

# **Toluene-MCH as a Two-Way Carrier for Hydrogen Transmission and Storage**

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**Project ID: H2058**

This presentation does not contain any proprietary, confidential, or otherwise restricted information.

# Overview

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## Timeline

- Project start date: Oct 2020
- Project end date: Sep 2020
- % Complete: 100

## Barriers

- H<sub>2</sub> Storage Barriers Addressed:
  - B: System Cost
  - C: Efficiency
  - K: Life-Cycle Assessments

## Budget

- FY20 Total Funding: \$100 K
- FY20 DOE Funding: \$50 K

## Partners/Interactions

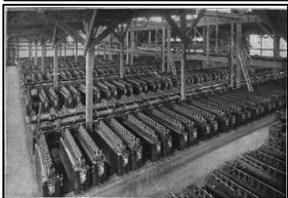
### *Industry & research collaborations*

- Chiyoda Corporation



# Relevance

Chlor-Alkali<sup>[1]</sup>



NGL Cracking<sup>[2]</sup>



Solar<sup>[3]</sup>



Wind<sup>[4]</sup>



Transmission by Rail<sup>[5-6]</sup>



Transmission by Ship<sup>[7-8]</sup>



## - Objectives

- Investigate the performance, regulated/unregulated greenhouse gas (GHG) emissions and cost advantages of using a two-way toluene-methylcyclohexane (MCH) carrier for hydrogen transmission and storage
- Develop and analyze specific hydrogen supply, transmission and demand scenarios that are particularly favorable for toluene-MCH carrier

MP °C	BP °C	H <sub>2</sub> Capacity		Production		Decomposition		
		wt%	g/L	P, bar	T, °C	P, bar	T, °C	ΔH kJ/mol-H <sub>2</sub>
<b>MCH</b>								
-127	101	6.1	47	10	240	2	350	68.3
				Non-PGM Catalyst		Pt/Al <sub>2</sub> O <sub>3</sub> Catalyst		

## - Tasks and Approach

- Develop models for cost and performance of toluene hydrogenation and dehydrogenation plants of 50-650 TPD (Metric Tons Per Day H<sub>2</sub> equivalent).
- H<sub>2</sub> supply scenarios: S<sub>1</sub> – byproduct H<sub>2</sub> from chlor-alkali plants, S<sub>2</sub> – byproduct H<sub>2</sub> from NGL steam cracking, S<sub>3</sub> and S<sub>4</sub> – renewable H<sub>2</sub> from solar and wind, respectively
- Develop models and/or use existing tools<sup>1</sup> and models for cost and performance of H<sub>2</sub> demand scenarios (D<sub>1</sub> - FC LDV, D<sub>2</sub> – FC HDV, D<sub>3</sub> – Power GTCC)
- Develop models for transmission, infrastructure and storage of MCH and toluene by rail or by ships (product tankers)
- For each case study, determine the performance (energy consumption, MJ/kg-H<sub>2</sub>), levelized cost (\$/kg-H<sub>2</sub>), and greenhouse gas emissions (kg-CO<sub>2</sub>/kg-H<sub>2</sub>)
- All pathway costs evaluated by H2A<sup>2</sup> guidelines and based on 2016 \$-year basis

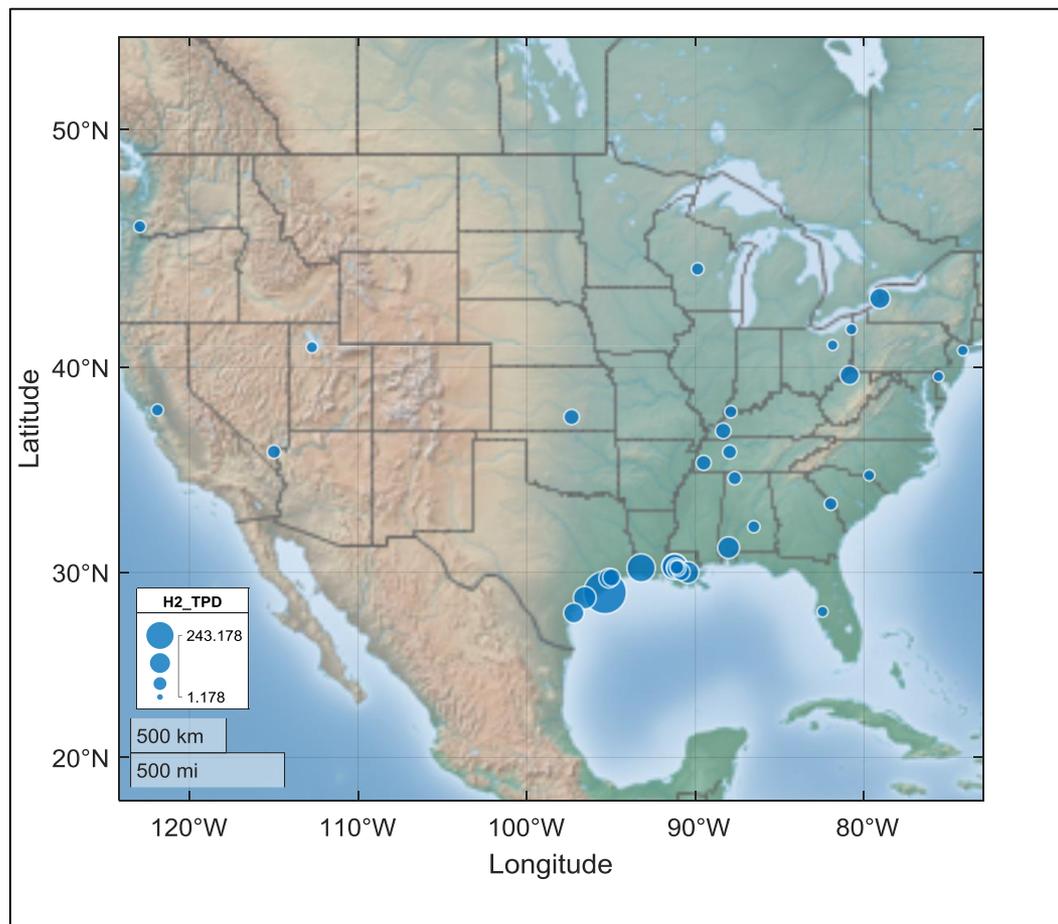
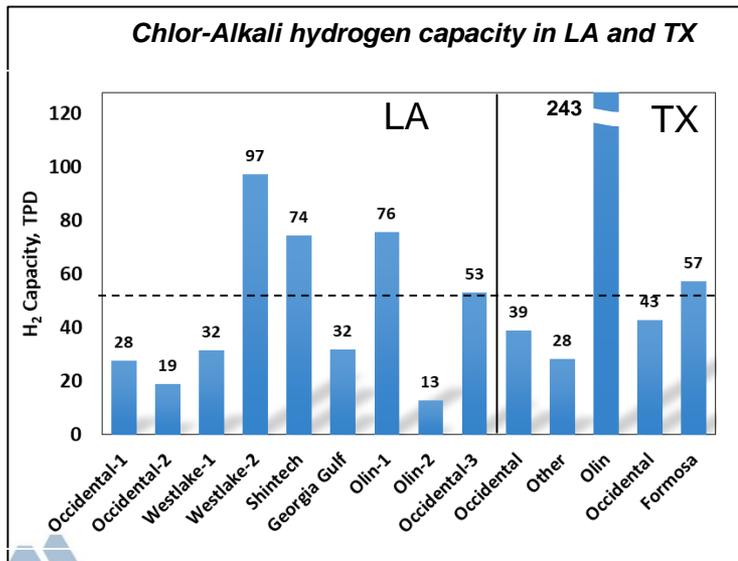
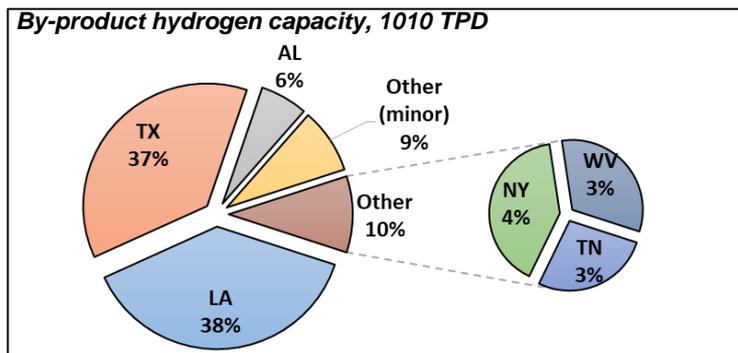
<sup>1</sup>Tools and methods: Matlab, GC-Tool, H2A, HDSAM, HDRSAM, SAM, Cost models (Internal Developed/Aspen/Literature)

<sup>2</sup>[https://www.hydrogen.energy.gov/h2a\\_analysis.html](https://www.hydrogen.energy.gov/h2a_analysis.html)



# (S<sub>1</sub>) - Utilization of by-Product H<sub>2</sub> from Chlor-Alkali plants<sup>1</sup>

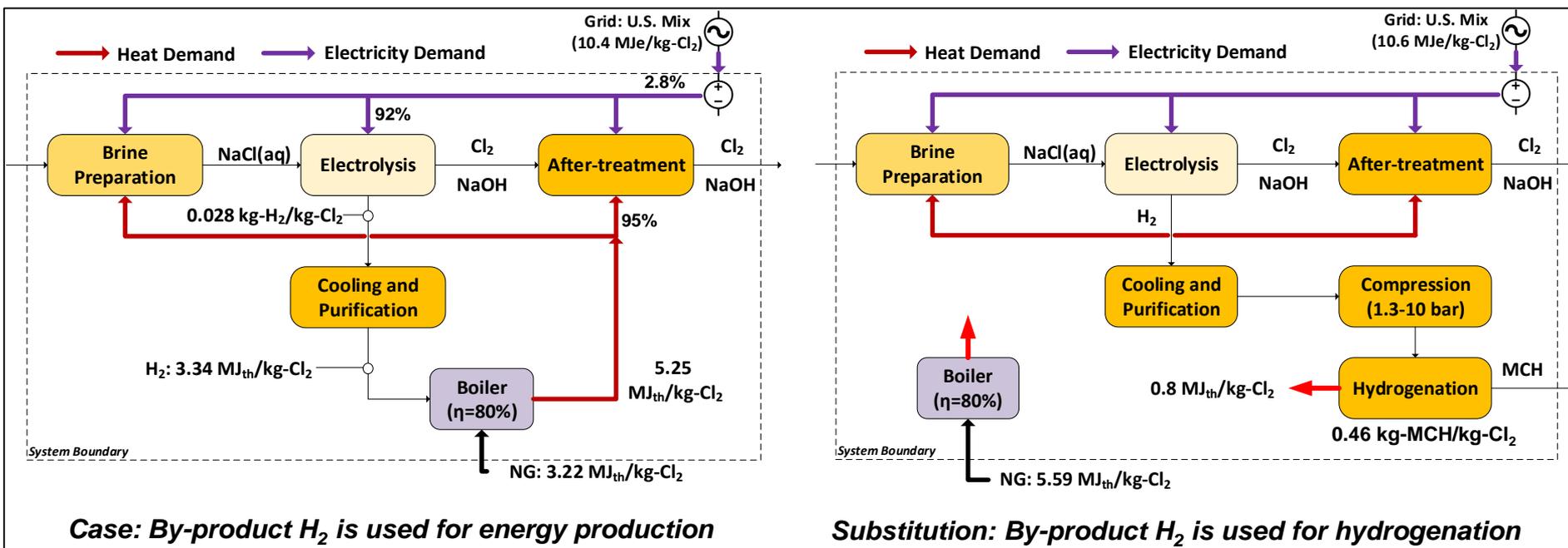
- An estimated 0.4 million metric tons of hydrogen is produced annually by the chlor-alkali industry in the U.S.
- Approximately 80% of the United States chlor-alkali capacity is in the Gulf region
- About 35% of by-product hydrogen is known to enter the merchant gas market. H<sub>2</sub> is combusted for steam generation or vented (~10-15%)



