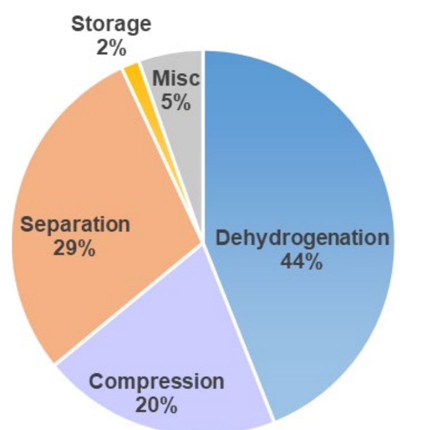
Losses

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

Feedstock/Utilities

- NG: 0.22 kWh_{th}/kWh_{th}-H_2
- Electricity: 0.04 kWh_e/kW_{th}-H_2

Capital Cost Factors: 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.

Levelized Costs: Carrier Production

Levelized production cost (LPC) lowest for methanol carrier ($1.22/kg-$H_2$)

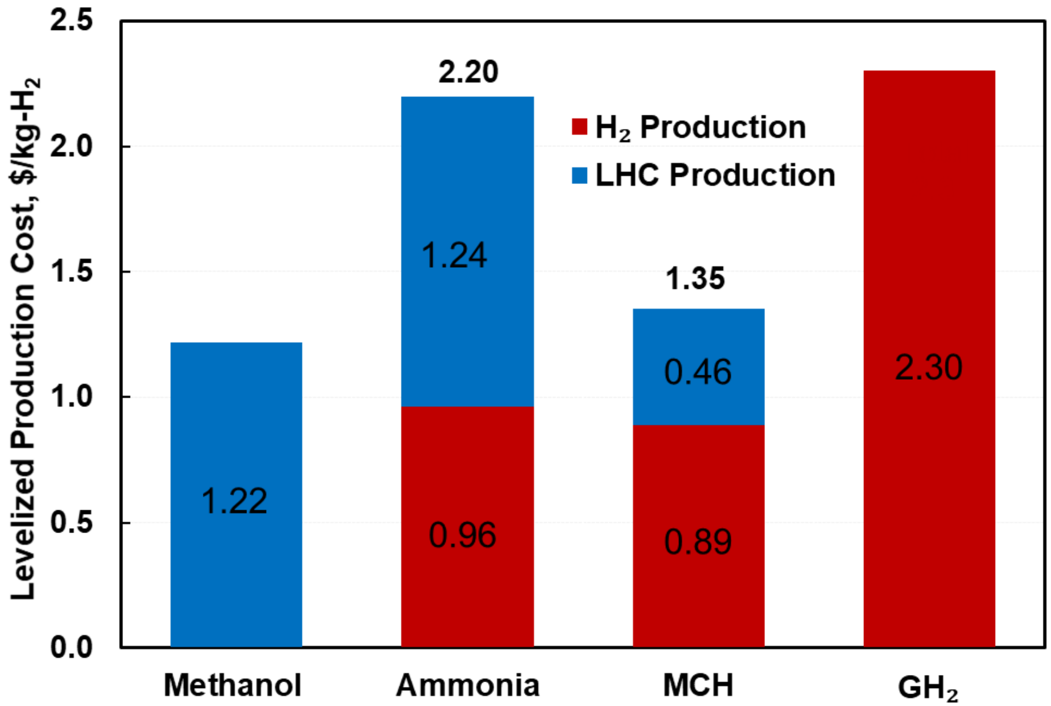
- Methanol produced by very large one-step ATR plant (10,000 tpd)
- Methanol produced from NG without an explicit step for pure H_2 production by SMR

LPC highest for ammonia carrier ($2.20/kg-$H_2$)

- Ammonia plants more capital intensive than methanol plants: 1.28 vs. $0.56/kg-$H_2$

LPC for MCH carrier competitive with methanol option ($1.35/kg-$H_2$)

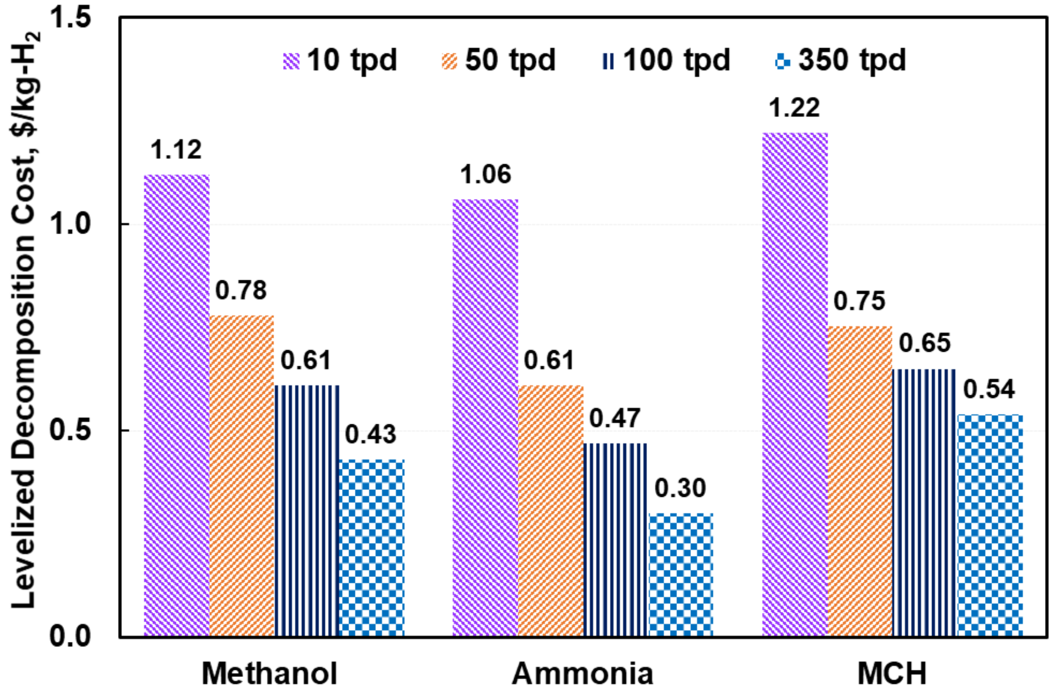
- MCH produced by a simple (exothermic) process for hydrogenating toluene
  Capital cost: $0.32/kg-$H_2$ for SMR, $0.30/kg-$H_2$ for hydrogenation



