Potential Carriers and Approaches for Hydrogen Delivery

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Matthew Hooks
Stefan Unnasch
Stephen Lasher

TIAX LLC
1601 S. D Anza Blvd.
Cupertino CA, 95014
Tel. 408-517-1550
Reference: D0348

The efficient delivery of hydrogen is necessary for the adoption of hydrogen as a transportation fuel, but numerous challenges must be met.

- Cost
- Density (wt. and vol.)
- Energy requirements
- Forecourt storage requirements
- Codes and standards

LH_2 Tank/ Fueling Station

H_2 Tube Trailer

H_2 Plant, Liquefier, LH_2 storage

"Conventional" delivery options are limited by volumetric density, processing energy, or handling issues.

"Conventional" Delivery	Examples	Refueling Type	On-Board Storage Type
Compressed Gaseous Hydrogen	• Pipeline • Low-P Tube Trailer • High-P Tube Trailer	• cH_2 (maybe with heat transfer)	• cH_2 Tank
Liquid Hydrogen	• LH_2 Truck • LH_2 Railcar	• LH_2 • cH_2 (maybe with heat transfer)	• cH_2 Tank • LH_2 Tank • Cryo-compressed Tank

Novel carriers are defined by the delivery method and storage material, as one storage material can be used for multiple delivery methods.

Novel Delivery	Example Materials
Liquid	▪ Liquid HC (APCI Material) ▪ Ammonia-Borane
Solid-Liquid Slurry	▪ All with liquid carrier: ▪ Chemical Hydrides (SBH, MgH_2) ▪ Metal Hydrides ($TiFe_{0.85}Mn_{0.15}$) ▪ Carbons?
Bricks	▪ Chemical Hydrides, Alanates? ▪ Metal Hydrides ▪ Carbons
Flowable Powder	▪ Metal Hydrides ▪ Chemical Hydrides ▪ Carbons

Sodium borohydride and magnesium hydride are chemical hydrides that can be used as either a flowable powder or in a liquid-slurry mixture.

- Pros:
  - Potentially higher gravimetric density than compressed or liquid hydrogen (when used dry and without consideration for reaction product weight)
  - Potentially easier to handle than compressed or liquid hydrogen
- Cons:
  - The product of the reaction is heavier than the hydride, limiting transport capacity
  - Regeneration process may require significant material cost
  - For ease of transport it may be necessary to add liquid carriers, thus reducing hydrogen yield (as a weight fraction)

Chem. Hydride	State	Hydrogen Yield	
NaBH4	Dry	wt. %, hydride	21.3%
		wt. %, spent mat.	12.3%
	Liquid / Slurry	wt. %, hydride	4.4%
		wt. %, spent mat.	4.4%
MgH2	Dry	wt. %, hydride	15.3%
		wt. %, spent mat.	6.9%
	Liquid / Slurry	wt. %, hydride	11.6%
		wt. %, spent mat.	6.1%

Assumptions: NaBH4: 26% solids loading, 80% on-board conversion
MgH2: 76% solids loading, 100% on-board conversion

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Alanates are not limited by the weight of reaction products, but have numerous issues that may hinder their adoption as hydrogen carriers.

- Sodium alanate is a popular type suggested for use as a hydrogen carrier
- Material will generally be used in the form of a powder with a modest packing density (60%) which reduces volumetric energy density
- Pros:
  - Potential for reversible hydrogen storage using waste heat to liberate hydrogen
  - Operates in a reasonable T-P space (2 bar/120°C desorption)
- Cons:
  - Low hydrogen yield (5.5 wt.% theoretical, 3.2 wt.% actual)
  - Adsorbtion/desorbtion requires significant heat transfer capability
  - Powder can be explosive and reacts with water and air, necessitating that this carrier always remain in the original container (either trailer or on-board storage tank)
- Due to their reactivity it is assumed that alanates will not be used as both an on-board and off-board carrier

Metal hydrides are similar to alanates in that hydrogen can be reversibly adsorbed/desorbed, but without some of the reactivity difficulties.

- Metal hydrides could be used in a number of applications, including flowable powder, bricks, and liquid slurries
- Each of these applications will be similarly affected by the characteristics of the metal hydride
- $TiFe_{0.85}Mn_{0.15}$ was selected as a likely metal hydride as it operates within a reasonable T-P space and is low-cost and has low energy requirements for desorbtion
- Pros:
  - Potential for reversible hydrogen storage using waste heat to liberate hydrogen
  - Operates in a reasonable T-P space
- Cons:
  - Very low hydrogen yield (3.0 wt.% actual, 1.5 wt.% slurry)
    - Other metal hydrides do generally not achieve any more than 5 wt.%
  - Metal hydrides often deteriorate with cycling
    - All the effects of cycling are not well known, especially in unique applications such as slurries

Certain carbon structures can easily bond with hydrogen under pressure and subsequently release hydrogen when heated.

