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

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U.S. DOE Hydrogen and Fuel Cells Program

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Project ID: H2058

Overview

Timeline

- Project start date: Oct 2020
- Project end date: Sep 2020

% Complete: 100

Barriers

- H_2 Storage Barriers Addressed:
  - B: System Cost
  - C: Efficiency
  - K: Life-Cycle Assessments

Budget

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

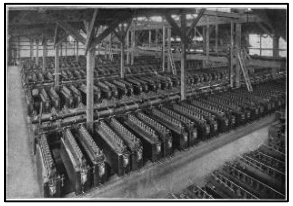
Partners/Interactions

Industry & research collaborations

- Chiyoda Corporation

Relevance

Chlor-Alkali[1]



NGL Cracking[2]

Solar[3]

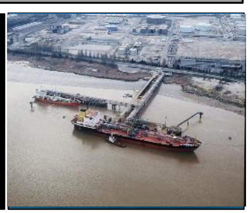
Wind[4]

Transmission by Rail[5-6]

Rail infrastructure

Transmission by Ship[7-8]

Ship unloading cargo at a Jetty



- **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	BP	H_2 Capacity		Production		Decomposition		
°C	°C	wt%	g/L	P, bar	T, °C	P, bar	T, °C	ΔH kJ/mol-H_2
MCH								
-127	101	6.1	47	10	240	2	350	68.3
				Non-PGM Catalyst		Pt/Al_2O_3 Catalyst		

Approach

- **Tasks and Approach**

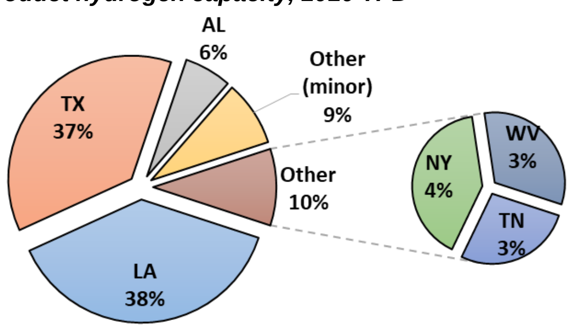
- Develop models for cost and performance of toluene hydrogenation and dehydrogenation plants of 50-650 TPD (Metric Tons Per Day H_2 equivalent).
- H_2 supply scenarios: S_1 – byproduct H_2 from chlor-alkali plants, S_2 – byproduct H_2 from NGL steam cracking, S_3 and S_4 – renewable H_2 from solar and wind, respectively
- Develop models and/or use existing tools[1] and models for cost and performance of H_2 demand scenarios (D_1 - FC LDV, D_2 – FC HDV, D_3 – 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_2), levelized cost ($/kg-$H_2$), and greenhouse gas emissions (kg-CO_2/kg-H_2)
- All pathway costs evaluated by H2A[2] guidelines and based on 2016 $-year basis

[1]***Tools and methods: Matlab, GC-Tool, H2A, HDSAM, HDRSAM, SAM, Cost models (Internal Developed/Aspen/Literature)***
[2]*https://www.hydrogen.energy.gov/h2a_analysis.html*

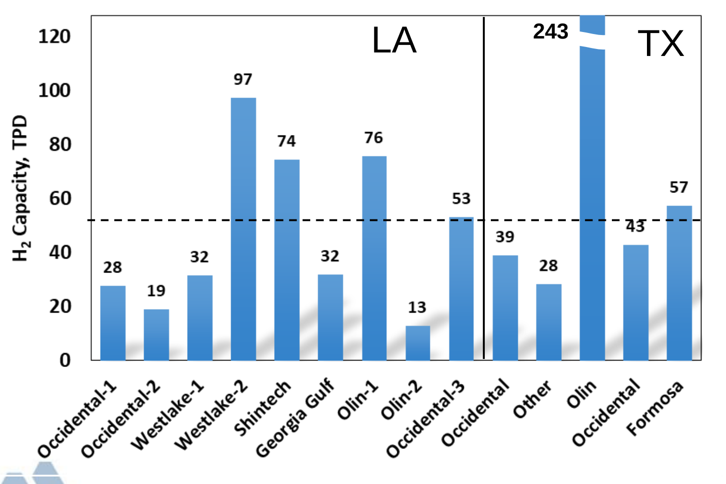
(S_1) - Utilization of by-Product H_2 from Chlor-Alkali plants[1]

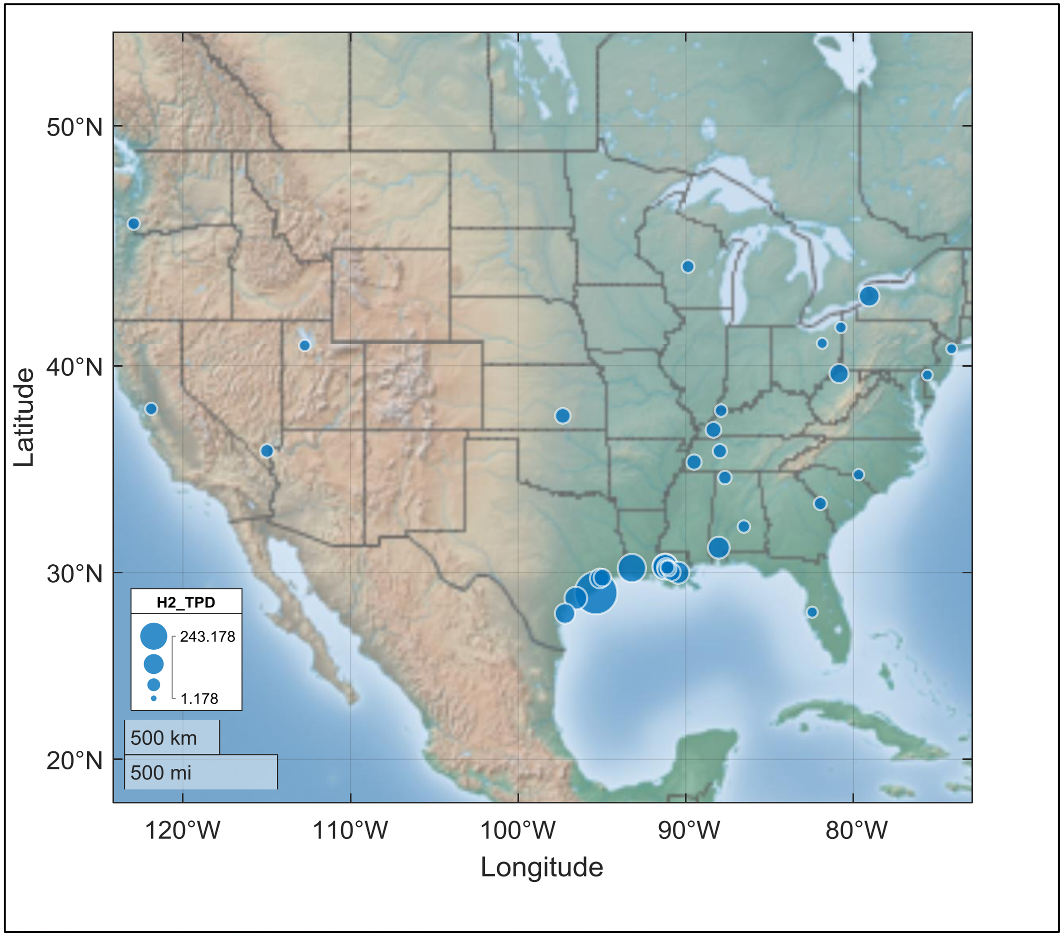
- An estimated 0.4 million metric tons of hydrogen is produced annually by the chlor-alkali industry in the U.S.
- Approximately 80% of the United States chlor-alkali capacity is in the Gulf region
- About 35% of by-product hydrogen is known to enter the merchant gas market. H_2 is combusted for steam generation or vented (~10-15%)

By-product hydrogen capacity, 1010 TPD



Chlor-Alkali hydrogen capacity in LA and TX

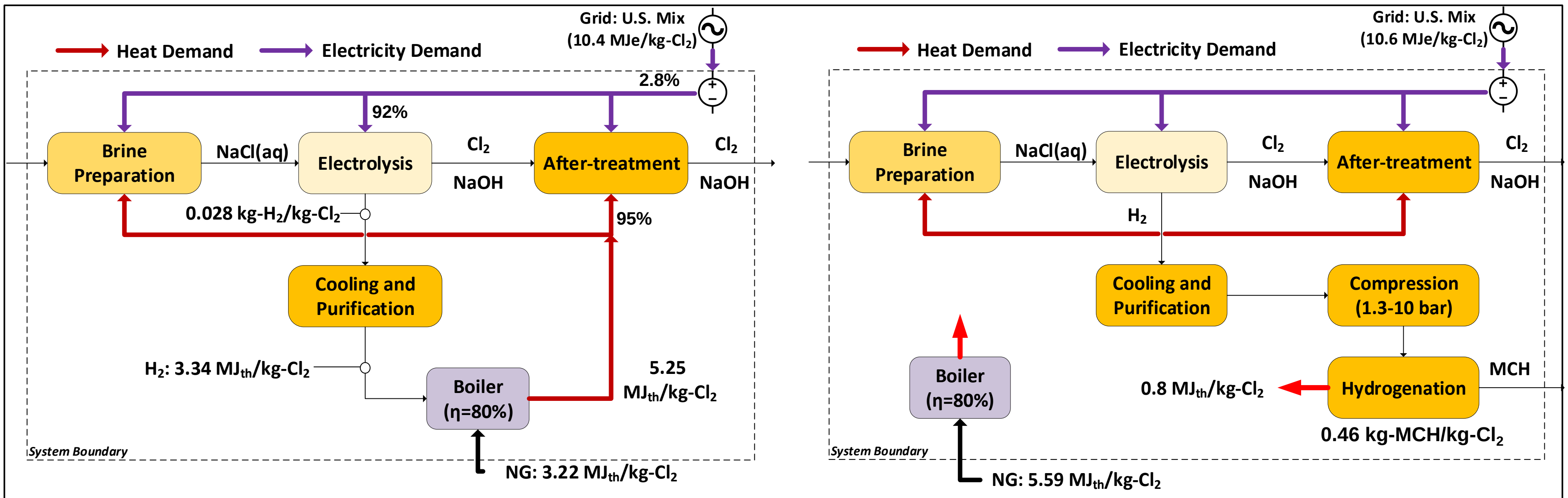




[1]Lee, D.Y. and Elgowainy, A., Dai Q. Life Cycle Greenhouse Gas Emissions of By-Product Hydrogen from Chlor Alkali Plants. ANL/ESD-17/27

