Chemical Carrier Concepts for Hydrogen Delivery

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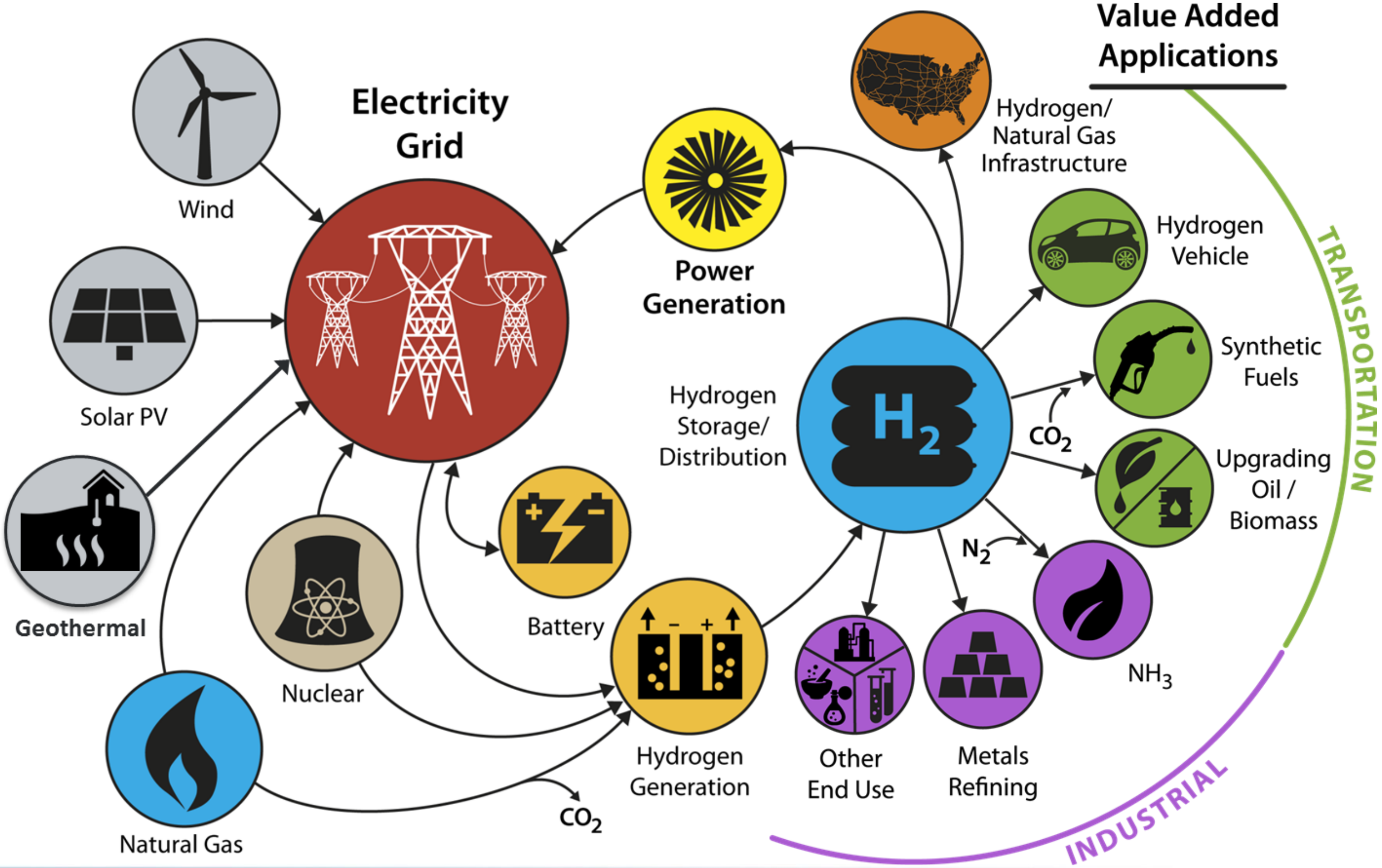
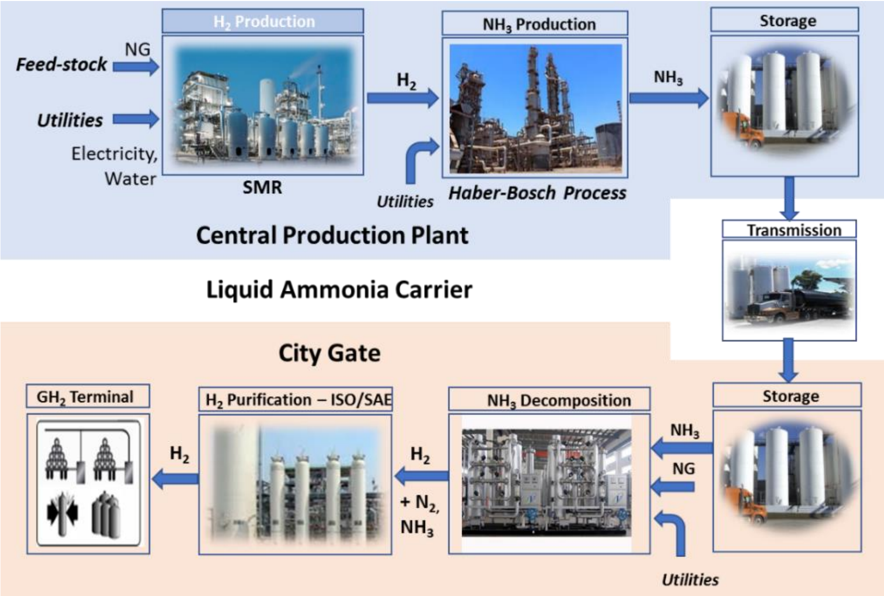
Conventional hydrogen transportation and storage methods have limitations