- Air Products has investigated the use of ethyl carbizol to fulfill this role as a liquid carbon carrier
  - Ethyl carbizol is a aromatic carbon ring with alternating single and double bonds that can achieve a theoretical capacity of 7.75 wt.% (6% realized without degradation)
- Pros:
  - Potential for reversible hydrogen storage
  - Achieves 6 wt.% with repeatability and little or no material degradation
  - Exothermic regeneration process can be used to generate steam for electricity cogeneration
- Cons:
  - Requires expensive precious metal catalyst that requires frequent replacing
    - Catalyst will be replaced bi-annually, however 90% of the cost can be recovered from the sale of the old catalyst material
  - Requires high pressure for hydrogenation (700 bar)

Using a slurry to transport hydrogen simplifies many transport functions, but also adversely effects the overall energy density.

- The primary candidate materials for use in a solid-liquid slurry are chemical and metal hydrides
  - Activated carbon may also be a potential for use in a slurry, but has not been proposed by a developer at this time
- For certain chemical hydrides the carrier solution may serve as one of the reactants in the process that liberates hydrogen from the carrier material
  - In these cases, additional solution may need to be added to the to the spent material in order to maintain a reasonable solids loading in the slurry
  - Certain slurries may also require the use of a stabilizer to keep the material suspended in the solution
- The addition of a liquid carrier to various hydrogen carrier materials allows for the carrier material to be pumped, both in the processing plant and at the forecourt
- Slurries have the potential to improve the stability/degradation of hydrogen storage materials, metal hydrides in particular
- Certain slurries can be “return-limited” when transported via truck, meaning that the spent carrier material will weigh more than the hydrided carrier material
  - Trucks will not be able to be shipped full if this is the case

Bricks are defined as self-contained carriers that are transferred to and from the vehicle in a rigid container.

- Any number of carrier types can be used in bricks, but metal hydrides or activated carbon structures are most likely as they do not need to undergo significant reprocessing as do chemical hydrides
- Bricks will likely have an integrated heat transfer mechanism, as most brick-compatible carriers will cycle hydrogen by changing the temperature and pressure of the carrier
- Pros:
  - Reduce the chance of contamination and/or material loss as the carrier is in a self-contained vessel
  - Makes for potentially simple material handling
- Cons:
  - Adds costs and weight to the carrier
  - Weight and volume of vessel reduces the volumetric and gravimetric capacity of the carrier system
  - The bricks will be very heavy – especially if 1 brick = 1 fill is assumed
    - Makes for very difficult loading and unloading

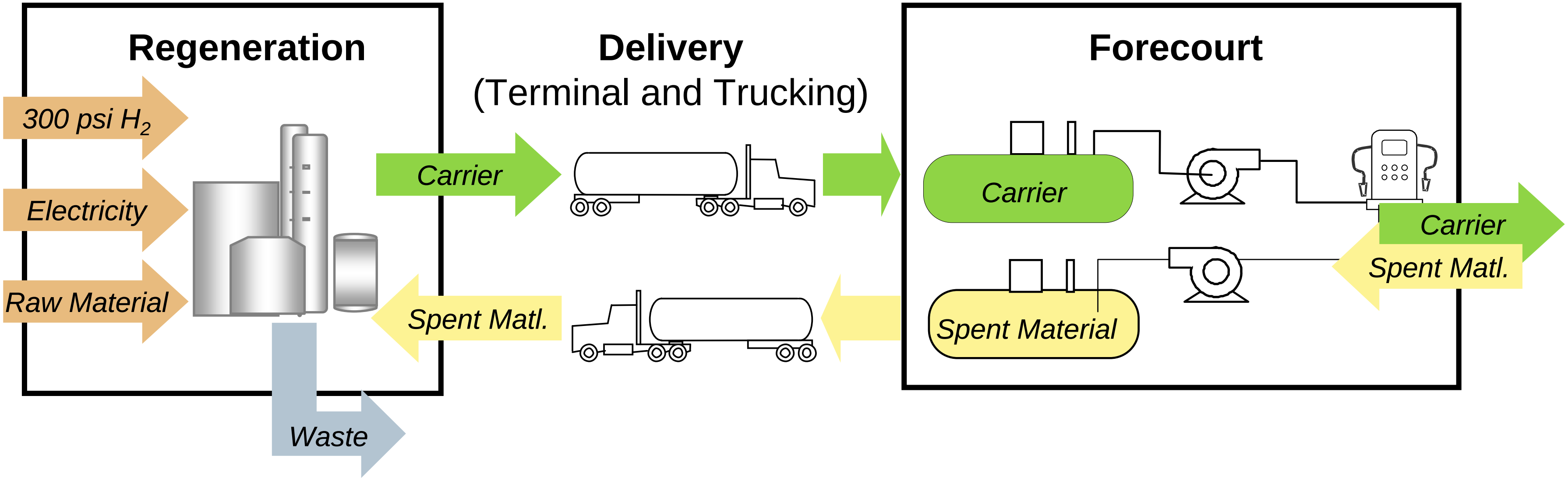
Flowable powders are solid hydrogen carriers that can be transferred as a powder from one transport mechanism to another.

