Chemical Hydrogen Storage Materials

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Hydrogen Storage Engineering
CENTER OF EXCELLENCE

U.S. Department of Energy
Energy Efficiency and Renewable Energy
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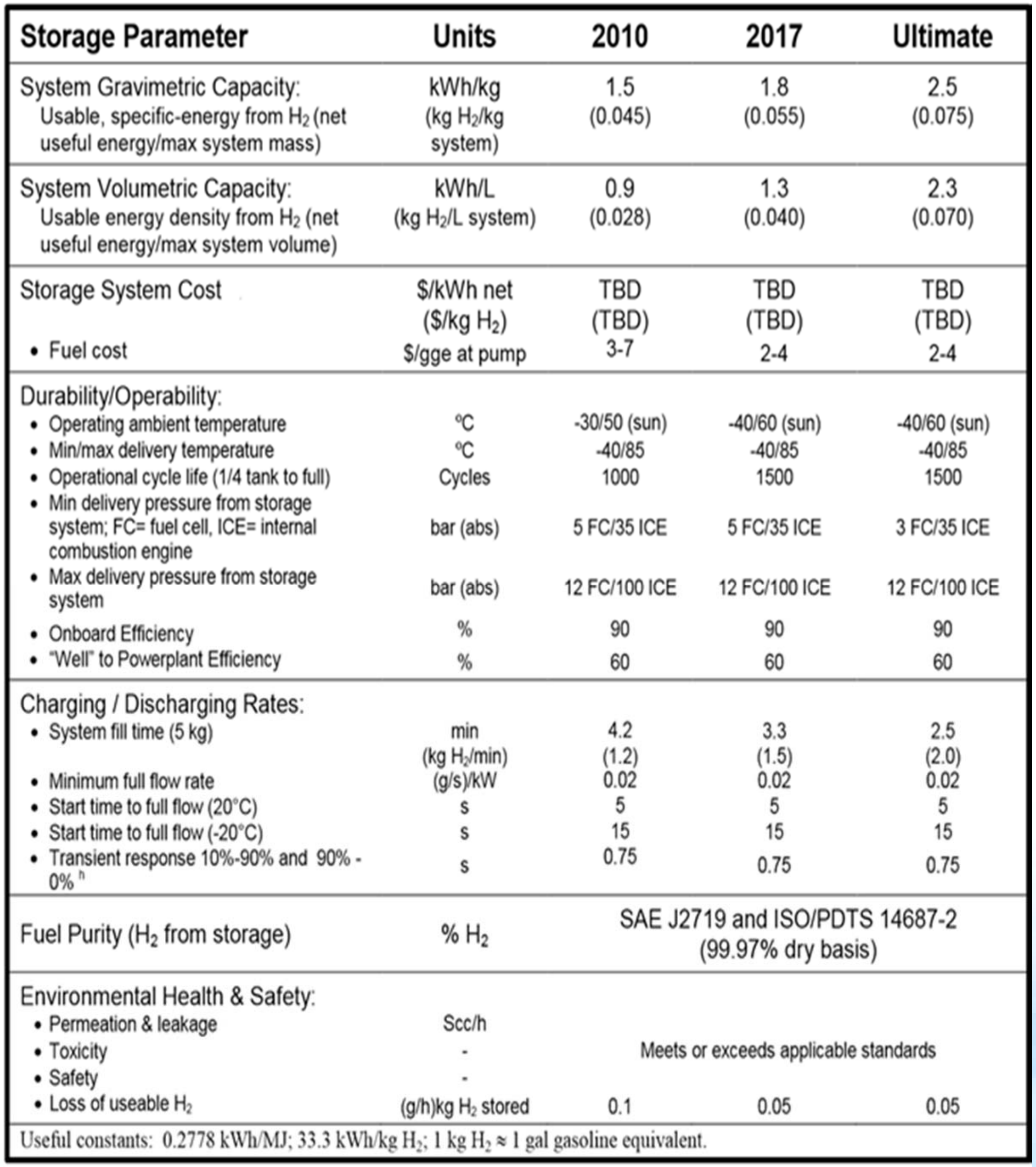
Objectives

1. Assess chemical hydrogen storage materials that can exceed 700 bar compressed hydrogen tanks
2. Status (state-of-the-art) of chemical hydrogen storage materials
3. Identify key material characteristics
4. Identify obstacles, challenges and risks for the successful deployment of chemical hydrogen materials in a practical on-board hydrogen storage and delivery system
5. Ask the hard questions

Presentation Caveats

- Presentation focused <u>solely</u> on the onboard storage of hydrogen for <u>light duty automotive applications</u>
- All DOE targets are equally weighted
- All DOE targets must be met concurrently
- Focused on the general class of chemical hydrogen storage materials



Storage Parameter	Units	2010	2017	Ultimate
System Gravimetric Capacity: Usable, specific-energy from H_2 (net useful energy/max system mass)	kWh/kg (kg H_2/kg system)	1.5 (0.045)	1.8 (0.055)	2.5 (0.075)
System Volumetric Capacity: Usable energy density from H_2 (net useful energy/max system volume)	kWh/L (kg H_2/L system)	0.9 (0.028)	1.3 (0.040)	2.3 (0.070)
Storage System Cost	\$/kWh net (\$/kg H_2)	TBD (TBD)	TBD (TBD)	TBD (TBD)
• Fuel cost	\$/gge at pump	3-7	2-4	2-4
Durability/Operability:				
• Operating ambient temperature	°C	-30/50 (sun)	-40/60 (sun)	-40/60 (sun)
• Min/max delivery temperature	°C	-40/85	-40/85	-40/85
• Operational cycle life (1/4 tank to full)	Cycles	1000	1500	1500
• Min delivery pressure from storage system; FC= fuel cell, ICE= internal combustion engine	bar (abs)	5 FC/35 ICE	5 FC/35 ICE	3 FC/35 ICE
• Max delivery pressure from storage system	bar (abs)	12 FC/100 ICE	12 FC/100 ICE	12 FC/100 ICE
• Onboard Efficiency	%	90	90	90
• "Well" to Powerplant Efficiency	%	60	60	60
Charging / Discharging Rates:				
• System fill time (5 kg)	min (kg H_2/min)	4.2 (1.2)	3.3 (1.5)	2.5 (2.0)
• Minimum full flow rate	(g/s)/kW	0.02	0.02	0.02
• Start time to full flow (20°C)	s	5	5	5
• Start time to full flow (-20°C)	s	15	15	15
• Transient response 10%-90% and 90% - 0% [h]	s	0.75	0.75	0.75
Fuel Purity (H_2 from storage)	% H_2	SAE J2719 and ISO/PDTS 14687-2 (99.97% dry basis)		
Environmental Health & Safety:				
• Permeation & leakage	Scc/h	Meets or exceeds applicable standards		
• Toxicity	-			
• Safety	-			
• Loss of useable H_2	(g/h)kg H_2 stored	0.1	0.05	0.05

Useful constants: 0.2778 kWh/MJ; 33.3 kWh/kg H_2; 1 kg H_2 ≈ 1 gal gasoline equivalent.

Introduction and Overview

Pre-Production Model Shown

7. How far can you drive on one fill-up in the Tucson Fuel Cell?

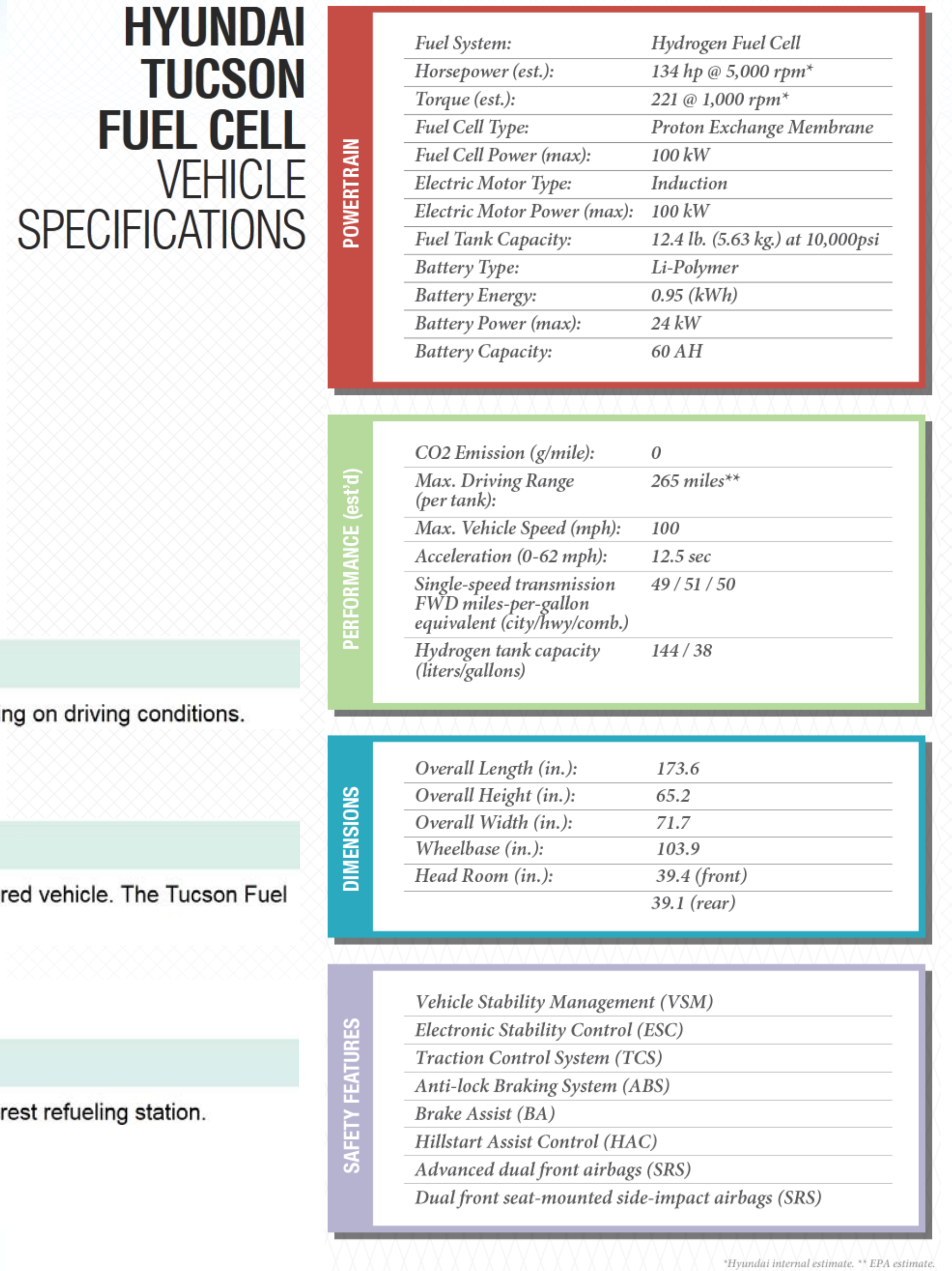
The Tucson Fuel Cell has an estimated driving range of 265 miles depending on driving conditions.