<sup>1</sup>Lee, D.Y. and Elgowainy, A., Dai Q. Life Cycle Greenhouse Gas Emissions of By-Product Hydrogen from Chlor Alkali Plants. ANL/ESD-17/27

# (S<sub>1</sub>) - Utilization of by-Product H<sub>2</sub> from Chlor-Alkali Plants<sup>1</sup>

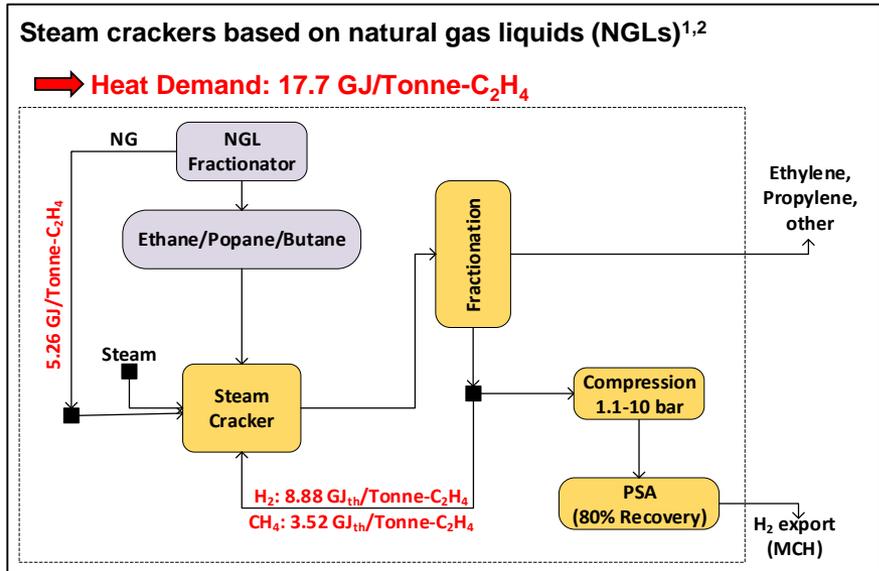
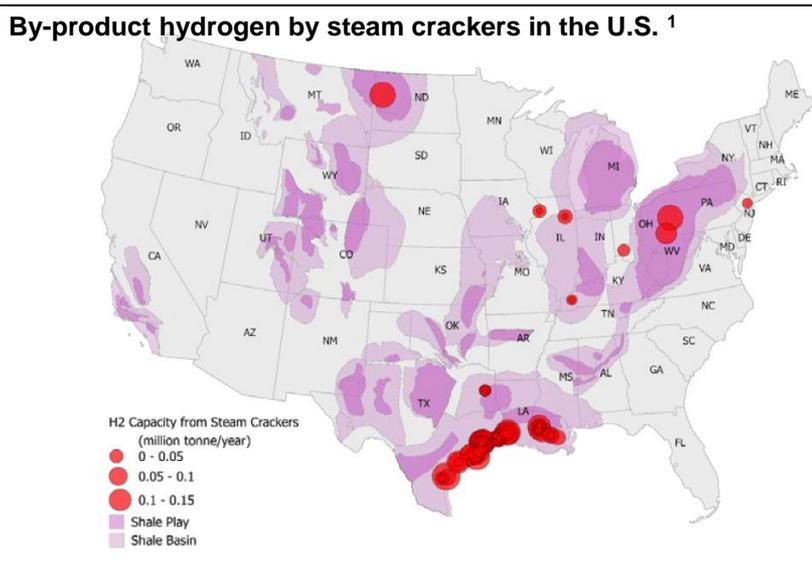
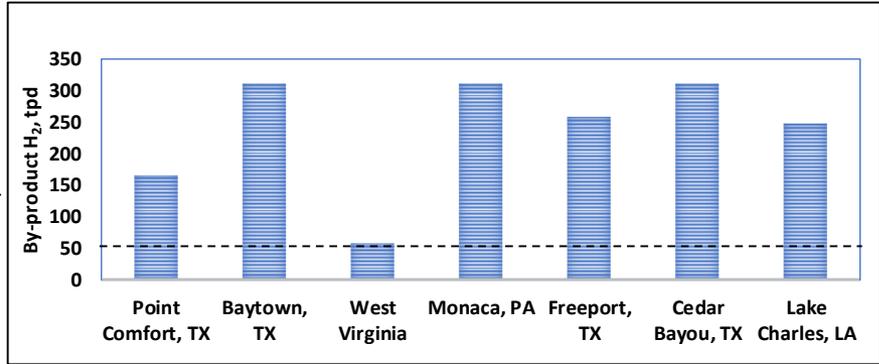
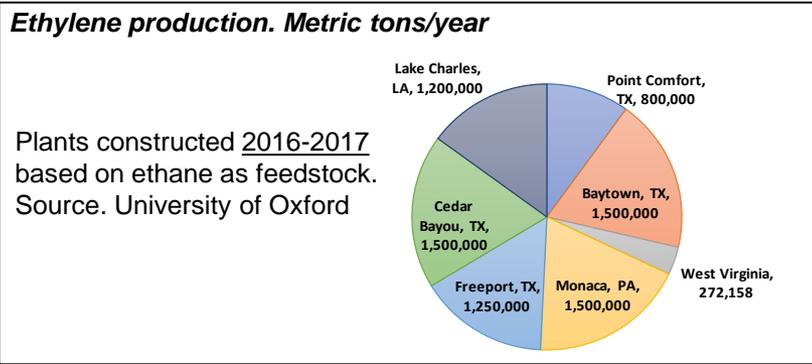
- About two-thirds (68%) of total electricity consumed by the U.S. chlor-alkali industry is from the bulk electricity market (or the grid);
- The remainder (32%) is sourced from on-site power generation. Most of the CHP units are in the Gulf Coast region, which all are topping cycle systems
- Steam is needed in the chlor-alkali production e.g. for salt preparation and concentration of caustic soda. NaOH after-treatment process accounts for the largest heat requirement (95%)
- By-product hydrogen can be exported or used for steam/electricity production
- Hydrogen used for hydrogenation needs to be substituted by NG to meet heat demand



<sup>1</sup>Lee, D.Y. and Elgowainy, A., Dai Q. Life Cycle Greenhouse Gas Emissions of By-Product Hydrogen from Chlor Alkali Plants. ANL/ESD-17/27

# (S<sub>2</sub>) - Utilization of by-Product H<sub>2</sub> - NGL Steam Cracking Plants<sup>1,2</sup>

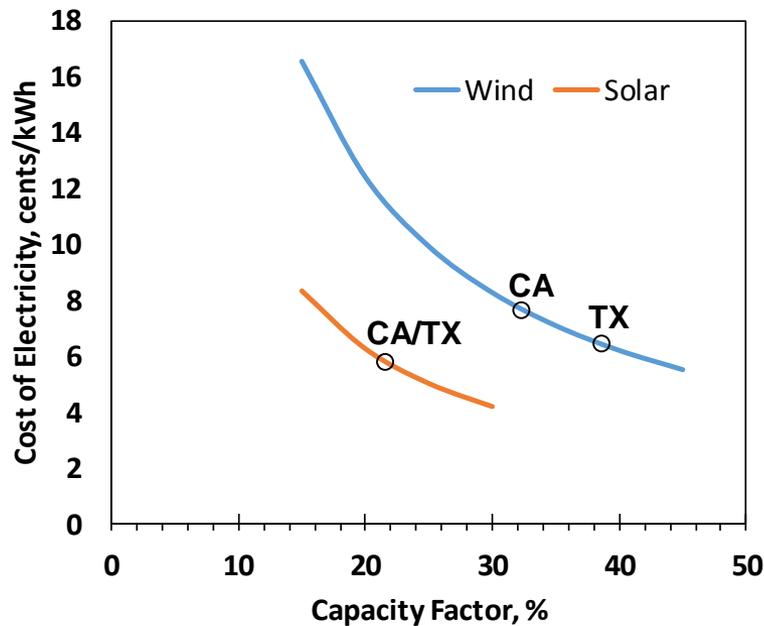
- An estimated 1.8 million metric tons per year (5,000 tpd) of by-product hydrogen is produced annually from NGL steam crackers in the U.S.
- Steam crackers in Texas and Louisiana makes up ~88% of the total by-product hydrogen
- As of 2017, ethane makes up 67% of the steam cracker feedstock in the U.S. (H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub>=7.6 wt.%)



<sup>1</sup>Lee, D.Y. and Elgowainy, A. International journal of hydrogen energy 43 (2018) 20143-20160

<sup>2</sup>The Lindgren Group, LLC, Production of Ethylene from Natural Gas, April 22, 2013