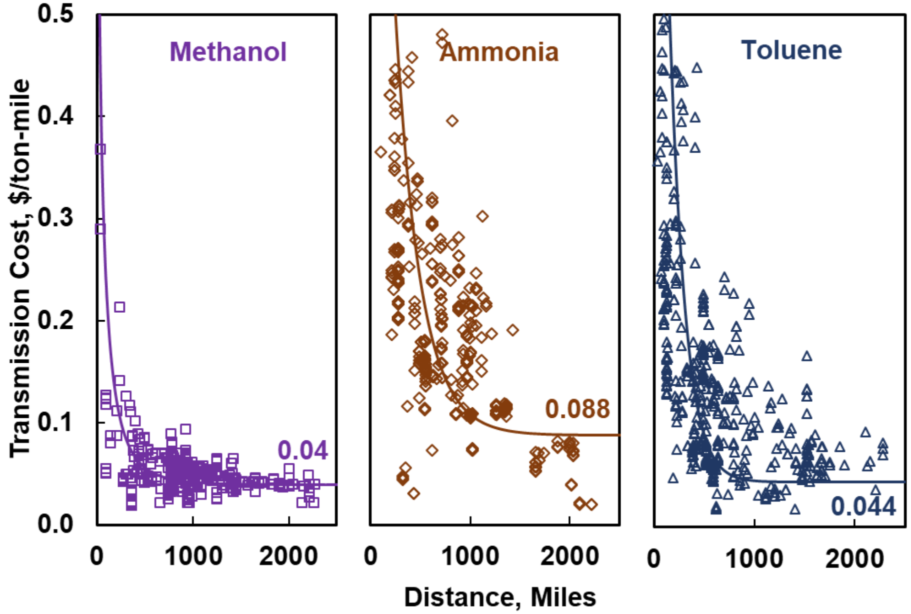
Levelized Costs: Carrier Decomposition

Levelized decomposition costs (LDC) are comparable for the three carriers: 0.61-0.78 \$/kg-H_2 at 50 tpd-H_2

- At high throughput, LDC decreases most for ammonia. However, ammonia decomposes at a high temperature (800^{o}C) using a catalyst (Ni) that may require further development and field testing
- Methanol decomposition method well established but requires steam reforming and water gas shift catalysts. Cost may decrease if methanol reformed at >3 atm.
- MCH decomposes at 2 bar using a PGM catalyst (Pt/Al_2O_3) and requires a large compressor



Levelized Costs: Transmission by Trains



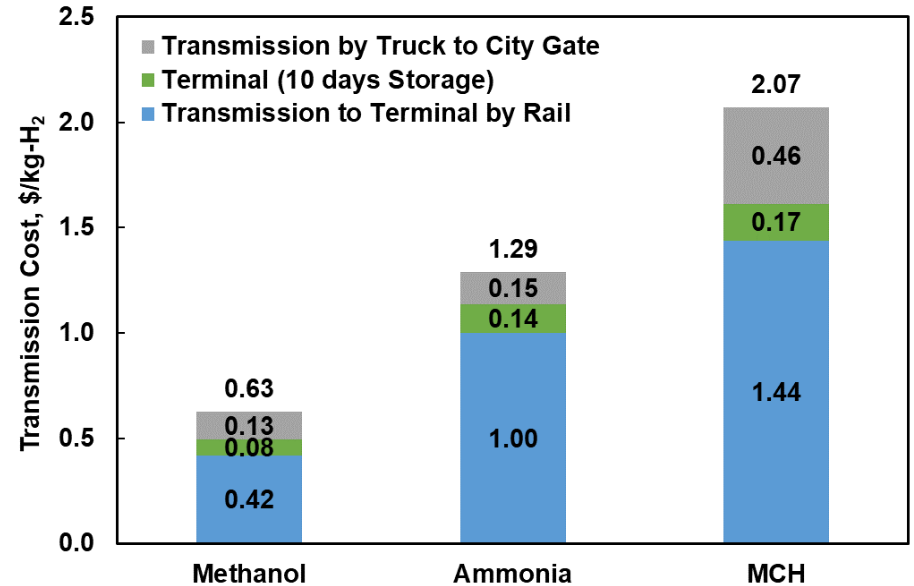
Railroad Waybill 2016 Data

- Rail transmission cost methanol < toluene << ammonia
- Fuel consumption: 380 ton-mile/gal