(S_1) - Utilization of by-Product H_2 from Chlor-Alkali Plants[1]

- 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



Case: By-product H_2 is used for energy production ***Substitution: By-product H_2 is used for hydrogenation***

[1] *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*

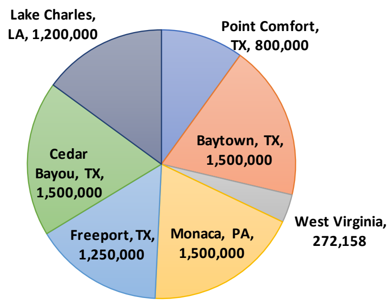
Approach

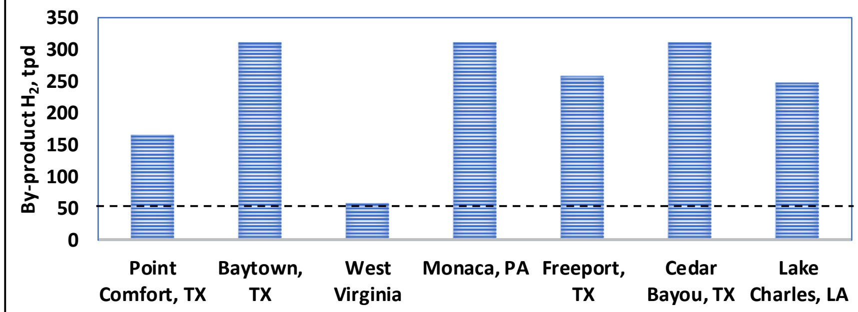
(S_2) - Utilization of by-Product H_2 - NGL Steam Cracking Plants[1,2]

- 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_2/C_2H_4=7.6 wt.%)

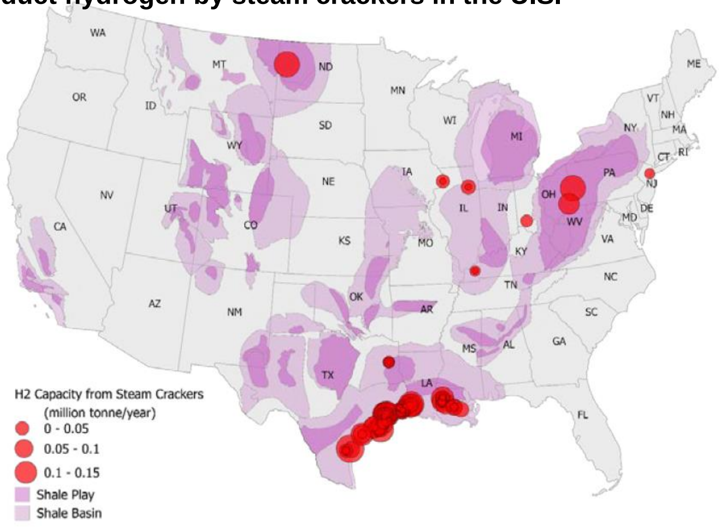
Ethylene production. Metric tons/year

Plants constructed <u>2016-2017</u> based on ethane as feedstock. Source. University of Oxford

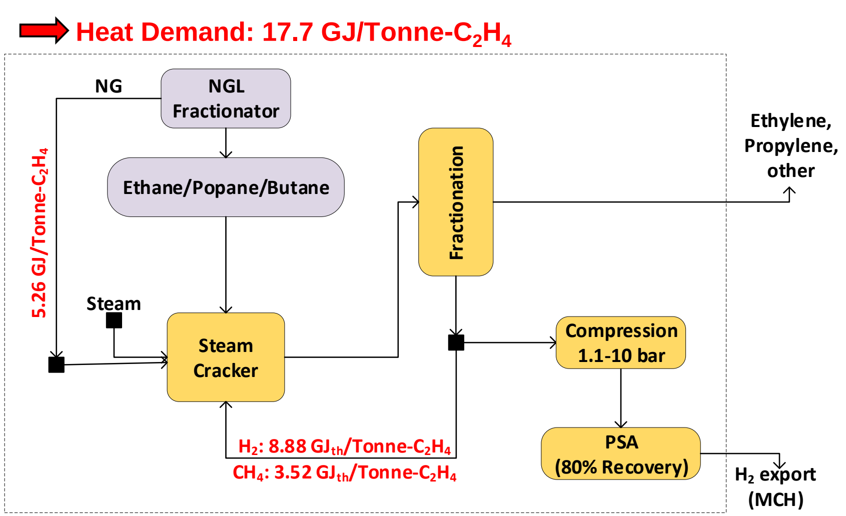




By-product hydrogen by steam crackers in the U.S. [1]

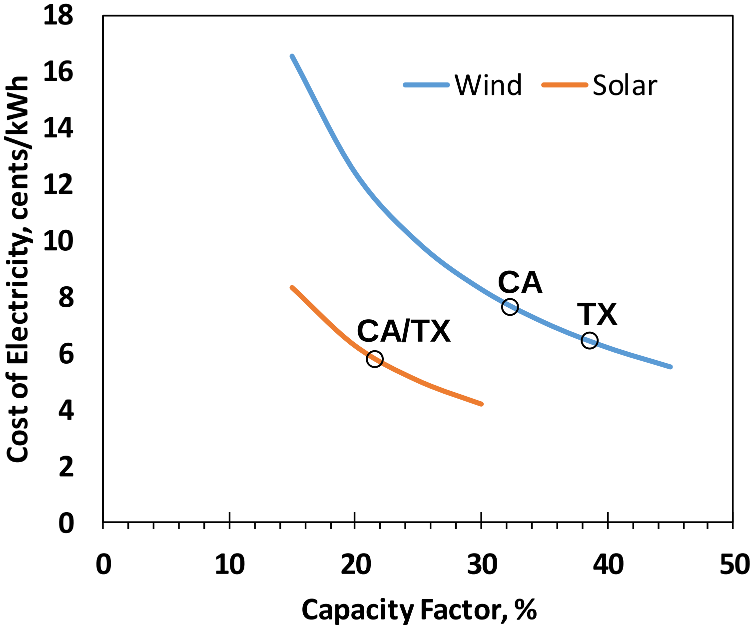


Steam crackers based on natural gas liquids (NGLs)[1,2]



[1]*Lee, D.Y. and Elgowainy, A. International journal of hydrogen energy 43 (2018) 20143-20160*
[2]*The Lindgren Group, LLC, Production of Ethylene from Natural Gas, April 22, 2013*

S_3 and S_4 - Cost of Electricity by Wind and Solar[1]



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
Total LCOE (cents/kWh)	***6.51***	***7.71***

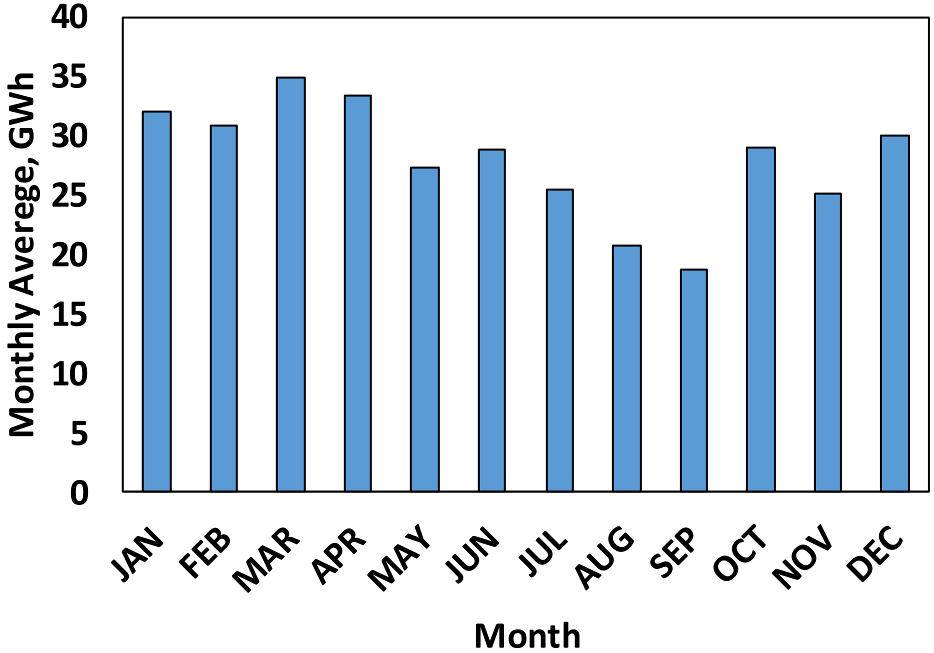
State	TX (SW)	CA (SE)
Resource	Solar (PV)	Solar (PV)
Array Type	1 Axis Tracking	1 Axis Tracking
Direct normal (kWh/m^2/day)	5.23	5.23
Inverter Efficiency (%)	96	96
CAPEX ($/kW)	1,040	1,040
OPEX ($/MWh)	4.8	4.8
Analysis Period (years)	25	25
IRR (%)	10	10
Capacity Factor (%)	21.1	21.4
CAPEX (cents/kWh)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