- Any number of carrier types can be used as flowable powders, but chemical hydrides or activated carbon structures are most likely as they generally do not require a closed environment
- The success of the flowable powder is primarily dependent on the characteristics of the carrier material
- Pros:
  - Does not have the added mass of a liquid slurrying-agent or metal vessel
- Cons:
  - Material handling may be difficult as material is more susceptible to loss or contamination

The analysis goals are set to fairly evaluate the energy requirements and costs for various novel carriers.

- Develop spreadsheet analysis tools to analyze component costs for novel carriers
  - Processing
  - Terminal Storage
  - Trucking
  - Forecourt
- Develop initial cost and performance inputs
- Develop any additional tools necessary to properly evaluate the unique traits of novel hydrogen carriers
  - Hydrogen yield calculations for:
    - $NaBH_4$ & MgH_2 Slurry
    - Bricks

All facets of the delivery process must be included in the analysis in order to equitably equate the various methods and carriers.



- H2 is supplied "over-the-fence"
- May include electrolysis
- Today's processes may not recycle all spent material

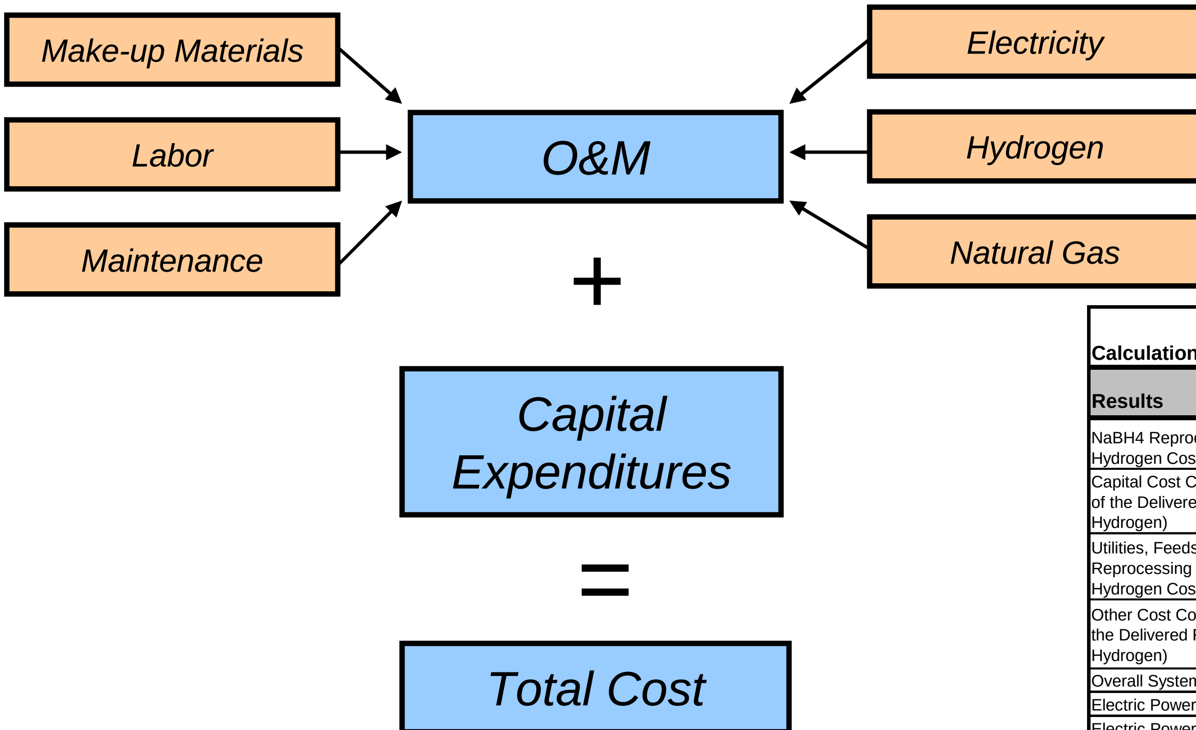
- Transportation of the carrier and spent material via truck
- Terminal storage may be required at the regeneration site

- May include carrier and spent material storage and dispensing (loading and off-loading)
- Or compressed hydrogen dispensing

Carrier model structure and most financial assumptions are maintained from original H2A Model to allow direct comparison with cH2 and LH2.