Transmission Cost

Transmission cost of carriers equivalent to 50-tpd H_2

- Methanol: 0.63 \$/kg-H_2
- Ammonia: 1.29 \$/kg-H_2
- MCH: 2.07 \$/kg-H_2



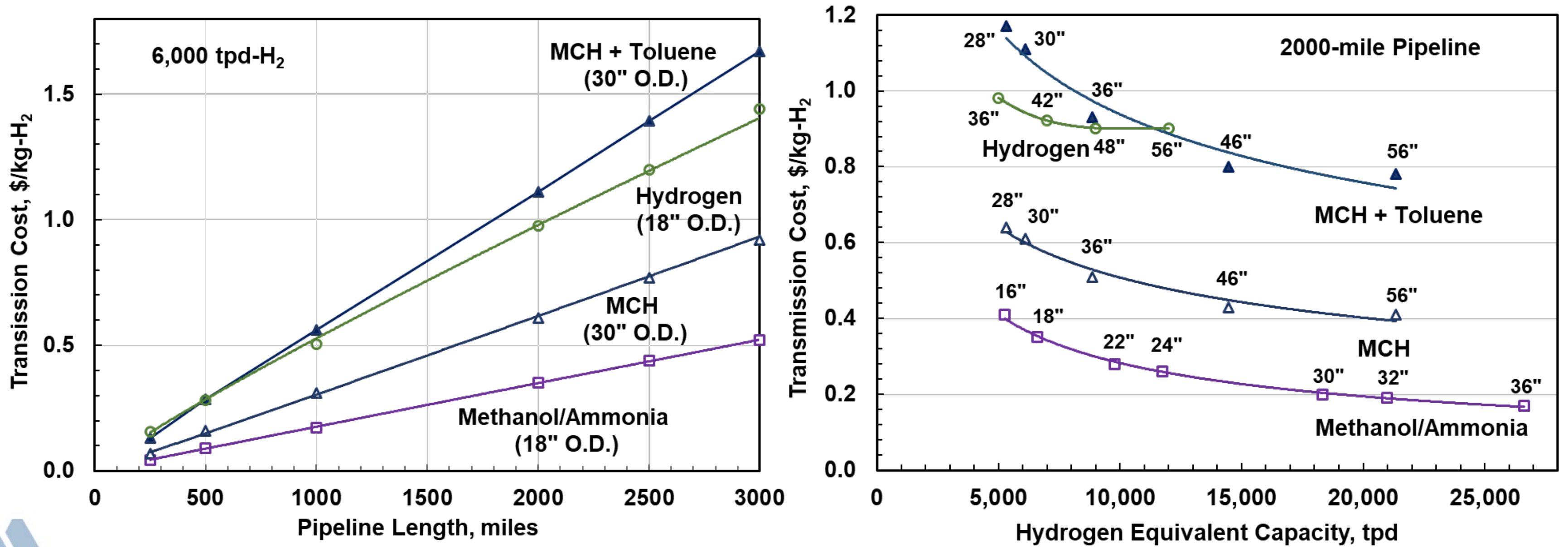
Levelized Costs: Transmission by Pipelines

Transmission Cost lowest for methanol and ammonia, similar for H_2 and MCH/toluene

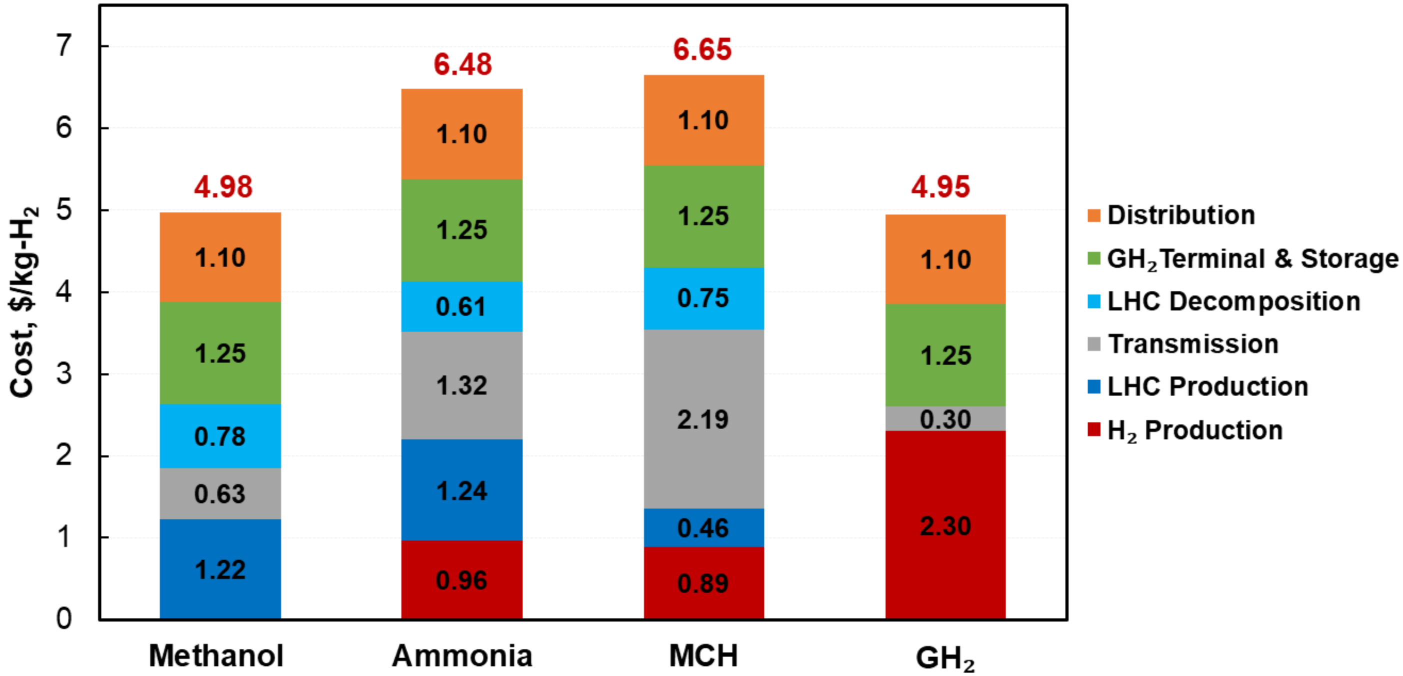
- Pipelines: API 5L Grade X52 tubes, 60-80 bar operating pressure, 20-bar pressure drop between pumping/compressor stations
- Max flow velocity: 20 m/s for H_2, 4 m/s for liquids
- Initial capital outlay for 6000 tpd-H_2 pipeline: 3.6M$/mile for H_2, 1.6M$/mile for liquids