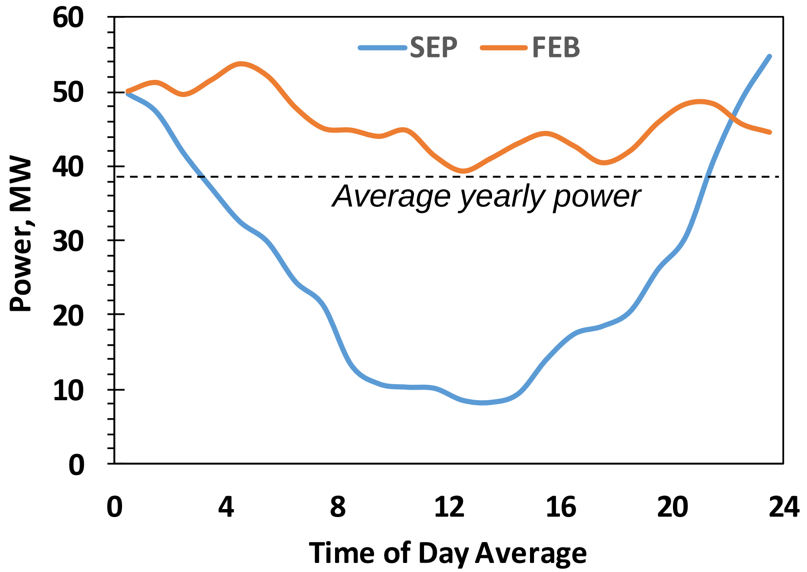
Projected Electricity Costs

- 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

[1]*Wind and solar techno-economics based on System Advisor Model (SAM). www.nrel.gov*

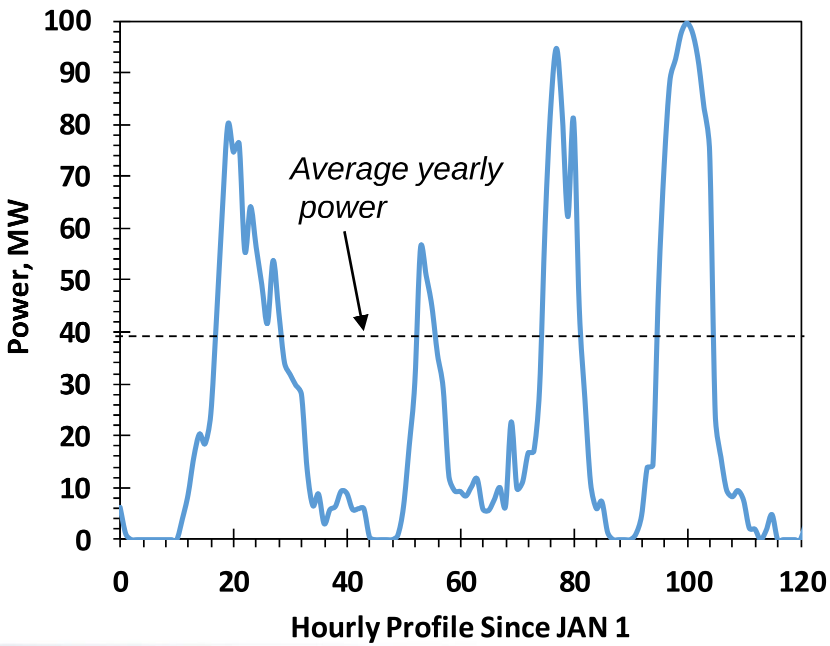
Utilization by Wind – Example Profiles in TX[1]





Renewable Power Intermittency

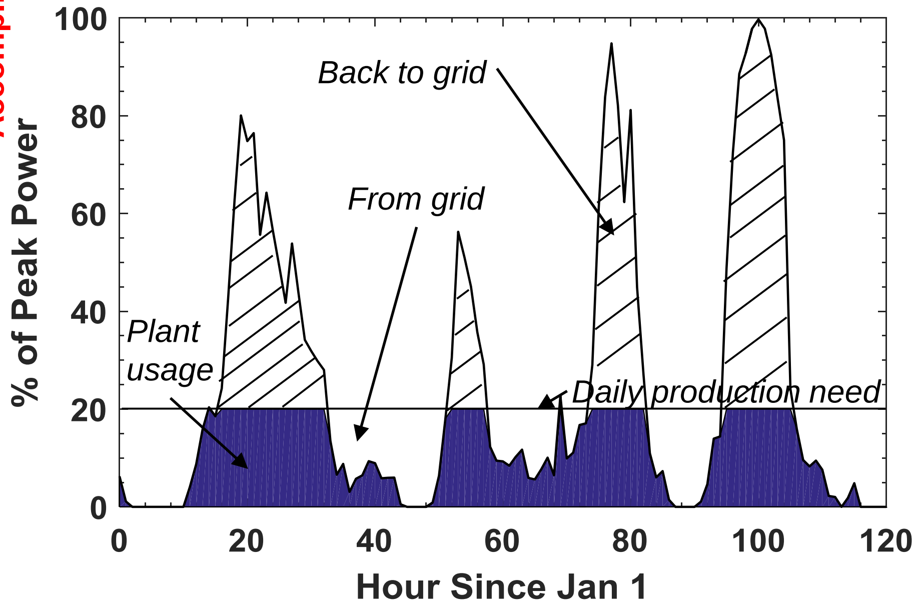
- Yearly, monthly and even hourly average values are not very useful metrics for analysis.
- Actual hourly profiles (e.g. wind) show sharp variability with 0-100% rated capacity and idling at hours.
- Using load following, the cost of hydrogen by electrolysis capital alone, will increase by 2-2.5 $/kg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

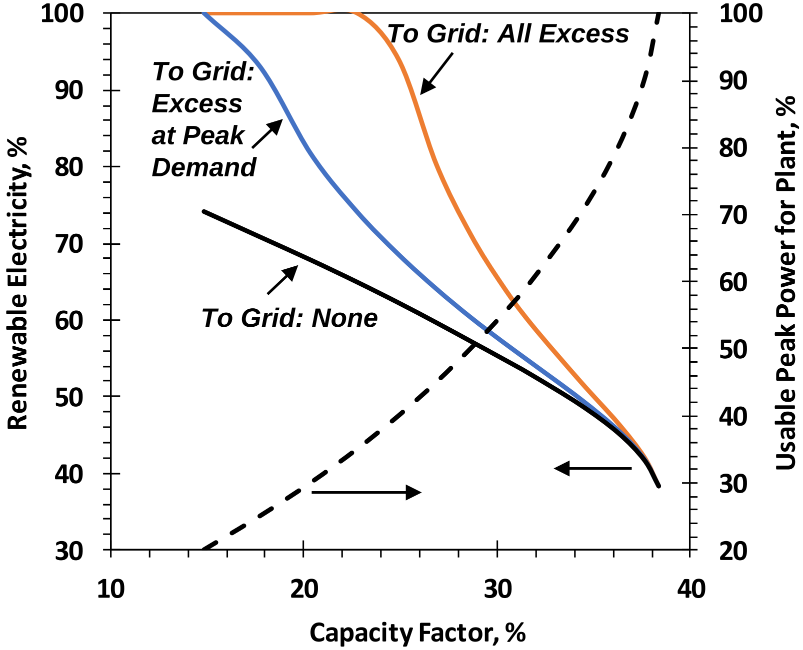


[1]Example 100 MW name-plate capacity

Capacity Factor = Annual energy produced/annual nameplate energy capacity

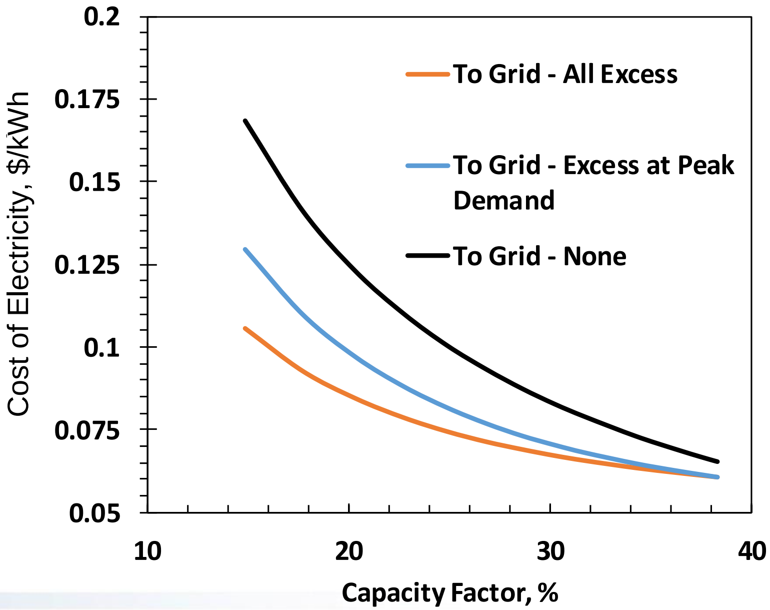
Utilization by Wind – Example Scenario Options





