

Contract No.:

This manuscript has been authored by Savannah River Nuclear Solutions (SRNS), LLC under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy (DOE) Office of Environmental Management (EM).

Disclaimer:

The United States Government retains and the publisher, by accepting this article for publication, acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this work, or allow others to do so, for United States Government purposes.

Hydrogen storage adsorbent systems acceptability envelope

Bruce Hardy^{1*}, David Tamburello¹, Claudio Corgnale^{1,2}

¹ *Savannah River National Laboratory, Aiken, SC 29808, USA*

² *Greenway Energy, Aiken, SC, 29803, USA*

Abstract

A methodology was developed to determine the range of coupled material parameters and operating conditions that allow an adsorbent based hydrogen storage system to meet performance targets. The range of acceptable parameters forms a multi-dimensional volume, or envelope. For this reason, the methodology is referred to as the Adsorbent Acceptability Envelope. The model evaluates the performance of the overall storage tank, comprised of the adsorbent material, the heat transfer system and the pressure vessel. Two cases were analyzed, both based on the flow-through cooling approach providing the cooling power required to charge hydrogen, with results presented and discussed. The first application (the forward problem) analyzed the gravimetric and volumetric performance of MOF-5[®] based hydrogen storage beds, under various operating conditions. Results demonstrated that the system can reach a gravimetric capacity of approximately 4 wt% and volumetric capacity of about 20 g/L within 200 s during the absorption process. The second application (the inverse problem) identified the range of selected material parameters, required to meet the U.S. Department of Energy targets for gravimetric and volumetric capacity. Results showed that the most important parameters are the maximum capacity and the density of the material. Adsorbents having a density on the order of twice that of nominal powder form MOF-5[®] can meet the 2020 DOE targets (i.e. system gravimetric capacity of 0.045 kg_{H2}/kg_{System} and system volumetric capacity of 0.030 kg_{H2}/L_{System}). A density of about 3-4.5 times the nominal value is required to meet the DOE 2025 targets (i.e.

* Corresponding author. Email address: bruce.hardy@srnl.doe.gov (B.Hardy)

system gravimetric capacity of $0.055 \text{ kg}_{\text{H}_2}/\text{kg}_{\text{System}}$ and system volumetric capacity of $0.040 \text{ kg}_{\text{H}_2}/\text{L}_{\text{System}}$). Likewise, a material with a maximum adsorption capacity approximately equal to three times that of nominal MOF-5[®] can meet the 2020 DOE targets, while a maximum capacity about 4.5 times the nominal value is required to meet the 2025 DOE targets.

Keywords

Hydrogen storage, Adsorption, Acceptability envelope, System modeling, Heat transfer

Nomenclature

AAE	=	Adsorbent acceptability envelope
α	=	Enthalpic contribution to the characteristic free energy of adsorption, E_a , (J/mol)
β	=	Entropic contribution to the characteristic free energy of adsorption, E_a , (J/mol-K)
c_{H_2}	=	Concentration of H_2 (mol/m ³)
C_p	=	Specific heat (J/kg-K)
DAR	=	Dubinin-Astakhov-Radushkevich
E_a	=	Characteristic free energy of adsorption from the Dubinin-Astakhov- Radushkevich model (J/mol). $\equiv \alpha + \beta T$
h	=	Molar enthalpy of H_2 (J/mol)
HSECoE	=	Hydrogen Storage Engineering Center of Excellence
$H_{exhaust}$	=	Total enthalpy of exhaust H_2 (J)
k	=	Thermal conductivity (W/m-K)
L_{bed}	=	Length of adsorbent bed (m)
m	=	Mass (kg)
\dot{m}	=	Mass flowrate (kg/s)
Δm	=	Mass variation (kg)
M_{H_2}	=	Molecular weight of H_2 (kg/g-mole)

- $n_a =$ Absolute adsorption (mol of H₂/kg_{ads})
- $n_{\max} =$ Limiting adsorption, the maximum hydrogen loading of the adsorbent
(mol/(kg_{ads}))
- $n_{total} =$ Total amount of hydrogen adsorbed and in the void space (mol H₂/kg_{ads})
- $N_{available} =$ Available mass of hydrogen between charge and discharge states
(kg H₂)
- $P =$ Pressure (P)
- $P_f =$ Pressure at charged state (Pa)
- $P_0 =$ Pressure at discharged state (Pa)
- $P_o =$ Pseudo-pressure for Dubinin-Astakhov model, or initial pressure (Pa)
- $Q =$ Heat transferred to system by means other than flow-through cooling (J)
- $t =$ Time (s)
- $T =$ Temperature (K)
- $T_f =$ Temperature at charged state (K)
- $T_0 =$ Temperature at discharged state (K)
- $T_{in} =$ Inlet temperature (K)
- $T_{out} =$ Outlet temperature (K)
- $u_0 =$ Molar internal energy of ideal free gas at the system temperature T (J/mol)
- $\Delta U_a =$ Internal energy of the condensed phase of H₂ at a temperature T and
pressure P relative to free gas at a temperature T and a pressure of 1 atm, per
mass of adsorbent (J/ kg adsorbent)

