Chemical Hydrogen Storage Material Property Guidelines for Automotive Applications

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Abstract

Chemical hydrogen storage is the sought after hydrogen storage media for automotive applications because of the expected low pressure operation (< 20 atm), moderate temperature operation ($< 200^{\circ}\text{C}$), system gravimetric capacities (> 0.05 kg H_2 /kg_{system}), and system volumetric capacities (> 0.05 kg H_2 /L_{system}). Currently, the primary shortcomings of chemical hydrogen storage are regeneration efficiency, fuel cost and fuel phase (i.e., solid or slurry phase). Understanding the required material properties to meet the DOE Technical Targets for Onboard Hydrogen Storage Systems is a critical knowledge gap in the hydrogen storage research community. This study presents a set of fluid-phase chemical hydrogen storage material property guidelines for automotive applications meeting the 2017 DOE technical targets. Viable material properties were determined using a boiler-plate automotive system design. The fluid-phase chemical hydrogen storage media considered in this study were neat liquids, solutions, and non-settling homogeneous slurries. Material properties examined include kinetics, heats of reaction, fuel-cell impurities, gravimetric and volumetric hydrogen storage capacities, and regeneration efficiency. The material properties, although not exhaustive, are an essential first step in identifying viable chemical hydrogen storage material properties—and most important, their implications on system mass, system volume and system performance.

Keywords: chemical hydrogen storage, fuel cells, hydrogen, material properties, chemical hydrides

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1.0 Introduction

An integrated fuel cell power system for automotive application is a topic that has continued interest because of its potential for increasing fuel efficiency. The primary drivers for the development and commercialization of integrated fuel cell power systems for automotive applications are both political and environmental. Political issues include the need to remove or relax the US's dependence on foreign oil which is accomplished by increasing efficiency, while environmental issues include reduction in vehicle emissions such as pollutants and greenhouse gases.

Hydrogen fuel cells for automotive applications offer unprecedented vehicle efficiencies around 60%. The shortcoming of hydrogen is the ability to store 5.6 kilograms of hydrogen on an automotive platform while meeting all the DOE technical targets.[1, 2] Liquid hydrogen offers increased volumetric capacities but requires storage temperatures around 20 K.[1, 2] For the cases of liquid hydrogen and cryo-compressed hydrogen, dormancy issues, gravimetric capacities and volumetric capacities are the critical challenges in storing neat hydrogen for automotive applications. In an attempt to remove the limitations imposed by the gravimetric and volumetric storage capacities of neat hydrogen, three material-based approaches to hydrogen storage are being researched; namely, adsorbents[3, 4], metal hydrides[5-13], and chemical hydrogen storage[14-17]. The successful commercialization of on-board hydrogen storage for light duty vehicles require that all of the DOE targets for on-board hydrogen storage systems for light-duty vehicles be met simultaneously. Unfortunately, the DOE targets are system targets, not material targets; thus, creating a knowledge gap in viable hydrogen storage material properties suitable for automotive applications.

The objective of this study was to develop a set of fluid-phase chemical hydrogen storage material property guidelines for automotive applications meeting the 2017 DOE technical targets. The fluid-phase chemical hydrogen storage media considered in this study were neat liquids, solutions, and non-settling homogeneous slurries. The fluid-phase material property guidelines are expected to aid material researchers in their materials development and/or discovery efforts. Until now, the materials researchers relied on system level targets to guide their materials research. Consequently, providing the materials research community with a viable set of chemical hydrogen storage materials properties fills a critical knowledge gap. Although the quantified set of material properties is not exhaustive, it is a necessary first step.

2.0 DOE 2017 System Targets

The Department of Energy has set forth system level targets for on-board hydrogen storage systems for light duty vehicles.[18] The technical system targets for on-board hydrogen storage system for light duty applications can be seen in Table 1. DOE targets for on-board hydrogen storage systems for light-duty vehicles.[18] The 2017 system level targets were used as design constraints for quantifying the material properties presented in this study.

3.0 Methodology

The methodology used for the determination of viable chemical hydrogen storage material properties is shown Figure 1. The ammonia borane system design developed by the Hydrogen Storage Engineering Center of Excellence was used as the boilerplate system design. The boilerplate system is presumed to contain the necessary components that will be common to all realizable fluid-phase chemical hydrogen storage media. Components of the ammonia borane system were identified as system

independent (*e.g.*, *fuel cost*), balance-of-plant (BOP)/material independent components (*e.g.*, *valves and pumps*), and material dependent components (MDC; *e.g.*, *reactor*). The term component is used loosely to not only represent physical components, but also quantities such as on-board efficiency, and regeneration efficiency.

System independent components are components invariant to the system design and *vice-versa*—examples include fuel cost and regeneration efficiency. Material independent components (referred to as balance-of-plant, BOP) include pumps, sensors, valves, tubing, etc. Because the BOP components were presumed to be material independent, the BOP components were grouped and treated as a constant with respect to mass, volume, durability, and operability. Material dependent components (MDC) are the components whose mass and volume are reliant upon the material properties, kinetics, and thermodynamics of the chemical hydrogen storage media. Material dependent components of interest are: reactor, heat exchanger, volume displacement tank, and hydrogen purification. To calculate viable material properties, the masses and volumes of the material dependent components were sized independent of the material. Given the *a priori* sizing of the MDC components and the BOP sizing, the minimum gravimetric and volumetric hydrogen capacities for slurries, solutions and neat liquids were calculated that would meet the DOE 2017 gravimetric and volumetric system targets (Table 1). *A priori* sizing of the MDC components permitted the calculation of material properties (*e.g.*, kinetics and heat of reaction) that meet the mass and volume estimates of the material dependent components (*vida infra*).

3.1 System design

The generalized chemical hydrogen storage automotive system design used for this study is represented in Figure 2. The automotive system design captures the essential unit operations and ancillary components required for the storage, production, and delivery of fuel-cell grade hydrogen generated from fluid-phase chemical hydrogen storage media. Two system design cases are presented in this study. Case 1 is the baseline case where the system design includes the envisaged system components necessary for automotive applications. The second case, Case 2, is an idealized case that has a lower system mass and system volume. The lower system mass and system volume for the idealized case stems from the fact that the hydrogen purification component was eliminated and the dehydrogenation reactor was reduced by 50%. Eliminating the hydrogen purification component assumes the gas-phase reaction selectivity for hydrogen is one (*i.e.*, *hydrogen is the only gas phase reaction product*) and the vapor pressure of the liquid hydrogen storage media is negligible. The idealized case can be viewed as the lower bound with respect to system mass and system volume—correlating to a lower bound on the required hydrogen storage media capacity to meet the 2017 DOE technical targets. The system masses and volumes assumed for both the baseline and idealized systems can be seen in Table 2. Component masses and volumes assumed for this study will be detailed in later sections.

3.1.1 System components

The overall system mass and volume are the primary drivers that dictate the necessary gravimetric and volumetric capacities of the hydrogen storage media to meet the DOE 2017 system technical targets. Based on the DOE 2017 system gravimetric target of 0.055 kg H₂ / kg_{system} and a hydrogen storage mass of 5.6 kg H₂, the total system mass cannot exceed 102 kg. The system mass is the sum of all masses of the system components and hydrogen storage media required to store and delivery fuel-cell grade hydrogen (Equation 1). Mathematically this can be written as

Equation 1

$$(M_{total})_{system}^{2017} = \sum_i m_i \leq 102 \text{ kg}$$

$i = \text{valves, pumps, reactor, media, gas-liquid separator, ...}$

The system components were grouped according to material independent, material dependent, and system independent components. Material independent components were assumed to be independent of material properties. In other words, the material independent components were sized based on operating conditions (*e.g., pressure, flow rates, and temperatures*), not material properties. Consequently, the masses and volumes of the material independent components were fixed for this analysis. Examples of material independent components include (but not limited to) filters, valves, sensors, regulators, and tubing. The material independent components are referred to as balance-of-plant components or BOP components. The total BOP component mass was fixed at 21.8 kg for all analyses. Mathematically the mass of BOP components is represented by Equation 2.

Equation 2

$$m_{BOP} = \sum_j (m_{BOP})_j = 21.6 \text{ kg}$$

$j = \text{valves, sensors, tubing, regulators, .}$

The material independent components are assumed to be invariant to the chemical hydrogen storage material and thus relevant to all chemical hydrogen storage system designs. The material dependent components are components that are material property dependent. Material properties such as thermodynamics and kinetics dictate the sizing of these components. Consequently, the material independent components are the critical components responsible for quantifying viable material properties necessary to meet the 2017 DOE technical targets. Typically, the engineering methodology is to design and size systems around known material properties and operating conditions. However, for this analysis the methodology is reversed. This analysis “reverse” engineers or quantifies the material properties necessary to meet the 2017 DOE technical targets using fixed component masses and volumes. *A priori* estimates of the masses and volumes for the material dependent components (*e.g., reactor*) are required to quantify the material properties that satisfy the *a priori* estimate of mass and volume. The material dependent components requiring *a priori* estimates are the dehydrogenation reactor, hydrogen purification, volume displacement tank (VDT) and heat exchangers. Similarly, the mass of the material dependent components (MDC) can be written as (Equation 3)

Equation 3

$$m_{MDC} = \sum_k (m_{MDC})_k$$

$k = \text{reactor, } H_2 \text{ purification, VDT, HX, .}$

The only system mass contribution not accounted for is the media mass. Accounting for the media mass, the governing system mass equation (Equation 4) can be written as

Equation 4

$$(M_{total})_{system}^{2017} = \sum_j (m_{BOP})_j + \sum_k (m_{MDC})_k + m_{media}$$

$j = \text{valves, sensors, tubing, regulators,}$

$k = \text{reactor, } H_2 \text{ purification, VDT, HX,}$

Solving for the media mass in Equation 4 and substituting the DOE 2017 total system mass of 102 kg results in the general equation (Equation 5) used to calculate the available media mass to meet the DOE 2017 technical targets.