8. How long does it take to fill up the Tucson Fuel Cell?

Refueling with hydrogen is similar to refueling a conventional gasoline powered vehicle. The Tucson Fuel Cell is capable of refueling from empty in less than 10 minutes.

9. What happens if I run out of fuel in the Tucson Fuel Cell?

If the vehicle runs out of fuel, it will need to be towed on a flatbed to the nearest refueling station.



HYUNDAI TUCSON FUEL CELL VEHICLE SPECIFICATIONS

POWERTRAIN

Fuel System:	*Hydrogen Fuel Cell*
Horsepower (est.):	*134 hp @ 5,000 rpm**
Torque (est.):	*221 @ 1,000 rpm**
Fuel Cell Type:	*Proton Exchange Membrane*
Fuel Cell Power (max):	*100 kW*
Electric Motor Type:	*Induction*
Electric Motor Power (max):	*100 kW*
Fuel Tank Capacity:	*12.4 lb. (5.63 kg.) at 10,000psi*
Battery Type:	*Li-Polymer*
Battery Energy:	*0.95 (kWh)*
Battery Power (max):	*24 kW*
Battery Capacity:	*60 AH*

PERFORMANCE (est'd)

CO2 Emission (g/mile):	*0*
Max. Driving Range (per tank):	*265 miles***
Max. Vehicle Speed (mph):	*100*
Acceleration (0-62 mph):	*12.5 sec*
Single-speed transmission FWD miles-per-gallon equivalent (city/hwy/comb.)	*49 / 51 / 50*
Hydrogen tank capacity (liters/gallons)	*144 / 38*

DIMENSIONS

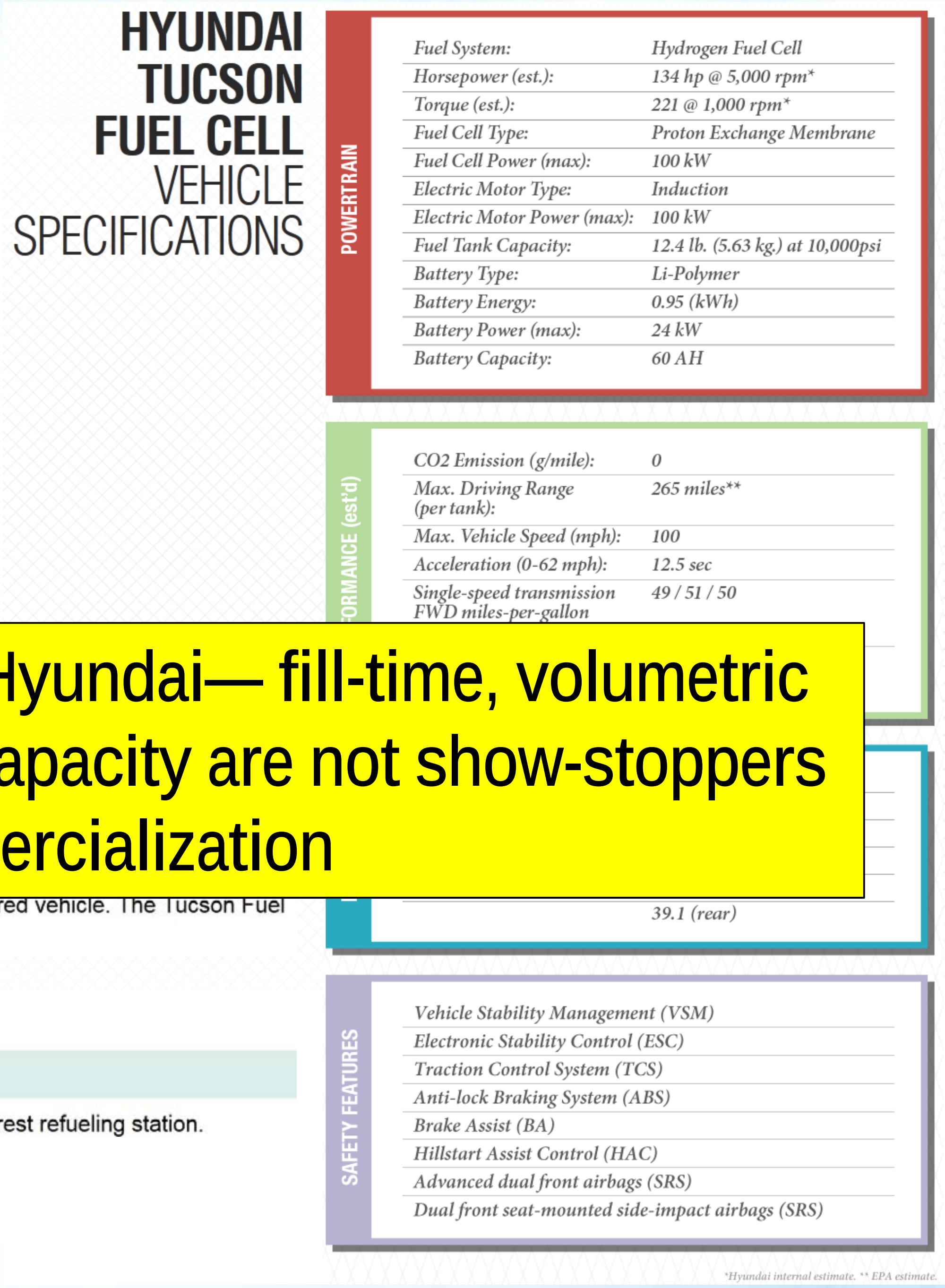
Overall Length (in.):	*173.6*
Overall Height (in.):	*65.2*
Overall Width (in.):	*71.7*
Wheelbase (in.):	*103.9*
Head Room (in.):	*39.4 (front)* *39.1 (rear)*

SAFETY FEATURES

- *Vehicle Stability Management (VSM)*
- *Electronic Stability Control (ESC)*
- *Traction Control System (TCS)*
- *Anti-lock Braking System (ABS)*
- *Brake Assist (BA)*
- *Hillstart Assist Control (HAC)*
- *Advanced dual front airbags (SRS)*
- *Dual front seat-mounted side-impact airbags (SRS)*

*Hyundai internal estimate. ** EPA estimate.

Introduction and Overview



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39.1 (rear)

SAFETY FEATURES

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**Hyundai internal estimate. ** EPA estimate.*

7.

8.

According to Toyota and Hyundai— fill-time, volumetric capacity and gravimetric capacity are not show-stoppers to commercialization

Refueling with hydrogen is similar to refueling a conventional gasoline powered vehicle. The Tucson Fuel Cell is capable of refueling from empty in less than 10 minutes.