Financial Assumptions - Regeneration Plant	Base Case
Assumed start-up year	2006
Reference year dollars	2005
After-Tax Real Discount Rate (%)	10.0%
Electrolyzer MACRS Depreciation Schedule Length (years)	10
Reactors and Separators MACRS Depreciation Schedule (years)	10
Remainder of Station MACRS Depreciation Schedule Length (years)	15
Electrolyzer Lifetime (years)	20
Reactors and Separators Lifetime (years)	20
Remainder of Plant Lifetime (years)	40
Analysis period (years)	40
Inflation Rate (%)	1.9%
State Taxes (%)	6.0%
Federal Taxes (%)	35.0%
Total Tax Rate (%)	38.9%

A Components Model tab was developed for calculating the regeneration cost and was based on other H2A modeling efforts.



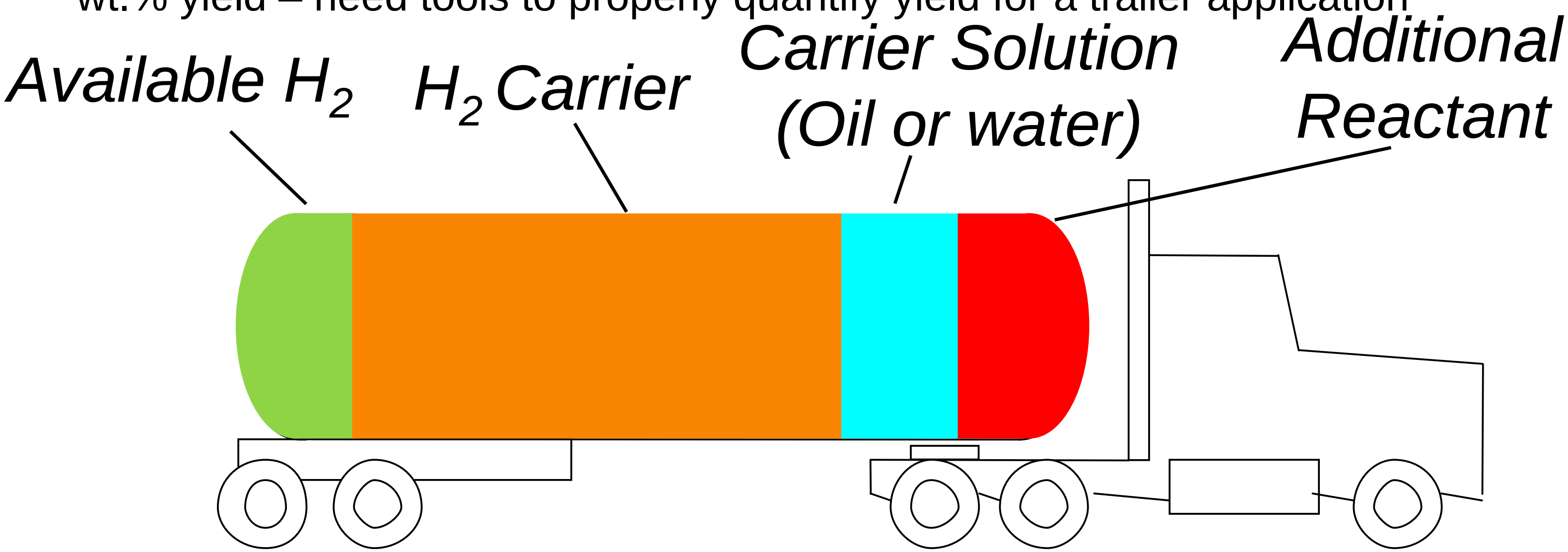
Calculation Outputs (Be sure ALL data is entered before checking)