Equation 5

$$m_{media} \leq 102 \text{ kg} - \left(\sum_j (m_{BOP})_j + \sum_k (m_{MDC})_k \right)$$

$j = \text{valves, sensors, tubing, regulators,}$

$k = \text{reactor, } H_2 \text{ purification, VDT, HX,}$

For our analyses, the total BOP mass was held constant at 21.6 kg. Using Equation 5 and the on-board storage of 5.6 kg of net usable hydrogen, the required hydrogen storage gravimetric capacity to meet the 2017 DOE technical target can be calculated using Equation 6.

Equation 6

$$\gamma_{media} \left[\frac{\text{kg } H_2}{\text{kg media}} \right] \geq \frac{(5.6 \text{ kg } H_2)_{net \text{ usable}}}{102 \text{ kg} - \left(\sum_j (m_{BOP})_j + \sum_k (m_{MDC})_k \right)}$$

$j = \text{valves, sensors, tubing, regulators,}$

$k = \text{reactor, } H_2 \text{ purification, VDT, HX,}$

Equation 6 is the governing equation for calculating the required hydrogen storage gravimetric capacity for a given system design (*i.e.*, *system component masses*). The *a priori* mass estimates and the associated material properties required to meet the mass estimates for the material dependent components are discussed in later sections. A similar approach was taken to account for the volume contributions of the system components and hydrogen storage media. Using the DOE 2017 technical targets for the system volumetric capacity (0.04 kg H₂/ L system) and the on-board storage of 5.6 kg of net usable hydrogen, the maximum total system volume (including media volume) is calculated using Equation 7.

Equation 7

$$(V_{total})_{system}^{2017} = \sum_i v_i \leq 140 \text{ L}$$

$i = \text{valves, pumps, reactor, media, gas-liquid separator,}$

In grouping the volume contributions of the material independent components, material dependent components, and the hydrogen storage media, the governing equations for the available media volume and the required media hydrogen storage density meeting the DOE 2017 technical targets are Equation 8 and Equation 9, respectively;

Equation 8

$$v_{media} \leq 140 L - \left(\sum_j (v_{BOP})_j + \sum_k (v_{MDC})_k \right)$$

$j = \text{valves, sensors, tubing, regulators,}$

$k = \text{reactor, } H_2 \text{ purification, VDT, HX,}$

and,

Equation 9

$$\phi_{media} \left[\frac{kg H_2}{L media} \right] \geq \frac{(5.6 kg H_2)_{net usable}}{140 L - \left(\sum_j (v_{BOP})_j + \sum_k (v_{MDC})_k \right)}$$

$j = \text{valves, sensors, tubing, regulators,}$

$k = \text{reactor, } H_2 \text{ purification, VDT, HX,}$

Where ϕ_{media} is the media hydrogen storage density (also referred to as the media volumetric storage capacity) and has the units of kilograms of net usable hydrogen per liter of media. The total volume of the BOP components was held constant at 8.9 L for all analyses. As expected, the volume contributions of system components are dictated by density. For a hydrogen storage media density as low as 0.75 g/mL, the system volumetric capacity target of 0.040 kg H_2 /L_{system} is achievable. In fact, in meeting the DOE 2017 gravimetric target, the chemical hydrogen storage system has in excess of 30 liters of unused system volume. In short, the chemical hydrogen storage system is not constrained by volume, but mass. The burden of meeting the DOE 2017 system gravimetric target resides in the media hydrogen storage capacity. Given the system component masses and volumes, Equation 6 and Equation 9 are the governing equations that were used to back out the necessary gravimetric and volumetric capacities of the chemical hydrogen storage media.

System independent components (or material properties) are independent of the system. Examples of system independent components include fuel cost, shelf-life, and regeneration efficiency. The system independent components do not impact the mass or volume of the system; however, they do impact the overall commercializability of the hydrogen storage media for automotive applications. In addition, the system independent components do not necessitate *a priori* mass or volume estimates for their quantification.

3.1.2 Materials Considered

This study only considers fluid phase chemical hydrogen storage media in the form of neat liquids, solutions, and non-settling homogeneous slurries. The chemical hydrogen storage media in

solution form was assumed to be a binary mixture of a solute and a solvent. The solute is the hydrogen bearing phase, while the solvent is a non-hydrogen bearing diluent used for dissolution (*e.g., ammonia borane dissolved in tetraglyme*). The slurry form was assumed to be a binary mixture of a hydrogen-bearing solid phase dispersed in a non-hydrogen bearing liquid matrix (*e.g., alane mixed with diethylene glycol dibutyl ether*). The neat liquids were assumed to only contain a hydrogen bearing liquid with no diluents. Throughout the text, the terms “media” and “material” are often used. The terms “media” and “material” are used to differentiate properties associated with the composition, to those of the material. The term “media” refers to the final fuel composition that includes both the hydrogen bearing and non-hydrogen bearing components. The term “material” refers to the hydrogen bearing component. For chemical hydrogen storage materials in the solution phase, “media” refers to the solution; while the term “material” refers to the solute (*i.e., the hydrogen bearing component*). For slurries, the term media refers to the overall slurry composition and the term “material” refers to the hydrogen bearing solid phase. The term “neat liquid” refers to a single component composition consisting of a hydrogen bearing component only. For the case of neat liquids, the terms “media” and “material” are used interchangeably.

4.0 Fluid-Phase Chemical Hydrogen Storage Material Capacities

The DOE system level volumetric and gravimetric storage capacities dictate the overall mass and volume of the system. The system volumetric capacity is defined as the net usable hydrogen mass per volume of system ($\text{kg H}_2 / \text{L system}$). The system gravimetric capacity is defined as the net usable hydrogen mass per mass of system ($\text{kg H}_2 / \text{kg system}$). The mass of net usable hydrogen stored on-board was taken to be 5.6 kg. To calculate the required gravimetric storage capacities of the chemical hydrogen storage media using Equations 6, the mass of the system hardware and the DOE 2017 system mass (102 kg) are all that are required. Similarly, to calculate the required volumetric storage capacities of the chemical hydrogen storage media using Equations 9, the volume of the system hardware and the DOE 2017 system volume (140 L) are needed. The system hardware includes all necessary system components (*i.e., BOP and MDC*) excluding the chemical hydrogen storage media.

4.1 Volumetric Capacity

The volume of the chemical hydrogen storage system is the sum of the volume contributions of the system hardware and the media. The system hardware is the grouping of the BOP and the MDC components. The media volume is a function of media density, material hydrogen storage capacity, and the loading mass fraction. The loading mass fraction for solutions and slurries is equivalent to the solute mass fraction and the slurry mass fraction, respectively. The loading mass fraction for neat liquids is identically one. Given a maximum DOE system volume of 140 L and 5.6 kg of stored net-usable hydrogen, the general equation used to calculate the maximum allowable system hardware volume as a function of material hydrogen capacity (γ_{material} , $\text{kg H}_2/\text{kg}_{\text{material}}$), loading mass fraction (χ , $\text{kg}_{\text{material}}/\text{kg}_{\text{composition}}$) and media density (ρ_{media} , $\text{kg}_{\text{media}}/\text{L}_{\text{media}}$) is shown in Equation 10.

Equation 10

$$V_{\text{system hardware}} \leq 140 - \left[\left(\frac{5.6 \text{ kg H}_2}{\gamma_{\text{material}} \chi} \right) \left(\frac{1}{\rho_{\text{media}}} \right) \right]$$

The term in brackets is the media volume. Equation 10 is system independent and can be used as a general tool to determine the maximum allowable system hardware mass for a given material capacity,

loading mass fraction and media density while meeting the DOE 2017 volumetric target of 140 L. For example, given a material hydrogen capacity of 0.10 kg H₂/kg_{material}, a loading mass fraction of 0.6 kg_{material}/kg_{composition}, and a media density of 1.0 g/mL, the maximum available system hardware volume meeting the DOE target is 47 L.

Figure 3a-c illustrates the graphical results of Equation 10 as a function of material capacity (0-0.25 kg H₂/kg_{material}), and loading mass fractions (0.0-1.0 kg_{material}/kg_{composition}) for given media densities of 0.5, 1.0, 1.5 g/mL. The surface plots represent the maximum system hardware volumes that satisfy the DOE volumetric system target of 140 L. Gaseous hydrogen storage stored over a wide range of storage temperatures and pressures. The only constraint for storing gaseous hydrogen is that the hydrogen density must be greater than 0.04 kilograms of hydrogen per liter of system (i.e., 5.6 kg H₂ / 140 L_{system}). The ordered pair of temperature and pressure satisfying the minimum constraint of 0.04 kg H₂/L_{system} can be mathematically written as Equation 11:

Equation 11

$$\left(\frac{T}{P}\right)_{Storage} > 0.05 \text{ L/mol } H_2 \left(\frac{1}{R Z_{P,T}}\right)$$

The constant 0.05 liters per mole of hydrogen is the hydrogen molecular weight (2 x 10⁻³ kg/mol) divided by the minimum hydrogen storage density (0.04 kg H₂ / L). For reference the maximum allowable system hardware for cryo-compressed normal gaseous hydrogen as a function of system pressure (bar) and temperature (K) is shown in Figure 3d. The volume of gaseous hydrogen was calculated using REFPROP 9.0 compressibility factors. At 80 K and 200 bar the volume of 5.6 kg of hydrogen is 117 L, resulting in a maximum allowable system hardware volume of 23 L. Cryo-compressed hydrogen storage is attractive because of the lower storage pressure option. Gaseous hydrogen storage represents the lower limit considered for chemical hydrogen storage media density (i.e., 0.04 kg H₂/L_{system}).