9. What happens if I run out of fuel in the Tucson Fuel Cell?

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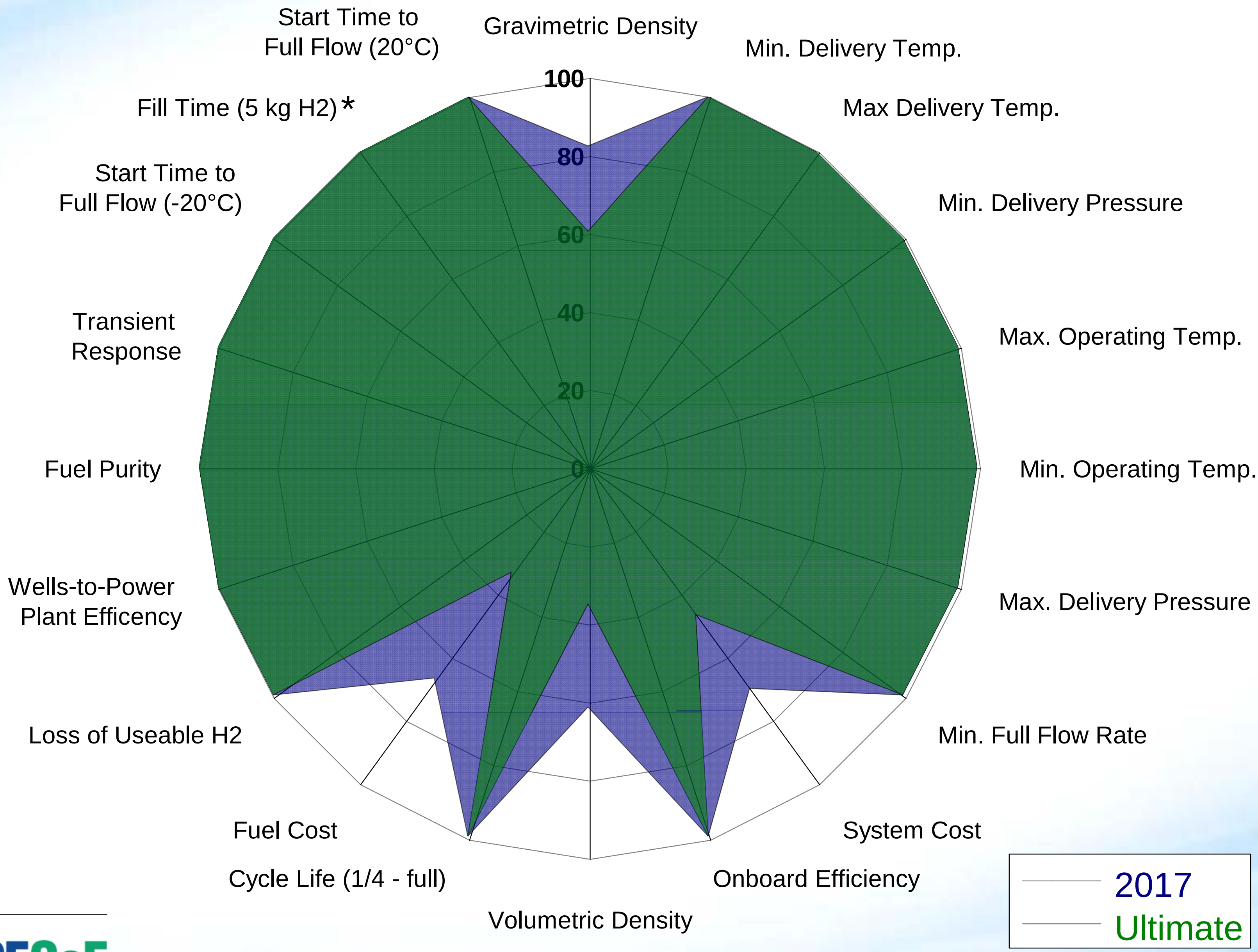
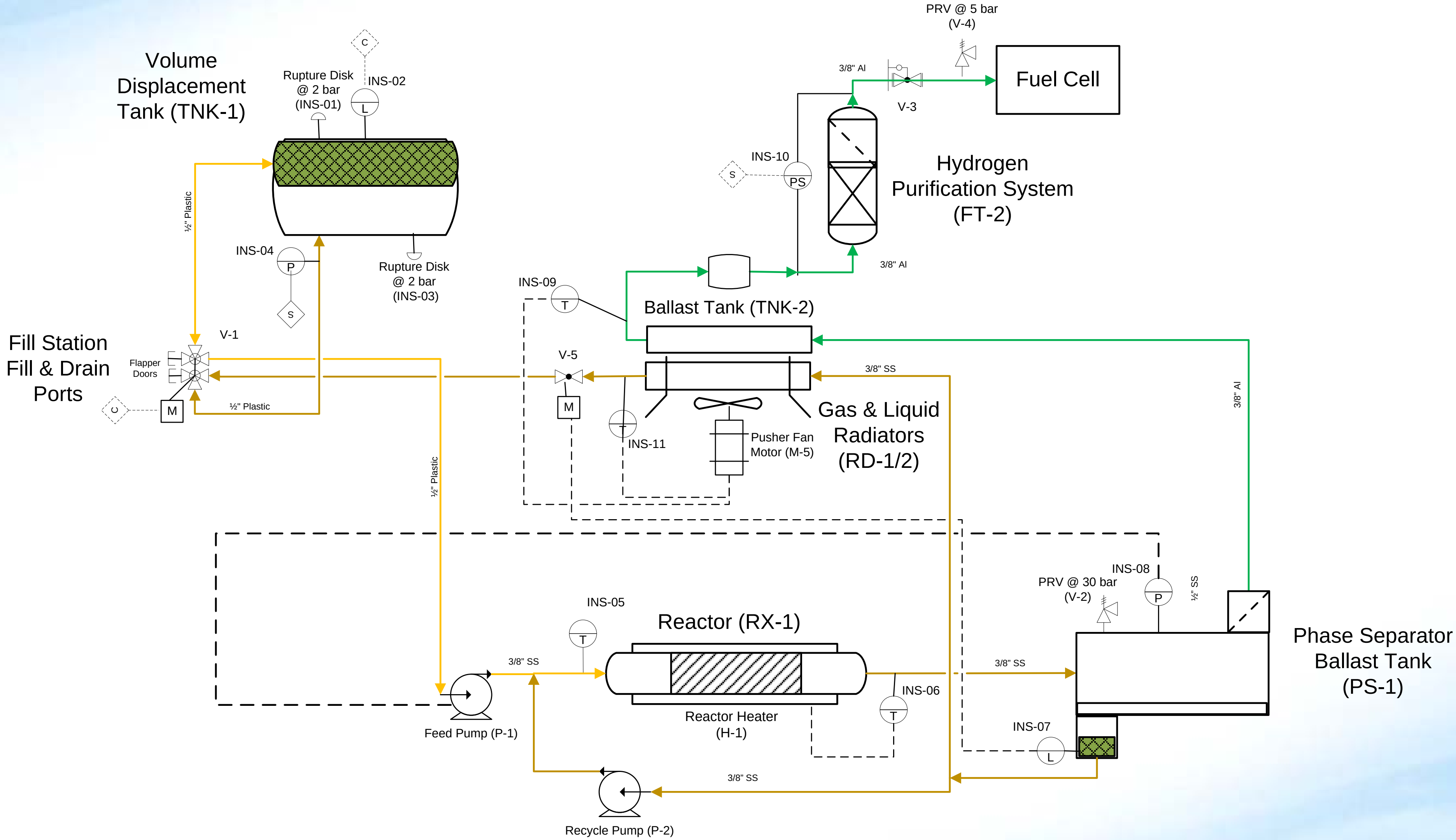
HSECoE

700 bar Compressed Hydrogen-*Commercialized Technology*



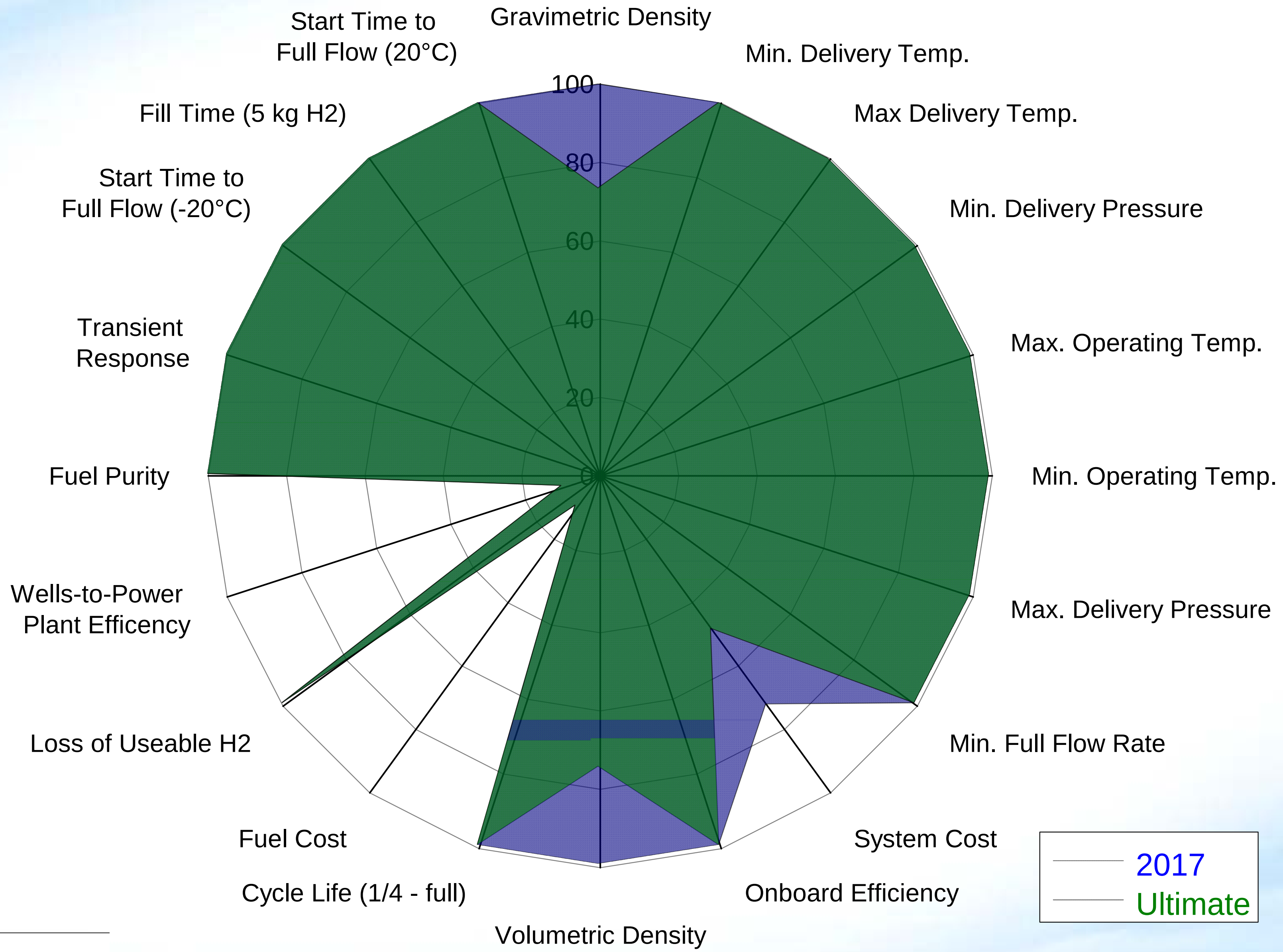
** Estimated fill times for Toyota FCHV ~ 5 min (5.8 kg H_2?), Hyundai Tucson ~ 10 min (5.8 kg H2)*