- cH_2 tube trailers: high pressures (200-500 bars), 250-1000 kg payload
- LH_2 trailers: 4000 kg payload but require multi-layer vacuum insulation
- cH_2 storage: Three geologic storage caverns in use in USA, compression costs
- LH_2 storage: Currently nine liquefaction plants in USA, energy intensive, boil-off losses



Hydrogen Carrier Pathways – Small Plants



Liquid Ammonia Carrier

Central Production Plant

H_2 Production

Feed-stock NG

Utilities Electricity, Water

SMR

H_2

NH_3 Production

Utilities

Haber-Bosch Process

NH_3

Storage

Transmission

City Gate

Storage

NH_3

NG

Utilities

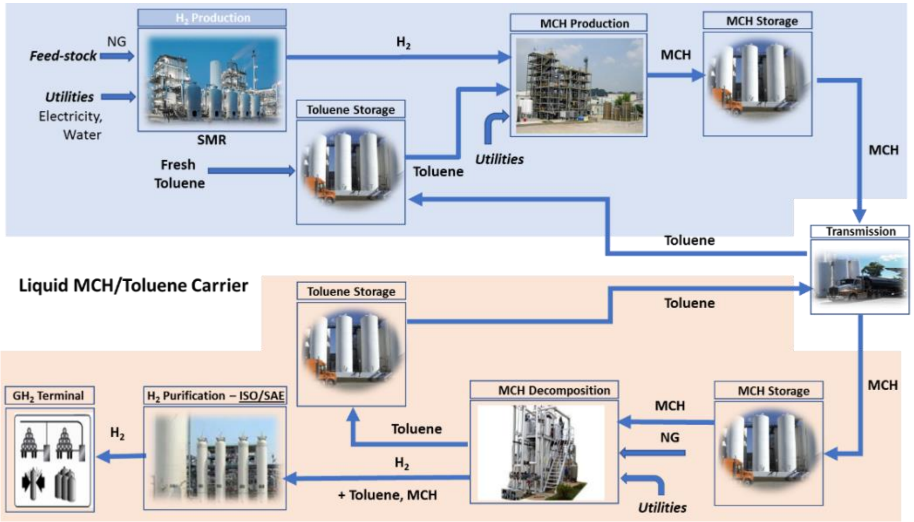
NH_3 Decomposition

H_2 + N_2, NH_3

H_2 Purification – ISO/SAE

H_2

GH_2 Terminal



Liquid MCH/Toluene Carrier

H_2 Production

Feed-stock NG

Utilities Electricity, Water

SMR

Fresh Toluene

Toluene Storage

Toluene

Utilities

H_2

MCH Production

MCH

MCH Storage

MCH

Transmission

Toluene

Toluene

Toluene Storage

MCH

MCH Storage

MCH

NG

Utilities

MCH Decomposition

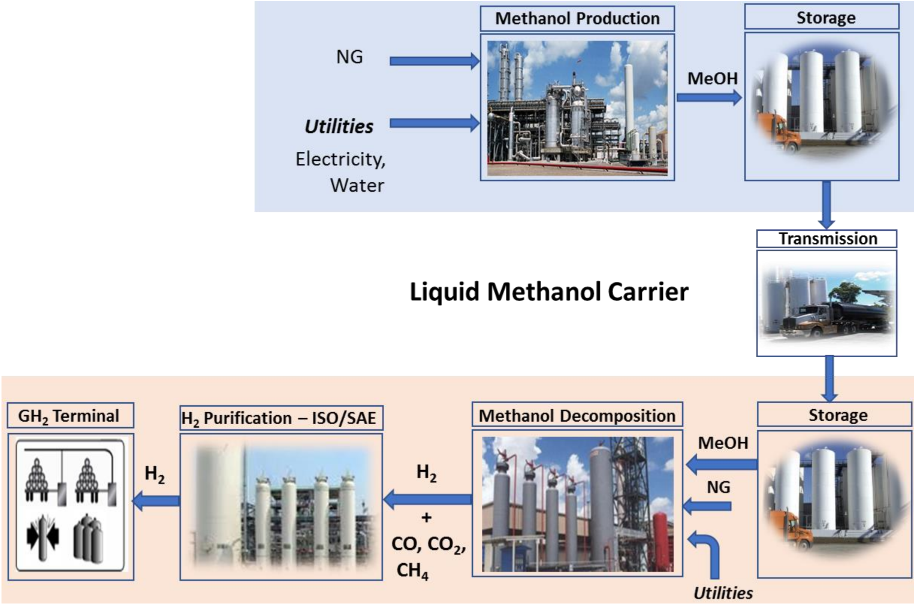
Toluene

H_2 + Toluene, MCH

H_2 Purification – ISO/SAE

H_2

GH_2 Terminal



Liquid Methanol Carrier

NG

Utilities Electricity, Water

Methanol Production

MeOH

Storage

Transmission

Storage

MeOH

NG

Utilities

Methanol Decomposition

H_2 + CO, CO_2, CH_4

H_2 Purification – ISO/SAE

H_2

GH_2 Terminal

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		

H_2 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)=15 yrs; Plant life=30 yrs; Construction period=3 yrs			
	NG	**Electricity**	**Water**	**Toluene**
Feedstock and Utilities	6.00 $/MBtu	5.74 ¢/kWh	0.54 ¢/gal	0.768 $/kg
H_2 Production by SMR, /kg-H_2	0.156 MBtu	0.569 kWh	3.35 gal	
Hydrogenation				
Ammonia	Haber-Bosch process and cryogenic air separation unit; 350 tpd;			
Methanol	Steam reforming of CH_4/CO_2 to synthesis gas $(H_2\text{-}CO)/(CO+CO_2)=2.05$;			
	Conversion to methanol; methanol purification; 320 tpd;			
Toluene	>99% conversion of toluene to MCH over non-PGM catalyst			
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	99% conversion of MCH to toulene; 2.5% make-up toluene			
	H_2 purification by PSA at 20 atm (90% recovery)			
Transmission	HDSAM v 3.1, Truck Liquid Delivery			
	Ammonia	**Methanol**	**MCH**	**GH_2**
Payload (kg)	22,500	22,500	22,500	1,042
Volume (m^3)	37	28	29	36
H_2 (kg)	3398	3465	1112	1042
GH_2 Terminal	HDSAM v 3.1, Compressed Gas H_2 Terminal			
H_2 Distribution	400 kg/day H_2 dispensing rate at refueling station			