Fluid phase chemical hydrogen storage media will have media densities far exceeding those of gaseous hydrogen. Comparing Figure 3(a-c) shows that increasing the media density (resulting in a lower media volume) correlates to an increase of the available system hardware volume for BOP and MDC components. Increasing the media density also expands the range of viable material capacities and loading mass fractions that will meet the DOE 2017 volumetric system target. For example, given a material capacity of 0.1 kg H₂/kg_{material}, a loading fraction of 0.5 kg_{material}/kg_{media}, and media density of 1.5 g/mL, the media volume is calculated to be 75 L which results in a maximum system hardware volume of 65 L. Using the same capacity and loading mass fraction, but with a media density of 0.5 g/mL, the calculated media volume is 224 L (84 L greater than the volumetric target). Media volumes greater than 140 L to store 5.6 kg of hydrogen will never meet the DOE 2017 volumetric system target. Media volumes exceeding 140 L occur in the region bounded by the surface and the x and y axes for a system hardware volume of 0 L. The locus of points where the media volume equals 140 L (i.e., available system hardware volume = 0 L) is the intersection of the xy plane (z = 0) and the surface plot. Because all hydrogen storage systems will require some system hardware volume, media volumes greater than or equal to 140 L will make it impossible for a system to meet the DOE 2017 volumetric system target. The expected media densities of fluid-phase chemical hydrogen storage media will likely be greater than 1

g/mL. This study assumes a media density of 1.0 g/mL for all fluid-phase compositions (neat liquids, slurries, and solutions) when calculating media volumes for the overall system volume. *Note: for a given material capacity and loading fraction, an increase in media density does not add to the overall system mass because the material capacities and loading fractions are normalized on a mass basis.*

For our baseline and idealized cases the volumes of the system hardware are 41.1 L and 35.1 L, respectively. Assuming a media density of 1.0 g/mL for the baseline and idealized cases, there is a large range in viable material capacities (0.05–0.25 kg_{material}/kg_{media}) and loading mass fractions (0.2–1 kg_{material}/kg_{media}) while still meeting the 2017 DOE volumetric system target. Mentioned previously, the fluid-phase chemical hydrogen storage system is not volume constrained, but mass constrained—this is expected for most (if not all) on-board hydrogen storage systems employing chemical hydrogen storage media. Because chemical hydrogen storage systems are mass constrained, viable material capacities and loading mass fractions will be derived from the plots of system hardware mass (*vida infra*).

4.2 Gravimetric Capacity

The mass of the chemical hydrogen storage system is the sum of the mass contributions of the system hardware and the media. The system hardware is the grouping of the BOP and the MDC components. The media mass is a function of media density, material hydrogen storage capacity, and the loading mass fraction. The loading mass fraction for solutions and slurries is equivalent to the solute mass fraction and the slurry mass fraction, respectively. The loading mass fraction for neat liquids is identically one. Given a maximum DOE system mass of 102 kg and 5.6 kg of stored net-usable hydrogen, the general equation used to calculate the maximum allowable system hardware mass as a function of material hydrogen capacity (γ_{material} , kg H₂/kg_{material}), and loading mass fraction (χ , kg_{material}/kg_{composition}) is shown in Equation 12.

Equation 12

$$M_{\text{system hardware}} \leq 102 - \left(\frac{5.6 \text{ kg } H_2}{\gamma_{\text{material}} \chi} \right)$$

The term in parentheses is the media mass. Equation 12 is system independent and can be used as a general tool to determine the maximum allowable system hardware mass for a given material capacity, and loading mass fraction while meeting the DOE 2017 volumetric target of 102 kg. For example, given a material hydrogen capacity of 0.10 kg H₂/kg_{material}, and a loading mass fraction of 0.6 kg_{material}/kg_{composition}, the maximum available system hardware mass is 8.7 kg. Figure 4 graphically illustrates the functional dependence of the system hardware mass on material capacity (kg H₂/kg_{material}) and loading mass fraction (kg_{material}/kg_{composition}).

The region bounded by the surface plot and the x and y axes for a system hardware mass of zero represent media masses that exceed the system target of 102 kg; thus, not meeting the DOE 2017 gravimetric target. The locus of points where the media mass equals 102 kg (*i.e.*, *available system hardware mass* = 0 kg) is the intersection of the xy plane ($z = 0$) and the surface plot. The three regions for media mass can be written mathematically as

$$\text{if } (\gamma_{\text{material}} \chi) \text{ is } \begin{cases} < 0.055 \Rightarrow m_{\text{media}} > 102 \text{ kg} \\ = 0.055 \Rightarrow m_{\text{media}} = 102 \text{ kg} \\ > 0.055 \Rightarrow m_{\text{media}} < 102 \text{ kg} \end{cases}.$$

The region of interest is where the product of the material gravimetric capacity and the loading mass fraction is greater than 0.055 [*i.e.*, $(\gamma_{\text{material}} \chi) > 0.055$]. Because all hydrogen storage systems will require some system hardware mass, media masses greater than or equal to 102 kg will pose difficulties for systems to meet the DOE 2017 gravimetric system target.

Figure 4 can be used as a general guide to determine the required system hardware mass for any class of hydrogen storage media (*i.e.*, *adsorbents, metal hydrides and chemical hydrogen storage*), given the material capacity and loading mass fraction. In this study we are assuming a system hardware mass to calculate the necessary material gravimetric capacities to meet the DOE 2017 gravimetric system target. The necessary material gravimetric capacities depend on the type of fluid-phase media considered (*e.g.*, *neat liquids, solutions, slurries*). The general case (Equation 12, Figure 4), was used as the basis for quantifying the necessary gravimetric capacities for neat liquids, solutions, and slurries to meet the DOE 2017 gravimetric system target.

4.3 Liquids

Chemical hydrogen storage media in the form of a neat liquid is the sought after media form for off-board regenerable processes. For this study, neat liquids were assumed to remain in the liquid phase under all operating conditions and processes—this includes the dehydrogenated fuel. The vapor pressures of the hydrogenated and dehydrogenated fuel forms were assumed negligible; thus requiring no additional components (*i.e.*, *mass and volume*) to address any vapor pressure implications. The equation for the system hardware mass for neat liquids is derived from Equation 12 by setting the loading mass fraction equal to one (Equation 13). Equation 13 represents the maximum system hardware mass to store 5.6 kg of net usable hydrogen as a function material capacity for neat liquids that meet the DOE 2017 gravimetric system target (102 kg).

Equation 13

$$M_{\text{system hardware}} \leq 102 - \left(\frac{5.6 \text{ kg } H_2}{\gamma_{\text{material}}} \right)$$

Figure 5 is the graphical representation of Equation 13. There are salient features of Figure 5 that are worth noting. The region shaded in red denotes gravimetric capacities (0–0.055 kg H₂ / kg_{media}) that will never meet the DOE 2017 gravimetric system target because the media masses alone are greater than the gravimetric system target of 102 kg. The grey line denotes the curve where the media mass equals the system hardware mass. Data lying to the left of the grey line indicates a system that is media heavy (*i.e.*, *the media mass is greater than the system hardware mass*) and data lying to the right indicates a system that is system hardware heavy (*i.e.*, *the system hardware mass is greater than the media mass*). The blue shaded region is the region containing viable material capacities that meet the DOE 2017 gravimetric system target; the boundary of this region is composed of the data where the sum of the media mass and the system hardware mass equal the DOE 2017 gravimetric target of 102 kg. Data lying within the

interior of the blue shaded region are composed of the data where the sum of the media mass and the system hardware mass is less than the DOE 2017 gravimetric system target of 102 kg.

The region of interest is the boundary of the blue shaded region because this will result in the lower bound of the required material capacity. The lower bound of the material capacity is a function of the system hardware mass. The assumed system hardware masses for the baseline and idealized system designs are 36.3 kg and 30.6 kg, respectively. A system hardware mass of 36.3 kg (baseline system) correlates to a minimum required material capacity of 0.085 kg H₂ / kg_{media} (denoted as the solid green line in Figure 5) for chemical hydrogen storage materials in the form of neat liquids. A system hardware mass of 30.6 kg (idealized system) correlates to a minimum required material capacity of 0.078 kg H₂ / kg_{media} (denoted as the dashed green line in Figure 5) for chemical hydrogen storage materials in the form of neat liquids. As expected, reducing the system hardware mass translates to a lowering of the materials capacities required to meet the DOE 2017 gravimetric system targets.

4.4 Slurries

Chemical hydrogen storage media in the form of slurries is assumed to be a two component mixture of a hydrogen-bearing solid phase dispersed in a non-hydrogen bearing liquid matrix. The slurry was assumed to be homogeneous and non-settling. Slurries of the settling type are heterogeneous mixtures that require active mixing to produce a pseudo-homogeneous mixture for processing. Chemical hydrogen storage media in the form of settling slurries will require additional hardware components (*i.e., mixers, impellers, motors, etc.*) that are not included in our baseline or idealized system designs. Properly accounting for the added hardware components for settling slurries requires additional information on the specific slurry of interest. Consequently, settling slurries are beyond the scope of this study. However, any additional hardware required for settling slurries would add to the overall system mass; thus, necessitating a decrease in mass of the other components or an increase in the media gravimetric capacity to maintain the 2017 gravimetric system target of 102 kg.