Results	
NaBH4 Reprocessing PlantPortion of the Delivered Real Levelized Hydrogen Cost ($(2005)/kg of Hydrogen)	$8.028
Capital Cost Contribution to the NaBH4 Reprocessing Plant Portion of the Delivered Real Levelized Hydrogen Cost ($(2005)/kg of Hydrogen)	$0.253
Utilities, Feedstock & Material Conribution to the NaBH4 Reprocessing Plant Portion of the Delivered Real Levelized Hydrogen Cost ($(2005)/kg of Hydrogen)	$7.721
Other Cost Contribution to the NaBH4 Reprocessing Plant Portion of the Delivered Real Levelized Hydrogen Cost ($(2005)/kg of Hydrogen)	$0.056
Overall System Energy Use (MJ/kg of H2 out)	106
Electric Power (J/J H2)	0.01
Electric Power (% Overall Energy)	0.68%
Natural Gas (J/J H2)	0
Natural Gas (% Overall Energy)	0%
Hydrogen (J/J H2)	0.88
Hydrogen (% Overall Energy)	99%
Real After-Tax IRR (%)	10%

Most processing plants can be evaluated based on capital costs and an understanding of the operating costs.

The trucking spreadsheet calculates the cost to transport a variety of novel carriers.

- The energy consumed by the truck (per kg_{H2}) varies primarily with trucking distance, fuel economy, vehicle speed, trailer cost, and truck capacity
  - For this analysis all variables were held constant except the truck capacity and trailer cost
  - Overall capacity is consistent with a 9,000 gal. gasoline truck (~25,000 kg)
- Truck capacity is the primary differentiator between trucking costs
  - A carrier with a 3 wt.% yield will costs twice as much to transport as a carrier with a 6 wt.% yield – need tools to properly quantify yield for a trailer application



Storage and forecourt tabs have been created to allow for simple comparisons of various carrier options.

- The storage terminal tab is geared toward carrier methods that can be stored in large storage tanks: liquids, liquid-slurries and flowable powders
  - Calculates the required storage for a two-day supply of fresh material and two-days of spent material – does not include cost of carrier material
- Forecourt cost calculations are separated into two tabs for the following scenarios:
  - Forecourts that distribute novel carriers to vehicle (desorbtion/dehydriding is performed on-board the vehicle)
  - Forecourts that distribute cH_2 carriers to vehicle (desorbtion/dehydriding is performed at the forecourt)

The Chem H_2 Truck Yield tool specifies the actual H_2 yield based on stoichiometry of the reaction and slurry composition for MgH_2 & $NaBH_4$.

- Determines whether additional reactants (e.g., water) are required and whether the system is return limited (i.e., spent material is heaver than hydride material)
- Inputs include carrier/slurry composition, reaction description, and on-board conversion efficiency
- Output is the actual H2 yield, which is used in other tabs

INPUTS:		
Truck Capacity	27,250	kg
On-Board Conversion	80%	
Water Recovery	89%	
Return Trip Water Addition	No	
NaBH4 Concentration	26.0%	wt
NaOH Concentration	3%	wt
H20 Concentration	71%	wt

	Mass		**Moles**	
Hydrogen Yield	1,208	kg	599.3	kmol
Hydrogen (frac of charged sol'n)	4.43%	wt		
Hydrogen (frac of truck capacity)	4.43%	wt		

In order to accurately quantify the effects of transporting hydrogen carriers in individual storage vessels a Brick Calculator was created.