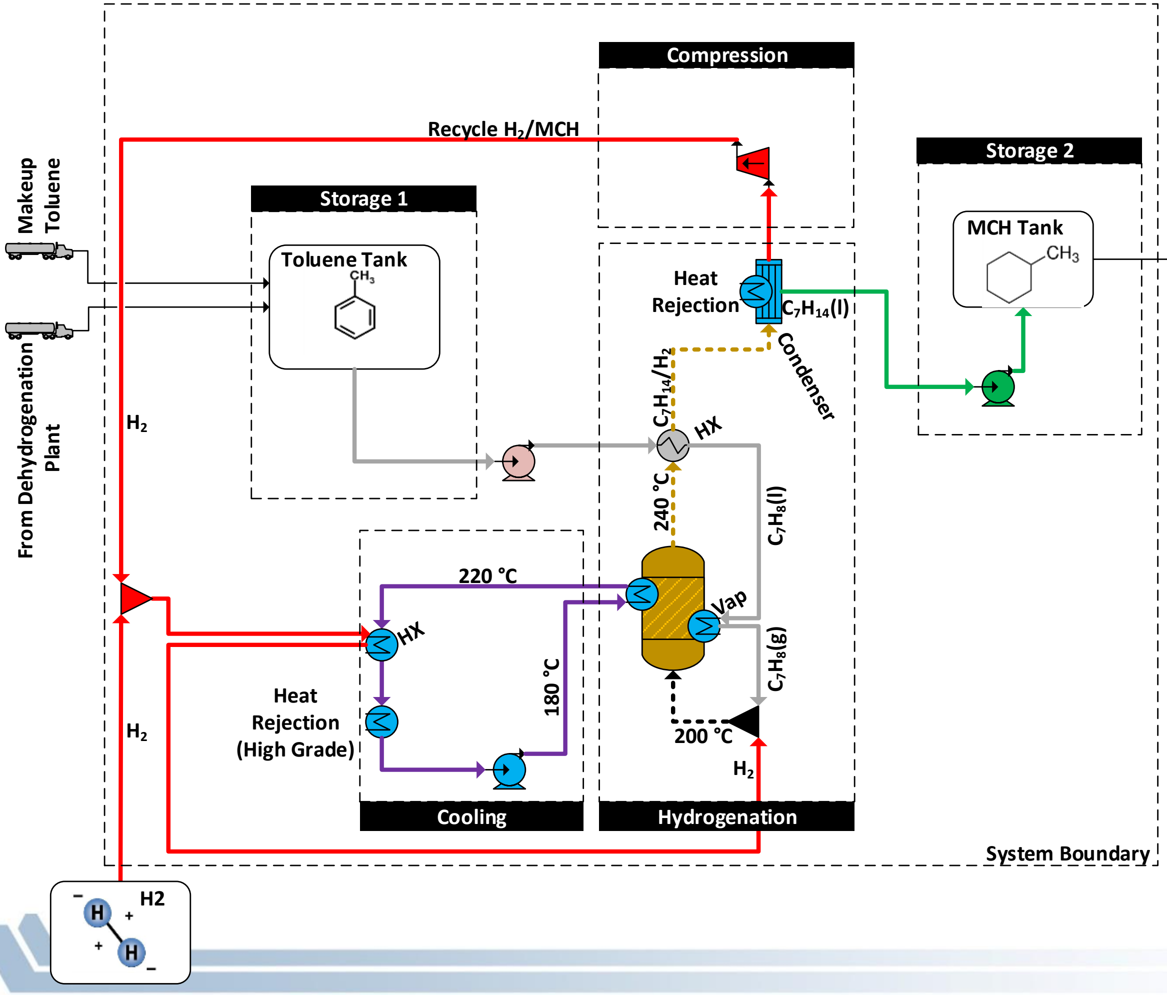
Rath, L. (2011). Cost and performance baseline for fossil energy plants: Coal to synthetic natural gas and ammonia. DOE/NETL-2010/1402.

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

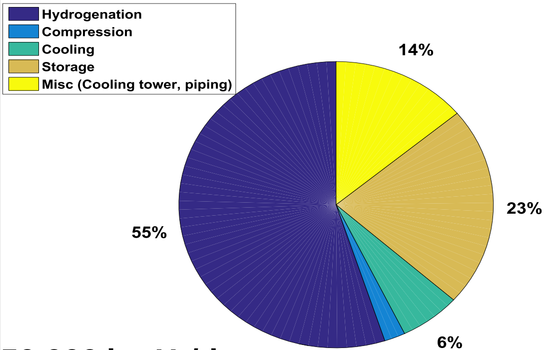
- Reactor operated at 240°C and 10 atm for nearly complete conversion. Conversion is kinetically limited. No side-reactions are considered.
- Allowing for 0.5 atm pressure drop, 98.5% of MCH condenses at 9.5 atm and 45°C
- Excess H_2 and MCH vapor recycled (H_2/Toluene ratio = 4/1)
- Toluene makeup = 2.52% (due to dehydrogenation losses)