# S<sub>3</sub> and S<sub>4</sub> - Cost of Electricity by Wind and Solar<sup>1</sup>



## Projected Electricity Costs

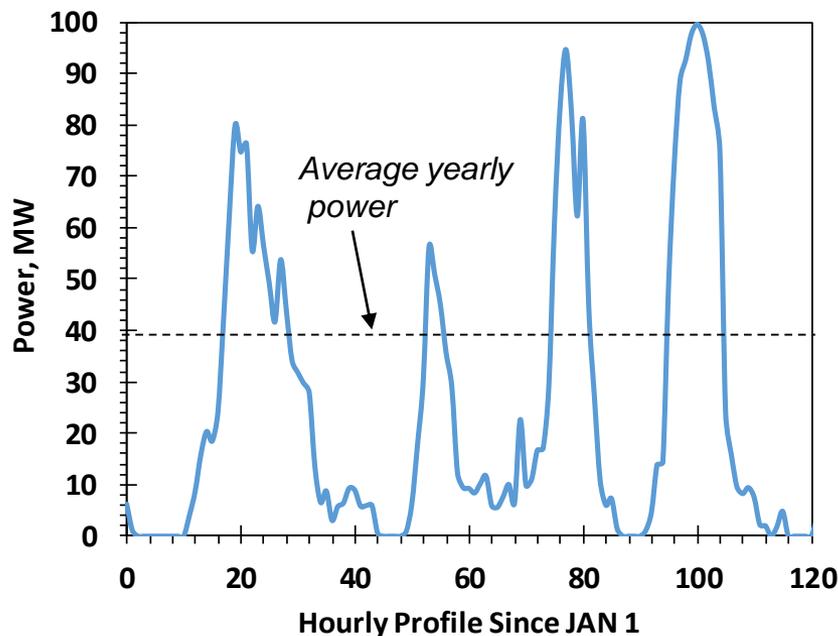
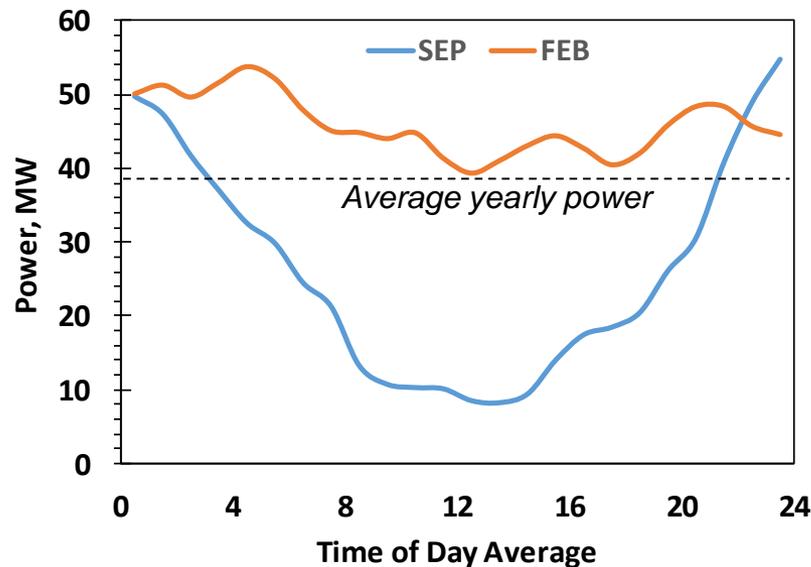
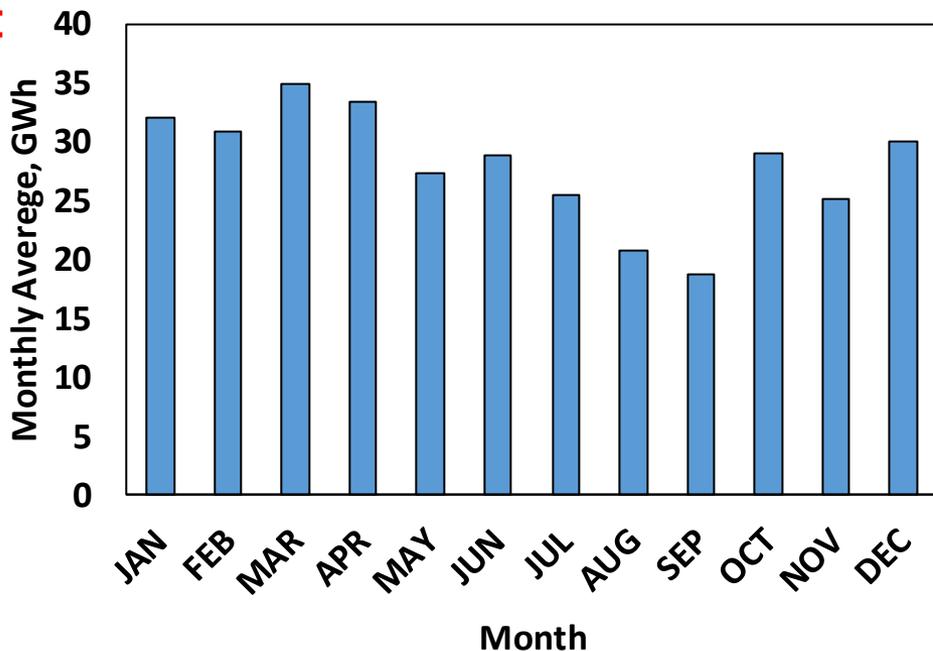
- Wind offers higher annual capacity factor than solar. Wind capacity : TX 38.1% vs 32.2% in CA
- Solar capacity factor near similar in TX and CA ~21%
- Cost of solar cheaper than wind in all cases: CAPEX and OPEX of solar less than wind

State	TX (SW)	CA (SE)
Resource	Wind	Wind
Turbine	General Electric 3.6sl	General Electric 3.6sl
Rated Capacity (kW)	3,600	3,600
Hub Height (m)	80	80
CAPEX (\$/kW)	1,695	1,695
OPEX (\$/MWh)	18.1	18.1
Analysis Period (years)	25	25
IRR (%)	10	10
Capacity Factor (%)	38.1	32.2
CAPEX (cents/kWh)	4.98	5.89
OPEX (cents/kWh)	1.53	1.81
<b>Total LCOE (cents/kWh)</b>	<b>6.51</b>	<b>7.71</b>

State	TX (SW)	CA (SE)
Resource	Solar (PV)	Solar (PV)
Array Type	1 Axis Tracking	1 Axis Tracking
Direct normal (kWh/m <sup>2</sup> /day)	5.23	5.23
Inverter Efficiency (%)	96	96
CAPEX (\$/kW)	1,040	1,040
OPEX (\$/MWh)	4.8	4.8
Analysis Period (years)	25	25
IRR (%)	10	10
Capacity Factor (%)	21.1	21.4
CAPEX (cents/kWh)	5.51	5.44
OPEX (cents/kWh)	0.49	0.48
<b>Total LCOE (cents/kWh)</b>	<b>6.00</b>	<b>5.92</b>

<sup>1</sup>Wind and solar techno-economics based on System Advisor Model (SAM). [www.nrel.gov](http://www.nrel.gov)

# Utilization by Wind – Example Profiles in TX<sup>1</sup>



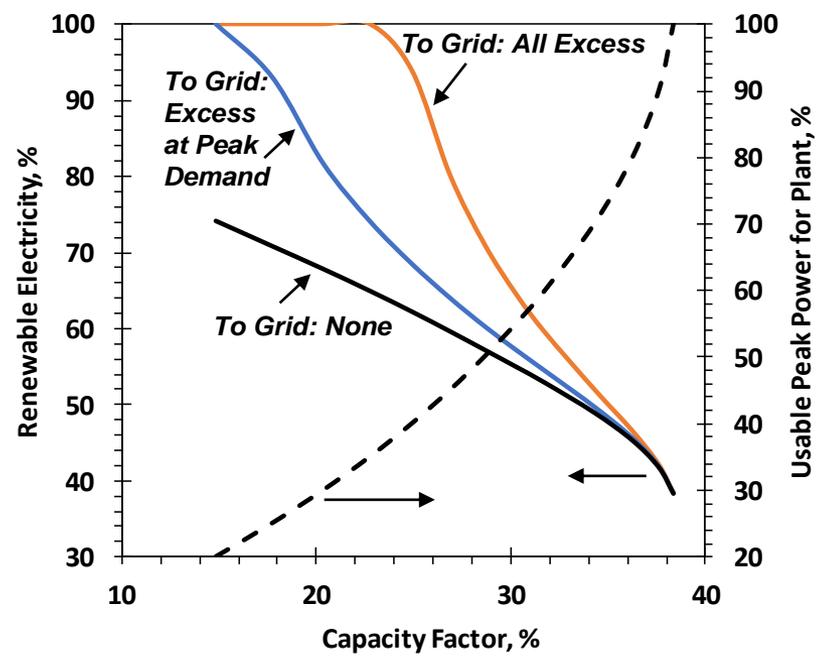
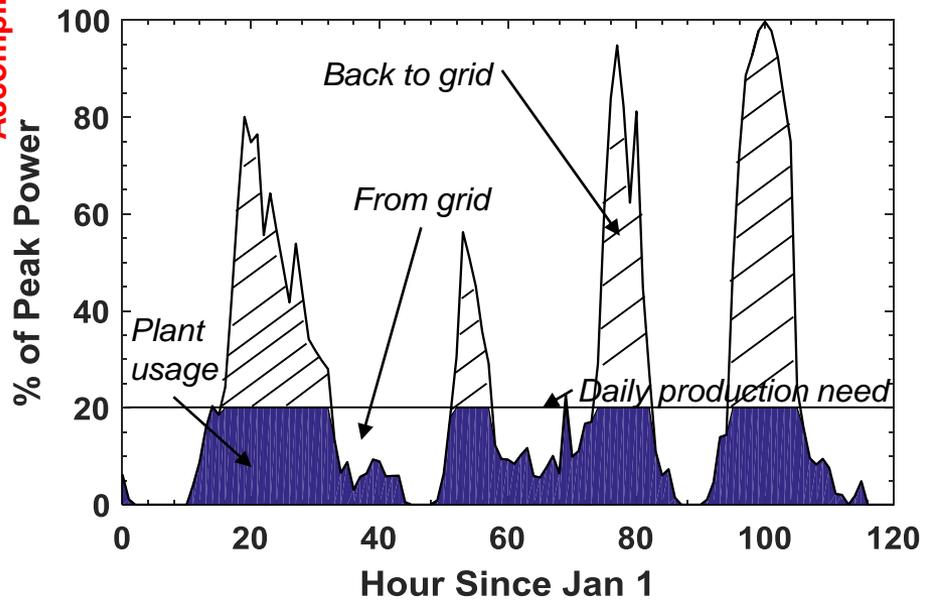
- Renewable Power Intermittency**
- Yearly, monthly and even hourly average values are not very useful metrics for analysis.
  - Actual hourly profiles (e.g. wind) show sharp variability with 0-100% rated capacity and idling at hours.
  - Using load following, the cost of hydrogen by electrolysis capital alone, will increase by 2-2.5 \$/kg (at 38%-32% capacity factor)

<sup>1</sup>Example 100 MW name-plate capacity

Capacity Factor = Annual energy produced/annual nameplate energy capacity

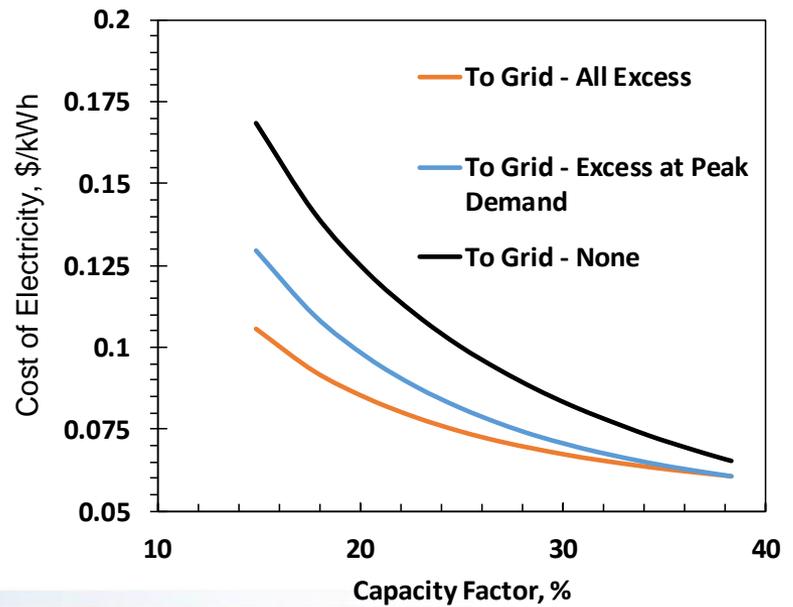
# Utilization by Wind – Example Scenario Options