The slurry mass to store 5.6 kg of net usable hydrogen is a function of material capacity (*i.e., hydrogen-bearing solid phase*) and the loading mass fraction. The loading mass fraction for slurries is referred to as the slurry mass fraction (denoted as $\phi_{slurry,m}$) and is defined as the ratio of the mass of hydrogen-bearing solids to the total mass of slurry composition. Equally important is the slurry volume fraction (denoted as $\phi_{slurry,v}$) and is defined as the ratio of the volume of hydrogen-bearing solids to the total volume of slurry composition. The slurry volume fraction was introduced to determine a realistic upper bound for the slurry mass fraction. As will be shown, the lower bound is dictated by the maximum expected gravimetric capacity of the material. The upper bound of the slurry mass fraction was used to back-out the minimum material gravimetric capacities for slurries meeting the DOE 2017 system gravimetric target. The slurry mass fraction is related to the slurry volume fraction by Equation 14.

Equation 14

$$\phi_{slurry,m} = \frac{1}{1 + \left(\frac{\rho_{solid}}{\rho_{liquid}} \right) \left(\frac{1}{\phi_{slurry,v}} \right) - \left(\frac{\rho_{solid}}{\rho_{liquid}} \right)}$$

Figure 6 is the graphical representation of Equation 14. When the density of the solid equals the density of the liquid carrier, Equation 14 reduces to $\phi_{\text{slurry},m} = \phi_{\text{slurry},v}$ (denoted as the solid green line in Figure 6). When the density of the solid is less than the density of the liquid carrier, the slurry mass fraction is greater than the slurry volume fraction (i.e., $\phi_{\text{slurry},m} > \phi_{\text{slurry},v}$, denoted as the upper bound in Figure 6). When the density of the solid is greater than the density of the liquid carrier, the slurry mass fraction is less than the slurry volume fraction (i.e., $\phi_{\text{slurry},m} < \phi_{\text{slurry},v}$, denoted as the lower bound in Figure 6). The upper bound was generated using a density ratio equal to two (i.e., $\rho_{\text{solid}}/\rho_{\text{liquid}} = 2$), while the lower bound was generated using a density ratio of 0.5 (i.e., $\rho_{\text{solid}}/\rho_{\text{liquid}} = 0.5$). For the purposes of this study, the upper bound of the slurry mass fraction was determined by imposing a maximum slurry volume fraction constraint of 0.5 (indicated by the vertical dashed line in Figure 6). A slurry volume fraction of 0.5 indicates that the volume of solid is equal to volume of liquid. If slurries are proven to be a viable option for hydrogen storage, then the rheological characteristics will ultimately determine the volume fraction—and hence mass fraction. The upper bound of the slurry mass fraction for a maximum slurry volume fraction of 0.5 and a density ratio of two was determined to be around 0.65.

The bounds on the slurry mass fraction (0.35-0.70) were used to determine viable gravimetric capacities of the hydrogen-bearing solids of the slurry composition for an idealized system hardware mass of 30.6 kg and a baseline system hardware mass of 36.3 kg (Figure 7). The dashed line in Figure 7, is the locus of points in the x-y plane given an idealized system hardware mass of 30.6 kg (refer to Figure 4). The solid line represents the locus of points for a baseline system hardware mass of 36.3 kg. For an idealized system hardware mass of 30.6 kg, the minimum gravimetric capacity of the hydrogen-bearing solid (0.11 kg H₂ / kg_{material}) occurs at the maximum slurry mass fraction loading (0.70 kg_{material} / kg_{slurry}). For the baseline system hardware mass of 36.3 kg, the minimum gravimetric capacity of the solid is 0.12 kg H₂ / kg_{material}. *Note: the gravimetric capacities represent the minimum capacities required to meet the DOE 2017 gravimetric system target of 102 kg.* Increasing the system hardware mass from 30.6 kg (idealized system) to 36.3 kg (baseline system) necessitates an increase in the material capacity to maintain a maximum overall system mass of 102 kg.

4.5 Solutions

Chemical hydrogen storage media in the form of solutions is assumed to be a two component mixture of a hydrogen-bearing solute dissolved in a non-hydrogen bearing liquid solvent. The approach in determining the minimum gravimetric capacities of the solute is similar to the approach used for slurries. The upper bound of the solute mass fraction was assumed to be 0.80 kg_{material} / kg_{solution}. In the absence of the solute-solvent chemistry, the maximum solute mass fraction was assumed to be on the order of a saturated solution of sugar dissolved in water (0.81 g_{sugar}/g_{water} @ 90 °C). Replotting Figure 7 with an upper bound of 0.80 kg_{material}/kg_{solution} results in Figure 8. Figure 8 shows the minimum hydrogen gravimetric capacities of the solute as a function of solute mass fractions (or loading mass fractions) for the idealized system design (dashed line) and the baseline system design (solid line). The minimum gravimetric capacity occurs at the maximum solute mass fraction (0.8 kg_{material} / kg_{solution}). For a system hardware mass of 30.6 kg (idealized system) and 36.3 kg (baseline system) the minimum gravimetric capacities are, respectively, 0.098 and 0.106 kg H₂ / kg_{solute}. The difference between Figure 7 and Figure 8 is the upper bound imposed on the loading mass fraction. The upper bound imposed on the solute mass fraction will likely be less than 0.81 g_{sugar}/g_{water} because of the temperature dependence on solubility and

the lower bound on the ambient operating temperature of the system (-40 °C, refer to Table 1). Solute-solvent thermodynamics will ultimately determine the maximum solubility of the solution.

5.0 Kinetics

Mentioned previously, the material dependent components were sized *a priori* to maintain a material independent system. *A priori* estimates on the mass and volume allow the material properties to be backed-out. The dehydrogenation reactor is a critical material dependent component responsible for generating hydrogen for fuel cell use. The two primary constraints used for the analyses were the reactor volume and the shelf-life of the hydrogen storage media. To quantify viable reaction kinetics, the reactor volume must be assumed. Our approach in choosing the reactor volumes were based on the fact that V6 internal combustion engines have displacements in the range of 2.5–4 L. For the purposes of this study, the baseline system consisted of a stainless steel reactor with a volume of 4 L and a mass of 5 kg; for the idealized system, the reactor was assumed to be 2 L and 2.5 kg. The dehydrogenation reactor was assumed to be an isothermal plug-flow reactor operating at 175°C. Assuming an isothermal PFR is a gross simplification that is unlikely to be encountered in practice. A primary contributor in the departure of an ideal PFR is the fact that the ratio of the hydrogen volumetric flow rate to the volumetric flow rate of the liquid is much greater than one. The ratio of the volumetric flow rates ($P = 1$ atm, 25 °C) approach values of 10,000 to 1 (neat liquid, 0.15 kg H₂/kg_{material}). The governing equation for the isothermal PFR reactor is

Equation 15

$$V_{PFR} \Big|_{X=99\%}^{T=175^{\circ}C} = F_{A_0} \int \frac{1}{-r_A(X, T)} dX \quad .$$

The rate expression (denoted as $-r_A$) is the relationship between the reaction rate, temperature and conversion. The conversion (denoted as X) is defined as the number of moles of A reacted per mole of A fed to the reactor. F_{A_0} is the molar feed rate of reactant A. The molar feed rate of reactant A was scaled to deliver a maximum hydrogen production rate of 0.4 moles of hydrogen per second (0.8 g H₂ / s)—half of what is dictated by the DOE targets (refer to Table 1). The system ballast tank is designed to accommodate transient operation for hydrogen rates greater than 0.4 moles of hydrogen per second. The ballast tank stores 15 liters of hydrogen at 20 bar.

The shelf-life constraint was imposed to eliminate unstable reaction media with fast reaction kinetics that offer limited practicality as an automotive fuel. The shelf-life is defined as the amount of time required to achieve a maximum conversion rate at a given temperature. The shelf-life constraint assumes the storage of a full tank of media for a minimum of 60 days at an ambient isothermal temperature of 60°C (refer to Table 1) with a maximum reactant conversion of 7.2%. The governing equation for the isothermal batch reactor is

Equation 16

$$t_{shelf-life} \Big|_{X=7.2\%}^{T=60^{\circ}C} = C_{A_0} \int \frac{1}{-r_A(X, T)} dX \quad .$$

The dehydrogenation reaction was assumed to be an uncatalyzed, irreversible single-step reaction represented by:

Species A is the hydrogen bearing reactant representing the neat liquid, solute or solid. Species I is the inert diluent used as the dissolution media for solutions or as the liquid carrier for slurries. In the case of neat liquids, species I is absent. Species I is an inert diluent that lowers the overall reaction rate by lowering the reactant inlet concentration. Assuming the same rate expression, conversion and operating temperature, a lowering of the reactant inlet concentration correlates to a larger reactor volume. An increase in reactor volume is also observed as the hydrogen gravimetric capacity of the material decreases because of the increased reactant throughput required to achieve the desired hydrogen flow rate.

The rate expressions assumed for this study were of the power-rate law form (Equation 17).

Equation 17

$$-r_A = k(T)(C_A)^n$$

$$k(T) = Ae^{\left(\frac{-E_a}{RT}\right)}$$

The sought after data are the Arrhenius parameters (activation energy, E_a and preexponential factor, A) and reaction orders (n) that satisfy the design constraints of reactor volume and shelf-life. The values of the reaction order ranged from 0-2. The values of the pre-exponential factor were bounded within the range of 10^5 – 10^{17} , and the values of the activation energy were bounded within the range of 100–155 kJ/mol. The analysis was performed by assuming a reaction order and then solving Equation 16 and Equation 17 for the Arrhenius parameters subject to the volume and shelf-life constraints. The results of the analyses are shown in Figure 9 in the form of Arrhenius plots for an assumed media composition with a 60 wt. % loading mass fraction and a hydrogen gravimetric capacity of 0.152 kg H_2 /kg_{material}; the required media volume to store 5.6 kg of H_2 is 71.3 L with a concentration of 17.2 moles of A per liter of media. The slope of the curve is $-E_a/RT$ and the y-intercept is the pre-exponential factor.