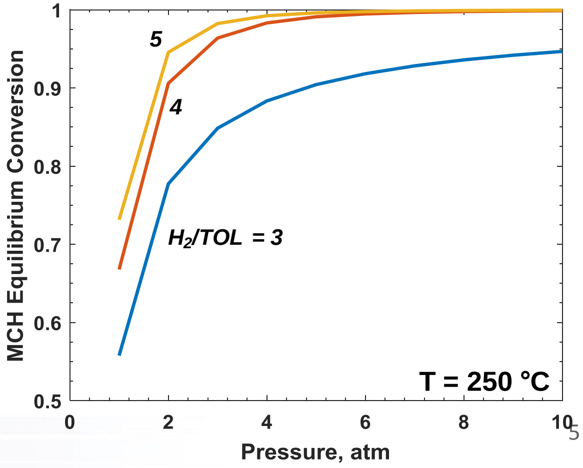
Feedstock/Utilities

- Toluene: 0.025 kg/kg-MCH
- Electricity: 0.04 kWh_e/kg-MCH

Capital Cost ($7.6 million)

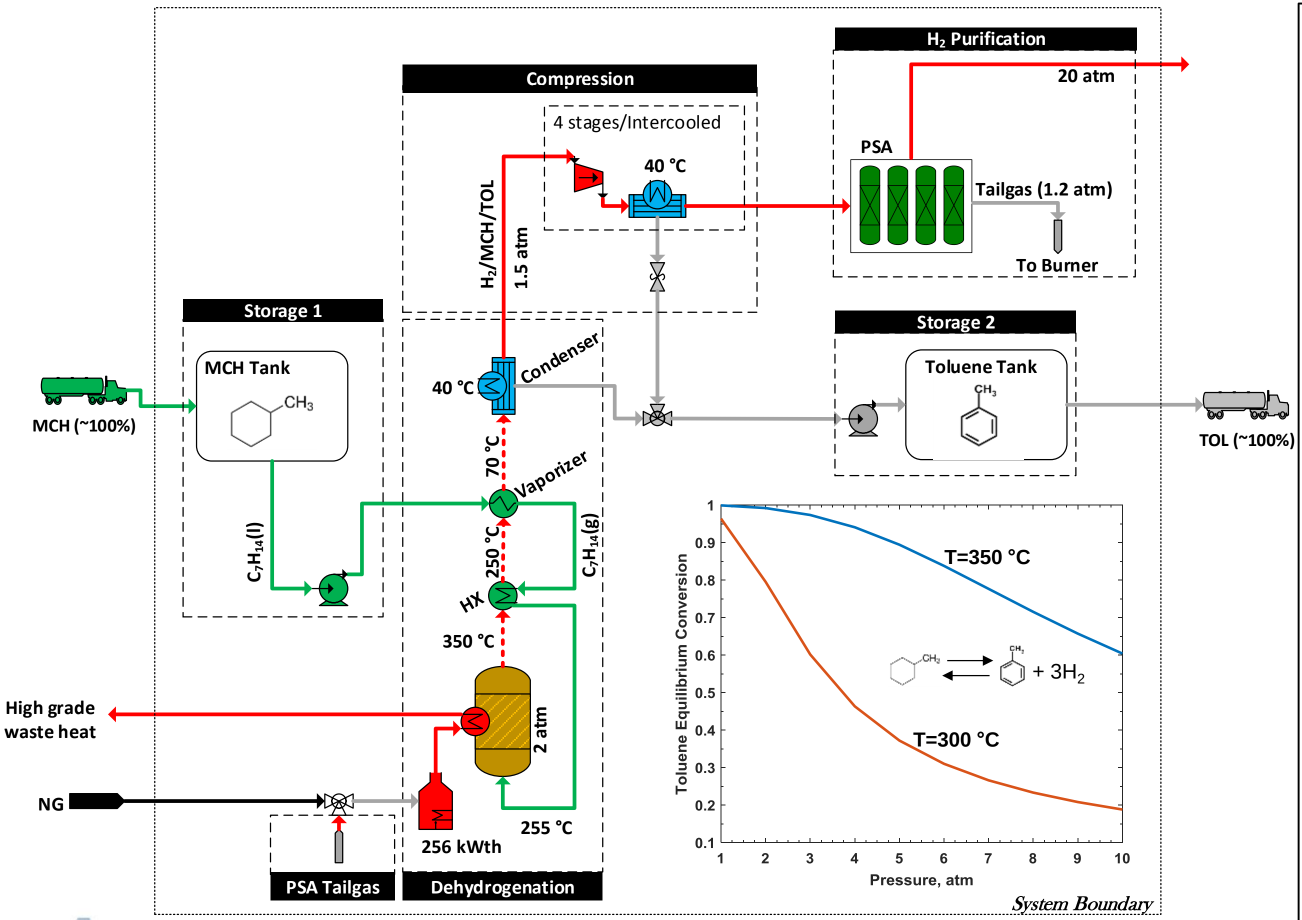


50,000 kg-H_2/day



Dehydrogenation of Methylcyclohexane

- Reactor operated at 350°C and 2 atm. Conversion is 99% and is equilibrium limited. 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)
- H_2 separation by PSA at 20 atm, 90% recovery (ISO/SAE H_2 quality)



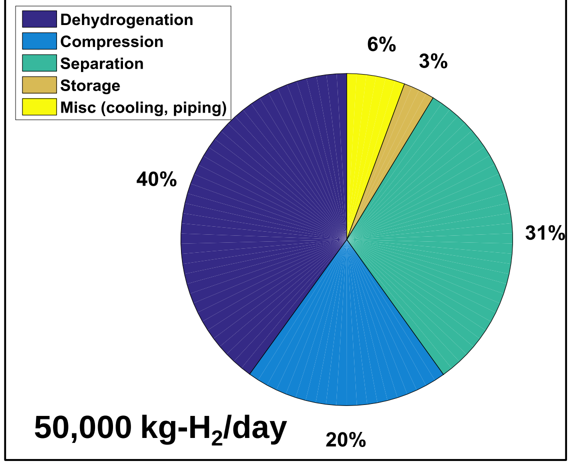
Losses

- Toluene+MCH: 2.52%
- Hydrogen: 11%
- 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 ($26.2 million)