Cost Factors

- Installed CapEx Factors: Pipe cost; labor; right of way (ROW); compressor/pumping stations
- Miscellaneous CapEx Factors: Eng. & design; project contingency; permitting & contractor
- Operating and Maintenance: Electricity (pumping and compression); maintenance



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



Large methanol scenario is competitive with the baseline GH_2 scenario

- Slightly cheaper combined production and decomposition cost ($0.30 $/kg-$H_2$), offset by 0.33 $/kg-$H_2$ higher transmission cost

As a carrier, ammonia is more expensive than methanol

- $0.81 $/kg-$H_2$ higher combined production and decomposition cost, 0.69 $/kg-$H_2$ higher transmission cost

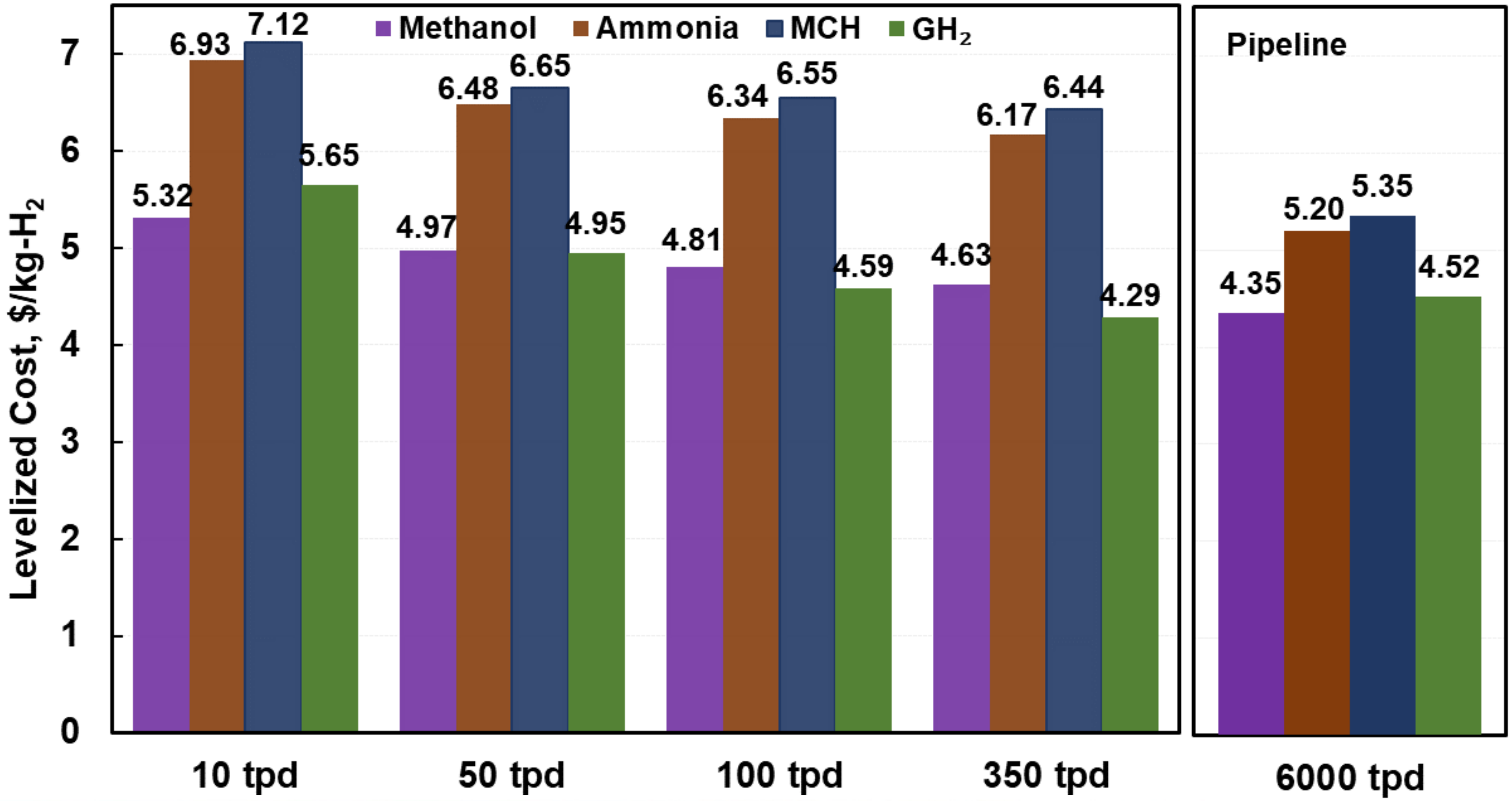
Centralized MCH production scenario slightly more expensive than ammonia