For a reaction temperature of 175 °C, the activation energies and pre-exponential factors for reaction orders less than 0.5 are around 117–121 kJ/mol and 10^9 – 10^{11} , respectively; For reaction orders of 0.5–1.0, the activation energies are around 146–150 kJ/mol with pre-exponential factors around 10^{14} – 10^{16} . Reaction orders greater than 1.0 did not result in Arrhenius parameters that satisfy both constraints (reactor volume and shelf-life) simultaneously for a reaction temperature of 175 °C, regardless of loading mass fraction. However, there were reaction orders greater than 1.0 that would satisfy the reactor volume constraint of 4.0 L, but not the 60 day shelf-life constraint. The 60 day shelf-life constraint proved to be the more demanding constraint. For example, consider a neat liquid with a material capacity of 0.15 kg H_2 /kg_{material}, a reaction temperature of 175 °C, a reaction order of 1.25, an activation energy of 146 kJ/mol, and a pre-exponential factor of 3.6×10^{15} ; the reactor volume equals 4.0 L, but the shelf-life is only 7.6 days. The minimum reactor volumes in Figure 9 are the reactor volumes in the absence of a volume

constraint, but still satisfying the shelf-life constraint. Activation energies greater than 36 kcal/mol will require higher reactor temperatures or the use of a catalyst to minimize the reactor volume.

Lower reaction temperatures are often viewed as being favorable, but in order to meet the volume constraint and shelf-life constraint, the reaction order for thermal decomposition reactions (Equation 17) at a reaction temperature of 175 °C cannot exceed 1.0. Increasing the reaction temperature beyond 175 °C increases the range of viable reaction orders that simultaneously meet the constraints of volume and shelf-life. However, increasing the reaction temperature may prove unfeasible because of potential trade-off scenarios with startup-time, on-board efficiency, side reactions, and heat exchanger mass. In other words, a lowering of the reaction temperature results in a smaller range of suitable reaction orders that satisfy the constraints of volume and shelf-life; in contrast, an increase in the reaction temperature results in an expanded set of suitable reactions orders. Examples of the maximum reaction orders as a function of reaction temperature for a neat liquid with a capacity of 0.15 kg H₂/kg_{material} satisfying the constraints of volume (4 L) and shelf-life (≥ 60 days) include: ($n_{\max} \approx 0.13$, $T_{\text{rxn}} = 100$ °C), ($n_{\max} \approx 1$, $T_{\text{rxn}} = 175$ °C), and ($n_{\max} \approx 2$, $T_{\text{rxn}} = 300$ °C). The intent of the kinetics analyses is to provide a general understanding of how the Arrhenius parameters, reaction temperatures and reaction orders affect the reactor volume and shelf-life. Ultimately, nature will provide the kinetics blueprint for the specific reaction of interest.

6.0 Heats of Reaction

The enthalpy of reaction (or heat of reaction) is a thermodynamic quantity relating the amount heat that is consumed or generated during a chemical reaction. Exothermic reactions (denoted as negative reaction enthalpies) release heat upon reaction. Endothermic reactions (denoted as positive reaction enthalpies) consume heat upon reaction. For automotive applications, exothermic dehydrogenation reactions afford increased on-board efficiencies, decreased startup times and faster transient response times. The disadvantages of exothermic reactions *may* include thermal runaway, waste heat and media stability (*i.e.*, shelf-life). Waste heat is the focal point for this analysis because the reaction exothermicity is directly proportional to the amount of waste heat generated, which in turn is directly proportional to the heat exchanger volume. The advantages of endothermic dehydrogenation reactions *may* include an increase in media stability, a reduced risk of thermal runaway, and a decrease in the amount of waste heat. The disadvantages *may* include decreased on-board efficiencies, increased startup times, and slower transient response times. For endothermic dehydrogenation reactions, the focal point is on-board efficiency. The enthalpy of reaction for endothermic reactions is an unrecoverable parasitic heat loss that impacts the on-board system efficiency. The DOE technical target for on-board system efficiency is 90% (Table 1).

6.1 Endothermic

The parasitic heat loss associated with the endothermic heat of reaction impacts the on-board system efficiency. This analysis only considers the impacts on system efficiency related to the endothermic heat of reaction, sensible heat of the media, the number of vehicle startups (*i.e.*, reactor) and the sensible heat of the reactor. This analysis did not include the parasitic losses associated with pumps, mixers, compressors, etc., because the goal was to isolate the effects of the heat of reaction to determine viable endothermic heats of reaction that have the potential to meet the on-board efficiency target of 90%. The on-board system efficiency is defined as the ratio of the lower heating value of hydrogen minus the parasitic losses divided by the lower heating value of hydrogen (Equation 18).

Equation 18

$$\varepsilon_{onboard} \equiv \frac{Q_{H_2}^{LHV} - Q_{parasitic}}{Q_{H_2}^{LHV}} \cdot 100$$

The basis of calculation was 5.6 kg of net usable hydrogen (*i.e.*, *one fuel tank*). Using the lower heating value of hydrogen (240 kJ/mol H₂) and 5.6 kg of net usable hydrogen stored, the total amount of energy contained in a full tank is 672,000 kJ (denoted as $Q_{H_2}^{LHV}$ in Equation 18). The parasitic losses (denoted as $Q_{parasitic}$) takes into account the heat required to raise the reactor temperature to the desired reaction temperature, the enthalpy of reaction, and the necessary heat required to raise the reaction media to the desired operating temperature (Equation 19).

Equation 19

$$Q_{parasitic} = \sigma * Q_{SS \text{ Reactor}} + Q_{rxn}^{total} + Q_{media}^{sensible}$$

The amount of heat required to raise the reactor to the desired reaction temperature is a function of the number of startups (denoted as σ), reactor mass, temperature difference (ΔT), and reactor heat capacity (Equation 20).

Equation 20

$$Q_{SS \text{ Reactor}} = m_{reactor} (C_p)_{SS} (\Delta T)$$

The reactors were assumed to be stainless steel having masses of 2.5 kg (idealized case) and 5.0 kg (baseline case). The temperature difference is the difference of the desired reaction temperature (*i.e.*, *final*) and the ambient temperature (*i.e.*, *initial*). The reaction temperature was assumed to be 175 °C and the ambient temperature was assumed to be 25 °C; therefore, the temperature difference is 150 °C. The number of startups (denoted as σ) is the number times the vehicle is started per day. For this study, cold startups were used; a cold startup assumes the reactor is heated from ambient temperature (25 °C) for each startup to a reactor temperature of 175 °C. In other words, we assumed the worst case scenario of no heat recovery/retention. Design efforts that recover sensible heat or attenuate the rate of heat loss to the surroundings will improve the overall system efficiency or allow for a larger range of viable endothermic heats of reaction. The heat contribution from the endothermic heat of reaction is accounted for by multiplying the net usable hydrogen stored (2800 moles H₂) and the enthalpy of reaction (Equation 21).

Equation 21

$$Q_{rxn}^{total} = n_{H_2} \cdot \Delta H_{rxn}$$

The sensible heat of the media ($Q_{media}^{sensible}$) takes into account the heat required to raise the temperature from ambient temperature to the desired reaction temperature. The sensible heat is a function of media composition and heat capacity (Equation 22).

Equation 22

$$Q_{media}^{sensible} = Q_{material}^{sensible} + Q_{carrier}^{sensible} = (m_{material} C_p^{material} \Delta T) + (m_{carrier} C_p^{carrier} \Delta T)$$

The masses of the material (hydrogen bearing) and carrier (non-hydrogen bearing) are a function of media type (*i.e.*, neat liquids, solutions, or slurries), material capacity (kg H₂/ kg_{material}) and loading mass fraction (kg_{material} / kg_{media}). For neat liquids, the carrier mass is zero. Additional information required to calculate the on-board efficiency include the average miles driven per day (41.1 miles / day) for light-duty vehicles and vehicle fuel economy (0.12 miles / mol H₂).[19] The driving range with 5.6 kilograms of hydrogen is 336 miles. Given 41.1 miles driven per day and a 336 mile driving range, the number of days of driving to utilize one tank containing 5.6 kilograms of hydrogen is 8.2 days.

Figure 10 shows the on-board efficiency as a function of endothermicity (2–18 kJ/mol H₂), reactor mass (2.5 and 5.0 kg), and the number of cold startups per day (2–8 SU/day). Given our assumptions, Figure 10 can be used to determine the maximum endothermic heat of reaction meeting a minimum on-board efficiency of 90% for a given number of startups per day; reaction enthalpies greater than the maximum result in on-board efficiencies less than the DOE target of 90%. Figure 10a and Figure 10b represent a neat liquid with hydrogen capacity of 0.10 kg H₂/kg_{material} for a reactor mass of 2.5 kg and 5.0 kg, respectively. Figure 10c and Figure 10d represent either a 50 wt. % slurry or solution that contains a hydrogen bearing component with a hydrogen capacity of 0.10 kg H₂/kg_{material} for a reactor mass of 2.5 kg and 5.0 kg, respectively. A mean heat capacity of 1.6 J/g K was used for all media compositions shown in Figure 10. Assuming four cold startups per day for a neat liquid with a hydrogen capacity of 0.10 kg H₂/kg_{material}, the maximum enthalpy of reaction to meet an on-board efficiency of 90% is +17 kJ / mol H₂ (Figure 10a).