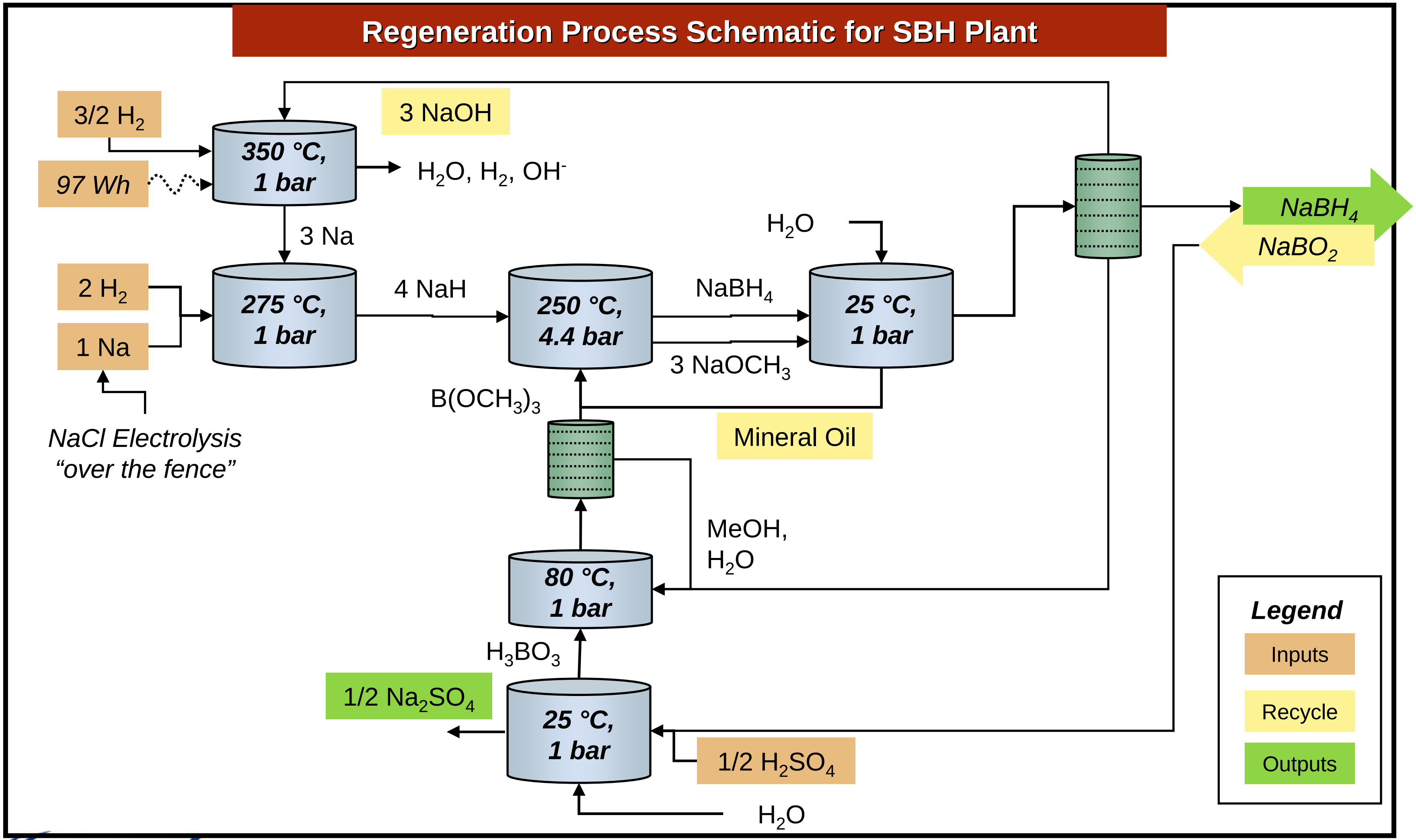
- The brick calculator estimates the weight and volume of the vessel; modeling it as a hollow cube that is the necessary volume to carry a single load of hydrogen and manufactured from a specified material: stainless steel, aluminum, or carbon fiber
- Includes inputs for weight and volume of heat exchange equipment
- The wt.% of the carrier as well as the density of the carrier all have significant effects on the overall sizes of these brick
- Output is the actual H2 yield, which is used in other tabs

H2 Contained (kg)	5.0
Wt%	5.00%
Density of Carrier (kg/m3)	1250
Box Material	Aluminum
Box Thickness (m)	0.0025
HX Equipment Weight (kg)	10
HX Equipment Volume (L)	8
Mass of Carrier (kg)	100
Volume (m3)	0.088
Length of Cube (m)	0.445
Surface Area (m2)	1.187
Volume of Box (m3)	0.003
Mass of Box Material (kg)	8.01
Actual Wt.%	4.24%
Actual Density (kg/m3)	1297
Percent Carrier	84.7%
Total Mass (kg)	123