Accomplishment



## Renewable Power Intermittency

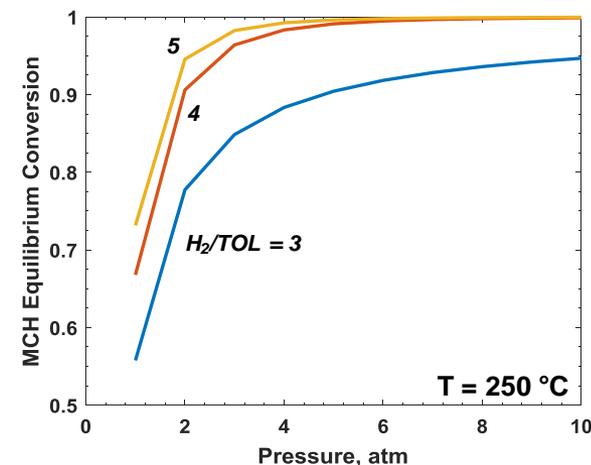
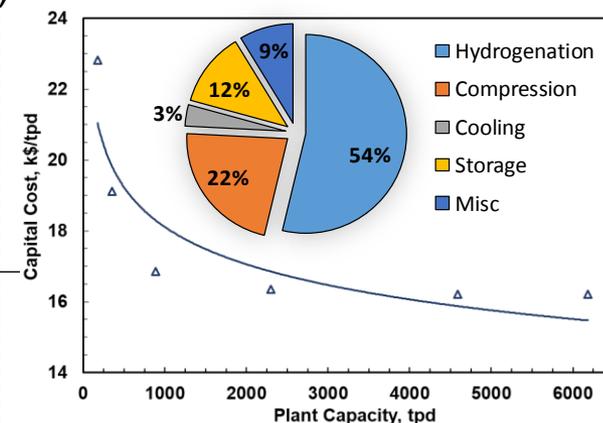
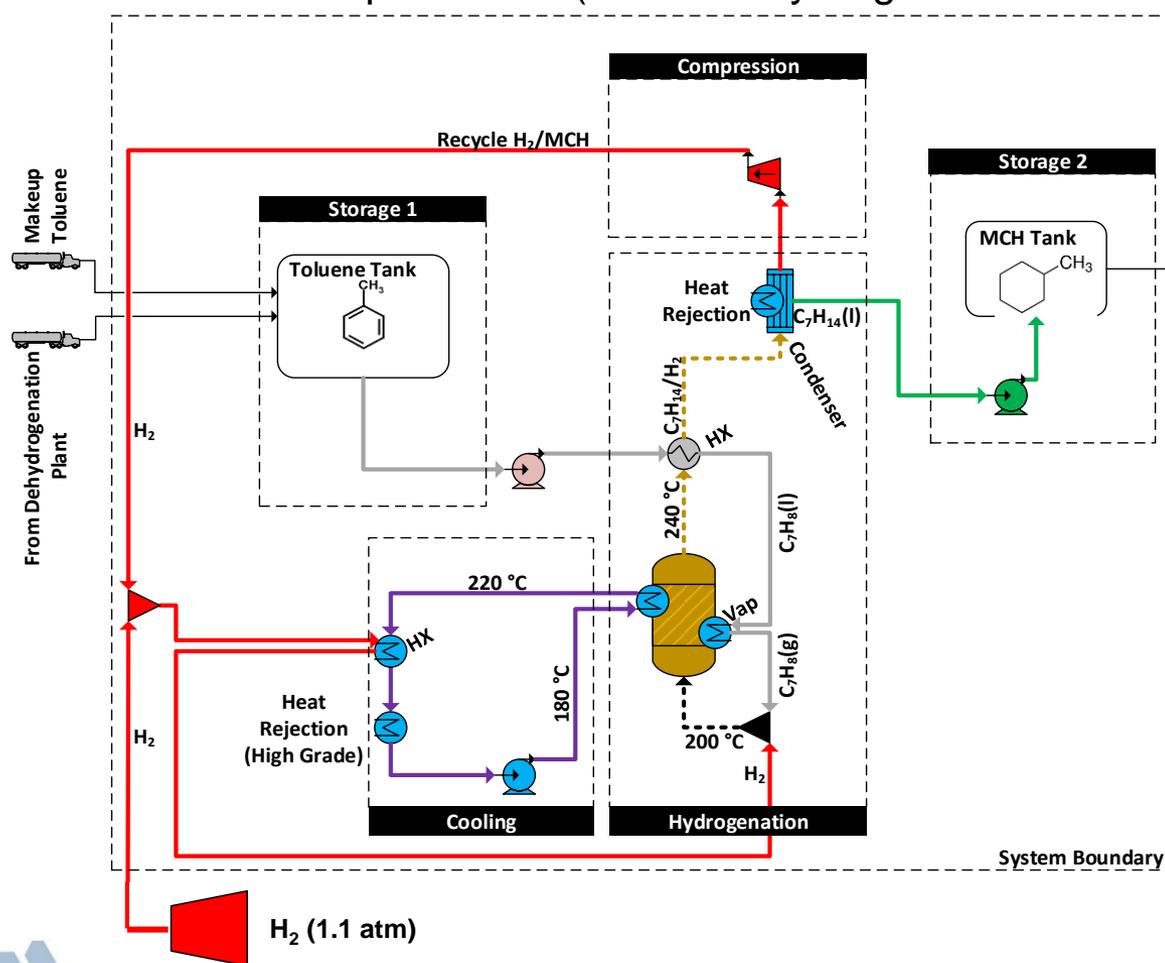
- Utilize a fraction of the rated power of the plant for hydrogen production
- Excess electricity is sold back to the grid (all excess, or excess during peak demand hours 8 am – 8 pm)
- At times when wind power is less than utilized for hydrogen production; import electricity from the grid
- Cost of grid power: 5.74 ¢/kWh, price of electricity sold: 2.5 ¢/kWh
- Renewable power: Offset import to export



Grid power assumes fossil based power and should not be confused with actual GHG emissions

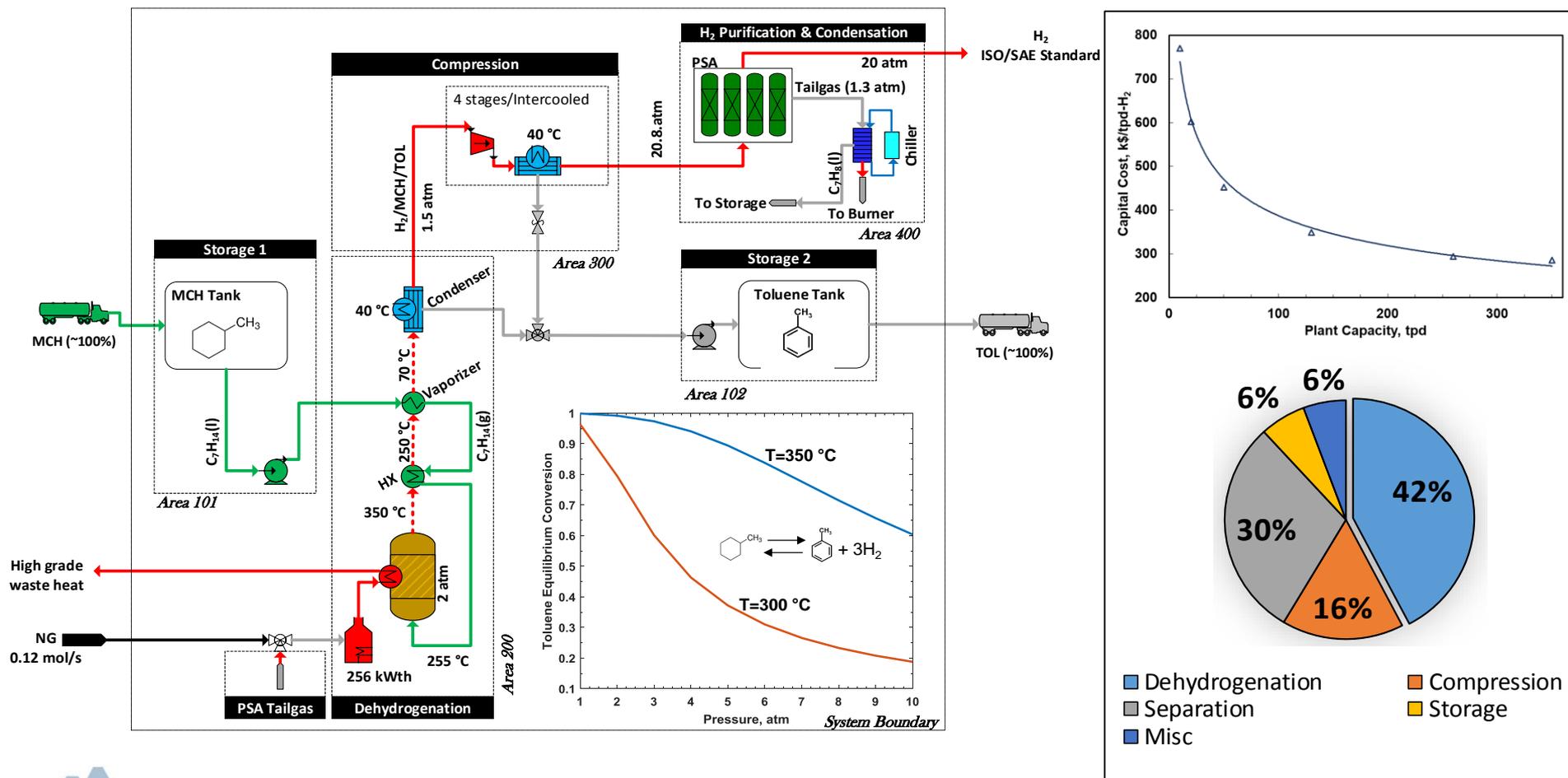
# Capital Cost of Toluene Hydrogenation Plant

- 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<sub>2</sub> and MCH vapor recycled (H<sub>2</sub>/Toluene ratio = 4/1)
- Toluene makeup = 0.22% (due to dehydrogenation losses)



# Capital Cost of Methylcyclohexane Dehydrogenation Plant

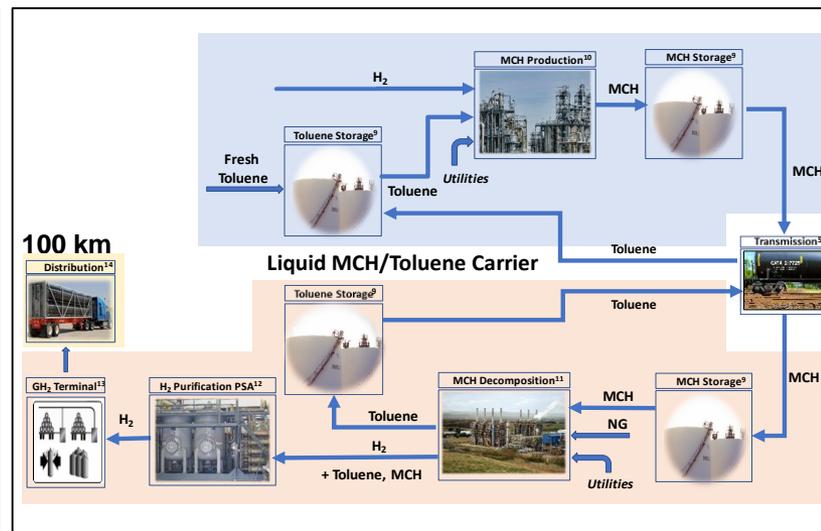
- Reactor operated at 350°C and 2 atm. Conversion is 98% with 99.9% toluene selectivity. No side-reactions considered.
- Allowing for 0.5 atm pressure, 80% of toluene condenses at 1.5 atm and 40°C, remaining during the compression cycle (4 stages) and chiller
- H<sub>2</sub> separation by PSA at 20 atm, 90% recovery (ISO/SAE H<sub>2</sub> quality)