HSECoE Chemical Hydrogen Storage Baseline System



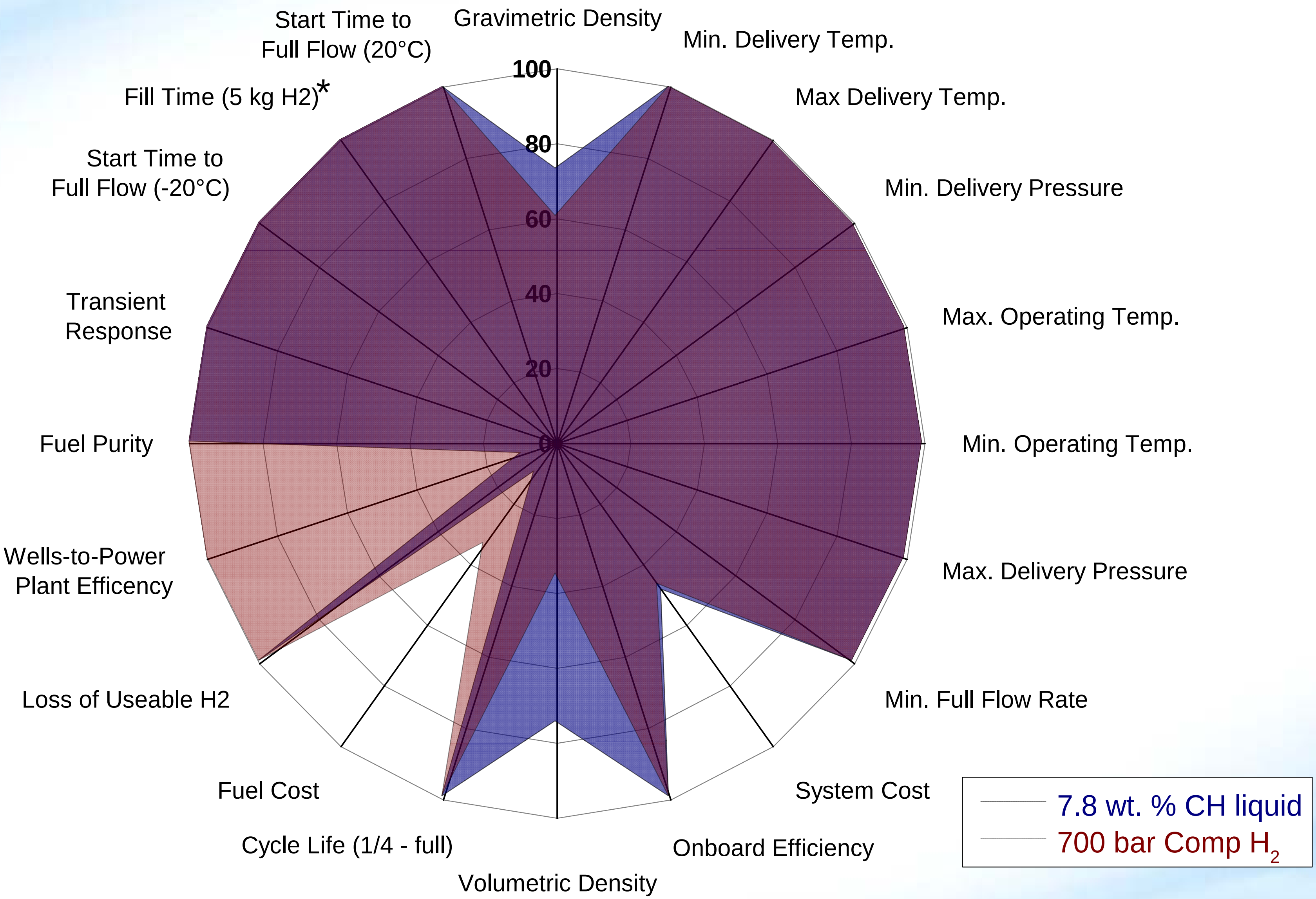
Baseline system developed for fluid-phase chemical hydrogen storage materials; neat liquids, non-settling homogeneous slurries, and solutions

7.8 wt. % Chemical Hydrogen Storage Material



ECoE estimates based on a neat liquid with 7.8 wt. % usable H2 and idealized system design of mass 30.6 kg and 35 L

700 bar H2 vs. 7.8 wt.% Chemical Hydrogen (ultimate targets)



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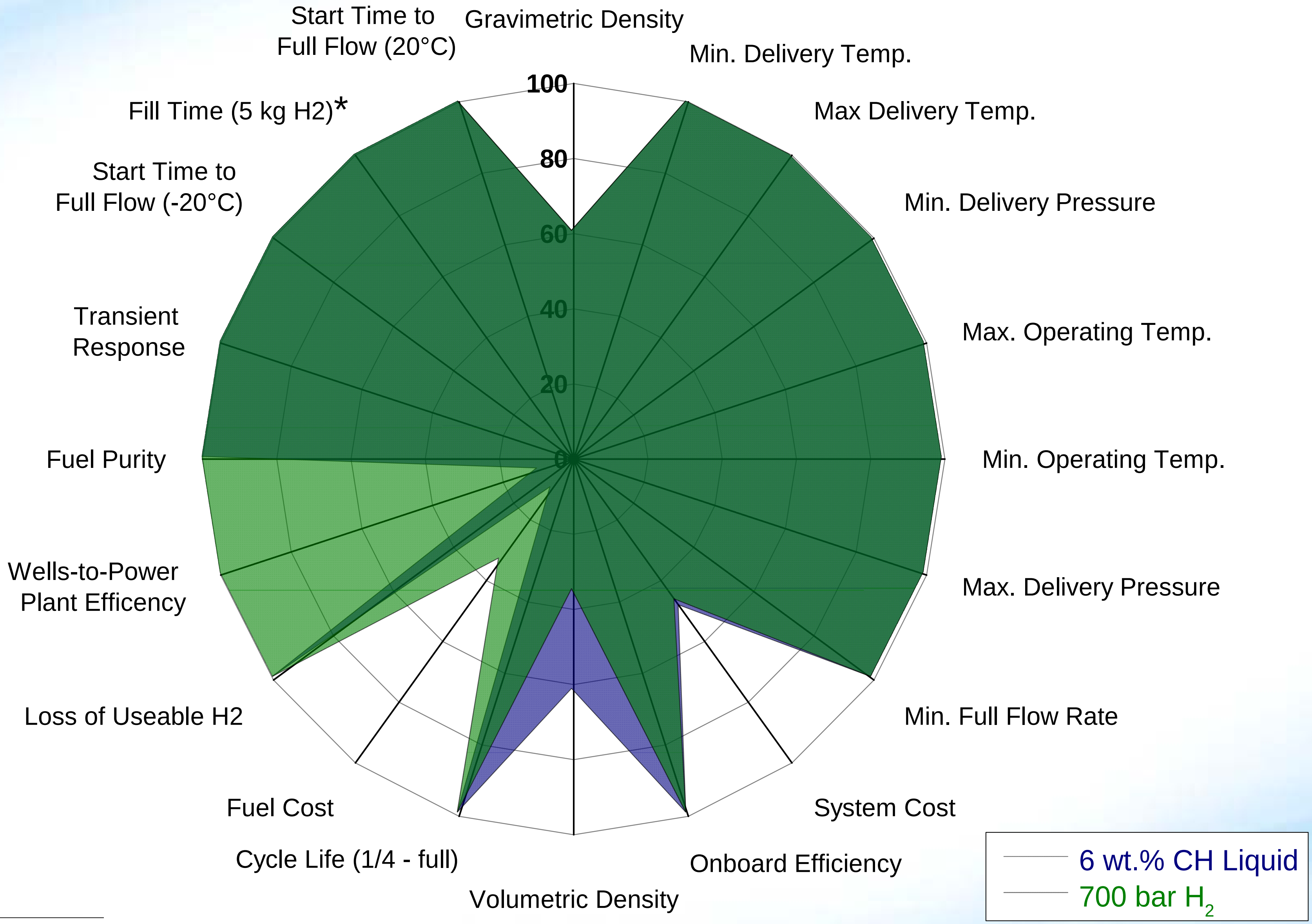
700 bar H2 vs. 6.0 wt. % Chemical Hydrogen (ultimate targets)