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

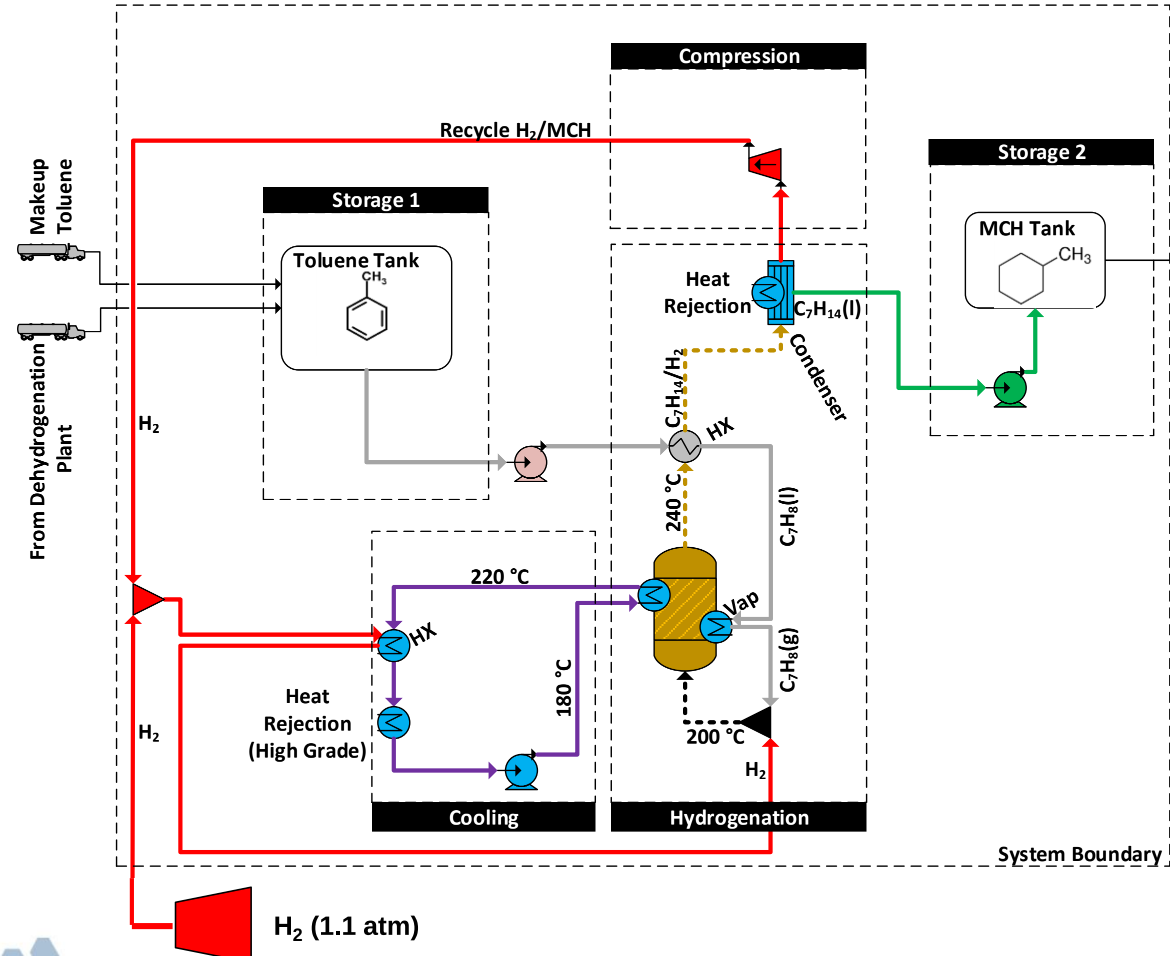


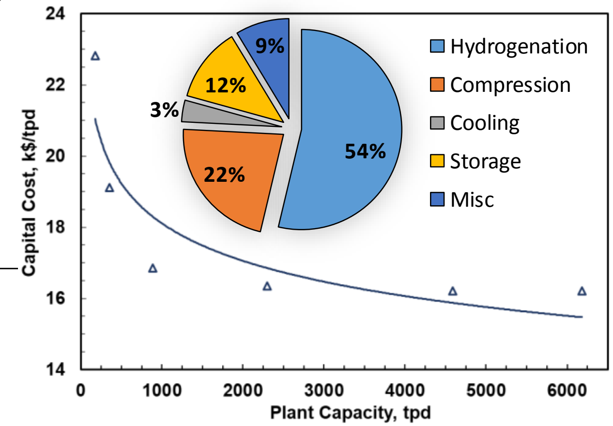
Grid power assumes fossil based power and should not be confused with actual GHG emissions

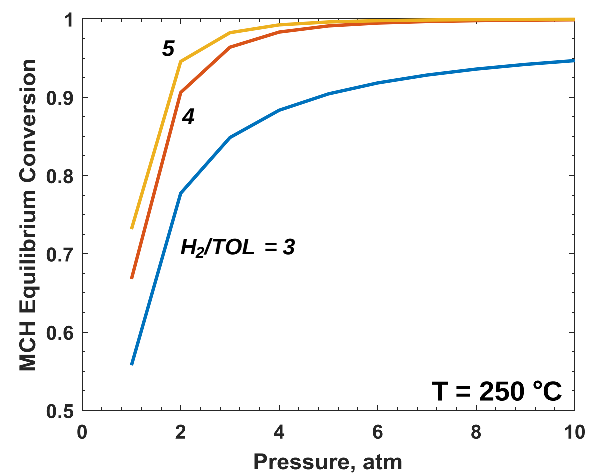
Accomplishment

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 = 0.22% (due to dehydrogenation losses)



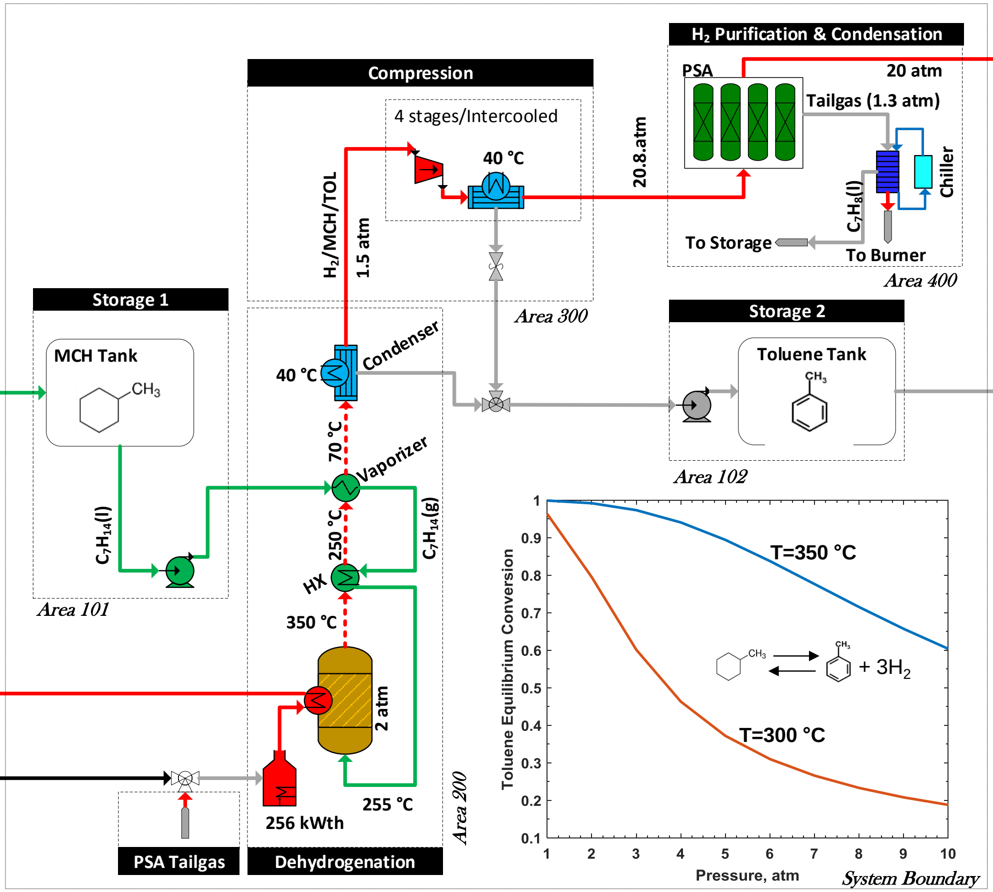


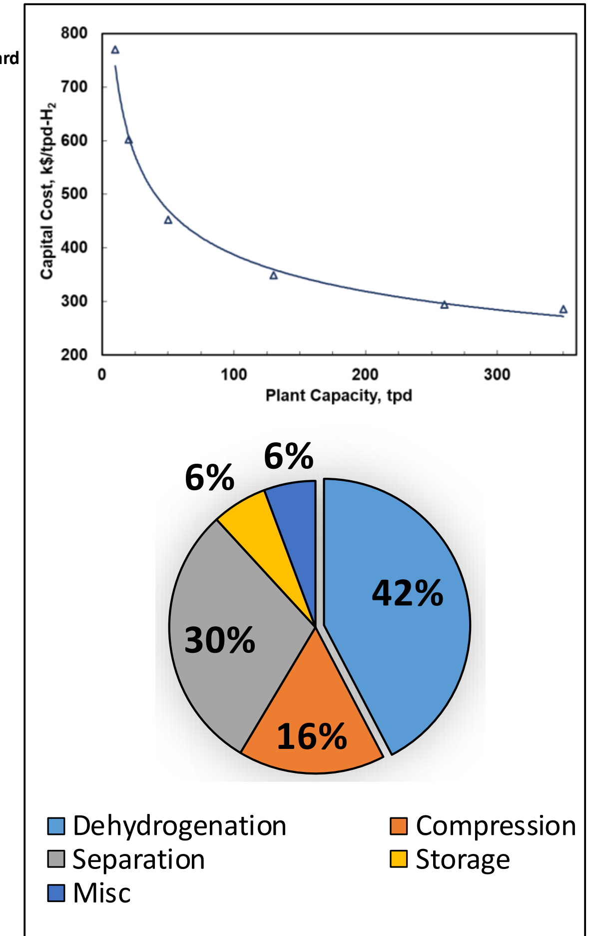


Lindfors, L.P. et. al. (1993). Kinetics of Toluene Hydrogenation on Ni/Al_2O_3 Catalyst. Chem. Eng. Sci., 48, 3813

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)