The heat required to raise the temperature of the reactor is directly proportional to the reactor mass—*e.g.*, doubling the reactor mass, doubles the required heat input (Equation 20). The additional heat correlates to a lowering of the maximum enthalpy of reaction to maintain an on-board efficiency of 90%. Comparing Figure 10a and Figure 10b shows the impact of increasing the reactor mass from 2.5 kg to 5.0 kg on the endothermic heats of reactions. Assuming four startups per day, the maximum reaction enthalpy is lowered from +17 kJ / mol H₂ to +15 kJ / mol H₂ with an increase in reactor mass from 2.5 kg to 5.0 kg. The energy losses associated in heating the reactor are more pronounced as the reactor mass and number of startup per day increase—evidenced by the lowering of the maximum enthalpy of reaction required for an on-board efficiency of 90%. Because neat liquids only contain a hydrogen-bearing component, neat liquids offer higher on-board efficiencies than slurries or solutions that contain a non-hydrogen bearing component. The quantity of heat required to raise the temperature of the non-hydrogen bearing component is inversely proportional to the loading mass fraction. Comparing Figure 10a and Figure 10c shows the impact of decreasing the loading mass fraction (kg_{material}/kg_{media}) from 1 to 0.5 on the endothermic heats of reaction meeting a minimum on-board system efficiency of 90%. Given four startups per day, a reactor mass of 2.5 kg and a loading mass fraction of 0.5, the maximum endothermic heat of reaction is around 12 kJ / mol H₂ (compared to 17 kJ / mol H₂ for a neat liquid). The largest decrease in the endothermic heat of reaction meeting an on-board efficiency of 90% is observed with a decrease in loading mass fraction and an increase in reactor mass (Figure 10a and Figure 10b).

The highest possible endothermic heat of reaction (while still meeting an on-board system efficiency of 90%) occurs when the endothermic heat of reaction is the only parasitic heat loss considered (*i.e., the system is adiabatic with 100% heat recovery*). For an adiabatic system with an on-board system efficiency of 90%, the maximum endothermic heat of reaction allowable is 24 kJ / mol H₂. Engineering design efforts to increase system efficiency include thermal integration (recuperators), thermal storage and heat loss mitigation (insulation); however, implementing these designs to increase efficiency may prove problematic in meeting the system mass and system volume targets. The easiest way to think about on-board efficiency is that there is a finite amount of energy available on-board. Using the lower heating value of hydrogen as the basis, the maximum amount of available energy is 672 MJ (*i.e., 5.6 kg H₂ times 120 MJ/kg H₂*). Consequently, any energy consuming processes (*e.g., heating, endothermic reaction enthalpies, pumps, compressors, waste heat, etc.,*) necessarily reduces the overall quantity of available energy, thus reducing the overall system efficiency. The heat capacity of the hydrogen storage media also impacts the overall on-board efficiency (Equation 22). An increase in the mean heat capacity from 1.6 J/g K to 6.4 J/g K reduces the on-board efficiency from 90% to 84%, respectively. Using water as a bounding case for heat capacity because water has one of the highest heat capacities (4.2 J/g K), on-board efficiency reductions less than or equal to 3% are expected—assuming no heat recovery.

6.2 Exothermic

The maximum exothermic heat of reaction, in contrast to endothermic heats of reaction, is not determined by on-board efficiency, but rather heat exchanger mass/volume. The heat exchanger mass/volume is a function of the amount of heat generated in the reaction, the material's heat capacity, and the required initial and final temperatures of both the reactants and the products. The total mass allocated to the heat exchangers was 3.7 kg (9.2 L) for both the baseline and idealized system designs. The parameters used for this analysis are shown in Table 3. The maximum hydrogen flow rate required was assumed to be 0.4 grams hydrogen per second (20 kW_e); which is the average hydrogen flow rate of the US06 drive cycle. The reaction light-off temperature was assumed to be 175°C. There are two heat exchangers in the system, one for the spent fuel and one for the hydrogen gas. The heat exchangers were sized to cool their respective fluids from the adiabatic reaction temperature to a target outlet temperature. The impact of heat of reaction on the mass of the radiators is calculated based on a three step process. First, the adiabatic temperature rise is calculated. Second, the length of the gas and spent fuel heat exchangers required to return their products back to the target temperatures is calculated. Finally, the total mass and volume of the heat exchangers is calculated. The adiabatic temperature rise is calculated based on the initial temperature T_{inlet}, the heat of reaction (ΔH_{rxn}), the heat capacities of the hydrogen and spent fuel, and the material hydrogen capacity (γ_χ) as shown in Equation 23

Equation 23

$$\Delta T_{adiabatic} = n_{H_2} \left(\frac{\Delta H_{rxn}}{C_{p,H_2} + C_{p,SF} / \gamma_{\chi}} \right)$$

The heat exchangers are a finned tube configuration consisting of a stainless steel tube with brazed aluminum fins. The heat exchanger lengths are calculated using the effectiveness-NTU method of heat exchanger analysis based on the assumption of a cross flow, single pass heat exchanger assuming the air is mixed and the flow in the radiator is unmixed in the form shown in Equation 24.[20]

Equation 24

$$\varepsilon = (1/C_r) \{1 - \exp\{-C_r[1 - \exp(-NTU)]\}\}$$

The heat transfer coefficient for the exterior of the finned tube is calculated for a cylinder in cross flow is shown in Equation 25

Equation 25

$$h_{\text{exterior}} = \frac{k_{\text{air}}}{d_{\text{hxOD}}} \left(0.3 + \frac{0.62 \text{Re}_d^{1/2} \text{Pr}_{\text{air}}^{1/3}}{\left[1 + (0.4/\text{Pr}_{\text{air}})^{2/3}\right]^{1/4}} \left[1 + \left(\frac{\text{Re}_d}{28200}\right)^{5/8}\right]^{4/5} \right)$$

Where $\text{Re}_d = \frac{\rho_{\text{air}} v_{\text{air}} d_{\text{hxOD}}}{\mu_{\text{air}}}$ and Pr_{air} , k_{air} , v_{air} , μ_{air} , and ρ_{air} are the Prandtl number, thermal conductivity,

velocity, viscosity, and density of air at the film temperature, respectively.[21] The increased surface area associated with these fin δ_{fin} can be calculated by Equation 26 as:

Equation 26

$$\delta_{\text{fin}} = [(d_{\text{fin}}^2 - d_{\text{hxOD}}^2) + 2d_{\text{hxOD}} p_{\text{fin}}] / (2d_{\text{hxOD}} p_{\text{fin}})$$

where d_{fin} is the outer diameter of the fin, d_{hxOD} is the outer diameter of the heat exchanger tube, and p_{fin} is the fin pitch. The fin efficiency (η_{fin}) was calculated for a circular fin.[22] The value of h_{interior} is Nusselt number for the tube interior with a swirl flow device and laminar flow in a uniformly heated tube as shown in Equation 27

Equation 27

$$\text{Nu}_{\text{interior}} = 5.172(1 + 0.005484 \cdot \text{Pr}^{0.7} (\text{Re}_d/y)^{1.25})^{1/2}$$

where y is the twist ratio of the turbulatorTM inside the heat exchanger tubes.[22] The parameters used in the radiator models are shown in Table 4. Additionally, the ambient air is assumed to be at 24°C and flowing past the radiator at 10 mph. The length of each heat exchanger is adjusted and the heat transfer calculated until the exit temperature achieves the target values. The mass and volume of the heat exchangers can then be calculated based on their length and the parameters above. The mass and volume of peripheral equipment such as fans and shrouds are not included in the calculation. Using these assumptions and the calculations described above, the exchanger mass was calculated as a function of gravimetric capacity of the storage media and the exothermic enthalpy of reaction (Figure 11). The size of the spent fuel heat exchanger is significantly larger than that of the hydrogen heat exchanger and dominates the calculations. As anticipated, the higher exothermic reaction enthalpy results a higher adiabatic temperature, increasing both the length and the mass of the heat exchangers. It is not linear because higher temperatures provide a larger driving force for heat transfer. For example, doubling the heat of reaction doubles the adiabatic temperature but does not double the required length of the heat exchangers. Because the hydrogen mass flow rate is constant for this calculation, the gravimetric capacity of the storage media is inversely proportional to the mass flow rate. As a result, with reduced gravimetric capacities, the flow rate of the storage media in the spent fuel heat exchanger increases to achieve the desired mass flow rate of hydrogen. The higher flow rates require that the heat exchanger be longer to bring the temperature down to its target temperature. Therefore, hydrogen storage media with the highest gravimetric capacities are beneficial in reducing the heat exchanger mass (and volume).

7.0 Volume Displacement Tank

The volume displacement tank (or bladder tank) is the storage vessel for both the fresh and spent hydrogen storage media. The fresh hydrogen storage media is the fully hydrogenated fuel and the spent material is the fully dehydrogenated material. A diaphragm is used within the volume displacement tank to isolate the fresh and spent fuel. The mass of the storage tank is proportional to the material of construction and the media volume. The material of construction assumed for the storage tank was polyethylene. The media volume is proportional to the media capacity and media density. The density of the spent fuel (*i.e., dehydrogenated media*) was assumed to be equal to the density of the fresh fuel (*i.e., hydrogenated media*). Our system design allocates 6.2 kilograms for the tank mass. Figure 12 shows the relationship of the media density and media hydrogen capacity on volume displacement tank mass. As expected, increasing the media density and hydrogen capacity results in a decrease of the storage tank volume and hence the storage tank mass. Because media densities are expected to be in the range of 1.0–1.5 g/mL with media hydrogen capacities greater than 0.08 kg H₂/kg media; the storage tank mass is expected to be below the 6.2 kilograms allocated for the mass of the storage tank.

8.0 Impurities

Fuel cell impurities generated from chemical hydrogen storage media require removal prior to reaching the fuel cell. The hydrogen delivered to the fuel cell must be greater than or equal to 99.97% (Table 1). The SAE J2719 hydrogen quality guidelines for fuel cell vehicles list a number of impurities and their maximum concentration.[23] Impurities can be classified as either fuel cell impurities or inert diluents. Inert diluents (*e.g., helium and nitrogen*) do not affect fuel cell durability. In contrast, fuel cell impurities such as carbon monoxide and sulfur compounds directly impact fuel cell operability and durability. The objective of this section is to determine the maximum fuel cell impurity concentration that can be scrubbed with a hydrogen purification unit having a mass of 3.2 kilograms (*i.e., baseline system*).

