H2@Scale: Outlook of Hydrogen Carriers at Different Scales


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

Denver Marriott West
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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

<table>
<thead>
<tr>
<th>MP °C</th>
<th>BP °C</th>
<th>H₂ Capacity wt%</th>
<th>Production</th>
<th>Decomposition</th>
<th>ΔH kJ/mol-H₂</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>P, bar</td>
<td>T, °C</td>
<td>P, bar</td>
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<tr>
<td>Ammonia</td>
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<tr>
<td>-78</td>
<td>-33.4</td>
<td>17.6</td>
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<td>Haber-Bosch Process</td>
<td>Fe Based Catalyst</td>
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<td>Methanol</td>
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<td>Cu/ZnO/Al₂O₃ Catalyst</td>
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<td>Steam Reforming</td>
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<tr>
<td>MCH</td>
<td>-127</td>
<td>101</td>
<td>6.1</td>
<td>47</td>
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<td>Non-PGM Catalyst</td>
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<td>Pt/Al₂O₃ Catalyst</td>
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Baseline Gaseous Hydrogen (GH₂) Pathway: 50 tpd-H₂

- 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-H₂;
- Operating capacity factor = 90%;
- Internal rate of return (IRR) = 10%;
- Depreciation (MACRS)=15 yrs;
- Plant life=30 yrs; Construction period=3 yrs

<table>
<thead>
<tr>
<th>Feedstock and Utilities</th>
<th>NG</th>
<th>Electricity</th>
<th>Water</th>
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</thead>
<tbody>
<tr>
<td>SMR Consumption, /kg-H₂</td>
<td>6.80 $/MBtu</td>
<td>12 ¢/kWh</td>
<td>0.54 ¢/gal</td>
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<td>GH₂ Terminal</td>
<td>HDSAM v 3.1, Compressed Gas H₂ Terminal</td>
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<tr>
<td>H₂ Storage</td>
<td>10-days geologic storage of H₂ for plant outages</td>
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<tr>
<td>H₂ Distribution</td>
<td>400 kg/day H₂ dispensing rate at refueling station</td>
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<tr>
<td>Tube Trailers</td>
<td>Payload</td>
<td>Volume</td>
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<tr>
<td></td>
<td>1042 kg</td>
<td>36 m³</td>
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</tbody>
</table>

DOE record: 13-16 $/kg-H₂ dispensed for very low production volume

- GH₂ scenario includes 10-d (500 t-H₂) 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 |
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 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

Linde Ammonia Concept (LAC)

- **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$/tdp at 2500 tpd

**Breakdown of Capital Costs (2,500 tpd)**

- **Reformer**: 26%
- **ASU**: 9%
- **NH3 Synthesis**: 37%
- **BOP**: 13%
- **Storage**: 9%
- **Electric plant**: 6%

Capital cost shown for LAC but are similar for the conventional ammonia process.
- Reactor operated at 240°C and 10 atm for nearly complete conversion. Excess \( \text{H}_2 \) and MCH vapor recycled (\( \text{H}_2/\text{Toluene} \) 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
- \( \text{H}_2 \): 350 tpd

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- Methanol steam-reformed at 3 bar, 290°C
- Capital cost decreases from 662k$/tpd at 50 tpd-H₂ to 396k$/tpd at 350 tpd-H₂
Capital Cost of Ammonia Decomposition Plant

- Ammonia cracked at 20 bar, 800°C on a Ni catalyst
- Capital cost decreases from 405k$/tpd at 50 tpd-H₂ to 257k$/tpd at 350 tpd-H₂

Ammonia Cracker with PSA for H₂ Purification

Area 101. Storage

Area 201. Ammonia Cracker

Area 301. Separation

Area 401. Burner

Capital Costs of Ammonia Decomposition Plant

Capital Cost Factors

50-tpd H₂

Storage 1%
Separation 31%
Cracker 59%
Misc 9%
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$/tpd at 50 tpd-H₂ to 286k$/tpd at 350 tpd-H₂.

**Losses**
- Toluene+MCH: 0.84%
- Hydrogen: 10%
- Heat: 0.36 kWhth/kWhth-H₂

**Feedstock/Utilities**
- NG: 0.22 kWhth/kWhth-H₂
- Electricity: 0.04 kWhe/kWth-H₂

**Capital Cost Factors: 50 tpd-H₂**

Levelized production cost (LPC) lowest for methanol carrier ($1.22/kg-H₂)
- Methanol produced by very large one-step ATR plant (10,000 tpd)
- Methanol produced from NG without an explicit step for pure H₂ production by SMR

LPC highest for ammonia carrier ($2.20/kg-H₂)
- Ammonia plants more capital intensive than methanol plants: 1.28 vs. $0.56/kg-H₂