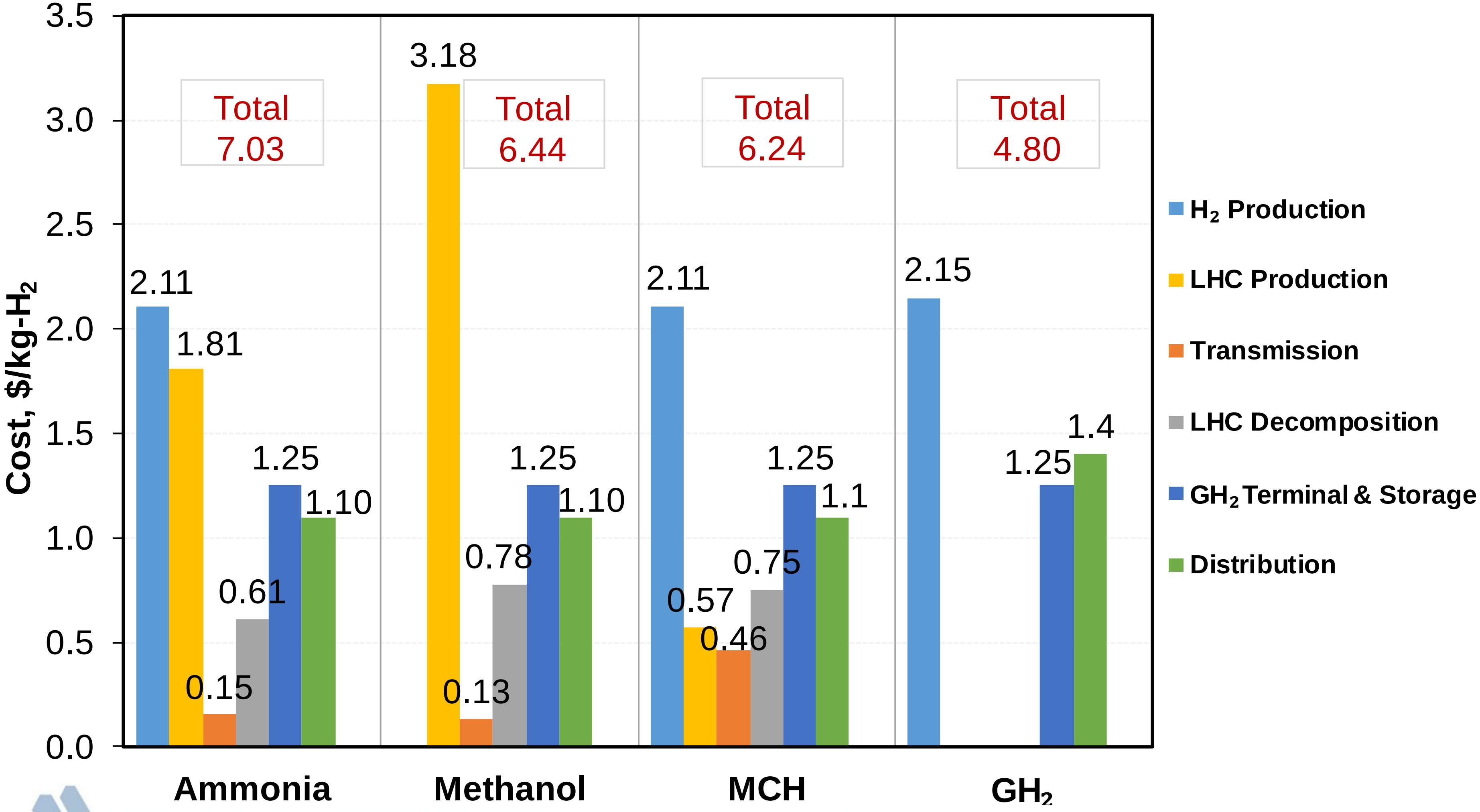


50,000 kg-H_2/day

Levelized Cost of H_2 Distributed to Stations (50,000 kg-H_2/d)

Liquid carrier options incur incremental costs of 1.44-2.23 \$/kg-H_2 (33 - 47%)

- LHC production costs (\$/kg-H_2): ammonia (1.81) > methanol (1.13) > MCH (0.57)
- LHC decomposition costs (\$/kg-H_2): methanol (0.78) ≅ MCH (0.75) > ammonia (0.61)
- Transmission & distribution (\$/kg-H_2): MCH (1.56) > GH_2 (1.40) > ammonia ≅ methanol (1.24)