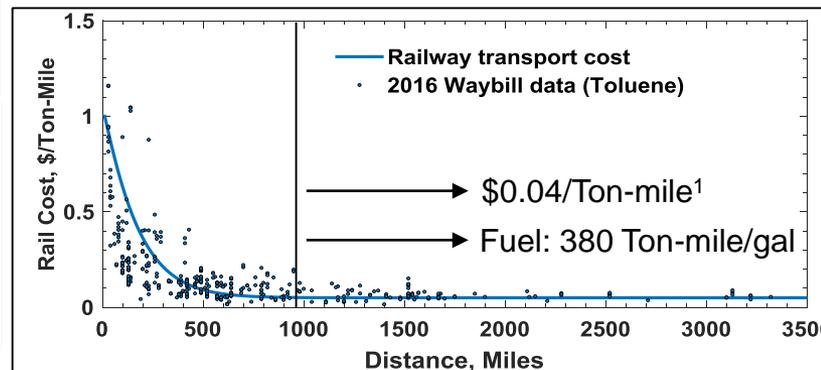
# (T<sub>1</sub>) - Transmission by Rail

Scenario: Hydrogen by-product from chlor-alkali and steam cracker plants

- Hydrogenation of toluene: 50, 130, 260 and 650 TPD
- Location: Hydrogenation in Gulf of Mexico. ~80% H<sub>2</sub> capacity (5,200 TPD)
- Transmission: Unit train or ships to dehydrogenation facility in northern California
- Distribution: H<sub>2</sub> distribution to LDV market by GH<sub>2</sub> trucks to a mid-size city (3 M)

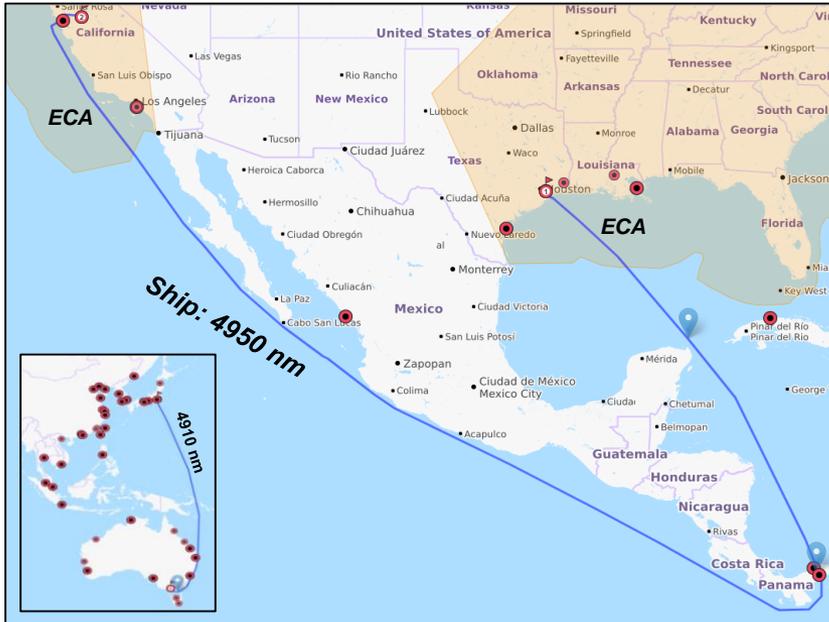


Byproduct H <sub>2</sub> from Gulf Coast						
H <sub>2</sub> Demand (TPD)	FC Vehicle Market (%)	Chlor Alkali (%)	Steam Cracker (%)	Train Frequency (days)	Storage (days)	Railcars
50	4	6.6	1.1	7	9	76
130	10	17.2	3.0	4	6	112
260	20	34.3	5.9	2	4	112
650	49	85.8	14.8	1	3	140



11 Short ton (ton) = 0.907 Metric ton (Tonne)

# (T<sub>2</sub>) – Transmission by Product Tanker



Tanker Specifications	50 TPD	130 TPD	260 TPD	650 TPD
Tanker Size (DWT)	35,000	92,615	92,615	115,000
Number of Ships per Route	1	1	2	4
Tanker MCH Capacity (Tonnes)	24,400	63,355	63,355	79,194
Tanker H <sub>2</sub> Capacity (Tonnes)	1,500	3,900	3,900	4,875
Tanker Length (m)	183	239	239	248
Tanker Width (m)	30	38	38	42
Tanker draught (m)	9	13	13	14
Storage (Days)	32	32	17	10

**Tanker size limited by LR2 size, not Neopanamax canal dimensions**

*Panamax locks: Length of up to 294 m (965'), beam of up to 32.31 m (106'), draught of up to 12.04 m (39.5').*

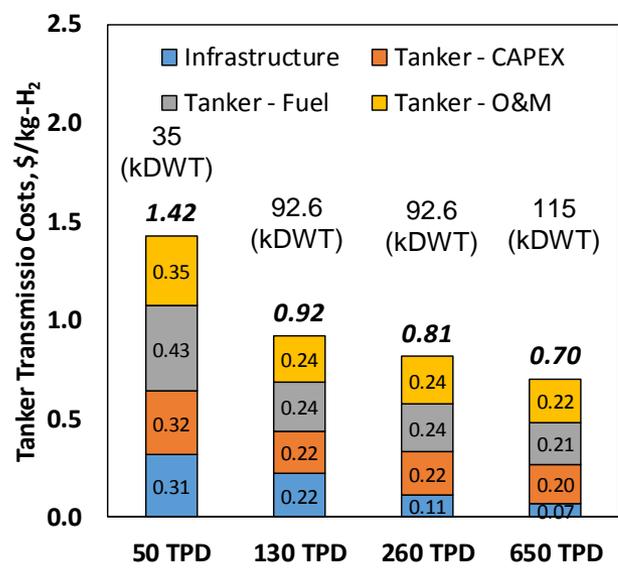
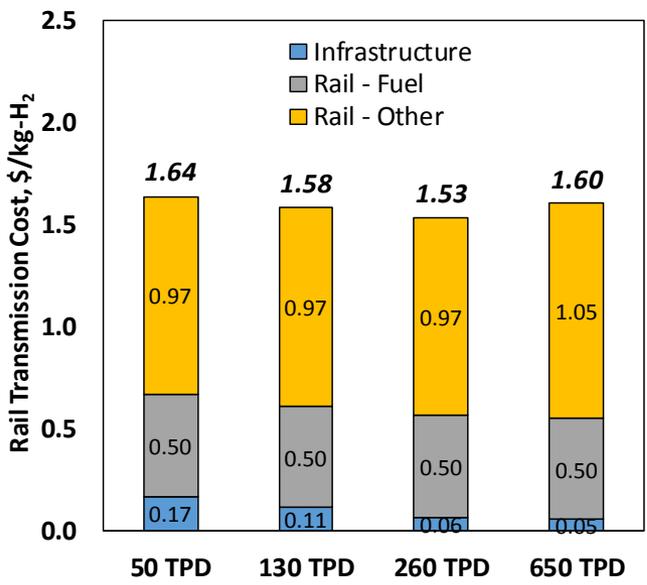
*Neopanamax locks: Length of up to 427 m (1,401'), beam of up to 52 m (170'), draught of up to 18.3 m (60').*

## MCH/Toluene tanker limited in capacity to 115 kDWT based on largest LR2 product tanker

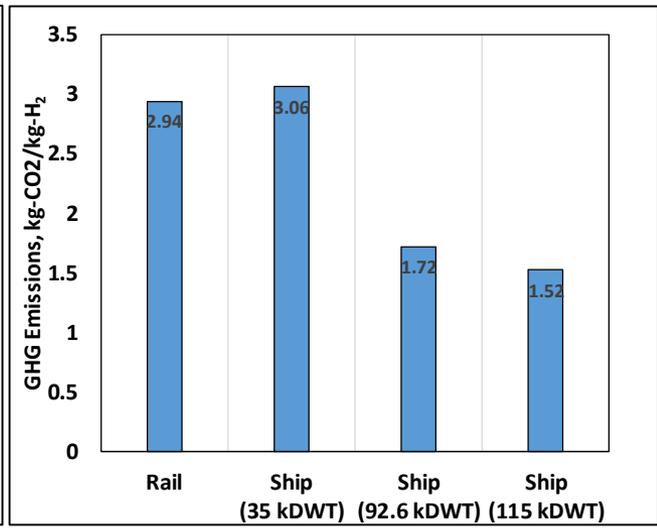
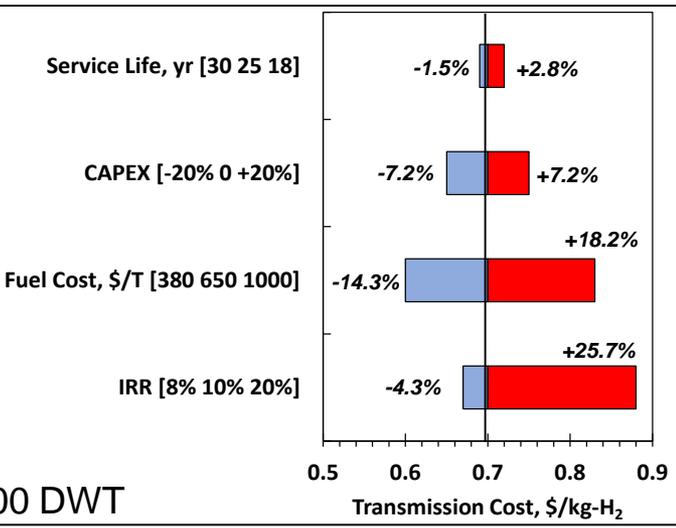
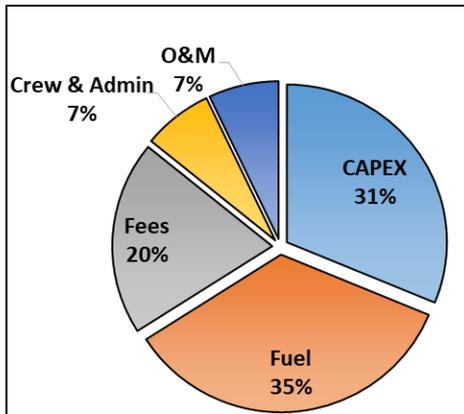
- Round-trip time: 30 days (15 knots at sail; 8 h to pass Panama Canal, 20 h to un-load and load shipment)
- From 2020, IMO regulations will cut sulfur dioxide emissions by 86%, reducing worldwide sulfur content in fuel from 3.5% (IFO) to 0.5% (MGO).
- Ships that operate in Emissions Control Areas (ECA) must limit sulfur content in fuel to <0.1% as in low-sulfur marine gas oil (LSMGO).
- Tanker will spend 27% of it's time in ECA zones (sail & at berth)
- Panama canal fees varies on ship length, width and laden conditions