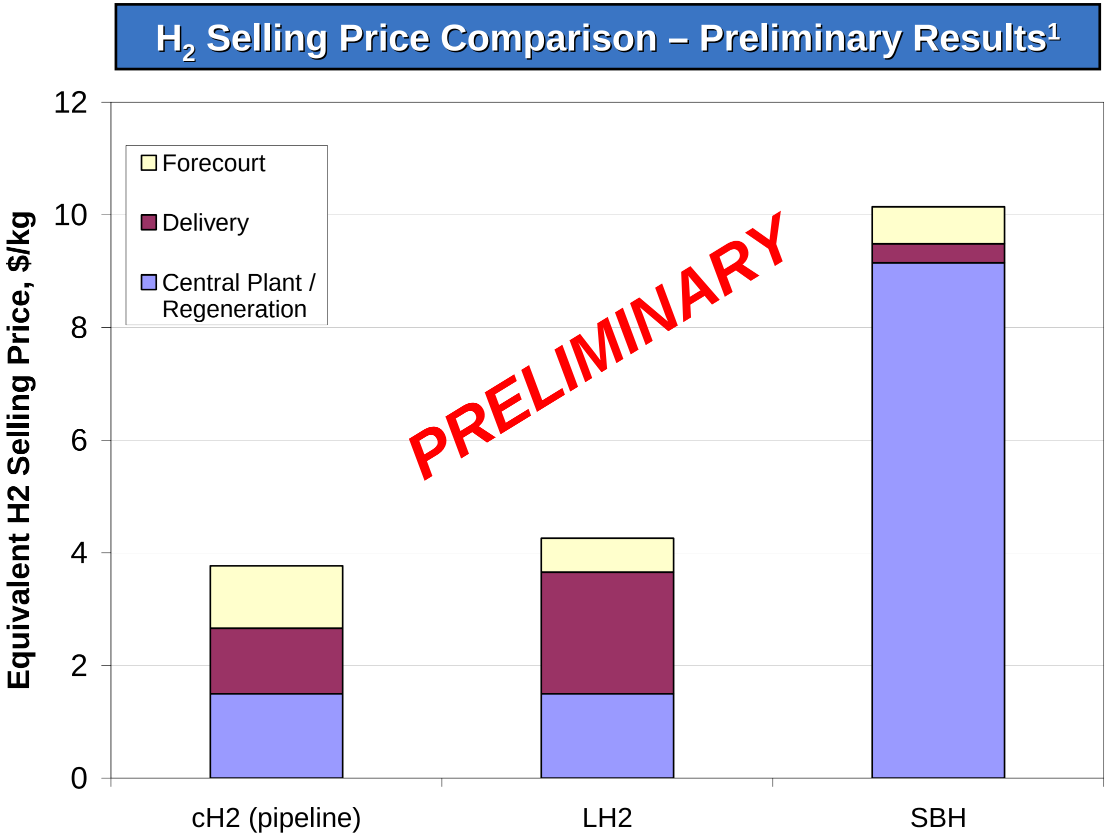
TIAX evaluated a regeneration process that reflects existing technology but is not currently being used at the industrial-scale.

- Today's SBH production
  - Use new sodium, boric acid, and hydrogen in Brown-Schlesinger process
  - Recycle methanol and mineral oil. No $NaBO_2$ is reprocessed.
- Existing technology, scaled up
  - Use sodium, boric acid, and hydrogen in Brown-Schlesinger process
  - Boric acid is recovered from $NaBO_2$. ½ mole Na_2SO_4 is waste material
  - Electrolyze 3 moles of NaOH at regeneration plant. Import 1 mole Na.
- Closed system with $NaBO_2$ electrolysis
  - Use sodium, boric acid, and hydrogen in Brown-Schlesinger process
  - Electrolyze $NaBO_2$ to produce boric acid and Na
  - Electrolyze 3 moles of NaOH at regeneration plant.
  - No waste material is produced
- One pot system
  - Directly electrolyze NaBO2 to $NaBH_4$, process data needs to be developed.

For the base case, we assume 3 moles of NaOH are recycled during regeneration with one additional mole of Na generated "over the fence".