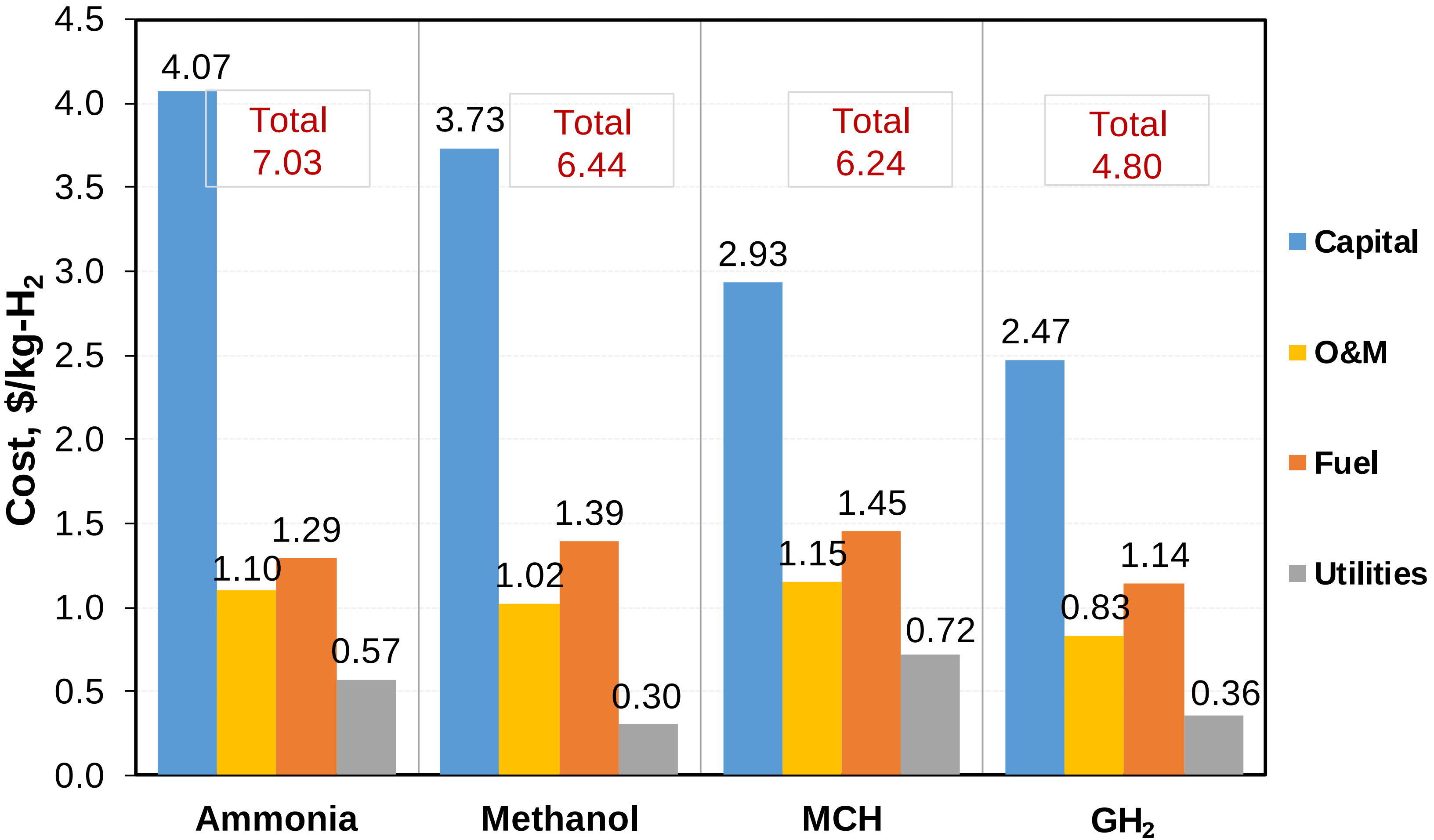


Baseline GH_2 scenario: Central SMR, H_2 compression & storage; truck transmission; GH_2 terminal

Breakdown of Levelized Cost of H_2 Distributed to Stations

Sources of increases in levelized costs compared to GH_2 scenario

- Ammonia: 72% capital; remaining equally between O&M, fuel and utilities
- Methanol: 77% capital; comparable O&M and fuel; small for utilities
- MCH: 32% capital; remaining equally between O&M, fuel and utilities