Previously mentioned, the system design is constrained by mass, not volume. Therefore, the mass of the purification unit is the primary constraint. The mass of the purification unit is a function of scrubbing capacity, impurity molecular weight, impurity concentration (molar basis), and replacement frequency. The replacement frequency of the hydrogen purification unit was assumed to be 1800 miles (analogous to an oil change). For the purposes of discussion, the hydrogen purification technology was assumed to be adsorbent based—although not necessary. However, the most important aspect in quantifying the impurity concentration is not an assumed hydrogen purification technology, but rather the assumed scrubbing capacity. The scrubbing capacity (or adsorbent capacity) is a mass based ratio that relates the mass of impurity (*e.g., adsorbate*) to the mass of hydrogen purification (*e.g., adsorbent*). The adsorbate was assumed to be irreversibly chemisorbed on the adsorbent—this assumption removes the thermodynamic constraints related to adsorption-desorption equilibrium which is presently unknown. The governing equations used to calculate the maximum impurity concentration for a given impurity molecular weight, adsorption capacity, adsorbent mass (*i.e., 3.2 kg*), and an 1800 mile replacement frequency is as follows. The adsorption capacity is defined as (Equation 28)

Equation 28

$$X_{adsorbent} = \frac{m_{adsorbate}}{m_{adsorbent}}$$

The mass of adsorbate (*i.e.*, impurity) to be removed is related to the impurity mole fraction and impurity molecular weight by Equation 29.

Equation 29

$$X_{adsorbent} = \frac{MW_i \left(\frac{\Delta y_i \cdot n_{H_2}}{1 - \Delta y_i} \right)}{m_{adsorbent}}$$

$$\Delta y_i = y_i^{inlet} - y_i^{outlet}$$

i = adsorbate (impurity)

The adsorbate (impurity) gas phase mole fraction and the impurity molecular weight are denoted as y_i and MW_i , respectively. The molecular weight was introduced to convert from a molar basis to a mass basis because gas phase concentrations are typically reported on molar (or volume) basis. The difference in the inlet and outlet impurity mole fractions (denoted as y_i) represents the number of moles to be scrubbed by the purification unit. The outlet impurity mole fraction (denoted as y_i^{outlet}) was taken as 0.0003, which satisfies the hydrogen mole fraction target of 0.9997 (Table 1). However, the maximum impurity outlet concentration will ultimately be determined from fuel cell durability studies. The number of moles of hydrogen (denoted as n_{H_2}) for an assumed 1800 mile replacement frequency is 16,800 moles H_2 (300 miles per tank, 6 tanks, 5.6 kg H_2 per tank). For example, given an adsorption capacity of 0.75 $g_{impurity} / g_{adsorbent}$ ($X_{adsorbent}$), an outlet mole fraction of 0.0003 (y_i^{outlet}), a target adsorbent mass of 3200 grams ($m_{adsorbent}$), an impurity molecular weight of 50 grams per mole (MW_i), and a replacement frequency of 1800 miles ($n_{H_2} = 16,800$ moles); the maximum impurity inlet mole fraction (y_i^{inlet}) is calculated to be 0.00315 (3147 ppm).

Figure 13 shows the maximum impurity inlet concentrations as a function of adsorbent capacity (0.2–1.0 $g_{impurity} / g_{adsorbent}$) and impurity molecular weight (10–90 g/mol) that satisfy the DOE hydrogen purity target (99.97%) and an adsorbent replacement frequency of 1800 miles. Note: Figure 13 was constructed under the assumption that the impurity is irreversible chemisorbed. In general, high scrubbing capacities and low molecular weight impurities afford the highest inlet concentrations. Impurity mole percentages exceeding 1% will be difficult to scrub, assuming a target mass of 3.2 kilograms and an adsorption capacity of one gram of impurity per gram of adsorbent. Because of the uncertainty in the chemical identity, purification technology, purification capacity and the fuel cell tolerance levels, *a priori* estimates of the maximum allowed impurity concentration cannot be quantified. In addition to hydrogen purification, mitigating approaches such as reaction selectivity via temperature, pressure, or catalysis may prove viable options in increasing the hydrogen reaction selectivity. Fuel cell impurities are a concern for all hydrogen storage media and may be the result of the fluid phase vapor pressure or reaction selectivity. Nonetheless, the impact of impurities generated from hydrogen storage materials should be examined on a case-by-case basis.

9.0 Regeneration Efficiency

The efficiency of spent fuel regeneration for hydrogen storage media requiring off-board regeneration via chemical processing is considered to be one of the more demanding technical challenges with chemical hydrogen storage media. DOE has set forth technical targets (Table 1) for both well-to-power plant (60%) and on-board efficiency (90%). Regeneration is the process by which the spent fuel (*i.e.*, *dehydrogenated*) undergoes chemical processing to convert the spent fuel back into hydrogenated fuel. The minimum regeneration efficiency for off-board regenerable hydrogen storage media is 66.67% (given an on-board efficiency of 90% and a well-to-power plant efficiency of 60%).

10.0 Summary

Table 5 summarizes the chemical hydrogen storage properties required to meet the DOE 2017 hydrogen storage system targets. The calculated values are based on our boilerplate system design and system designs assumptions.

11.0 Conclusions

Realizable material properties related to chemical hydrogen storage for automotive applications meeting the 2017 DOE technical targets were presented in this paper. The material properties were calculated assuming a generalized, material-independent, fluid-phase chemical hydrogen storage system design. The presented material properties were developed within the constraints of our system design, component sizing, assumptions, system operating conditions and the DOE 2017 system targets. 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. Viable material properties including gravimetric capacities, kinetics, heats of reaction, and impurity concentrations were calculated assuming neat liquids, solutions and non-settling slurries. The material properties presented should not be taken as hard targets, but rather soft guidelines because of potential system trade-off scenarios. In fact, property values that fall within the presented material property values do not guarantee a commercializable media form. Likewise, material property values just outside the material property ranges do not imply that a material is not capable of meeting the system performance targets, but rather that the material will require further examination. Providing the materials research community with a viable set of chemical hydrogen storage material properties fills a critical knowledge gap in the search for novel chemical hydrogen storage media. The guidelines set forth, although not exhaustive, are an essential first step in identifying viable chemical hydrogen storage material properties—and most important, their implications on system mass, system volume and system performance.

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References

- [1] M. Klell, Storage of Hydrogen in the Pure Form, in: Handbook of Hydrogen Storage, Wiley-VCH Verlag GmbH & Co. KGaA, 2010, pp. 1-37.
- [2] D.J. Durbin, C. Malardier-Jugroot, International Journal of Hydrogen Energy, 38 (2013) 14595-14617.
- [3] B. Hardy, C. Corgnale, R. Chahine, M.-A. Richard, S. Garrison, D. Tamburello, D. Cossement, D. Anton, International Journal of Hydrogen Energy, 37 (2012) 5691-5705.
- [4] L. Simpson, Final Report for the DOE Hydrogen Sorption Center of Excellence, National Renewable Energy Laboratory, 2010.
- [5] M. Dornheim, Tailoring Reaction Enthalpies of Hydrides, in: Handbook of Hydrogen Storage, Wiley-VCH Verlag GmbH & Co. KGaA, 2010, pp. 187-214.
- [6] J. Graetz, J.J. Reilly, V.A. Yartys, J.P. Maehlen, B.M. Bulychev, V.E. Antonov, B.P. Tarasov, I.E. Gabis, Journal of Alloys and Compounds, 509 (2011) S517-S528.
- [7] T.Q. Hua, R.K. Ahluwalia, International Journal of Hydrogen Energy, 36 (2011) 15259-15265.
- [8] J. Huot, Metal Hydrides, in: Handbook of Hydrogen Storage, Wiley-VCH Verlag GmbH & Co. KGaA, 2010, pp. 81-116.
- [9] J.K. Lenny Klebanoff, Final Report for the DOE Metal Hydride Center of Excellence, Sandia National Laboratory, 2012.
- [10] B. Sakintuna, F. Lamaridarkrim, M. Hirscher, International Journal of Hydrogen Energy, 32 (2007) 1121-1140.
- [11] A. Shariati, S. Raeissi, C.J. Peters, Clathrate Hydrates, in: Handbook of Hydrogen Storage, Wiley-VCH Verlag GmbH & Co. KGaA, 2010, pp. 63-79.
- [12] C. Weidenthaler, M. Felderhoff, Complex Hydrides, in: Handbook of Hydrogen Storage, Wiley-VCH Verlag GmbH & Co. KGaA, 2010, pp. 117-157.
- [13] R. Zidan, Aluminum Hydride (Alane), in: Handbook of Hydrogen Storage, Wiley-VCH Verlag GmbH & Co. KGaA, 2010, pp. 249-277.
- [14] T. Ichikawa, Amides, Imides and Mixtures, in: Handbook of Hydrogen Storage, Wiley-VCH Verlag GmbH & Co. KGaA, 2010, pp. 159-185.
- [15] H. Li, Q. Yang, X. Chen, S.G. Shore, Journal of Organometallic Chemistry, 751 (2014) 60-66.
- [16] F. Mertens, G. Wolf, F. Baitalow, Ammonia Borane and Related Compounds as Hydrogen Source Materials, in: Handbook of Hydrogen Storage, Wiley-VCH Verlag GmbH & Co. KGaA, 2010, pp. 215-247.
- [17] K.C. Ott, Final Report for the DOE Chemical Hydrogen Storage Center of Excellence, Los Alamos National Laboratory, 2012.
- [18] DOE-EERE, Targets for Onboard Hydrogen Storage Systems for Light Duty Vehicles, 2009.
- [19] U.S. Department of Transportation, Highway Statistics 2011 (2013).
- [20] W.M. Kays, A.L. London, Compact heat exchangers, 3rd ed., New York : McGraw-Hill, New York, 1984.
- [21] F.P. Incropera, D.P. DeWitt, Fundamentals of heat and mass transfer, 5th ed., New York : J. Wiley, New York, 2002.
- [22] W.M. Rohsenow, J.P. Hartnett, Y.I. Cho, Handbook of heat transfer, 3rd ed., New York : McGraw-Hill, New York, 1998.
- [23] SAE International, SAE J2719_201109-Hydrogen Fuel Quality for Fuel Cell Vehicles, 2011.