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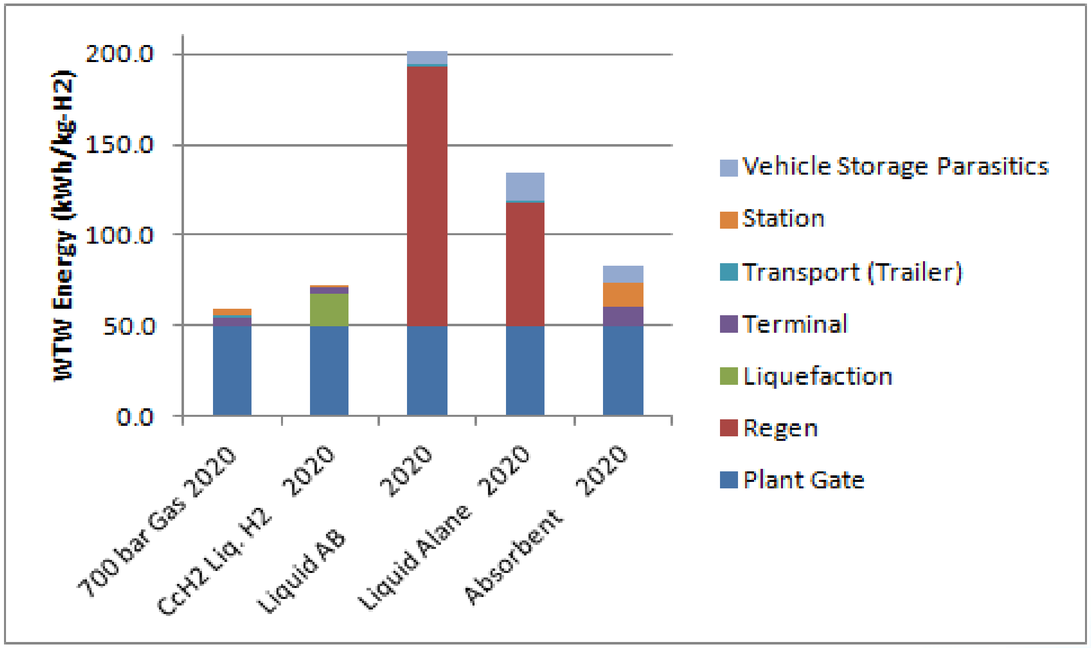
ECoE estimates based on a neat and idealized system design of mass 30.6 kg and 35 L

Well-to-Wheels Energy Breakdown

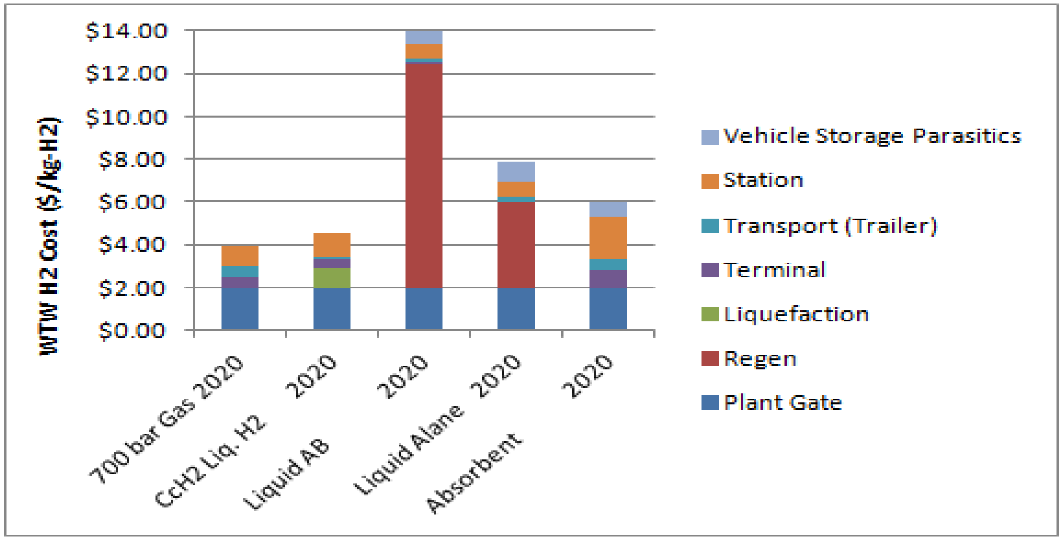
WTW Energy Breakdown kWh/kg-H2	700 bar Gas 2020	CcH2 Liq. H2 2020	Liquid AB 2020	Liquid Alane 2020	Absorbent 2020
Plant Gate	50.3	50.3	50.3	50.3	50.3
Regen	0.0	0.0	143.0	67.8	0.0
Liquefaction	0.0	17.5	0.0	0.0	0.0
Terminal	4.5	3.2	0.3	0.2	10.4
Transport (Trailer)	0.6	0.1	0.3	0.3	0.3
Station	3.6	0.6	0.0	0.0	13.0
Vehicle Storage Parasitics	0.0	0.0	8.1	16.2	9.5
Total	59.0	71.8	202.0	134.8	83.5



M. Paster, et. al. Liquid Carrier and Adsorbent Systems WTW Analyses for the HSECoE, February 2013

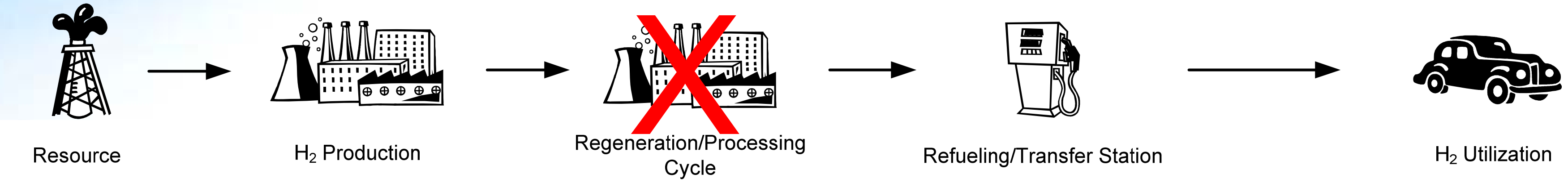
Well-to-Wheels Cost Breakdown

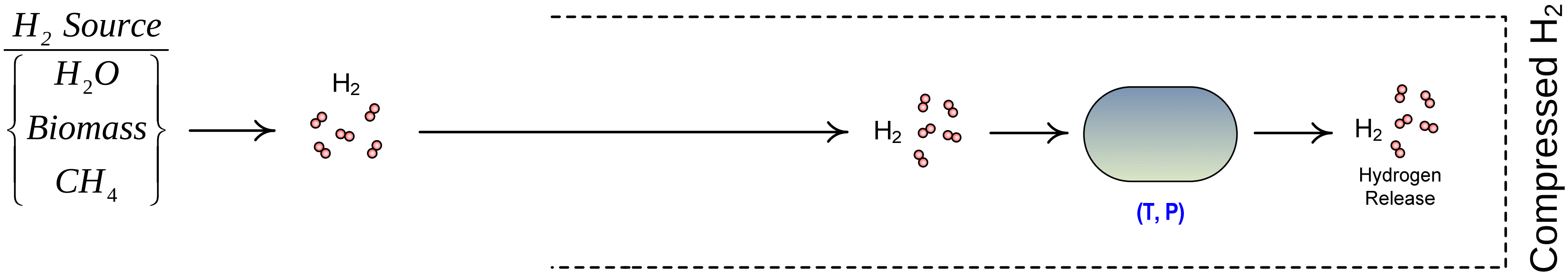
WTW Cost Breakdown	700 bar Gas 2020	CcH2 Liq. H2 2020	Liquid AB 2020	Liquid Alane 2020	Absorbent 2020
Plant Gate	$1.95	1.95	1.95	1.95	1.95
Regen	$0.00	$0.00	$10.46	$4.00	$0.00
Liquefaction	$0.00	$0.96	$0.00	$0.00	$0.00
Terminal	$0.52	$0.40	$0.08	$0.07	$0.84
Transport (Trailer)	$0.50	$0.12	$0.23	$0.24	$0.51
Station	$0.93	$1.07	$0.68	$0.68	$2.01
Vehicle Storage Parasitics	$0.00	$0.00	$0.56	$0.95	$0.68
Total	$3.91	$4.50	$13.96	$7.88	$6.00



