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Toluene-Methylcyclohexane as Two-Way Carrier for Hydrogen Transmission and Storage

Final CRADA Report

Energy Systems Division

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Participants: Argonne National Laboratory and Chiyoda International Corporation

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Non Proprietary

Final CRADA Report

For the Office of Scientific and Technical Information (OSTI)

CRADA Number: 19122
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DOE Program or Other Government Support
Program office: Energy Efficiency & Renewable Energy – Hydrogen & Fuel Cell Technologies
Program manager name: Zeric Hulvey
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Argonne National Laboratory

Argonne PI(s): Rajesh, K. Ahuwalia and Dionissios, D. Papadias

Funding Table

To add rows, right-click in bottom row and select “Insert” “rows above”.

	Planned Funding	Actual Funding	In-Kind
Government	50,000 $	50,000$	
Argonne National Laboratory	$	$	$
Chiyoda Int. Corporation	50,000$	50,000$	$
Click or tap here to enter text.	$	$	$
Total	**100,000$**	**100,000$**	**$**

Nature of Work

Describe the research (summary of Scope of Work and principal objectives of the CRADA):

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 and demand scenarios that are particularly favorable for toluene-MCH carrier.

DOE mission area(s):
Energy and Environmental Science and Technology
Choose an item.
Choose an item.

Conclusions drawn from this CRADA; include any major accomplishments:
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.
- 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.

Technology Transfer-Intellectual Property
Argonne National Laboratory background IP:
None

Participant(s) background IP:
None

Identify any new Subject Inventions as a result of this CRADA:
None

Summary of technology transfer benefits to industry and, if applicable, path forward/anticipated next steps towards commercialization:
None

Other information/results (papers, inventions, software, etc.):
Presented at the U.S. DOE Hydrogen and Fuel Cells Program 2020 Annual Merit Review and Peer Evaluation Meeting Washington, D.C. 30 May 2020. Project ID: H2058

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Summary of Research Results:

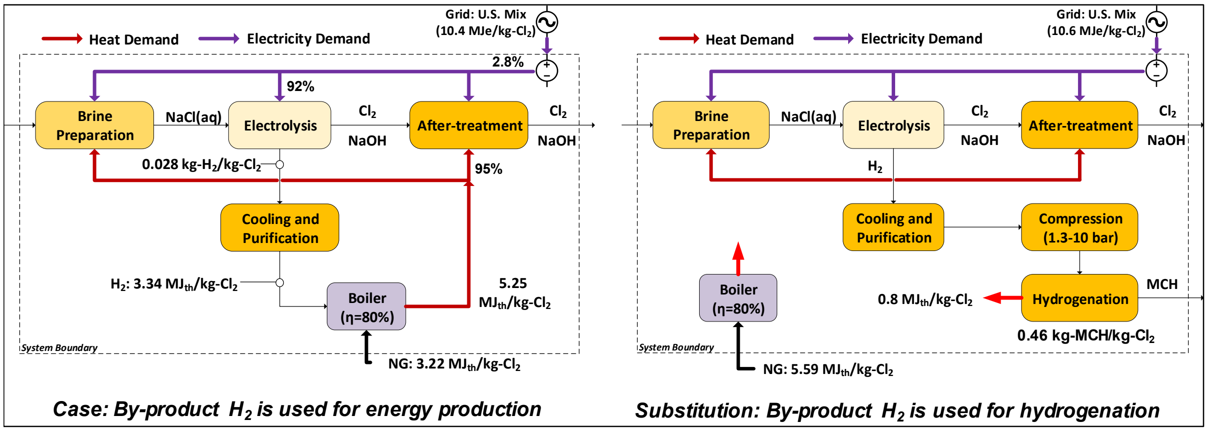
Recognizing the potential role of liquid hydrogen carriers in overcoming the inherent limitations in transporting and storing gaseous and liquid hydrogen, a complete production and use scenario is postulated and analyzed for a two-way carrier. MCH is produced at commercially viable scales in a central location in Texas (TX) by hydrogenation of toluene and transmitted by rail or chemical tankers to northern California (CA), see Fig. 1. MCH is dehydrogenated near city gates to generate fuel-cell quality hydrogen, and toluene is transmitted back to TX.