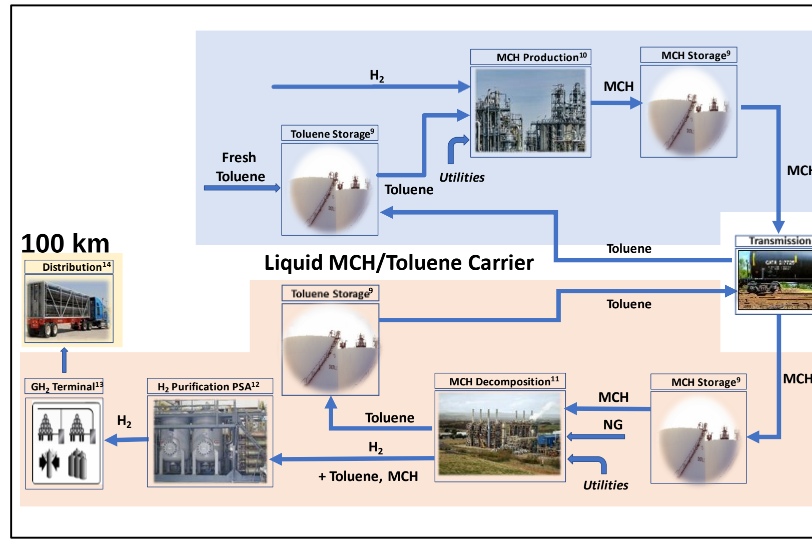
Okada, Y. et. al. (2006). Development of Dehydrogenation Catalyst for Hydrogen Generation in Organic Chemical Hydride Method. Int. J. Hydrogen Energy, 31, 1348.

Accomplishment

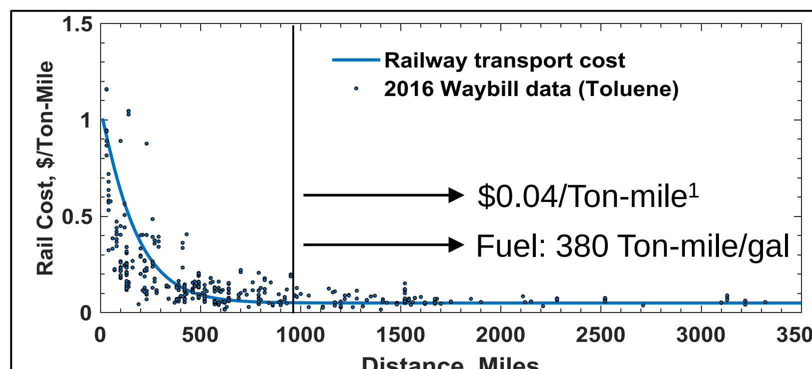
(T_1) - Transmission by Rail

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_2 capacity (5,200 TPD)
- Transmission: Unit train or ships to dehydrogenation facility in northern California
- Distribution: H_2 distribution to LDV market by GH_2 trucks to a mid-size city (3 M)



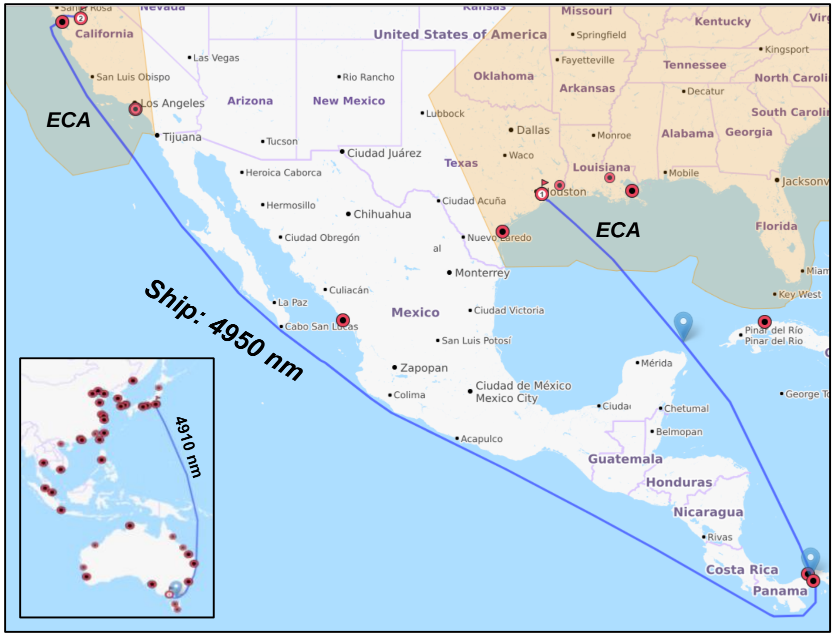
		Byproduct H_2 from Gulf Coast				
H_2 Demand (TPD)	FC Vehicle Market (%)	Chlor Alkali (%)	Steam Cracker (%)	Train Frequency (days)	Storage (days)	Railcars
50	4	6.6	1.1	7	9	76
130	10	17.2	3.0	4	6	112
260	20	34.3	5.9	2	4	112
650	49	85.8	14.8	1	3	140



www.stb.gov: sample of carload waybills for all U.S. rail traffic submitted by those rail carriers terminating 4,500 or more revenue carloads annually.

[1]1 Short ton (ton) = 0.907 Metric ton (Tonne)

(T_2) – 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_2 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´).

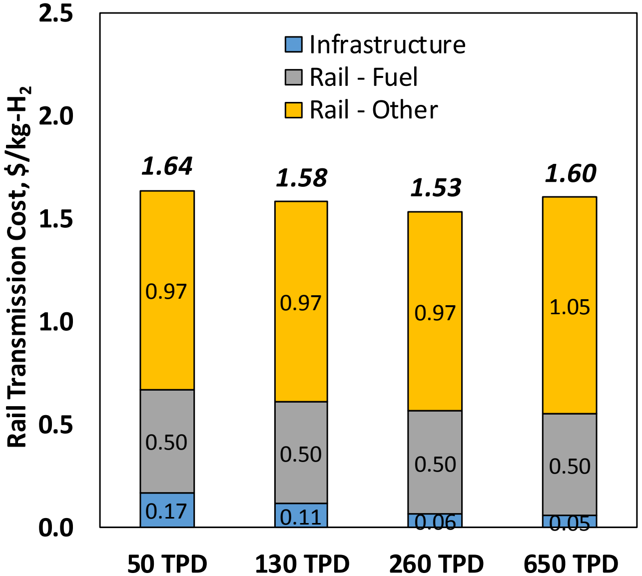
Neopanamax locks: Length of up to 427 m (1,401´), beam of up to 52 m (170´), draught of up to 18.3 m (60´).

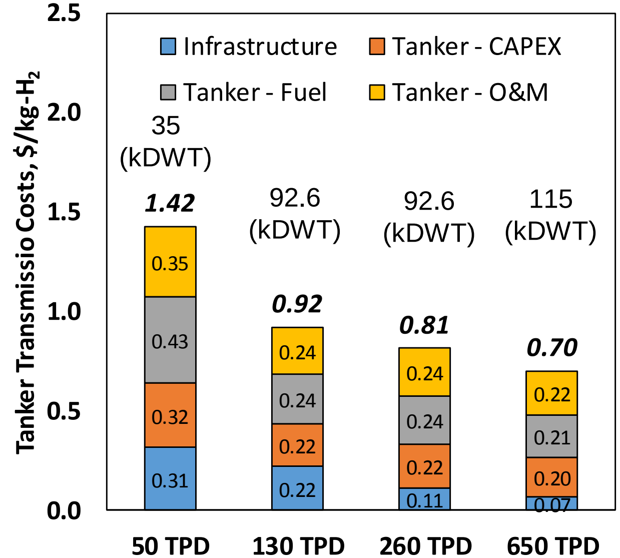
MCH/Toluene tanker limited in capacity to 115 kDWT based on largest LR2 product tanker

- 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

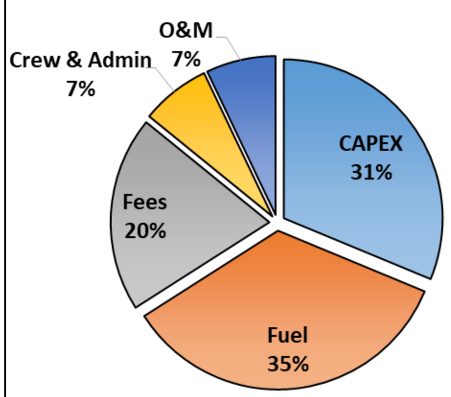
Accomplishment

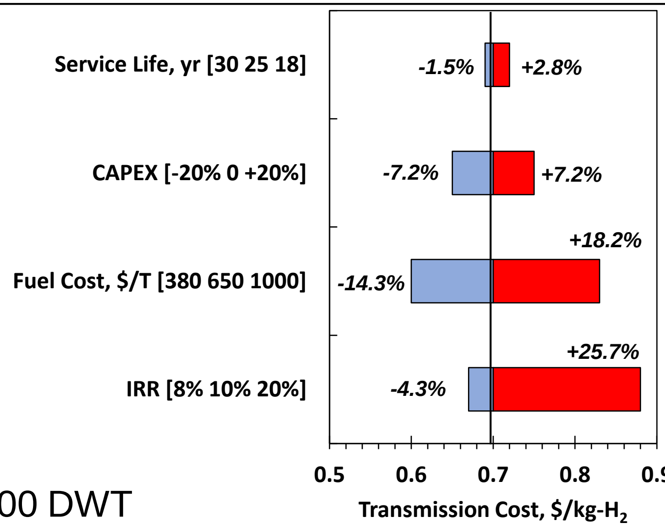
Tanker (T_2) Transmission Cost Relative to Rail (T_1)