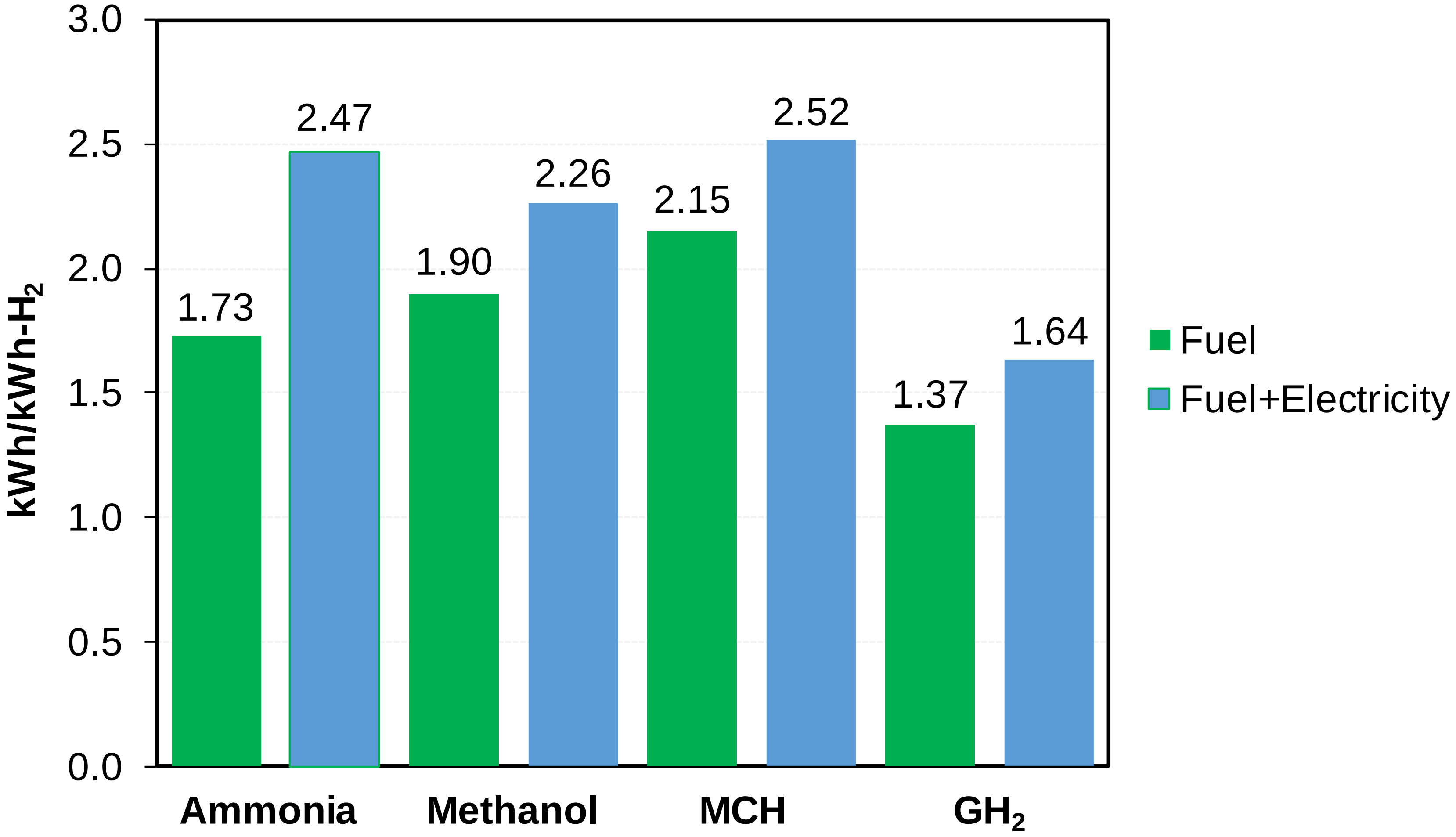


For cost breakdown, fuel refers to natural gas (NG); utilities include electricity, water & make-up toluene

Energy Efficiency

Endothermic dehydrogenation step including PSA at city gate is the largest contributor to the 38-54% 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 ≅ ammonia (2.52) > methanol (2.26) > GH_2 (1.64)

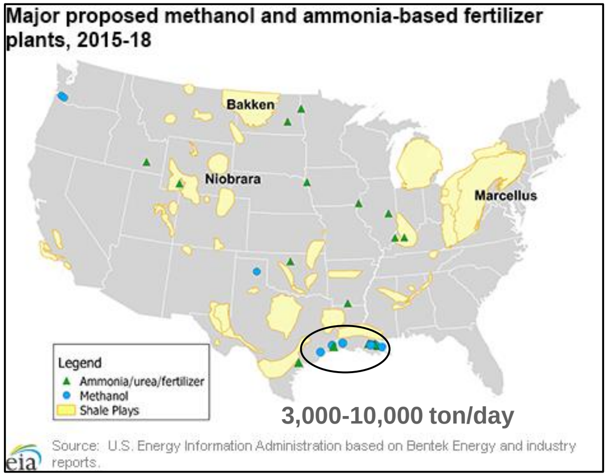


For calculating energy efficiency, make-up toluene is included with fuel

Hydrogen Carrier Pathways – Large Plants

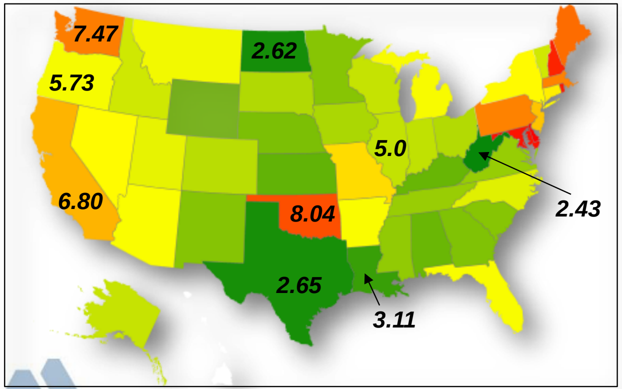
Scenario: Large hydrogenation plant for economy of scale

- 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 to storage terminal in California (3250 km); local transmission by truck (150 km) to city gate