Production Methods

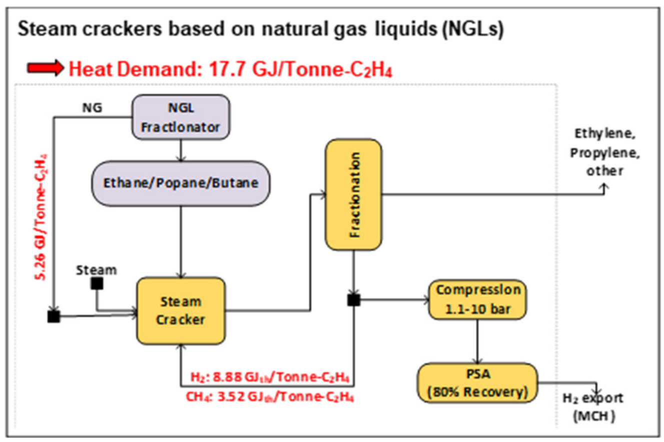
We considered the following four methods of producing hydrogen at capacities from 50 to 650 tonnes-H_2/day (tpd).

- S_1: Byproduct hydrogen from chlor-alkali plants in Gulf of Mexico
- S_2: Byproduct hydrogen from steam cracking of natural gas liquids in Gulf of Mexico
- S_3: Renewable hydrogen from excess wind-generated electricity in Texas
- S_4: Renewable hydrogen from excess solar-generated electricity in Texas

Figure 1 Transmission of MCH/toluene by rail or ships from Texas to northern California



(a) Chlor-alkali plant



(b) Steam cracker

Figure 2 Utilization of byproduct H_2 from chlor-alkali plants and steam crackers

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. Most of the byproduct hydrogen is combusted for steam generation or vented and only 35% is known to enter the merchant gas market[1]. Steam is needed in chlor-alkali plants in various process steps including salt preparation and concentration of caustic soda. NaOH after-treatment process accounts for the largest heat requirement (95%). Byproduct hydrogen can be exported and used for hydrogenation, if the heat required in the plant for raising steam (2.27 MJ/kg-Cl_2) is made up by natural gas (NG) combustion, see Fig. 2a.

An estimated 1.8 million metric tons (5,000 tpd) of byproduct hydrogen is produced annually in U.S. in natural gas liquid (NGL) steam crackers. Steam crackers in Texas and Louisiana account for ~88% of the total byproduct hydrogen. As of 2017, ethane makes up 67% of the steam cracker feedstock in the U.S[2]. The incremental NG energy requirement (8.88 MJ/kg-C_2H_4) for exporting byproduct hydrogen is shown in Fig. 2b.

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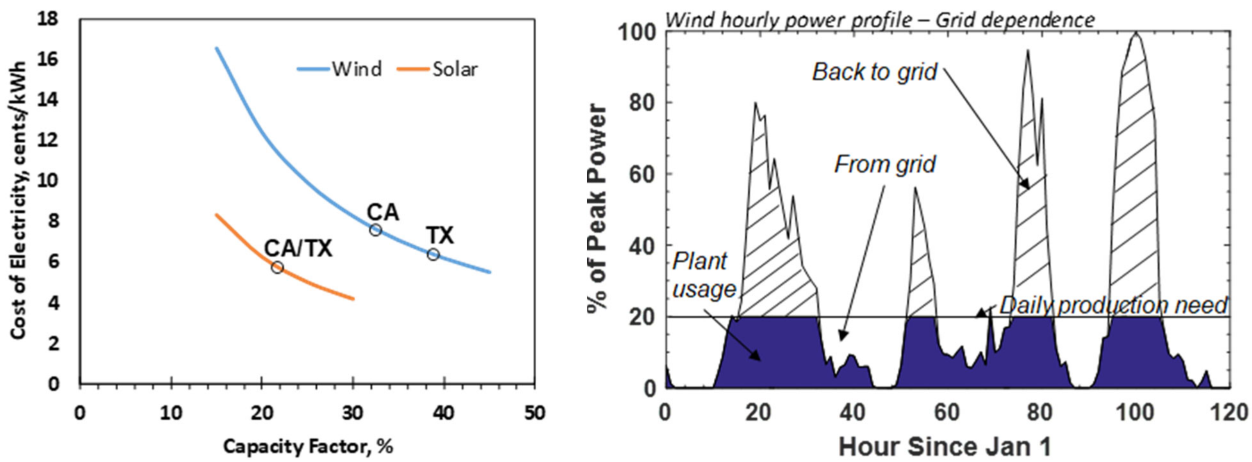
[1] *Lee, D.Y. and Elgowainy, A., Dai Q. Life Cycle Greenhouse Gas Emissions of By-Product Hydrogen from Chlor Alkali Plants. ANL/ESD-17/27*