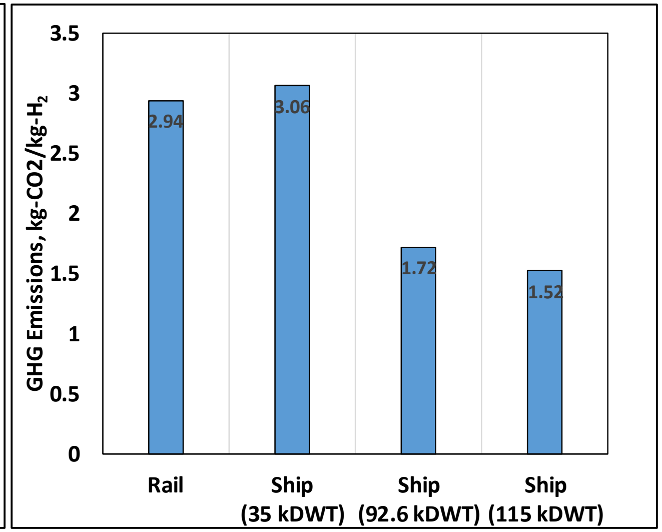


- Economy of scale favors large tankers (single ship per route)
- Tankers more favorable for transmission than rail >50 TPD
- GHG Emissions lowest for Tanker>50 TPD demand





Tanker specific costs 92,600 DWT



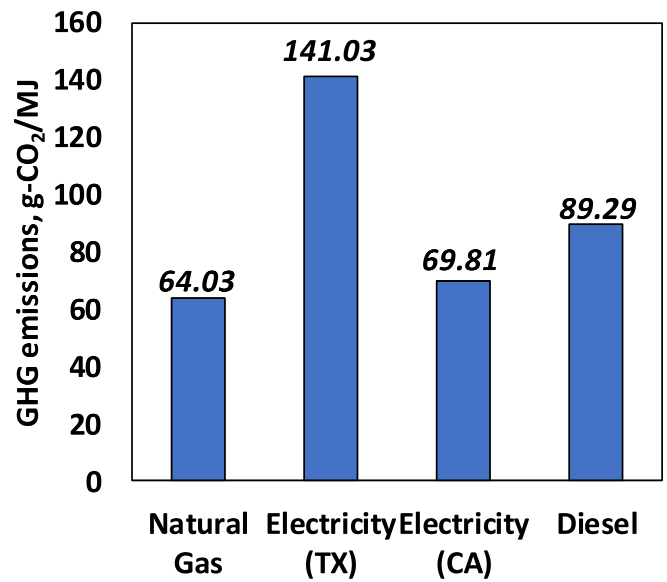
Approach

Pathway Costs and Green-House Gas Emissions

Electricity Production Mix GREET 2019

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



Allocation

Chlor-Alkali Allocation			
Chlor-Alkali	Cl_2	NaOH	H_2
Co-products (kg/kg H2)	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%

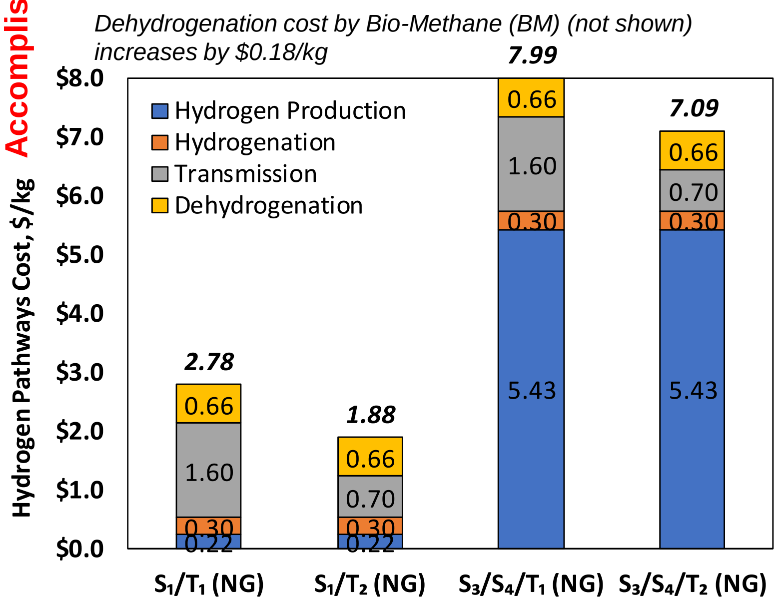
Ethane Crackers - Allocation			
Products	Formula	kg/kg-H2	Mass Share
Ethylene	(C2H4)	13.158	83.20%
Propylene	(C3H6)	0.25	1.58%
Methane	(CH4)	0.895	5.66%
Butadiene	(C4H6)	0.368	2.33%
Butene	(C4H8)	0.039	0.25%
Benzene	(C6H6)	0.092	0.58%
Toluene	(C7H8)	0.013	0.08%
Hydrogen	(H2)	1	6.32%
Total		***15.815***	***100.00%***

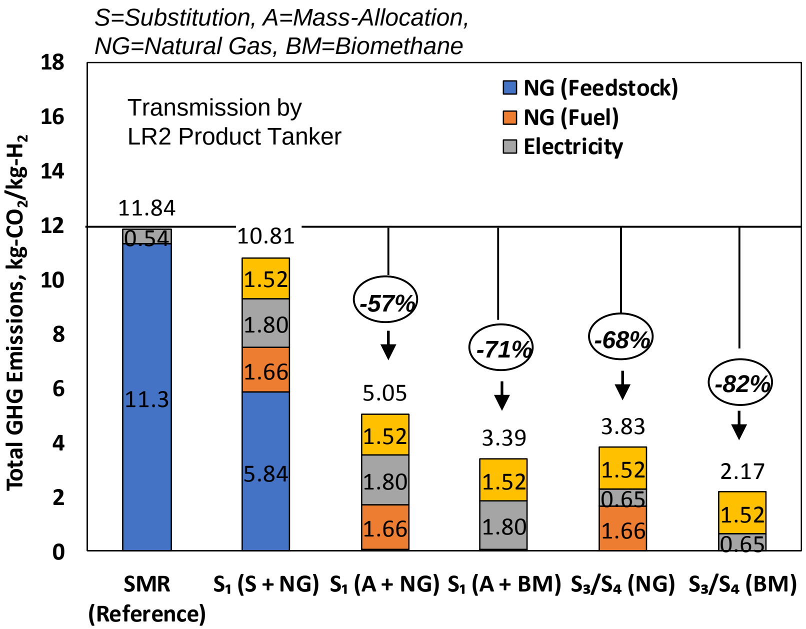
Emissions and Energy

- 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_2 by-product emissions will be compared on substitution (NG consumption) as well as on mass-allocation basis (CO_2 emissions split on all co-products)
- For brevity, costs are compared for a large demand case (650 TPD). All cost break-downs are available in separate spreadsheet.

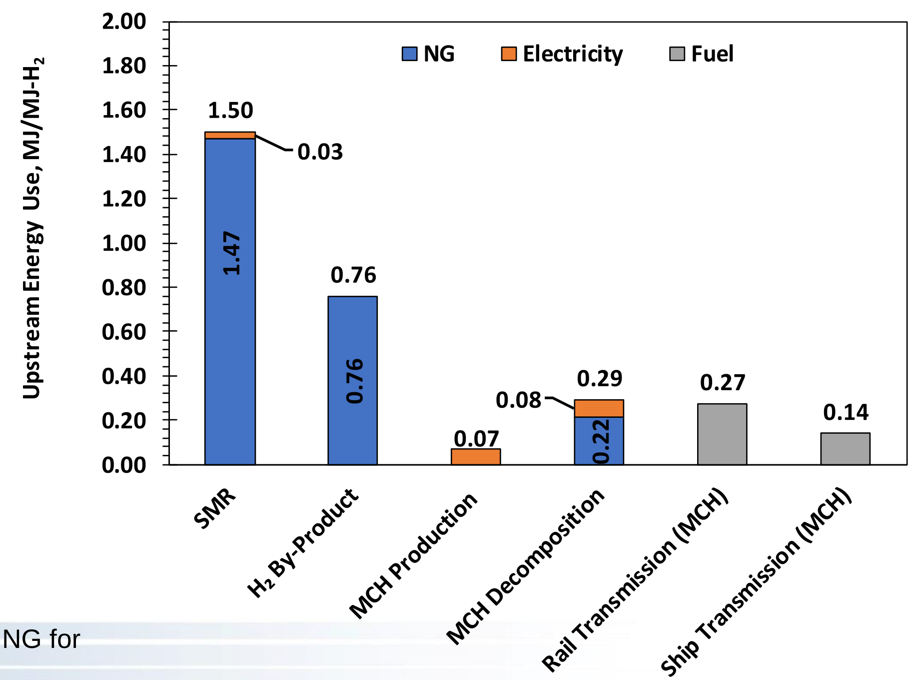
Accomplishment

Cost, Up-stream Energy Use and Emissions: Summary



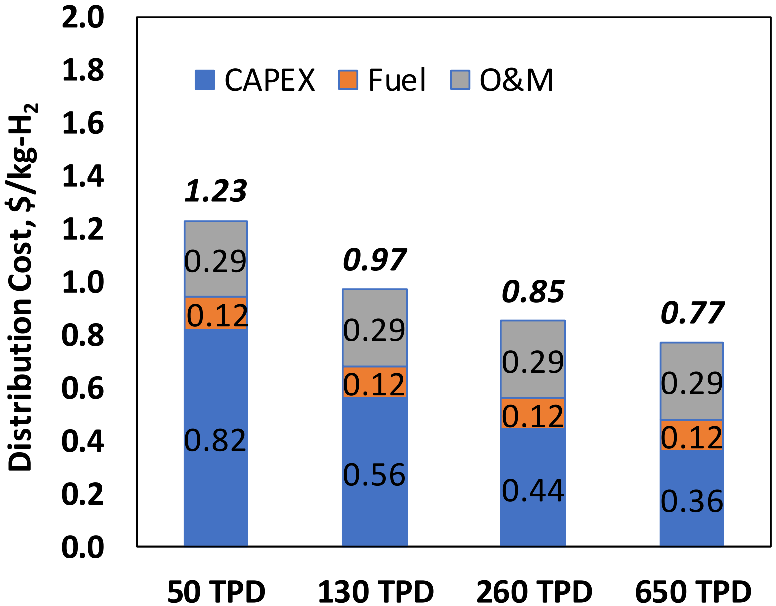


- By-product H_2 incurs the lowest cost among the pathways analyzed. Using ships as transmission mode, the cost could potentially be below $2/kg[1]
- By-product H_2 could reduce GHG by 57-71% relative to SMR if emissions are mass-allocated to all co-products and if bio-methane is available for dehydrogenation.
- Producing renewable H_2 in TX for dehydrogenation in CA will be at best cost competitive ($7.26/kg in CA) but incur higher emissions.