M. Paster, et. al. Liquid Carrier and Adsorbent Systems WTW Analyses for the HSECoE, February 2013

Compressed Hydrogen Pathway

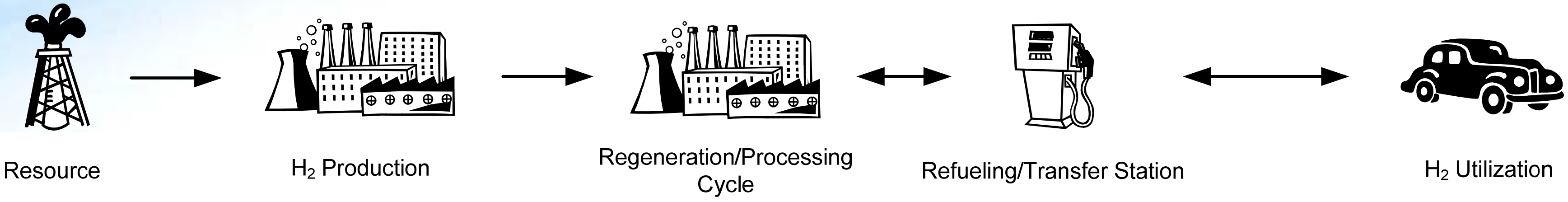


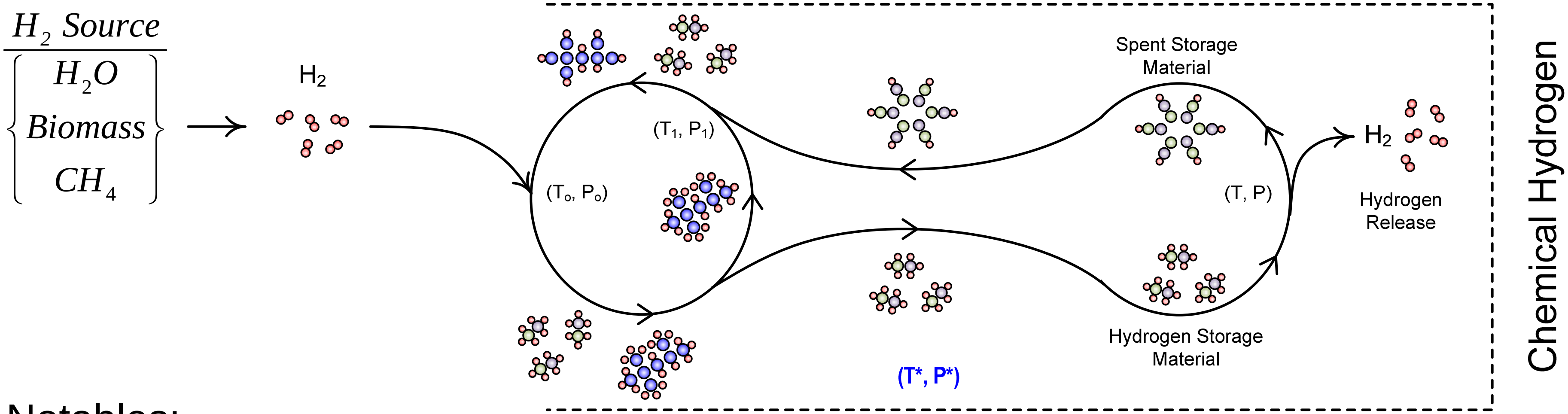


Notables:

- No regeneration schemes necessary
- Unidirectional processing pathway

Chemical Hydrogen Processing Pathway





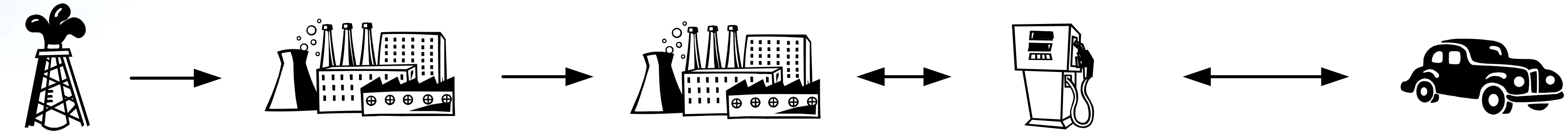
Notables:

- Bidirectional processing pathway
- Added complexity and processing steps

……energy consuming and costly

Chemical Hydrogen Processing Pathway

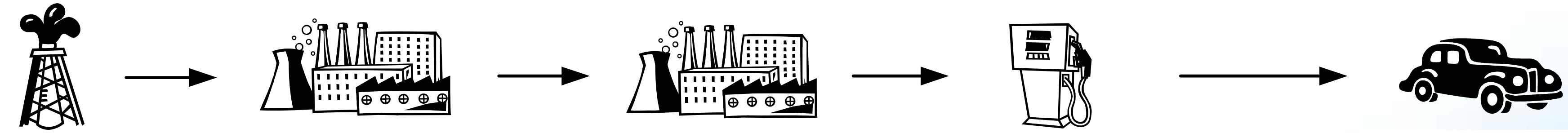
¿Bidirectional processing pathway?



Resource → H_2 Production → Regeneration/Processing Cycle ↔ Refueling/Transfer Station ↔ H_2 Utilization

OR

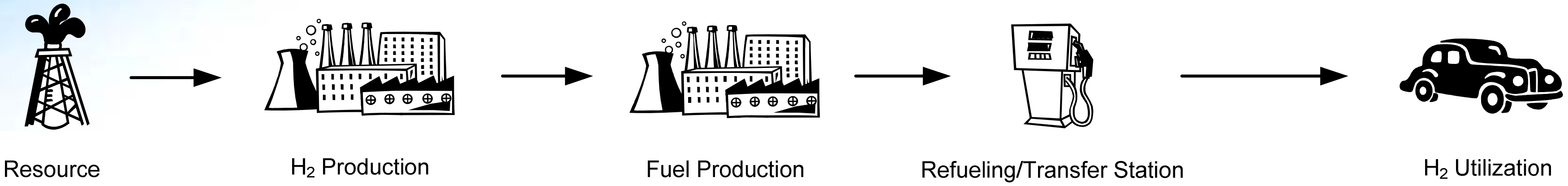
¿Unidirectional?



Resource → H_2 Production → Fuel Production → Refueling/Transfer Station → H_2 Utilization

Chemical Hydrogen Processing Pathway

¿Unidirectional?



Resource

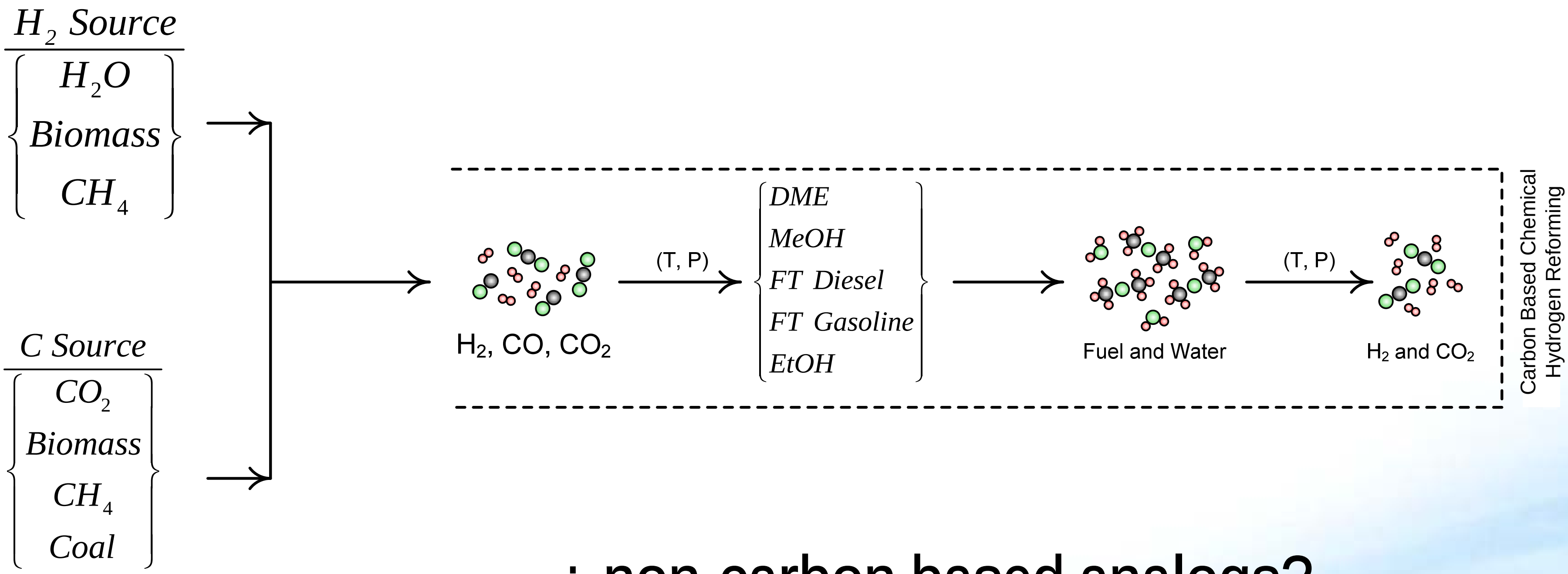
H_2 Production

Fuel Production

Refueling/Transfer Station

H_2 Utilization

……. *for example*



H_2 Source

H_2O

Biomass

CH_4

C Source

CO_2

Biomass

CH_4

Coal

H_2, CO, CO_2

(T, P)

DME

MeOH

FT Diesel

FT Gasoline

EtOH

Fuel and Water

(T, P)