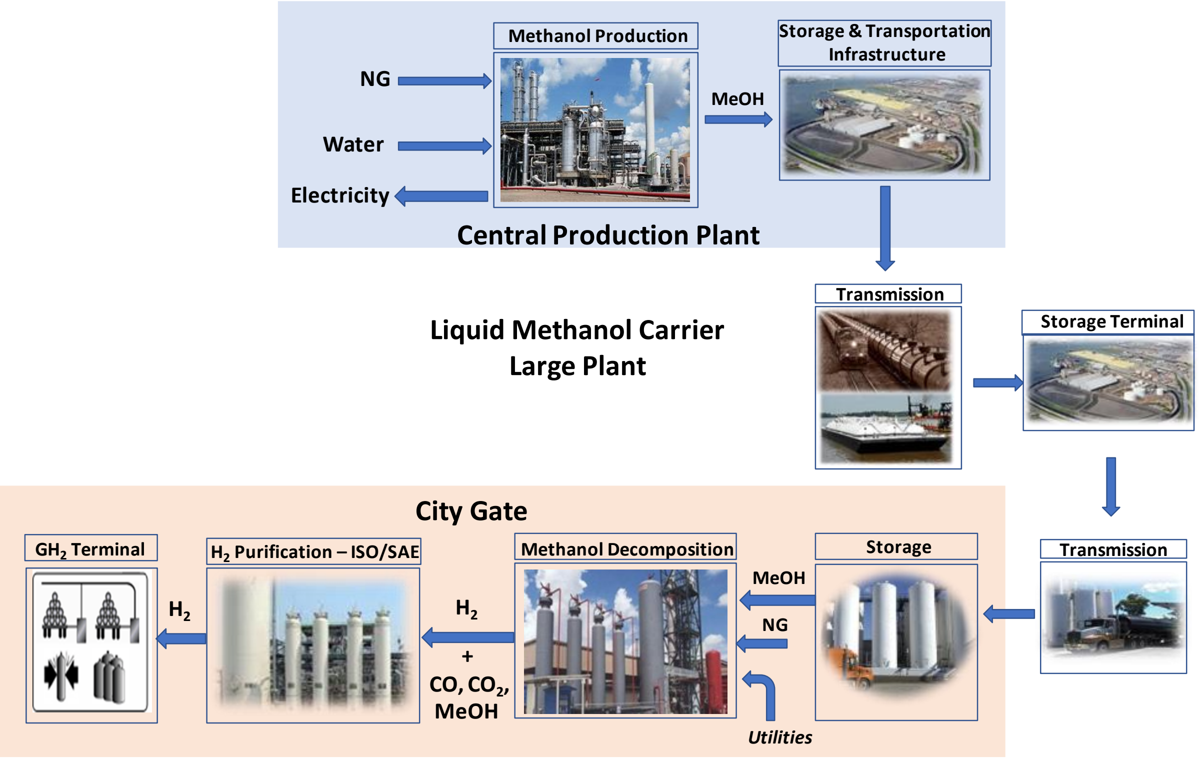

Major proposed methanol and ammonia-based fertilizer plants, 2015-18

3,000-10,000 ton/day

Source: U.S. Energy Information Administration based on Bentek Energy and industry reports.



EIA: Industrial NG $/MBtu (2017 average)


Methanol Production

Storage & Transportation Infrastructure

NG

Water

Electricity

MeOH

Central Production Plant

Transmission

Liquid Methanol Carrier Large Plant

Storage Terminal

City Gate

GH_2 Terminal

H_2 Purification – ISO/SAE

Methanol Decomposition

Storage

Transmission

H_2

H_2 + CO, CO_2, MeOH

MeOH

NG

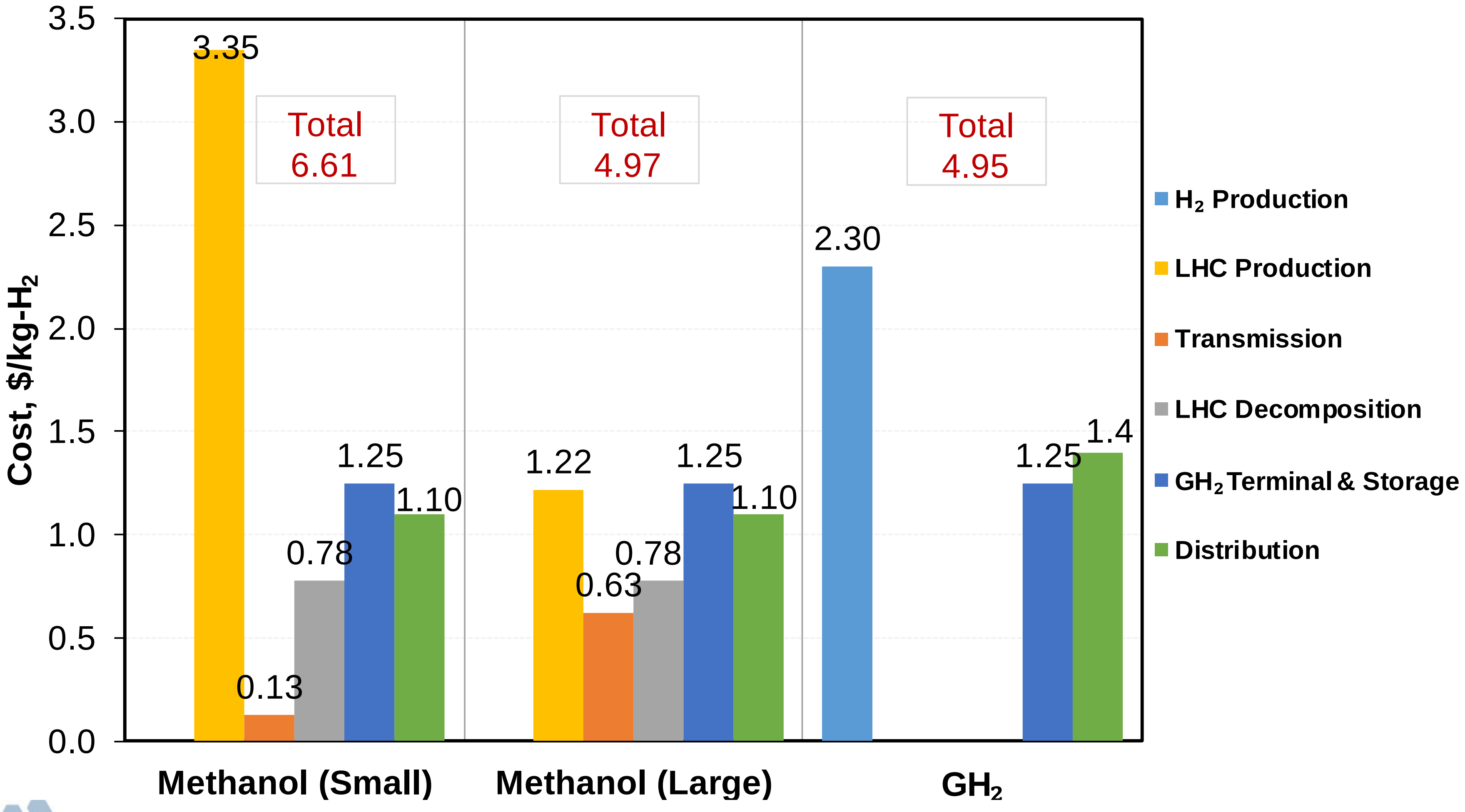
Utilities

Levelized Cost of H_2 Distributed to Stations (50,000 kg-H_2/d)

Liquid carrier can be competitive with the baseline GH_2 scenario.

Large (10,000 tpd) vs. small (320 tpd) methanol production plants

- 0.92 \$/kg-H_2 lower LHC production capital cost
- 0.86 \$/kg-H_2 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 supply and demand 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