[1] This is the lowest cost reflected by hydrogen substituted by NG for heat demand, and not assigning a "market" value for H_2

(D_1) - GH_2 Terminal and Distribution Costs



LDV GH_2 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_2 Demand (TPD)	50	130	260	650
H_2 LDV Market Penetration (%)	4	10	19	49
H_2 LDV Fleet	87,700	219,000	416,000	1,075,000
# of H_2 Stations in City	168	280	400	822
Distance Between Stations (km)	3.36	2.6	2.18	1.52
H_2 Stations displacing Gas Stations (%)	11	18	26	53
# of TrucksRequired Per Day	32	80	151	388
# 540 bar Trailers	187	310	441	907
Tube trailers/H_2 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)

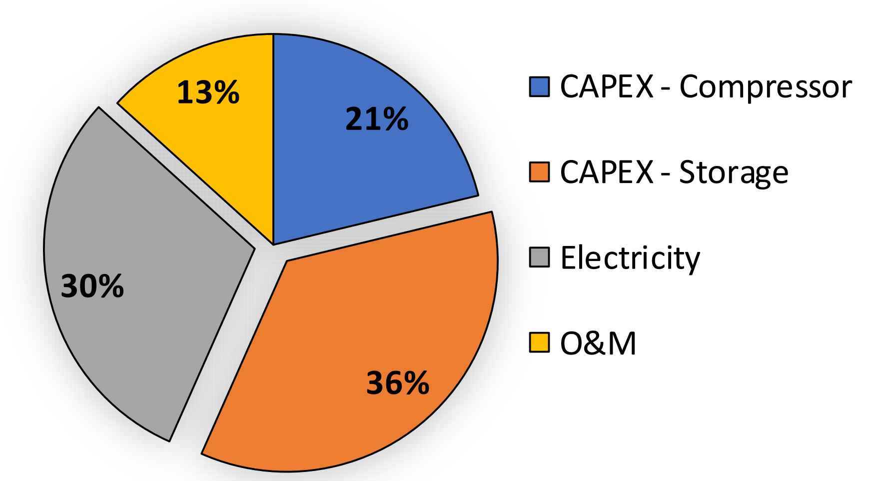
Distribution (400 vs 1000 kg/day)

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

- Gaseous H_2 terminal

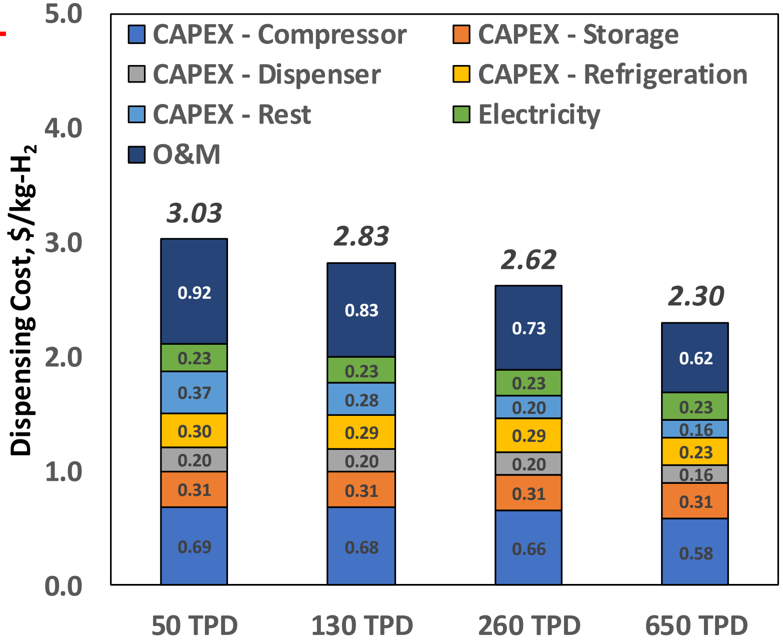
- Cost not affected by market penetration rate. Buffer storage accounts for 36% of the cost (required to fill 540 bar/1,040 kg-H_2 within 10 hours)

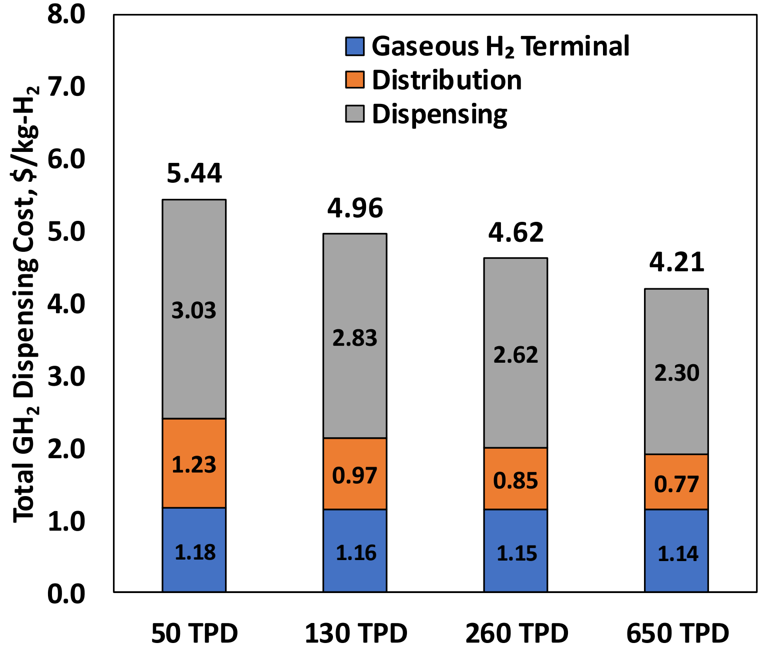
GH_2 Terminal Cost: $1.14/kg-$H_2$



Accomplishment

(D_1) - GH_2 Total Dispensing Costs and Emissions



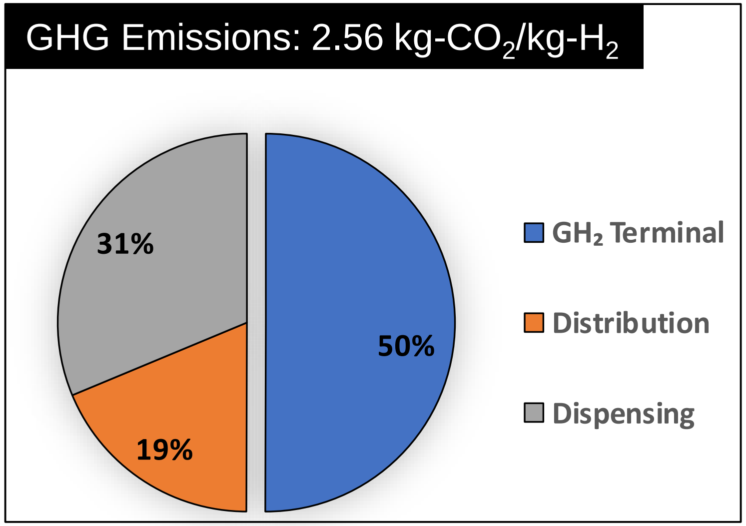


Total Dispensing Cost (400 vs 1000 kg/day)

- 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_2/kg-H_2 for GH_2 refueling pathway. GH_2 terminal account for 50% of GHG emissions.



Summary and Conclusions

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_2 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_1/T_2)
- By-product H_2 pathway could reduce GHG by ~58% relative to H_2 produced by SMR if emissions are mass-allocated to all co-products (5.05 kg-CO_2/kg-H_2 vs 11.84 kg-CO_2/kg-H_2). Potentially, GHG emissions could be reduced by a total of 71% with biogas available for dehydrogenation
- Producing renewable H_2 for hydrogenation in TX and dehydrogenation in CA could be cost competitive with renewable H_2 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_2/kg-H_2
- 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.