- 0.71 $/kg-$H_2$ cheaper production and decomposition cost < 0.87 $/kg-$H_2$ higher transmission cost

Levelized Cost of H_2 Distributed to Stations at Different Demands*

All carriers produced from natural gas as feedstock at commercially viable scale, independent of H_2 demand at city gate

- Methanol as hydrogen carrier may involve lower risk and be attractive in the transition phase, <50-tpd H_2 demand
- With pipelines, levelized cost decreases by ~1 $/kg-$H_2$ for ammonia and MCH, methanol slightly cheaper than H_2
- Comparison between GH_2 and LHC scenarios sensitive to NG price differential

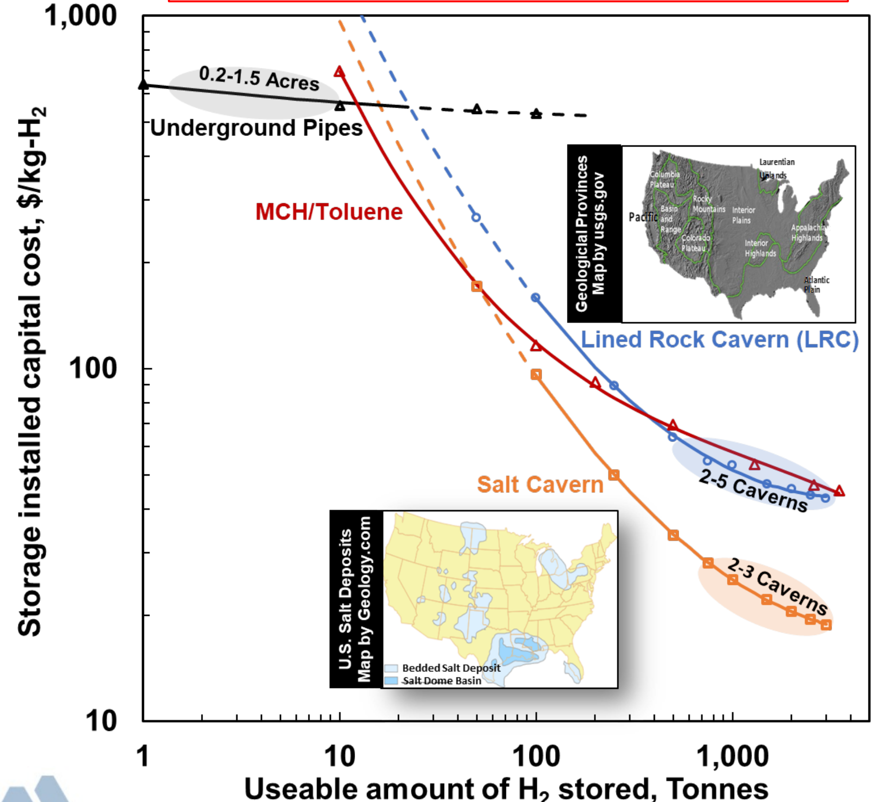


For simplicity in presentation, all levelized costs include fixed 1.10$/kg-$H_2$ distribution cost independent of demand

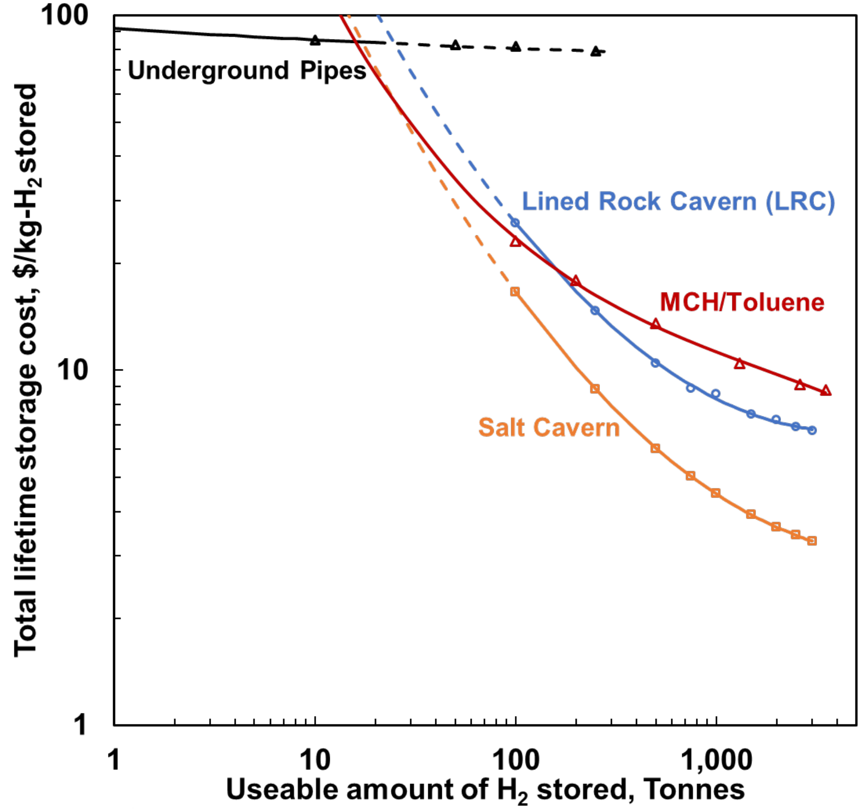
Bulk H_2 Storage: Outlook

- 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
- Possible role of carriers as bulk hydrogen storage medium when caverns not available