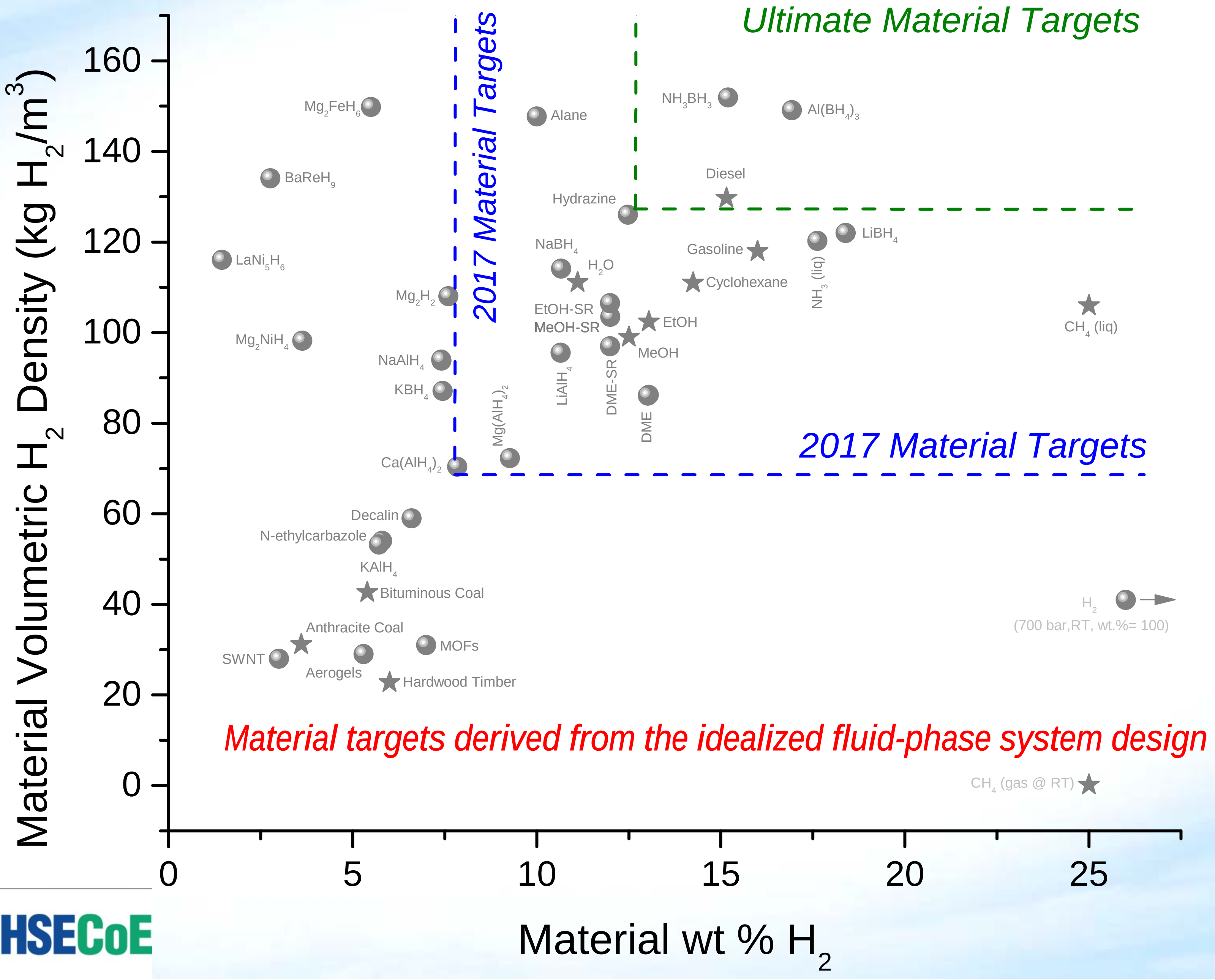
H_2 and CO_2

Carbon Based Chemical Hydrogen Reforming

¿ non-carbon based analogs?

Chemical Hydrogen Status

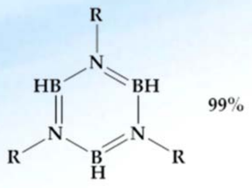
★ *Values denote maximum theoretical wt. % H_2 (i.e., all hydrogen removed)*



Material targets derived from the idealized fluid-phase system design

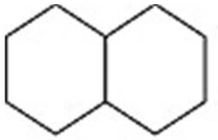
HSECoE

Chemical Hydrogen Materials



R = hexyl, methoxypropyl

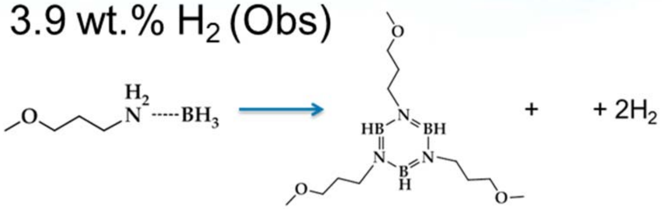
R = hexyl: 2.1 wt.% H_2 (Obs)
R = methoxypropyl: 3.9 wt.% H_2 (Obs)

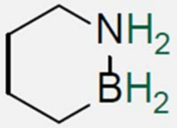


decalin

7.2 wt. H_2 (Obs)
mpt: -43 °C
MW: 138

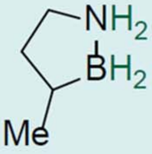
3.9 wt.% H_2 (Obs)





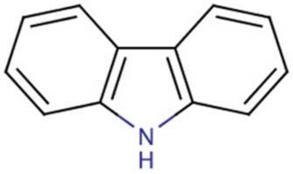
Mw = 85

9.4 wt% (Theor)
47 g H_2/L
d: 1.00 g/mL
mp: 75 °C

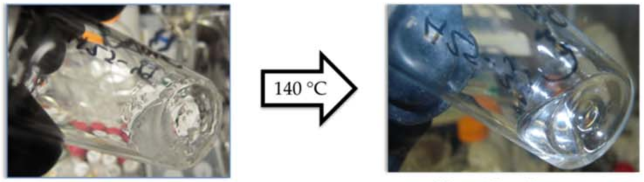


Mw = 85

4.7 wt% H_2 (Obs)
42 g H_2/L
d: 0.89 g/mL
viscosity: 25 cP
mp: −18 °C
ΔH(exp) = −9.1



6.7 wt. H_2 (Obs)
mpt: 246 °C
MW: 167



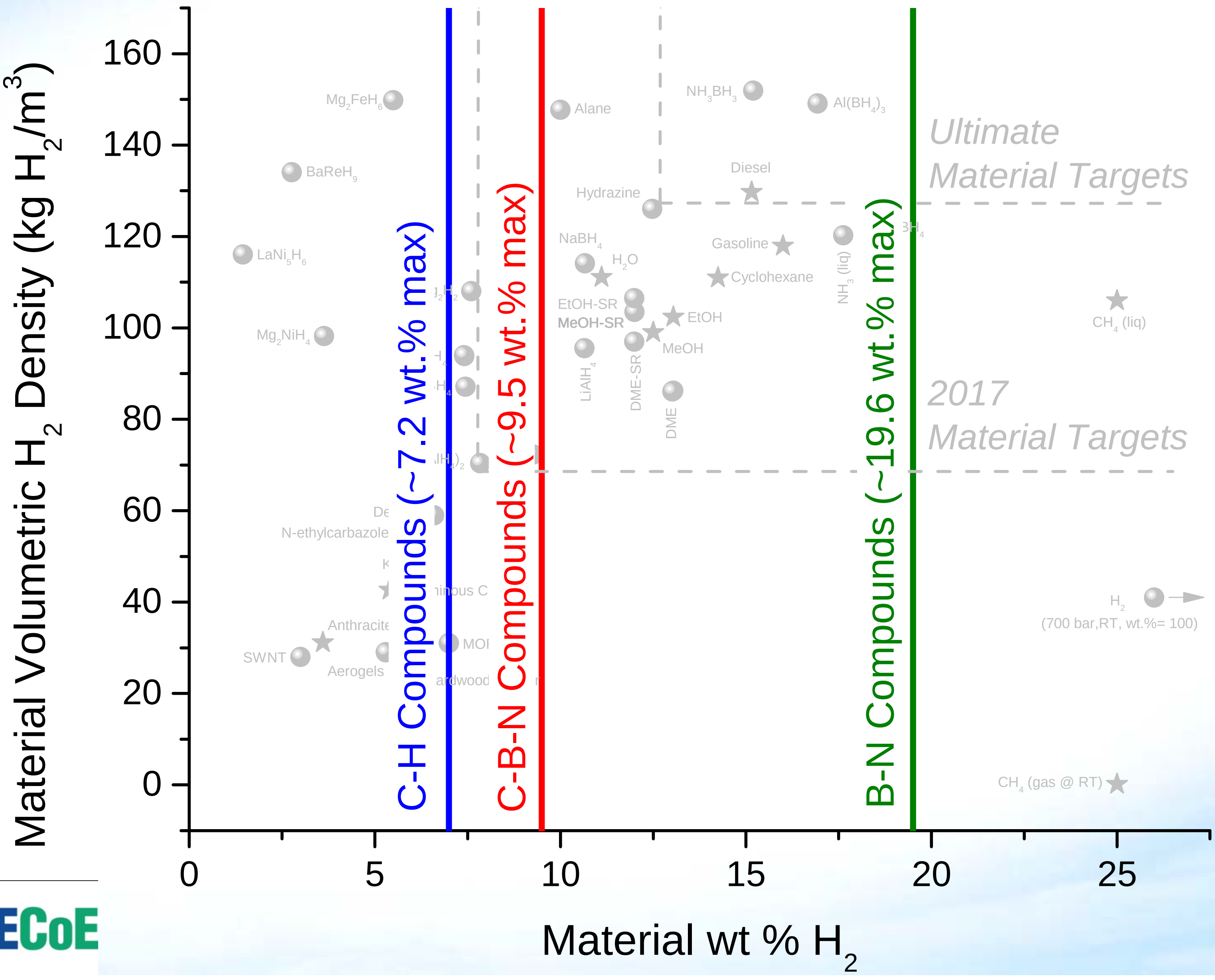
Picture @ Room Temperature

20 wt. AB/Hexyl AB
6.0 wt.% H_2 (Obs)

Chemical hydrogen storage materials have the highest potential in meeting the gravimetric and volumetric targets, but thermodynamics and kinetics are preventing their realization

State-of-the-Art

C-H Compounds: reversible conjugated diene systems (7.2 wt. % theoretical, 7.2 wt. % observed)
C-B-N Compounds: reversible CBN backbones (9.5 wt. % theoretical, ~4.5 wt. % observed)
B-N Compounds: 19.6 wt.% theoretical, ~15.5 wt. % observed)
★ *Values denote maximum theoretical wt. % H_2 (i.e., all hydrogen removed)*
Material targets derived from the idealized fluid-phase system design