# Tanker (T<sub>2</sub>) Transmission Cost Relative to Rail (T<sub>1</sub>)



- Economy of scale favors large tankers (single ship per route)
- Tankers more favorable for transmission than rail >50 TPD
- GHG Emissions lowest for Tanker >50 TPD demand



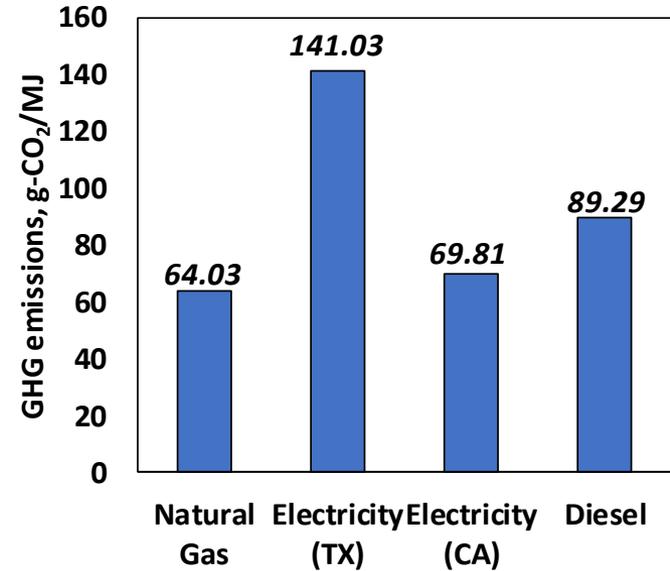
# Pathway Costs and Green-House Gas Emissions

Electricity Source (%)	U.S. Mix	TRE (TX) Mix	CA Mix
Residual oil	0.5%	0.1%	0.0%
Natural gas	29.8%	45.5%	41.3%
Coal	32.7%	28.9%	6.3%
Nuclear power	20.6%	11.5%	9.7%
Biomass	0.1%	0.0%	0.5%
Renewable	16.3%	14.0%	42.2%

Electricity Source (g-GHG/kWh)	U.S. Mix	TRE (TX) Mix	CA Mix
Residual oil	4.06	1.06	0.24
Natural gas	126.53	193.54	175.63
Coal	325.56	287.72	62.89
Nuclear power	0.00	0.00	0.00
Biomass	0.00	0.00	0.00
Renewable	0.00	0.00	0.00
Total (g/kWh)	480.16	507.71	251.32
Total (g/MJ)	133.38	141.03	69.81

Electricity Production Mix  
GREET 2019



Chlor-Alkali Allocation			
Chlor-Alkali	Cl <sub>2</sub>	NaOH	H <sub>2</sub>
Co-products (kg/kg H <sub>2</sub> )	35.09	39.65	1
Market Values (\$/kg)	0.26	0.44	1
Mass share	46.33%	52.35%	1.32%
Market value share	32.62%	63.74%	3.65%

Ethane Crackers - Allocation			
Products	Formula	kg/kg-H <sub>2</sub>	Mass Share
Ethylene	(C <sub>2</sub> H <sub>4</sub> )	13.158	83.20%
Propylene	(C <sub>3</sub> H <sub>6</sub> )	0.25	1.58%
Methane	(CH <sub>4</sub> )	0.895	5.66%
Butadiene	(C <sub>4</sub> H <sub>6</sub> )	0.368	2.33%
Butene	(C <sub>4</sub> H <sub>8</sub> )	0.039	0.25%
Benzene	(C <sub>6</sub> H <sub>6</sub> )	0.092	0.58%
Toluene	(C <sub>7</sub> H <sub>8</sub> )	0.013	0.08%
Hydrogen	(H <sub>2</sub> )	1	6.32%
<b>Total</b>		<b>15.815</b>	<b>100.00%</b>

Allocation

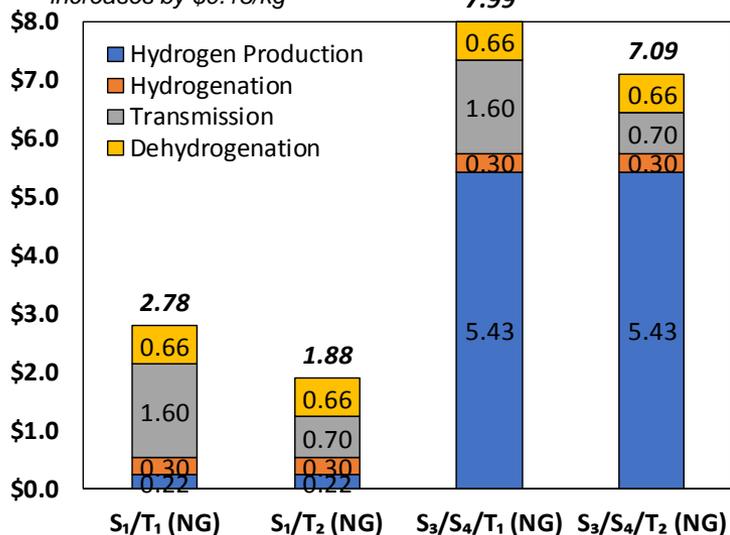
## Emissions and Energy

- Emissions and energy use include well to point of use metrics according to latest GREET model 2019
- Electricity emissions used for TRE region (TX) and CA with a mix of energy sources
- H<sub>2</sub> by-product emissions will be compared on substitution (NG consumption) as well as on mass-allocation basis (CO<sub>2</sub> emissions split on all co-products)
- For brevity, costs are compared for a large demand case (650 TPD). All cost breakdowns are available in separate spreadsheet.

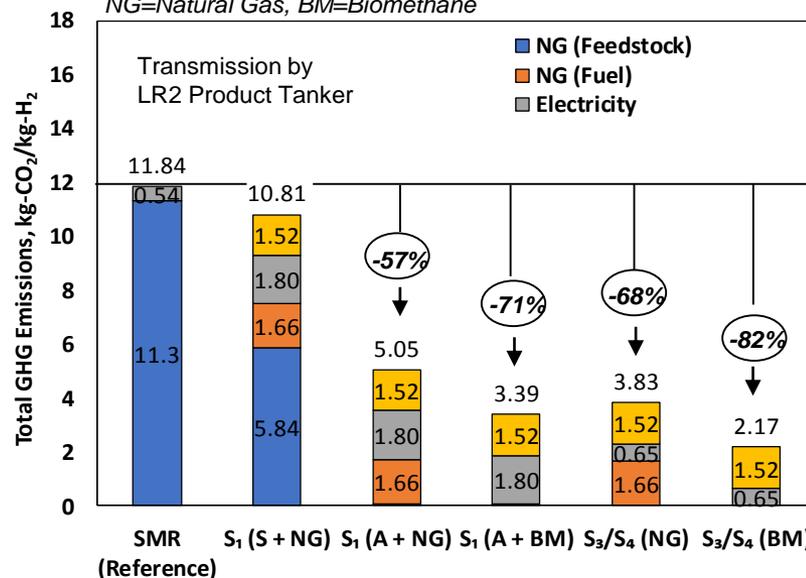


# Cost, Up-stream Energy Use and Emissions: Summary

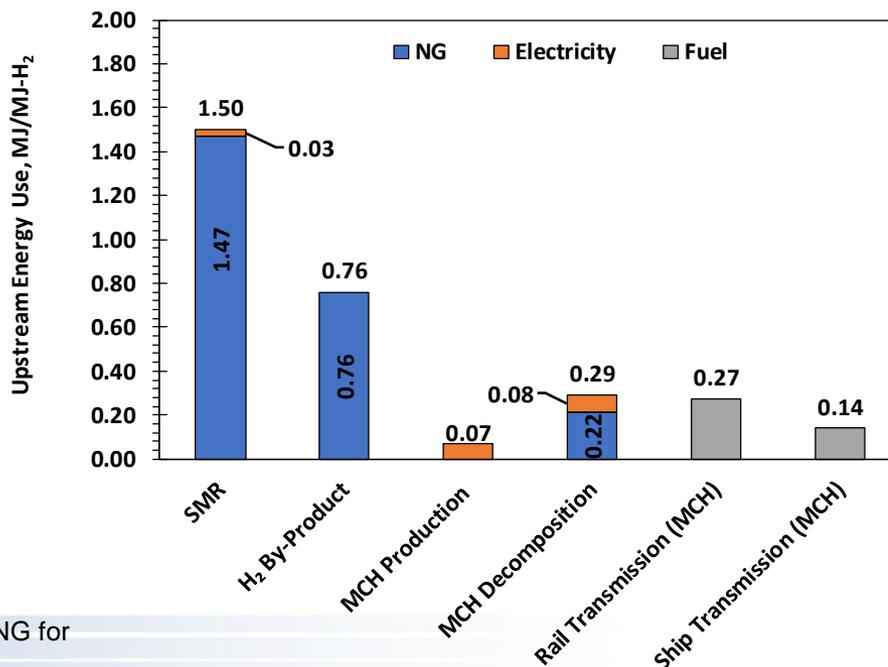
Dehydrogenation cost by Bio-Methane (BM) (not shown) increases by \$0.18/kg



S=Substitution, A=Mass-Allocation, NG=Natural Gas, BM=Biomethane

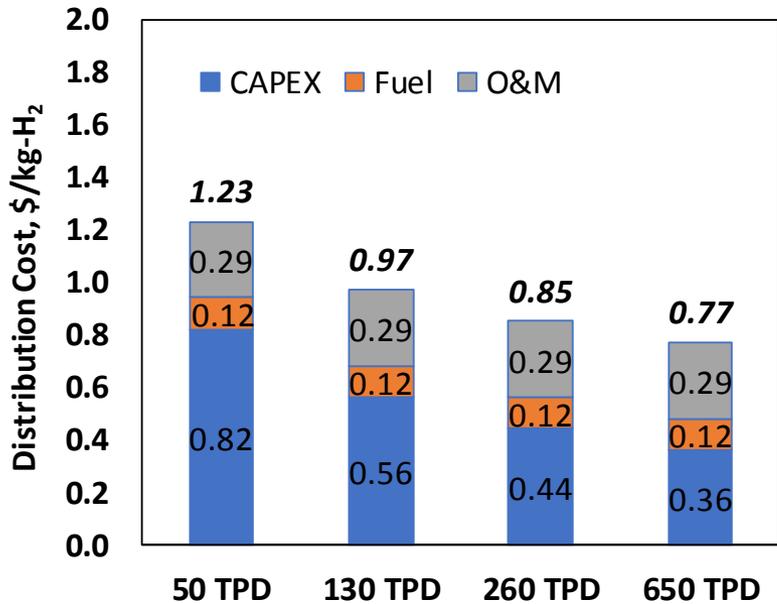


- By-product H<sub>2</sub> incurs the lowest cost among the pathways analyzed. Using ships as transmission mode, the cost could potentially be below \$2/kg<sup>1</sup>
- By-product H<sub>2</sub> could reduce GHG by 57-71% relative to SMR if emissions are mass-allocated to all co-products and if bio-methane is available for dehydrogenation.
- Producing renewable H<sub>2</sub> in TX for dehydrogenation in CA will be at best cost competitive (\$7.26/kg in CA) but incur higher emissions.