Installed Capital Cost
- Underground pipes: 100 bar
- LRC and salt caverns: 150 bar

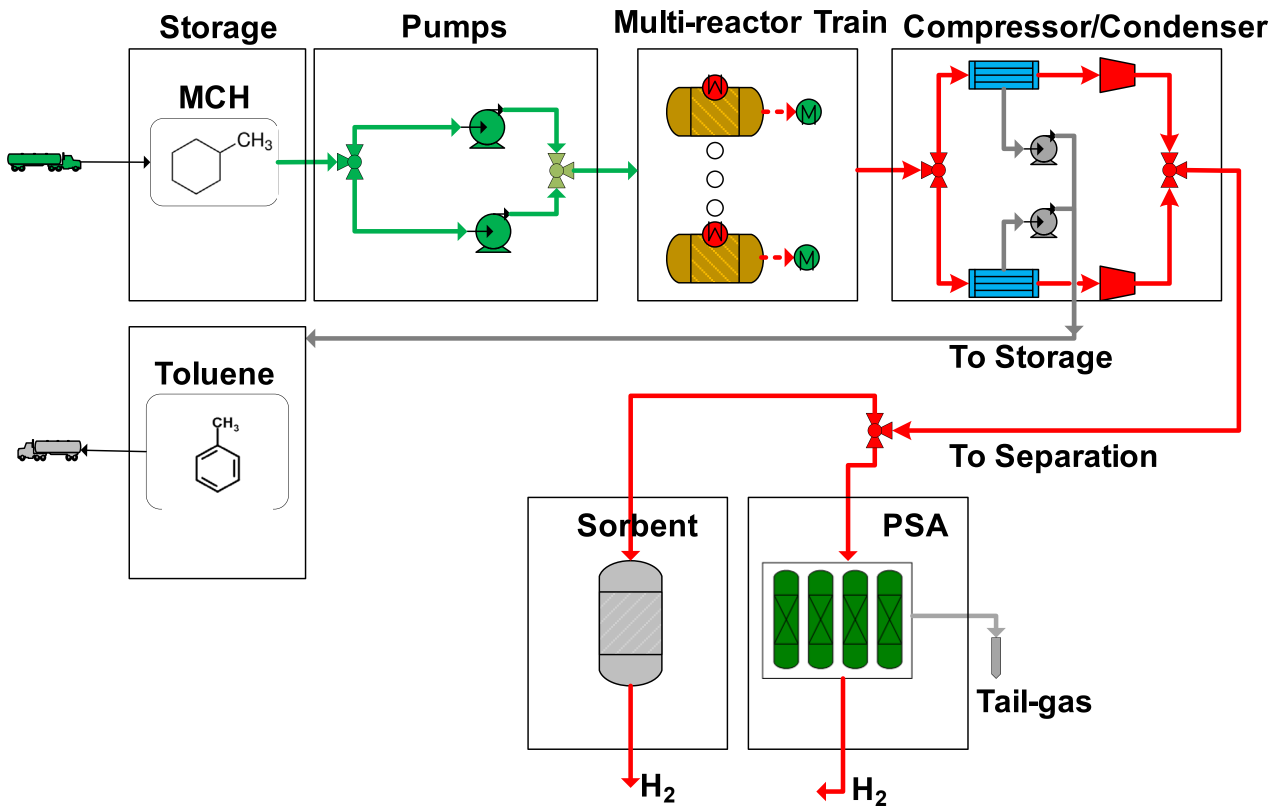


Yearly Storage Cost
- Inclusive of CAPEX and operating & maintenance cost



Reducing H_2 Bulk Storage Requirement with Liquid Carriers

Parallel dehydrogenation steps



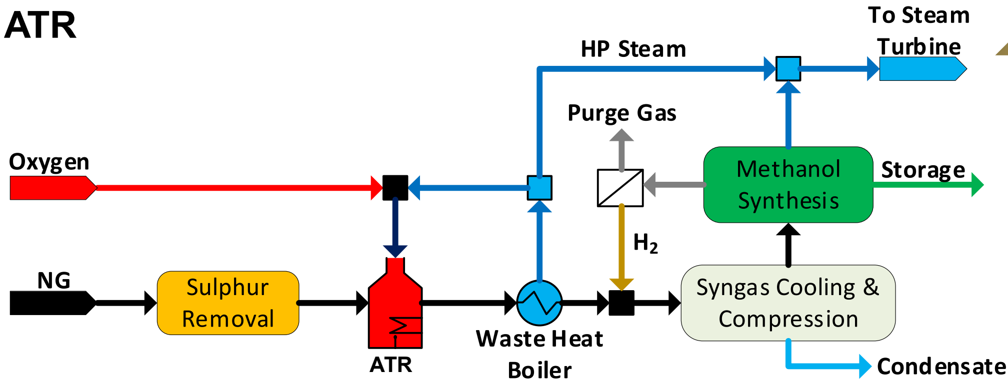
- Desirable to have a carrier (low ΔG and ΔH) that can be dehydrogenated under mild operating conditions
- Liquid phase decomposition at high pressures to ease compression requirements
- Minimal or no side products, simple purification steps