[2] *Lee, D.Y. and Elgowainy, A. International journal of hydrogen energy 43 (2018) 20143-20160*



(a) Cost of electricity (b) Wind hourly profiles

Figure 3 Renewable H_2 production from wind and solar electricity: cost and utilization factors

For renewable hydrogen production by central low-temperature polymer electrolyte membrane (PEM) water electrolysis, we consider a consider a central case of 50 tpd unit train discussed in DOE H2A current technology status report[3]. The total system electrical usage is 54.3 $kWh_e/kg\text{-}H_2$, 93% of which is consumed in the electrolyzer stack. Wind and solar techno-economics is based on System Advisor Model (SAM)[4]. Considering wind and solar annual profiles in Fig. 3a, wind offers a higher annual capacity factor than solar. For example, wind capacity factor is 38.1% in TX and 32.2% in CA, whereas solar capacity factor is similar in TX and CA, ~21%. Despite the lower solar capacity factor, electricity generated from solar is less expensive than wind due to lower capital and operational costs of solar plants.

Due to solar/wind intermittency and the need to hydrogenate at a constant hourly rate, the renewable farms are connected to the grid. As shown in Fig. 3b for wind energy, we utilize a fraction of the rated power of the plant for hydrogen production. Excess electricity during 8 am – 8 pm peak demand hours is sold to the grid at ¢2.5/kWh. At times when wind power is less than required for hydrogen production, we import electricity from the grid at ¢5.43/kWh, thus offsetting the amount of electricity exported during peak demand periods. For zero grid electricity balance, the capacity factor in the wind scenario decreases from 38% to 23%, thus increasing the net cost of electricity.

Cost and energy requirements of hydrogenation and dehydrogenation plants was evaluated from process models. For more details regarding the process and costs, please refer to Papadias et al. (2021)[5].

Transmission Modes

We consider two modes of transmitting MCH/toluene by rail (T_1) and by ships (T_2). Federal Railway Administration (FRA) regulations currently only permit shipping of liquid carriers by rail, but not gaseous or liquid hydrogen.