<sup>1</sup>This is the lowest cost reflected by hydrogen substituted by NG for heat demand, and not assigning a "market" value for H<sub>2</sub>

# (D<sub>1</sub>) - GH<sub>2</sub> Terminal and Distribution Costs



LDV GH <sub>2</sub> Refueling Infrastructure				
California City Case Size Population (Million)	3	3	3	3
Station Utilization (%)	80	80	80	80
Station Dispensing Capacity (kg/day)	400	600	800	1000
H <sub>2</sub> Demand (TPD)	50	130	260	650
H <sub>2</sub> LDV Market Penetration (%)	4	10	19	49
H <sub>2</sub> LDV Fleet	87,700	219,000	416,000	1,075,000
# of H <sub>2</sub> Stations in City	168	280	400	822
Distance Between Stations (km)	3.36	2.6	2.18	1.52
H <sub>2</sub> Stations displacing Gas Stations (%)	11	18	26	53
# of Trucks Required Per Day	32	80	151	388
# 540 bar Trailers	187	310	441	907
Tube trailers/H <sub>2</sub> Daily demand (#/TPD)	3.7	2.4	1.7	1.4
Cost of Electricity - CA (\$/kWh)	0.125	0.125	0.125	0.125

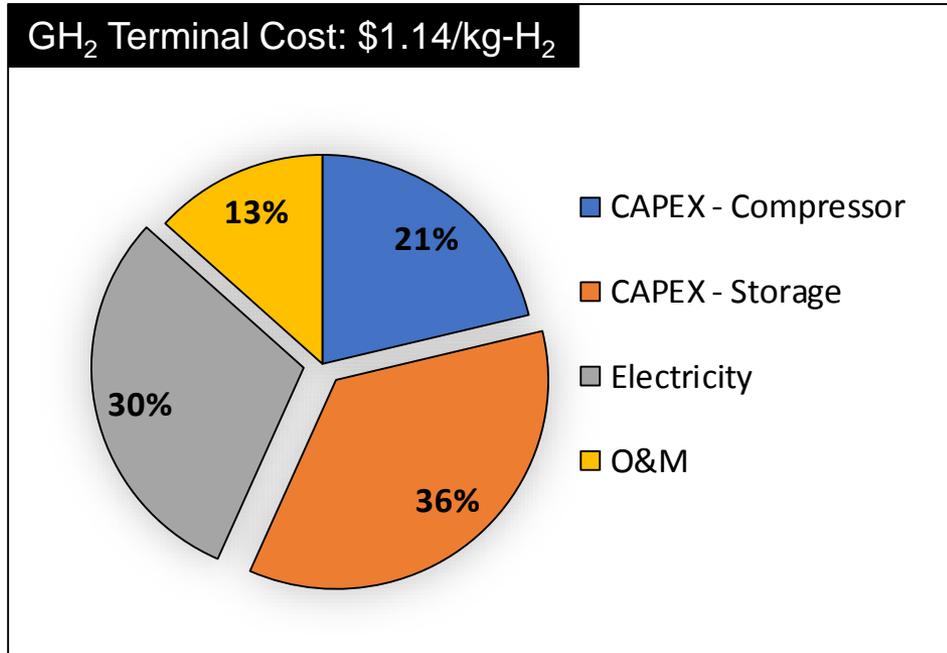
**Distribution costs are affected by the station capacity (dispensing rate)**

**Distribution (400 vs 1000 kg/day)**

- Lower cost as number of tube trailers are reduced per daily demand

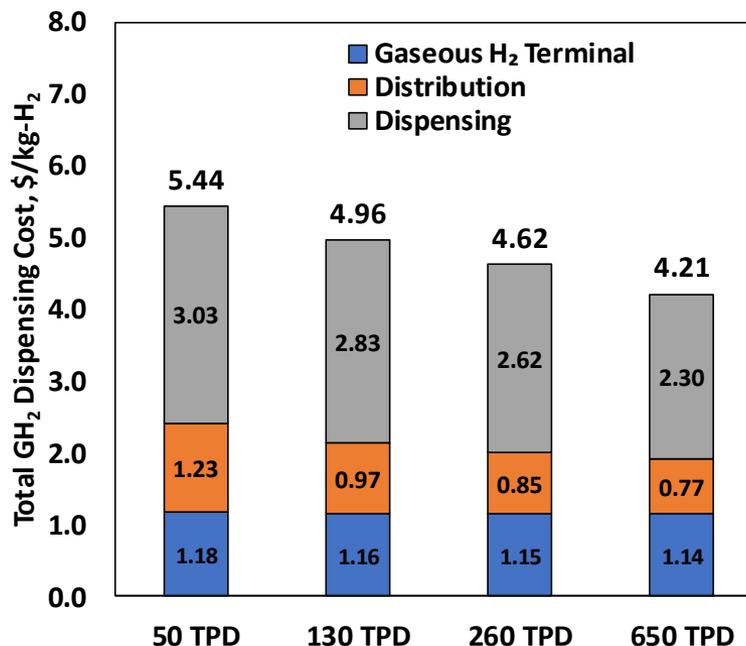
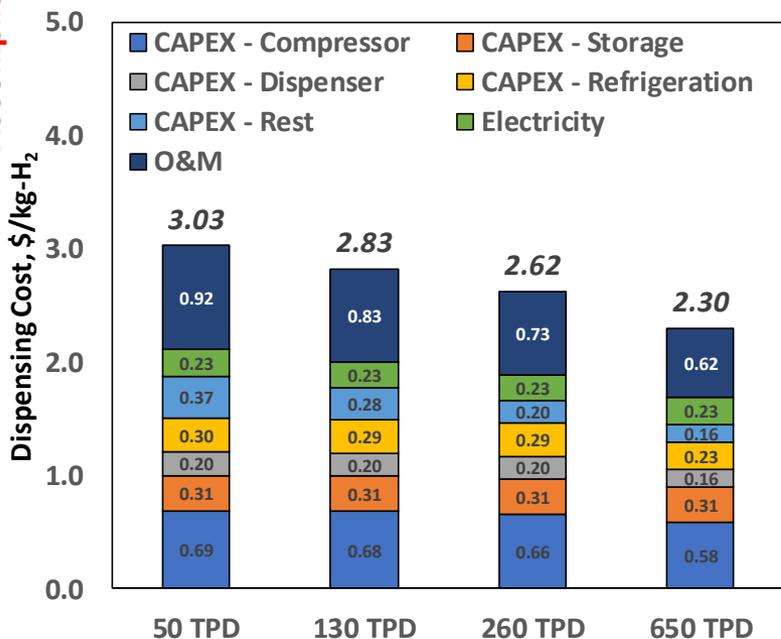
**- Gaseous H<sub>2</sub> terminal**

- Cost not affected by market penetration rate. Buffer storage accounts for 36% of the cost (required to fill 540 bar/1,040 kg-H<sub>2</sub> within 10 hours)



# (D<sub>1</sub>) - GH<sub>2</sub> Total Dispensing Costs and Emissions

Accomplishment

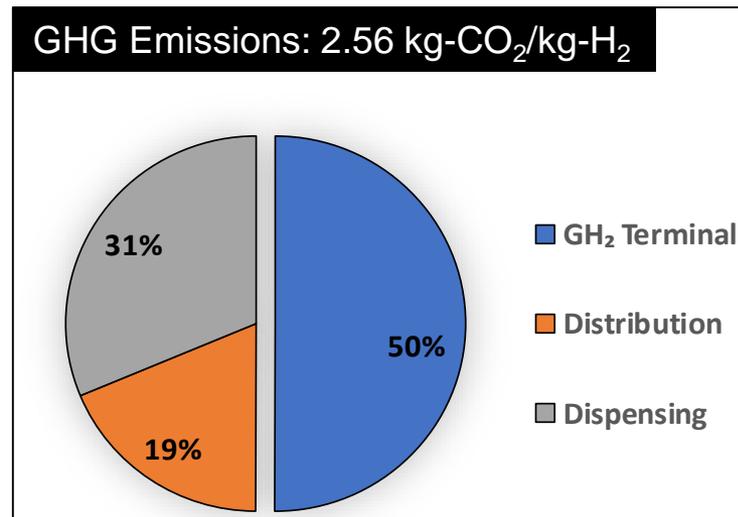


## Total Dispensing Cost (400 vs 1000 kg/day)

- Cost reduction by \$1.23/kg as station capacity increases due to lower transmission and dispensing costs

## - Emissions

- A total of 2.56 kg-CO<sub>2</sub>/kg-H<sub>2</sub> for GH<sub>2</sub> refueling pathway. GH<sub>2</sub> terminal account for 50% of GHG emissions.



## Summary and Conclusions

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The performance, regulated/unregulated greenhouse gas (GHG) emissions and cost advantages of using a two-way toluene-methylcyclohexane (MCH) carrier for hydrogen transmission and end use was analyzed for different scenarios

- By-product H<sub>2</sub> incurs the lowest cost among the pathways analyzed. Using ships as transmission mode, the cost, reflected by NG substitution only, could potentially be below \$2/kg (\$1.88/kg S<sub>1</sub>/T<sub>2</sub>)
- By-product H<sub>2</sub> pathway could reduce GHG by ~58% relative to H<sub>2</sub> produced by SMR if emissions are mass-allocated to all co-products (5.05 kg-CO<sub>2</sub>/kg-H<sub>2</sub> vs 11.84 kg-CO<sub>2</sub>/kg-H<sub>2</sub>). Potentially, GHG emissions could be reduced by a total of 71% with biogas available for dehydrogenation
- Producing renewable H<sub>2</sub> for hydrogenation in TX and dehydrogenation in CA could be cost competitive with renewable H<sub>2</sub> locally produced in CA (\$7.09/kg vs \$7.26/kg in CA). GHG emissions due to transmission and dehydrogenation will increase by 3.83 kg-CO<sub>2</sub>/kg-H<sub>2</sub>
- Transmission of MCH/Toluene by large product tankers (115,000 DWT) is 50% less expensive than transmission by rail (\$0.7/kg vs \$1.53/kg). Emissions utilizing ships for transmission are reduced by half relative to rail.