Summary and Discussion

1. Methanol as hydrogen carrier may involve lower risk and be attractive in the transition phase, <50-tpd H_2 demand
2. Ranking of the three carriers by levelized production costs
   - Methanol (1.22 \$/kg-H_2)<MCH (1.35 \$/kg-H_2)<<Ammonia (2.20 \$/kg-H_2)
3. H_2 capacity of the carrier is an important factor in determining the transmission cost by trains
   - Toluene has nearly the same train transmission cost as methanol on tpd basis, but is >3X costlier on kg-H_2 basis
4. Toxicity and handling are also important factors in determining train transmission costs
   - Ammonia has nearly the same H_2 capacity as methanol but is >2X costlier to move by train
5. Long H_2 or carrier pipelines (>1000 mile) do not offer significant cost savings
   - Pipelines may not be economically viable for two-way carriers
6. Further study needed to evaluate the role of carriers as medium for bulk hydrogen storage

Methanol Production Plant Configurations

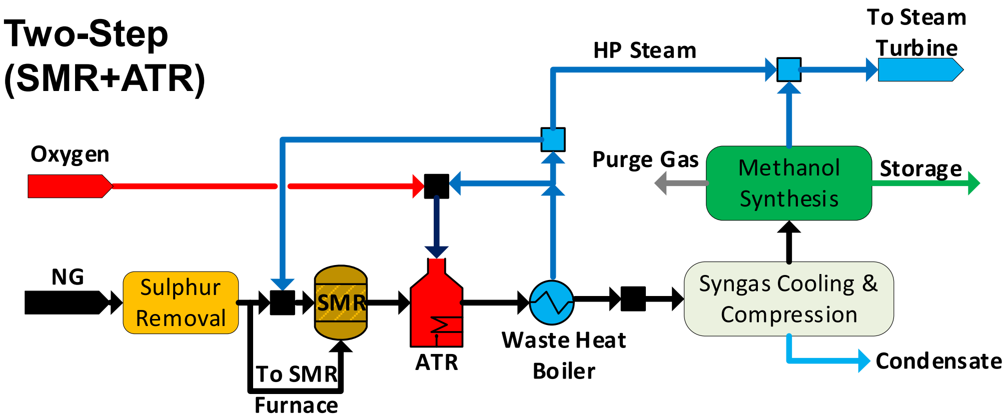
ATR



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

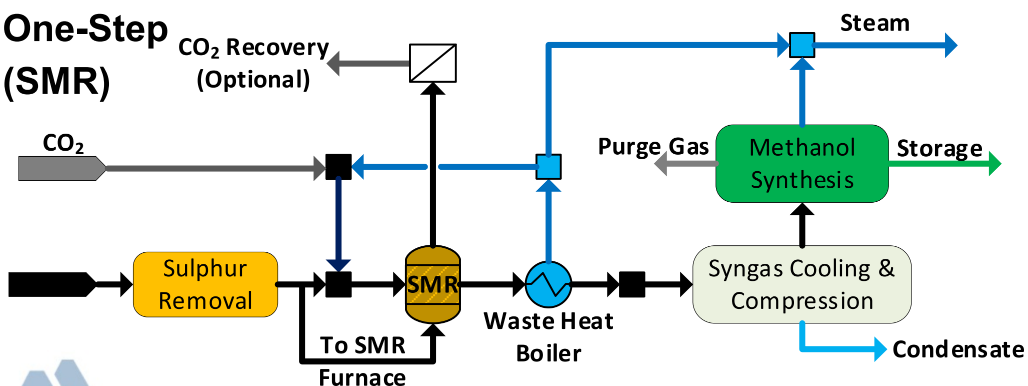
Two-Step (SMR+ATR)