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

[4] *https://sam.nrel.gov/.*

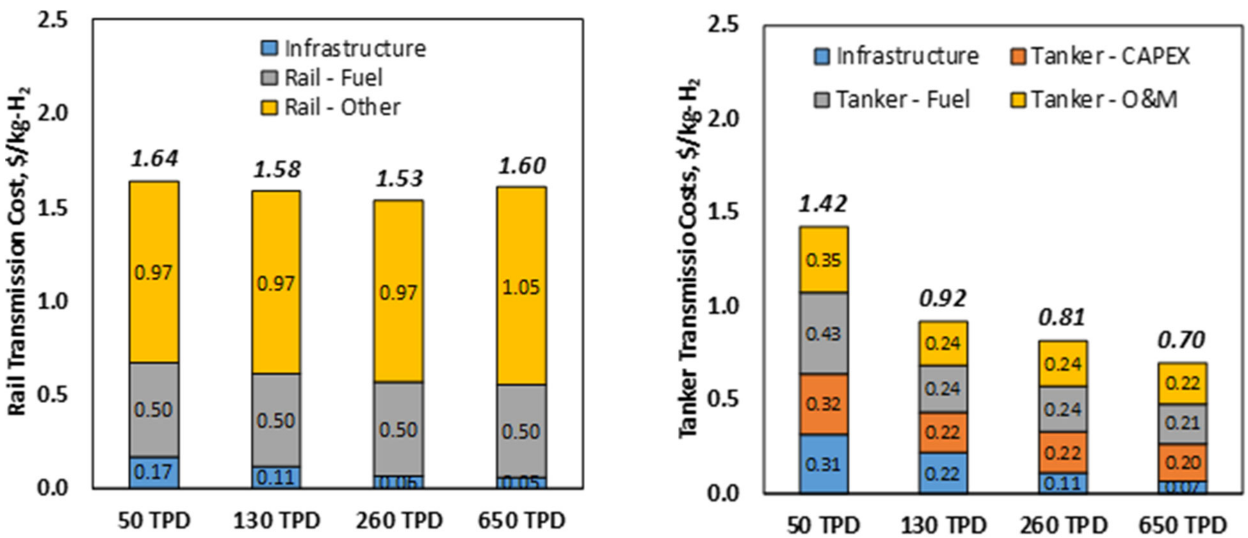
[5] *Dionissios, D. Papadias, Jui-Kun, Peng and Rajesh, K., Ahluwalia. (2021). Hydrogen carriers: Production, transmission, decomposition, and storage. International Journal of Hydrogen Energy, 46, 24169-24189.*

We used actual cost data for transmission of toluene/MCH by rail. U.S. rail carriers shipping over 4,000 carloads annually are mandated to supply a sample of the waybill for carloads and commodities shipped. We used the 2018 waybill data[6] and correlated the transmission cost in terms of \$/ton-mile as a function of shipping distance. The freight revenue in \$/ton-mile generally decreases with distance and number of freight cars per train. The limiting rail transmission cost is related to the fuel consumption, about 380 ton-mile/gal, fuel cost, perceived hazard in transporting material, and for distances greater than 1,000 miles is 0.044/ton-mile for toluene.

For ships, we consider chemical tankers up to 115,000 deadweight ton (DWT). The capital cost of the ship as function of size (DWT) is estimated using statistical data from global shipyards. Additional cost of 20% is included to account for U.S. maritime commerce regulation requiring ships to be produced domestically if sailing from two U.S. ports. Panama Canal fees per roundtrip are estimated on laden conditions and additional port fees are included at \$0.52/DWT-day. The crew complement consists of 2 deck officers, 4 engineers, and 24 deckhands for a total crew of 30. Infrastructure costs are included to account for the costs of constructing and operating railyards for loading and unloading MCH/toluene to and from the railcars, jetty system which allows the ships to anchor away from the shore, and pipelines to transfer the MCH/toluene to the shore.

Shown in Fig. 4 are the transmission costs for rail and ships as function of daily demand. Transmission costs by rail do not show any significant cost reduction with capacity and total to about 1.53-1.64 \$/kg-H_2. The main cost is due to fuel and delivery charges incurred by the railroad.

Despite a longer route, 4,950 miles compared to 1,950 miles by rail, transmitting by ships is more economical. As the demand increases, the ships get bigger and more economical. The transmission cost at the lowest demand (50 tpd) is close to that by rail, \$1.42/kg-H_2, but decreases to \$0.70/kg-H_2 for a demand of 650 tpd, which is less than half the transmission cost by rail.