Tables

Table 1. DOE targets for on-board hydrogen storage systems for light-duty vehicles.[18]

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% ^a	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	Sc/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.				

Table 2. Baseline and idealized system component masses and volumes for fluid-phase chemical hydrogen storage media used in this study.

Component	Baseline Case		Idealized Case	
	Mass (kg)	Volume (L)	Mass (kg)	Volume (L)
Media + Tank	≤ 65.5	≤ 98.9	≤ 71.5	≤ 104.9
Reactor ^a	5	4	2.5	2
H ₂ Purification ^a	3.2	4	0	0
Heat Exchangers ^a	3.7	9.2	3.7	9.2
Ballast Tank ^a	2.6	15	2.6	15
BOP ^b	21.8	8.9	21.8	8.9

^a component masses or volumes were sized independent of material to maintain a material independent system

^b BOP mass and volume were fixed for both system cases

Table 3 Fluid properties used for heat exchanger design.

Parameter	Value	Units	Gas Parameter	Value	Units
Hydrogen Flow Rate	0.4	g/s	Reactor Inlet Temperature	175	°C
Operating Pressure	20	atm	Spent Fuel Target Outlet Temperature	60	°C
Spent Fuel Heat Capacity	1.6	J/g/K	Gas Target Outlet Temperature	85	°C
Spent Fuel Thermal Conductivity	0.2	W/m/K	Spent Fuel Viscosity	500	cP

Table 4 Heat exchanger dimensions.

Spent fuel Parameter	Value	Units	Gas Parameter	Value	Units
Fin Diameter (d_{fin})	0.025	m	Fin Diameter (d_{fin})	0.016	m
Heat Exchanger Tube Diameter (d_{hxOD})	0.0095	m	Heat Exchanger Tube Diameter (d_{hxOD})	0.00635	m
Fin Thickness	0.00046	m	Fin Thickness	0.00046	m
Fin Pitch (p_{fin})	0.0023	m	Fin Pitch (p_{fin})	0.0023	m
Twist Ratio (y = diameters/180° twist)	9.84		Twist Ratio (y = diameters/180° twist)	9.84	

Table 5. Summary of chemical hydrogen material properties required to meet the 2017 DOE Targets for Onboard Hydrogen Storage Systems for Light Duty Vehicles

Parameter	Symbol	Units	Range*	Assumptions	Section
Minimum Material capacity (liquids)	γ_{mat}	$\text{g}_{\text{H}_2} / \text{g}_{\text{material}}$	$\sim 0.078 (0.085)^{\dagger}$	<ul style="list-style-type: none"> System mass (excludes media) = 30.6 kg (36.3 kg) 5.6 kg of net-usable hydrogen Liquid media (neat) Media density = 1.0 g/mL 	§ 4.3
Minimum Material capacity (solutions)	γ_{mat}	$\text{g}_{\text{H}_2} / \text{g}_{\text{material}}$	$\sim 0.098 (0.106)^{\dagger}$	<ul style="list-style-type: none"> System mass (excludes media) = 30.6 kg (36.3 kg) Solute mass fraction = 0.80 Solution density = 1.0 g/mL 	§ 4.5
Minimum Material capacity (slurries)	γ_{mat}	$\text{g}_{\text{H}_2} / \text{g}_{\text{material}}$	$\sim 0.112 (0.121)^{\dagger}$	<ul style="list-style-type: none"> System mass (excludes media) = 30.6 kg (36.3 kg) Non-settling homogeneous slurry Slurry mass fraction = 0.70 Slurry volume fraction = 0.5 Slurry density = 1.0 g/mL 	§ 4.4
Kinetics: Activation Energy	E_a	kJ / mol	117–150	<ul style="list-style-type: none"> Reactor volume ≤ 4 L Shelf life ≥ 60 days Reaction order, $n = 0.13$ (100°C), 0.5 (125)°C, 1 (175°C), 2 (300°C) 	§ 5.0
Kinetics: Preexponential Factor	A		$4 \times 10^9 - 1 \times 10^{16}$		
Endothermic Heat of Reaction	ΔH_{rxn}	kJ / mol H_2	$\leq +17 (15)^{\dagger}$	<ul style="list-style-type: none"> On-board Efficiency = 90% Number of cold startups = 4 $\Delta T = 150$ °C with no heat recovery Neat liquid ($C_p = 1.6$ J/g K) Reactor mass = 2.5 kg SS (5.0 kg SS) 	§ 6.1
Exothermic Heat of Reaction	ΔH_{rxn}	kJ / mol H_2	≤ -27	<ul style="list-style-type: none"> Maximum Temperature = 250°C Recycle ratio = 50% 	§ 6.2
Maximum Reactor Outlet Temperature	T_{outlet}	°C	250	<ul style="list-style-type: none"> Liquid radiator = 2.08 kg Gas radiator = 0.3 kg Ballast tank = 2.6 kg 	§ 6.2
Impurities Concentration	y_i	ppm	No <i>a priori</i> estimates can be quantified	<ul style="list-style-type: none"> Adsorbent mass ≤ 3.2 kg 	§ 8.0
Media H_2 Density	$(\gamma_{\text{mat}})(\phi_{\text{m}})(\rho_{\text{mat}})$	kg H_2 / L	≥ 0.07	<ul style="list-style-type: none"> HD polyethylene tank ≤ 6.2 kg 	§ 4.1
Regen Efficiency	η_{regen}	%	$\geq 66.6\%$	<ul style="list-style-type: none"> On-board Efficiency = 90% WTPP efficiency = 60% 	§ 9.0
<p>* (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</p> <p>[†] values outside of parentheses are the values that correlate to the idealized system design (i.e., 30.6 kg) and the values in parentheses are those that correlate to the baseline system design (36.3 kg)</p>					

Figures

Figure 1. Modeling methodology flow chart.

Figure 2. Automotive system design for off-board regenerable chemical hydrogen storage media.

(a)

(b)

(c)

(d)

Figure 3. Maximum system hardware volume required to meet DOE 2017 volumetric system target of 140 L as a function of material hydrogen capacity and loading mass fraction for (a) media density of 0.5 g/mL, (b) media density of 1.0 g/mL, and (c) media density of 1.5 g/mL [for reference, the maximum system hardware available for storing gaseous hydrogen as a function of storage temperature and storage pressure is also shown (d)].

Figure 4. Maximum available system hardware mass to meet DOE 2017 system gravimetric target of 102 kg as a function of material hydrogen capacity and loading mass fraction.

Figure 5. Maximum available system hardware mass as a function of media hydrogen capacity (neat liquids, solutions or slurries); the dashed green line represents the minimum gravimetric capacity for the idealized system (30.6 kg), the solid green line represents the minimum gravimetric capacity for the baseline system (36.3 kg), the blue shaded region is the region that satisfy the DOE 2017 system gravimetric target of 102 kg.

Figure 6. Slurry mass fraction as a function of slurry volume fraction for a density ratio of 0.5 (lower bound), a density ratio of 1 (solid green line), a density ratio of 2 (upper bound); density ratio = $\rho_{solid}/\rho_{liquid}$.

Figure 7. Slurries: minimum material gravimetric capacities of the hydrogen bearing solid component as a function of slurry mass fractions for the idealized system (dashed green line) and the baseline system (solid green line) satisfying the DOE 2017 system gravimetric target of 102 kg.

Figure 8. Solutions: minimum material gravimetric capacities of the hydrogen bearing solute as a function of solute mass fractions for the idealized system (dashed green line) and the baseline system (solid green line) satisfying the DOE 2017 system gravimetric target of 102 kg.

Figure 9. Arrhenius plots as a function reaction order and temperature that satisfy the design constraints of reactor volume (≤ 4 L) and a shelf-life (≥ 60 days) simultaneously given a loading mass fraction of 60 wt. %, a material capacity of $0.152 \text{ kg H}_2 / \text{kg}_{\text{material}}$, and a reaction temperature of 175°C .

(a)

(b)

(c)

(d)

Figure 10. On-board system efficiencies as a function of endothermic heat of reaction and number of startup per day for (a) neat liquid with 2.5 kg SS reactor, (b) neat liquid with 5.0 kg SS reactor, (c) 50 wt. % slurry with 2.5 kg SS reactor, and (d) 50 wt. % slurry with 5.0 kg SS reactor (*Assumptions: material capacity = 0.10 kg H_2 /kg_{material}, mean heat capacity = 1.6 J/g K for all compositions, no heat recovery, and $\Delta T = 150$ °C*).

Figure 11. Total heat exchanger mass (kg) as a function of exothermic heat of reaction (kJ/mol H₂) and the hydrogen gravimetric capacity of the storage material (g H₂ / g_{mat}).

Figure 12. Mass of storage tank as a function of media density and media hydrogen capacity (note: media refers to the overall composition of the hydrogen storage media).

Figure 13. Maximum impurity concentration as a function of scrubbing capacity and impurity molecular weight for a fixed scrubber mass of 3.2 kg and an 1800 mile replacement frequency.