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

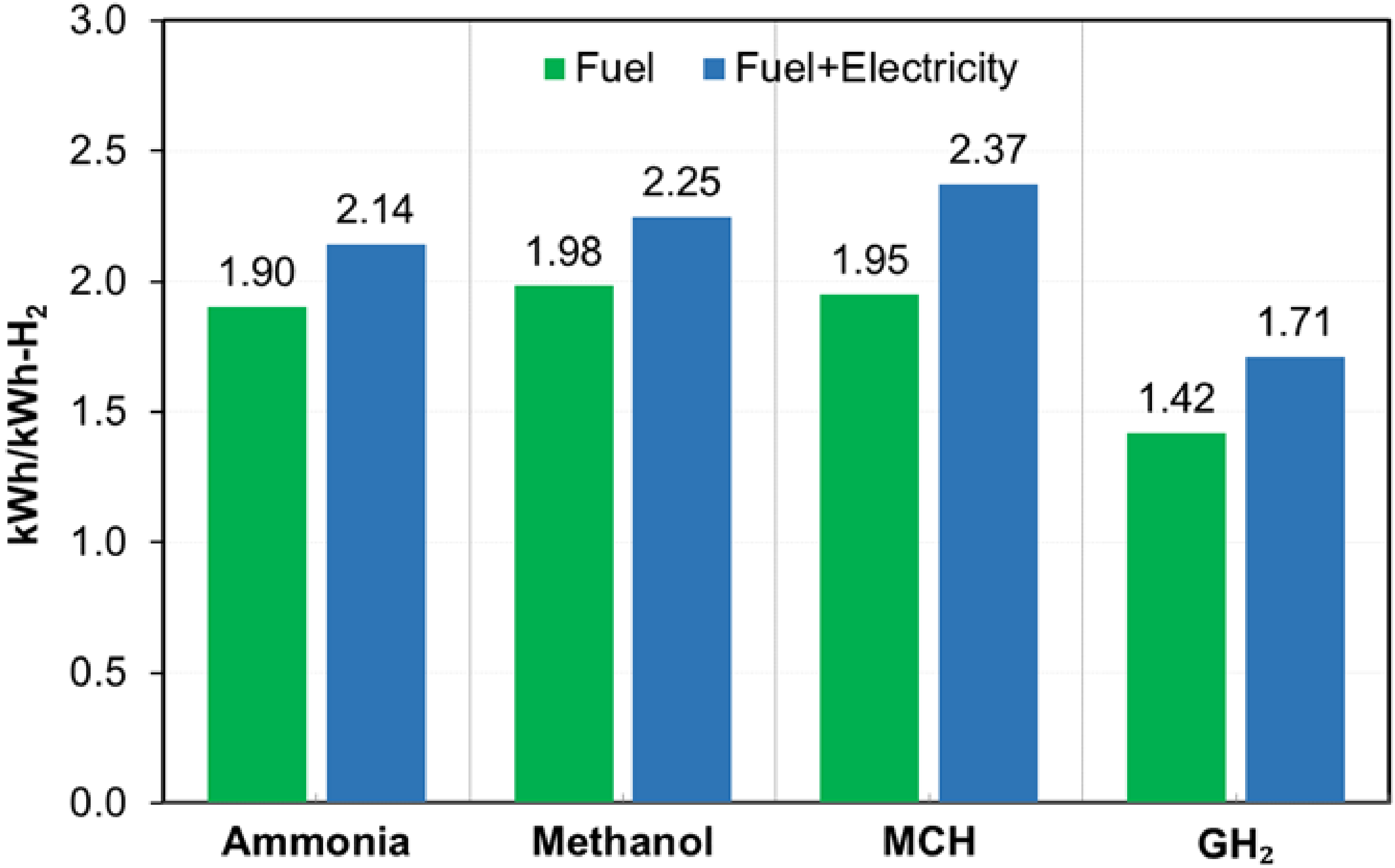
- $CO_2/C=0.3$, $H_2O/C=3.5$
- M (reformer): 2.05
- 1 BWR or Quench reactor
- Electricity demand: 0.14 kWh_e/kg-MeOH
- Steam Turbine: *Not economical*

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

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-H_2): MCH (2.37) > ammonia (2.25) > methanol (2.14) > GH_2 (1.71)



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

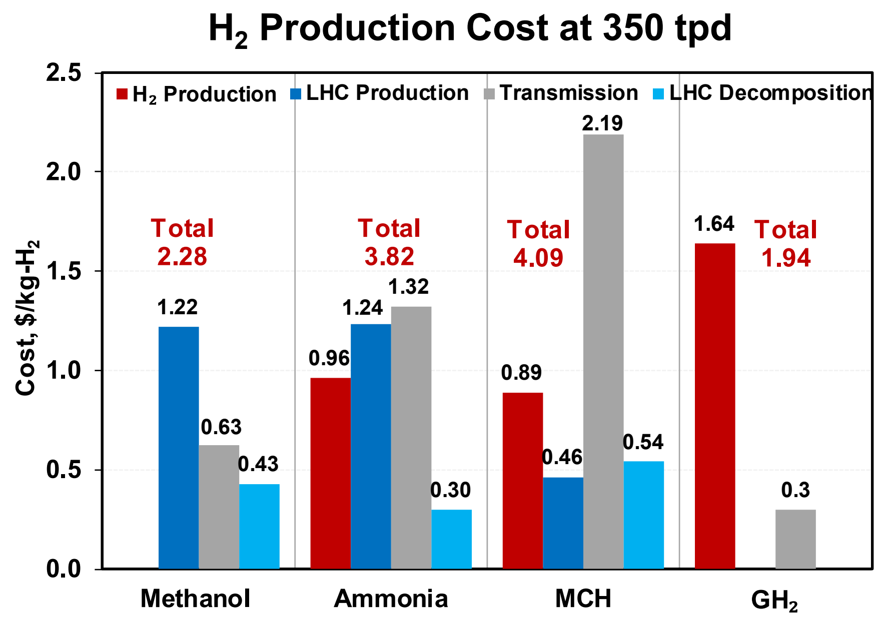
Hydrogen Carriers: Outlook

Proposed LHC Targets for $2/kg H_2 Production Cost

- $1/kg-$H_2$ LHC production: at 50 tpd, $1.22 for methanol and $0.89 for fuel cell quality H_2
- $0.50/kg-$H_2$ LHC transmission: at 50 tpd, $0.63 for methanol
- $0.50/kg-$H_2$ LHC decomposition and H_2 purification: at 50 tpd, $0.61 for methanol

Current Status at 50 tpd: $2.63 for methanol, $4.13 for ammonia, $4.29 for MCH/toluene

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



	Levelized Cost at Station ($/kg-$H_2$), 50 tpd				
	Methanol	Ammonia	MCH / Toluene	GH_2	Comments
H_2 Production		0.96	0.89	2.30	Ammonia more expensive to produce than MCH from toluene
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 MCH is only 47 g/L
GH_2 Terminal & Storage	1.25	1.25	1.25	1.25	Ideally, LHC 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	