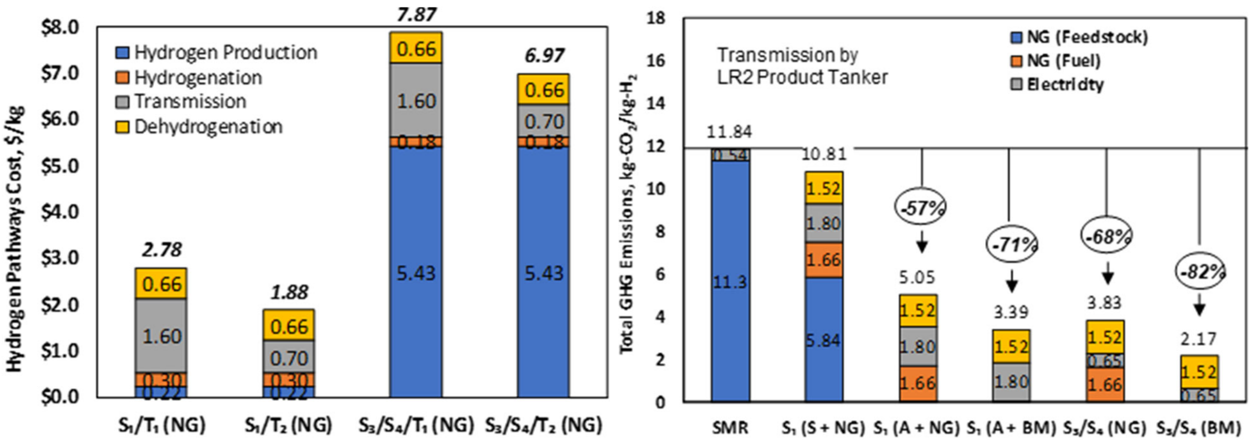
(a) Rail (b) Ships

Figure 4 Transmission costs from TX to CA by rail and by chemical tankers

[6] https://prod.stb.gov/

Cost and GHG Emissions

Figure 5a presents the breakdown of the levelized costs in terms of the individual process steps for hydrogen production, toluene hydrogenation, transmission and MCH dehydrogenation. The byproduct hydrogen cost is calculated from the calorific value of replacement NG data in Fig. 2 and the assumed \$2.65/million-Btu 2018 NG cost for TX. Renewable hydrogen production cost was estimated from the capital and operating costs of PEM electrolysis and wind or solar farms. GHG emissions were estimated from and energy use and well to point of use metrics according to latest GREET model 2019[7]. Byproduct H_2 emissions were compared on the bases of NG substitution and mass-allocation (i.e., CO_2 emissions split to all co-products).



(a) Pathway costs (b) GHG Emissions

Figure 5 Pathway costs of hydrogen and GHG emissions at a daily production rate of 650 tpd. S: substitution; A: mass-allocation, NG: natural gas; BM: biomethane

The levelized cost of hydrogen for a few scenarios is shown in Fig. 5a. For brevity, costs are only presented for the large demand case, 650 tpd. Because the costs of byproduct hydrogen from chlor-alkali plants (S_1) and NGL steam cracking plants (S_2) are about the same, we only show results for the S_1 scenario. Similarly, because the costs of producing hydrogen by wind and solar are about the same, we group the pathway costs for S_3 and S_4 routes. By-product H_2 incurs the lowest cost among the pathways analyzed. Using ships (T2) as transmission mode, the byproduct H_2 pathway cost can potentially be as low as \$1.88/kg-H_2. The \$0.22/kg cost of byproduct H_2 only reflects the cost of NG substitution for heat demand. For comparison, the cost of H_2 production by a large steam methane reformer (SMR) in CA is ~\$1.25/kg. The cost of renewable hydrogen pathway is \$6.97/kg-H_2 with ships as transmission mode. The \$5.43/kg cost of renewable H_2 is dominated by the estimated ¢7.9/kWh cost of electricity generation by solar and wind.

The equivalent GHG emissions in kg-CO_2/kg-H_2 are shown in Fig. 5b for S1, S3 and S4 with chemical tankers as transmission mode. For comparison, we also show the GHG emissions from a large-scale SMR in CA. In case of NG substitution for by-product hydrogen, the GHG emissions are similar to the SMR case. 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. In case of biomethane, hydrogen produced from wind and solar can reduce the

[7] *Argonne GREET Mode. lhttps://greet.es.anl.gov*

emission by up to 82% relative to the SMR. Transmission by ship accounts for the majority of GHG emissions (1.52 kg-CO_2/kg-H_2).

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)
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