Notable Shortcomings-*in general*

Chemical Hydrogen

- Dehydrogenation kinetics
- Shelf-life
- Phase or phase change
- Vapor pressure
- Gravimetric capacity
- Regeneration efficiencies
- Fuel cost
- Noble metal catalysis
- Impurities
- Durability and operability

700 bar Hydrogen

- Gravimetric capacity
- Volumetric capacity
- Fill time
- High pressure

Key Material Properties

- Neat liquids with >7.8 wt. % H_2
  - Solid, slurry or solution phase compositions are highly improbable

    …….*if not impossible*

- Maintaining fluid phase through dehydrogenation
- Very low/negligible vapor pressure (e.g., ionic liquids)
- Suitable dehydrogenation kinetics with high conversions
  - fast kinetics (> 0.4 moles H_2/s, T = 125-200°C)
  - high hydrogen selectivities ($S_{H2} > 0.997$)
  - extended shelf-life greater than 60 days @ 60°C, X < 7.2%)
- Melting points: $T_{mpt} < -40°C$
- Energy efficient regeneration routes (WTPP > 66.6%)

  …….*likely to be less efficient than compressed hydrogen*

- Fuel cost

  …….*likely to cost more than hydrogen*

- *Fuel Cell Impurities (i.e., reaction selectivity)*
  - *recycle vs. replenish*

HSECoE

Summary: Material Property Guidelines

Parameter	Symbol	Units	Range*	Assumptions
Minimum Material capacity (liquids)	γ_{mat}	$g_{H2} / g_{material}$	~ 0.078	• System mass (excludes media) = 30.6 kg (36.3 kg) • 5.6 kg of H_2 stored • Liquid media (neat) • Media density = 1.0 g/mL
Minimum Material capacity (solutions)	γ_{mat}	$g_{H2} / g_{material}$	~ 0.098	• System mass (excludes media) = 30.6 kg (36.3 kg) • Solute mass fraction = 0.35 ~ 0.80 • Solution density = 1.0 g/mL
Minimum Material capacity (slurries)	γ_{mat}	$g_{H2} / g_{material}$	~ 0.112	• System mass (excludes media) = 30.6 kg (36.3 kg) • Non-settling homogeneous slurry • Slurry mass fraction = 0.35 ~ 0.70 • Slurry volume fraction = 0 ~ 0.5 • Slurry density = 1.0 g/mL
Kinetics: Activation Energy	E_a	kcal / mol	28–36	• $V_{reactor} \leq 4$ L • Shelf life ≥ 60 days • Reaction order, n = 0 – 1
Kinetics: Preexponential Factor	A		$4 \times 10^9 – 1 \times 10^{16}$	
Endothermic Heat of Reaction	ΔH_{rxn}	kJ / mol H_2	$\Delta H_{rxn} \leq +17$	• On-board Efficiency = 90% • # Cold Startups = 4 • ΔT = 150 °C with no heat recovery • neat liquid (Cp = 1.6 J/g K) • Reactor mass = 2.5 kg SS (5.0 kg SS)
Exothermic Heat of Reaction	ΔH_{rxn}	kJ / mol H_2	$\Delta H_{rxn} \geq -27$	• T_{max} = 250°C • Recycle ratio @ 50%
Maximum Reactor Outlet Temperature	T_{outlet}	°C	250	• Liquid Radiator = 2.08 kg • Gas Radiator = 0.3 kg • Ballast Tank = 2.6 kg
Impurities Concentration	y_i	ppm	No *a priori* estimates can be quantified	• $m_{adsorbent} \leq 3.2$ kg
Media H_2 Density	$(\gamma_{mat})(\phi_m)(\rho_{mat})$	kg H_2 / L	≥ 0.07	• HD polyethylene tank ≤ 6.2 kg
Regen Efficiency	η_{regen}	%	≥ 66.6%	• On-board Efficiency = 90% • WTPP efficiency = 60%
Viscosity	η	cP	≤ 1500	None

** (a) parameter values are based on a specific system design and component performance with fixed masses and volumes (b) values outside these ranges do not imply that a material is not capable of meeting the system performance targets (c) the material property ranges are subject to change as new or alternate technologies and/or new system designs are developed (d) the minimum material capacities are subject to change as the density of the composition changes due to reductions in the mass and volume of the storage tank or reductions in system mass are realized material values correlate to the idealized system design (i.e., system mass = 30.6 kg, excludes media and tank mass)*

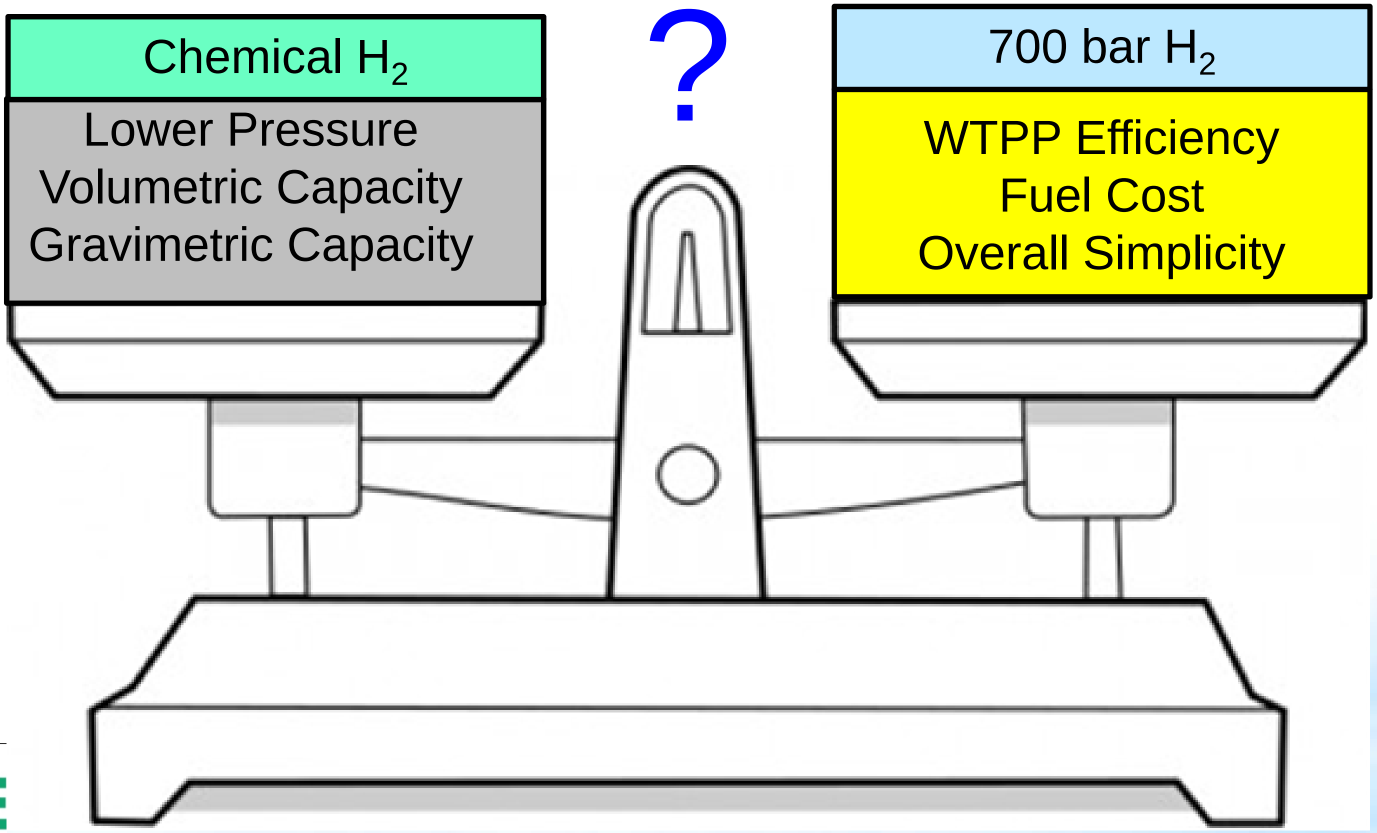
The Tough Questions

- Assuming an ideal chemical hydrogen material with all of the required material properties, is that enough to supplant compressed hydrogen?
- Can chemical hydrogen storage materials ever be as efficient or better than hydrogen production?
- Can chemical hydrogen storage materials be cost competitive with hydrogen?
- What efficiency and cost are needed to favor chemical hydrogen over compressed hydrogen?

Notable Shortcomings-*in general*

¿ What are the ultimate advantages of chemical hydrogen storage materials over 700 bar compressed hydrogen?

- Lower Pressure
- Volumetric Capacity
- Gravimetric Capacity



Chemical H_2

Lower Pressure
Volumetric Capacity
Gravimetric Capacity

?

700 bar H_2

WTPP Efficiency
Fuel Cost
Overall Simplicity

Acknowledgements

Fuel Cell Technologies Office

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Disclaimer

- The material properties detailed in this presentation were prepared in order to provide general guidance for chemical hydrogen storage researchers and therefore should not be taken as rigid constraints.

- The presented material properties were developed within the constraints of our system design, component sizing, assumptions, and system operating conditions. In addition, the ranges in material properties are not specific to a particular material, and therefore can be applied to the general class of chemical hydrogen storage media.

- Material property values just outside the material ranges presented do not imply that a material is not capable of meeting the system performance targets, but rather that the material will require further examination.

- The material property ranges are subject to change as new technologies and/or new system designs are developed.

- The minimum material capacities are subject to change if the density of the composition changes because of reductions in the mass and volume of the storage tank.

- Material properties that fall within the presented material properties do not establish commercial viability or commercial success.