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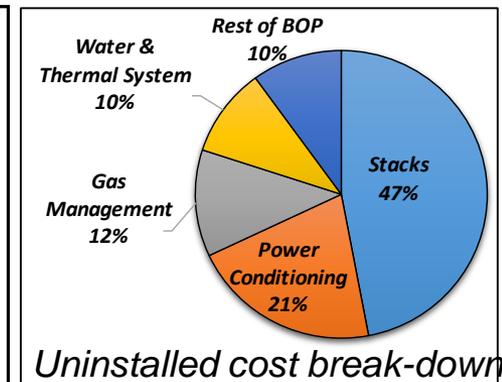
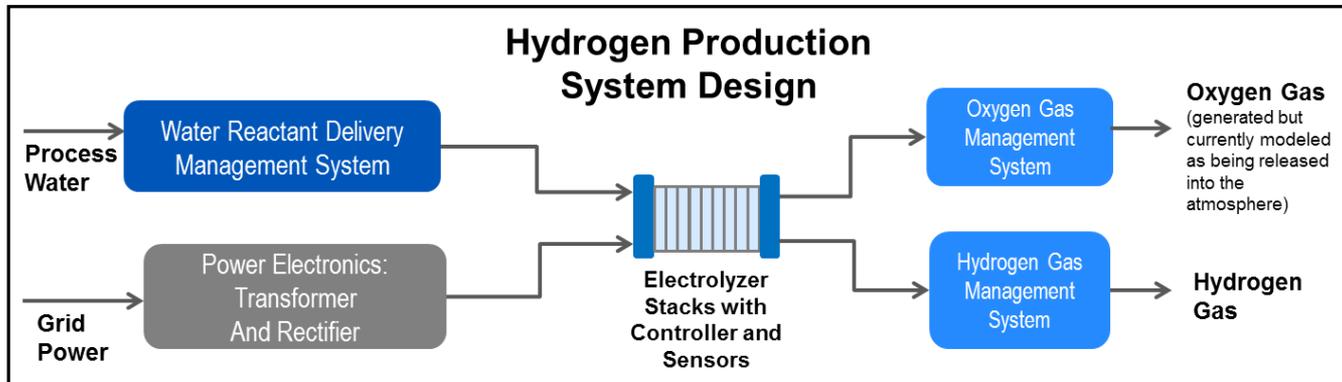




# H<sub>2</sub> Production – PEM Electrolysis

We are using DOE H2A as the reference model for electrolysis cost<sup>1</sup>

- Hydrogen production by PEM electrolysis, central case 50 TPD unit train according to DOE H2A current technology status.
- Uninstalled cost of \$900/kW, stacks contribute 47% of cost.
- Cell voltage 1.75V, 70.3% voltage efficiency (as % of fuel LHV)
- Hydrogen drying losses: 3% of gross hydrogen
- Total system electrical usage: 54.3 kWh<sub>e</sub> /kg-H<sub>2</sub> (stack contributes 93%)
- Unless specified, electricity cost is  $\phi$ 5.74/kWh in TX and  $\phi$ 12.5/kWh in CA (industrial cost, 2019 average, EIA.gov)

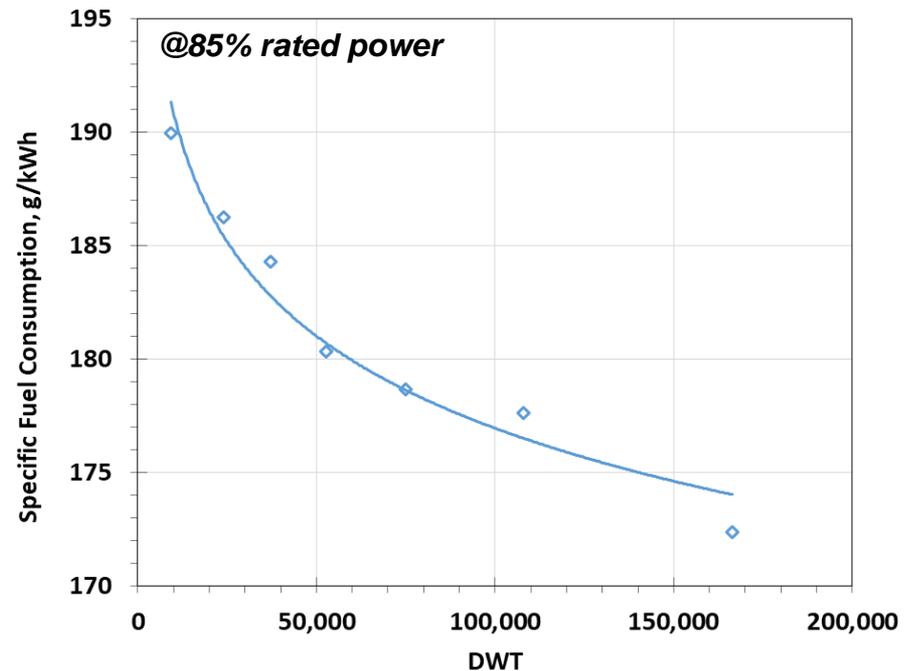
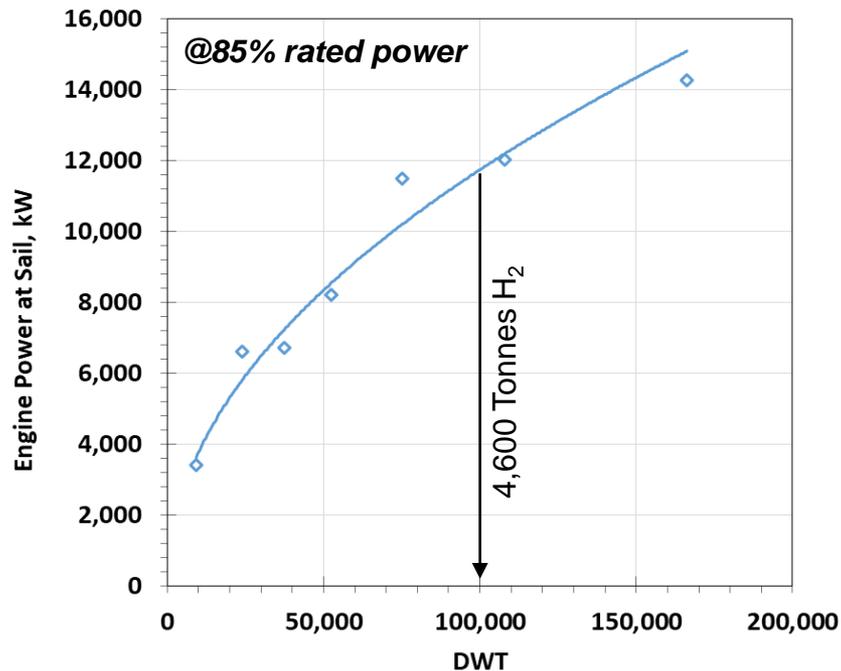


<sup>1</sup>[https://www.hydrogen.energy.gov/h2a\\_analysis.html](https://www.hydrogen.energy.gov/h2a_analysis.html)

## (T<sub>2</sub>) – Tanker Cost Factors (Fuel)

We are using LSMGO as the reference fuel for maritime applications considered in this study.

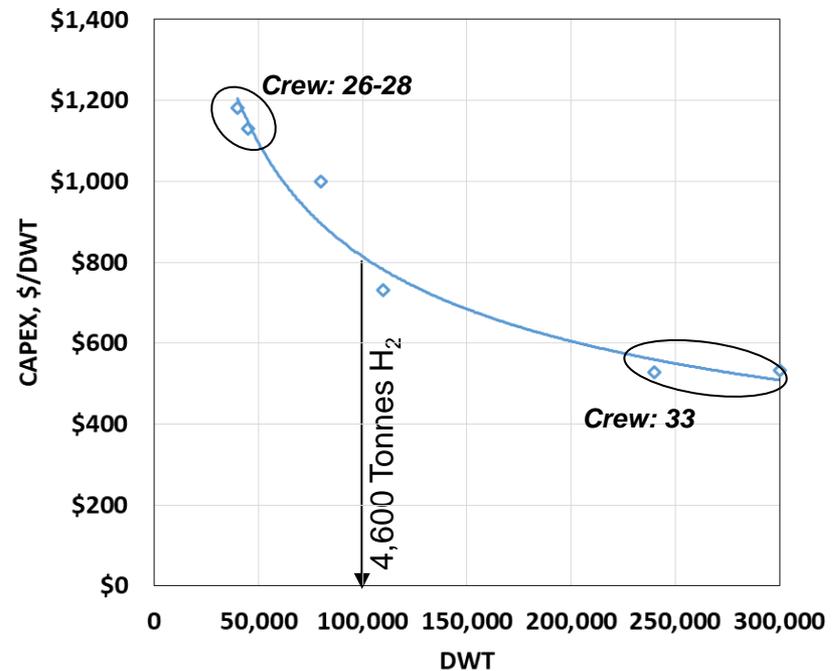
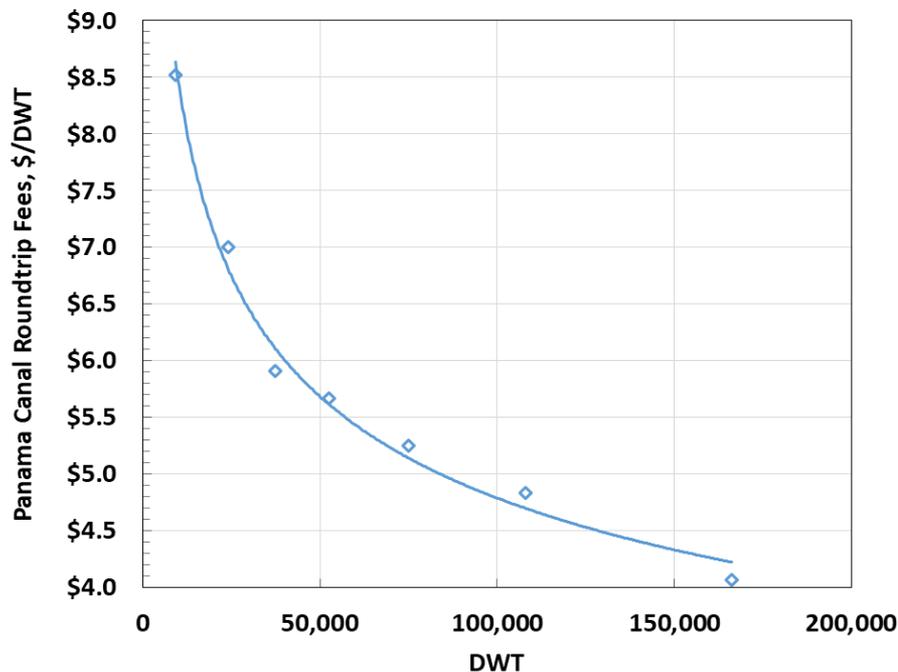
- Small difference in price of MGO and LSMGO. As of end of 2019 cost of LSMGO is \$650/Tonne (LHV = 42.8 MJ/kg, 900 m<sup>3</sup>/kg)
- Main fuel consumption occurs at sail. Engine operates at 85% of rated power for maximum fuel efficiency.
- Specific fuel consumption decreases with engine size (bigger engines operate at low RPM ~100 with efficiencies approaching 50%)



## (T<sub>2</sub>) – Tanker Cost Factors (Capex + Opex)

### Panama canal fees per roundtrip are based on laden conditions (MCH/Toluene)

- Canal fees decrease (on DWT basis) as ship increases in cargo capacity.
- Additional port fees included at \$0.52/DWT-day.
- Capex of ship as function of size (DWT) based on statistical data around global shipyards. Additional cost of 20% will be included due to maritime commerce between U.S. ports<sup>1</sup>
- Crew size complement: 2 Deck officers, 4 engineers, rest as deckhand



<sup>1</sup> The **Jones Act** requires goods shipped between U.S. ports to be transported on ships that are built, owned, and operated by United States citizens or permanent residents