Picture Licenses/References

[1] Courtesy by Eric Burgers, from Flickr: https://www.flickr.com/photos/uw-eric/2890255375/in/photostream/
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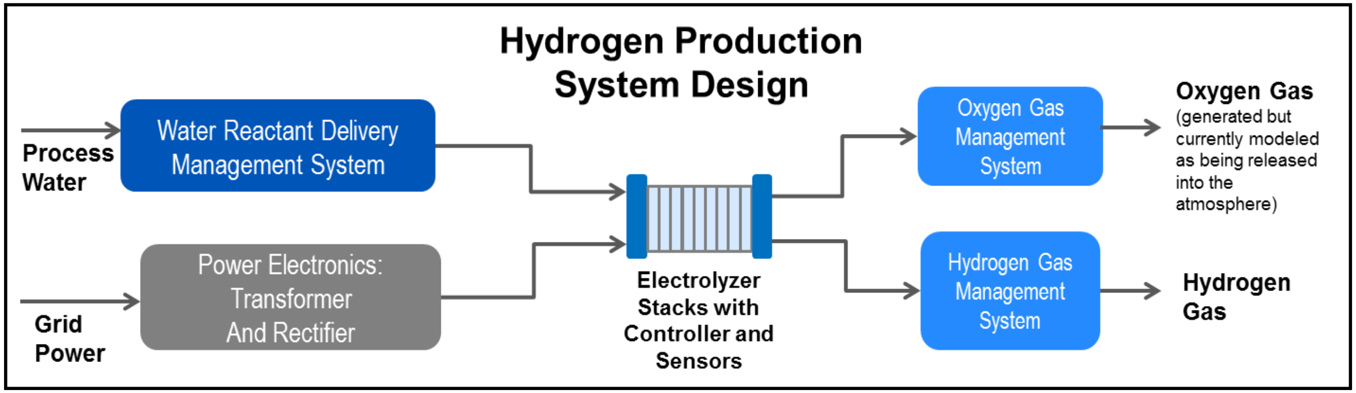
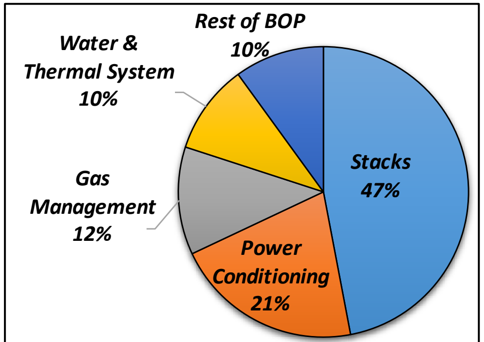
Technical Backup Slides

H_2 Production – PEM Electrolysis

We are using DOE H2A as the reference model for electrolysis cost[1]

- 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_e /kg-H_2 (stack contributes 93%)
- Unless specified, electricity cost is ¢5.74/kWh in TX and ¢12.5/kWh in CA (industrial cost, 2019 average, EIA.gov)





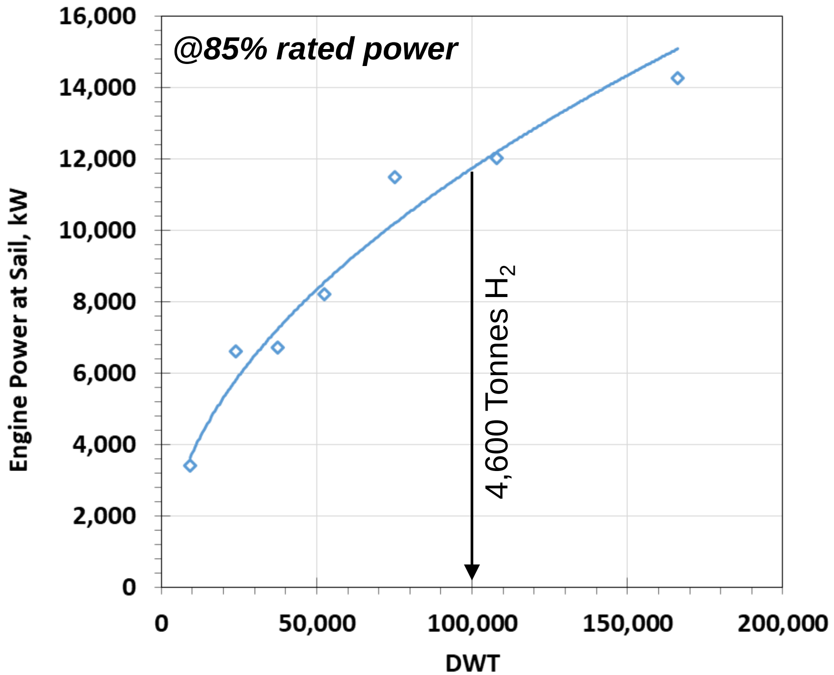
Uninstalled cost break-down

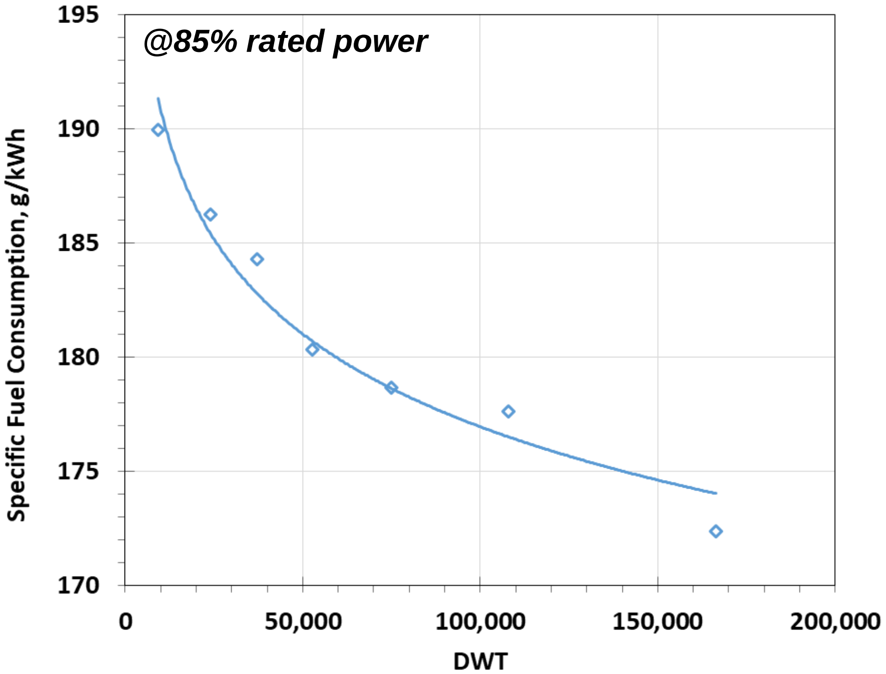
[1]***https://www.hydrogen.energy.gov/h2a_analysis.html***

(T_2) – 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^3/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%)

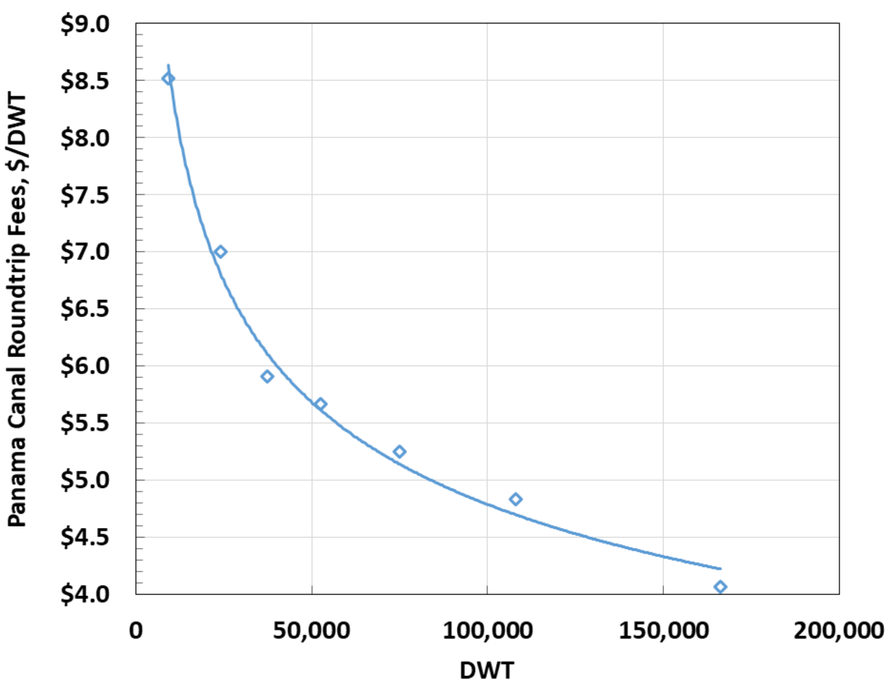


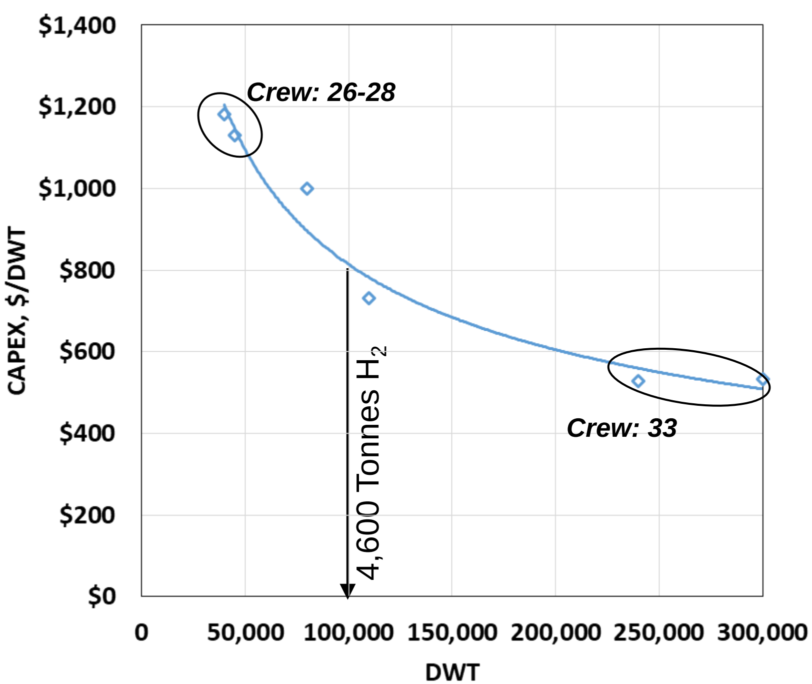


(T_2) – Tanker Cost Factors (Capex + Opex)

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[1]
- Crew size complement: 2 Deck officers, 4 engineers, rest as deckhand





[1] *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*