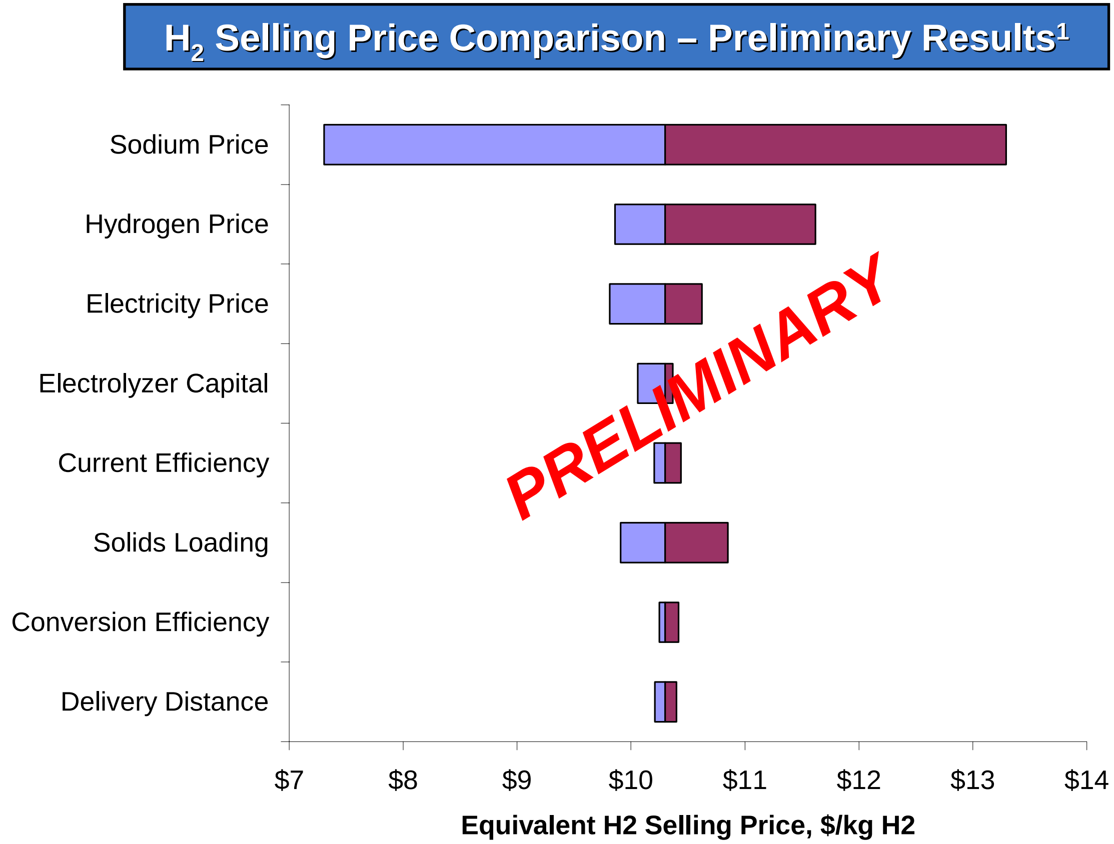


Preliminary results illustrate that SBH processing requires optimization, but potential delivery costs benefits exist.



[1] These results are based on natural gas steam reforming as the sources for the hydrogen. Production and delivery efficiency (LHV) assumptions include: steam reformer = 74%, pipeline power = 3 kWh/kg, liquefier power = 8.6 kWh/kg. Cost assumptions include: 100 km truck delivery from a central plant to the forecourt designed for 1500 kg/day H_2, SBH plant = 470 TPD (100 TPD H_2 equivalent), Hydrogen plant = 300 TPD.

The developed models were used to perform a sensitivity analysis for SBH in a slurry that illustrates large effects of sodium and hydrogen cost.



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For SBH to serve as a viable hydrogen delivery mechanism further development of the regeneration process is necessary to reduce cost.

- Hydrogen-assisted electrolysis of NaOH provides a lower cost and less power intensive approach for recovering Na
  - However, the process still requires make-up sodium, which is not inexpensive – we assumed this was delivered as pure sodium
- Future process advancements are necessary to reduce the continuous consumption of materials (Na, H_2SO_4) to reduce cost
  - Direct electrolysis of $NaBO_2$ would reduce Na cost, but will likely result in higher electricity requirements
- Molten salt electrolysis of NaOH is the key capital cost driver
  - We are still investigating the electrolyzer capital cost
  - Preliminary estimates are $62-665/kWe
- Currently, we have assumed the system must operate under warm (20°C) ambient conditions to avoid precipitation of $NaBO_2$
  - Adding water or heating the material can help prevent precipitation
  - Is some precipitation acceptable during delivery and forecourt storage?

TIAX has completed a number of tasks aimed at providing computational tools and the proper inputs for evaluating novel carriers.

- H2A spreadsheets have been modified to create tabs that evaluate the processing, storage, trucking and forecourt costs for novel carriers
- Capital/operating inputs have been provided for the trucking tab for various carriers
- Reprocessing capital costs, process description, and operating costs have been determined in detail for the following carriers:
  - NaBH4
- Tool has been developed to determine the material requirements and actual hydrogen yield for the following chemical hydrides:
  - NaBH4
  - MgH2
- Tool has been designed to calculate the additional weight and volumetric/gravimetric density penalties associated with the addition of a brick storage vessel
- Hydrogen yields have been determined for a number of novel carriers and presented in the trucking spreadsheet to illustrate the effects on transportation energy for the various carriers

Future work remains to clearly define the present state and future potential of the novel carriers defined by the project overview.

- To the extent possible, compare pathways using a constant “test” material to evaluate the pathway viability, independent of the material
- Determine whether materials will be best suited for use as on-board storage, off-board storage/delivery, or both
- Establish Base and Best cases for each of the viable material/pathway options
- Evaluate and compare cost, energy inputs, and GHG emissions for each option
- Review and discuss with Delivery team and industry representatives (ongoing iterative process)
- Fully integrate Carrier Analysis into H2A models

Thank You

- DOE
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- Colleagues at TIAX, Nexant, and NREL
- Audience