LPC for MCH carrier competitive with methanol option ($1.35/kg-H₂)
- MCH produced by a simple (exothermic) process for hydrogenating toluene
  Capital cost: $0.32/kg-H₂ for SMR, $0.30/kg-H₂ for hydrogenation
Levelized decomposition costs (LDC) are comparable for the three carriers: 0.61-0.78 $/kg-H₂ at 50 tpd-H₂

- At high throughput, LDC decreases most for ammonia. However, ammonia decomposes at a high temperature (800°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/Al₂O₃) 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 H₂
- Methanol: 0.63 $/kg-H₂
- Ammonia: 1.29 $/kg-H₂
- MCH: 2.07 $/kg-H₂
Levelized Costs: Transmission by Pipelines

Transmission Cost lowest for methanol and ammonia, similar for H₂ 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 H₂, 4 m/s for liquids
- Initial capital outlay for 6000 tpd-H₂ pipeline: 3.6M$/mile for H₂, 1.6M$/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
Large methanol scenario is competitive with the baseline GH₂ scenario
- Slightly cheaper combined production and decomposition cost ($0.30 \$/kg-H₂), offset by 0.33 \$/kg-H₂ higher transmission cost

As a carrier, ammonia is more expensive than methanol
- $0.81 \$/kg-H₂ higher combined production and decomposition cost, 0.69 \$/kg-H₂ higher transmission cost

Centralized MCH production scenario slightly more expensive than ammonia
- 0.71 \$/kg-H₂ cheaper production and decomposition cost < 0.87 \$/kg-H₂ higher transmission cost
All carriers produced from natural gas as feedstock at commercially viable scale, independent of H₂ demand at city gate

- Methanol as hydrogen carrier may involve lower risk and be attractive in the transition phase, <50-tpd H₂ demand
- With pipelines, levelized cost decreases by ~1 $/kg-H₂ for ammonia and MCH, methanol slightly cheaper than H₂
- Comparison between GH₂ and LHC scenarios sensitive to NG price differential

For simplicity in presentation, all levelized costs include fixed 1.10$/kg-H₂ distribution cost independent of demand.
Bulk H₂ Storage: Outlook

- Underground pipes more economical than geological storage for <20-t usable stored H₂
- At large scale, salt caverns generally more economical than lined rock caverns
- Storing >750-t usable H₂ 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
Parallel dehydrogenation steps

- Desirable to have a carrier (low $\Delta G$ and $\Delta H$) 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 H₂ demand

2. Ranking of the three carriers by levelized production costs
   - Methanol (1.22 $/kg-H₂)<MCH (1.35 $/kg-H₂)<<Ammonia (2.20 $/kg-H₂)

3. H₂ 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-H₂ basis

4. Toxicity and handling are also important factors in determining train transmission costs
   - Ammonia has nearly the same H₂ capacity as methanol but is >2X costlier to move by train

5. Long H₂ 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

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BWR = Boiling Water Reactor
ASU = Air Separation Unit
Syngas stoichiometric molar ratio ($M$) = $(H_2\text{-}CO_2)/(CO\text{+}CO_2)$
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-H₂): MCH (2.37) > ammonia (2.25) > methanol (2.14) > GH₂ (1.71)

For calculating energy efficiency, make-up toluene is included with fuel
Proposed LHC Targets for $2/kg H₂ Production Cost

- $1/kg-H₂ LHC production: at 50 tpd, $1.22 for methanol and $0.89 for fuel cell quality H₂
- $0.50/kg-H₂ LHC transmission: at 50 tpd, $0.63 for methanol
- $0.50/kg-H₂ LHC decomposition and H₂ 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

<table>
<thead>
<tr>
<th>Hydrogen Carriers: Outlook</th>
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<tbody>
<tr>
<td>Methanol Ammonia MCH / Toluene GH₂ Comments</td>
</tr>
<tr>
<td>H₂ Production 0.96 0.89 2.30 Ammonia more expensive to produce than MCH from toluene</td>
</tr>
<tr>
<td>LHC Production 1.22 1.24 0.46 Methanol produced directly from NG under mild conditions</td>
</tr>
<tr>
<td>LHC Transmission 0.63 1.32 2.19 Refrigerated rail cars needed for ammonia</td>
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<tr>
<td>LHC Decomposition 0.78 0.61 0.75 H-capacity of MCH is only 47 g/L</td>
</tr>
<tr>
<td>GH₂ Terminal &amp; Storage 1.25 1.25 1.25 1.25 Ideally, LHC should decompose at PSA operating pressure</td>
</tr>
<tr>
<td>Distribution 1.10 1.10 1.10 1.40 GH₂ distributed from production site to refueling station</td>
</tr>
<tr>
<td>Total 4.98 6.48 6.65 4.95</td>
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</tbody>
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H₂ Production Cost at 350 tpd

- H₂ Production
- LHC Production
- Transmission
- LHC Decomposition

Cost, $/kg H₂

<table>
<thead>
<tr>
<th>Methanol</th>
<th>Ammonia</th>
<th>MCH / Toluene</th>
<th>GH₂</th>
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<td>1.22</td>
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