$v_f =$	Adsorbent volumetric capacity ($\text{kg}_{\text{H}_2}/\text{L}_{\text{ads}}$)
$v_{bed} =$	Superficial velocity of hydrogen in the adsorbent (m/s)
$v_{in} =$	Inlet hydrogen velocity (m/s)
$V =$	Total volume of adsorbent (m^3)
$V_v =$	Total void volume (m^3/kg adsorbent)
$V_a =$	Adsorbed volume (m^3/kg adsorbent)
$V_{bed} =$	Volume of adsorbent (m^3)
$W =$	Work done on system (J)
$w_f =$	Gravimetric capacity of the adsorbent ($\text{kg}_{\text{H}_2}/(\text{kg}_{\text{ads}} + \text{kg}_{\text{H}_2})$)
$W =$	Work done on system (J)
$Z =$	Compressibility factor
$\epsilon =$	Porosity
$\rho_{ads} =$	Bulk adsorbent density (kg/m^3)

Subscripts

ads =	Relative to the adsorbent material
sys =	Relative to the system tank (i.e. including material, multilayer insulation, pressure vessel, balance of plant)
i =	Relative to component 'i'
in =	Inlet (referred to pressure, mass flow rate and temperature) or into the system volume (referred to Δm)

out = Outlet (referred to pressure, mass flow rate and temperature) or out of the system volume (referred to Δm)

1. Introduction

There has been significant interest in the use of hydrogen and natural gas as alternatives to traditional petrochemical fuels for light duty vehicles. Onboard storage of gases has proved to be problematic. To attain parity with the energy density of traditional petrochemical fuels, densification of the gas is required. Although this could be accomplished through cryo-compression, a significant amount of energy would be required to put the gas into this state. For pure compression of hydrogen, pressures on the order of 350-700 bar are required, necessitating a significant amount of work [1,2]. Although hydrogen liquefaction results in high gravimetric densities at low pressures the process is more expensive than pure compression due to the amount of power needed to cool the hydrogen to sufficiently low temperatures (approximately 20 K at 1 bar) [1,3]. Further, for liquefied hydrogen, there is an issue with boil-off during periods of dormancy and a corresponding reduction in efficiency.

As an alternative to cryo-compression, it is possible to utilize a media that, at a given temperature and pressure, uptakes and stores greater quantities of gas than by compression alone. In addition to its requirements for uptake, the media must readily release the stored gas as needed. Storage media fall into 3 general classifications: chemical hydrides, which are recharged offboard the vehicle; adsorbents which uptake hydrogen via physisorption; and metal hydrides which undergo chemical reactions during the charging process and are refueled onboard the vehicle. All media-based storage systems undergo complex, coupled physical processes during hydrogen uptake and discharge, making the use of numerical models essential for design and evaluation. A number of configuration-specific models have been developed to evaluate the performance of particular system designs and adsorbents [4-15]. Model development, however, requires a significant expenditure of time. Therefore, it is desirable to

have an efficient numerical tool capable of identifying general coupled media and storage system designs that are most likely to meet target performance requirements, prior to conducting detailed evaluations. With regards to adsorbents, Bhatia and Myers [16] discussed the optimization of an adsorbent for an isothermal process for which adsorption could be characterized by either the Langmuir or Unilan isotherms.

This paper focuses on adsorbent based hydrogen storage. Keeping in mind the need to assess adsorbent and storage system performance prior to committing to development of a detailed model, a methodology was developed to assess the ability of a given adsorbent and storage vessel to meet design targets. Because the methodology takes into account the coupled physical processes occurring during the operation of the storage system, the impact of all components on the overall system performance are evaluated rather than the attributes of a single component. The additional components include the balance of tank items, namely the vacuum insulation system, the pressure vessel system and the heat transfer system. The mass and volume occupied by the balance of plant components was assessed using a lumped parameter model, developed in Matlab[®]. The overall methodology can be used to identify the required range of operating conditions, adsorbent material properties, and heat transfer design parameters. The range of acceptable parameters forms a multi-dimensional volume, or envelope. For this reason, the methodology is referred to as the Adsorbent Acceptability Envelope (AAE). This approach is analogous to that developed in reference [17] for metal hydrides. The AAE addresses the performance of an adsorption-based storage system, which includes the adsorbent and other functional components, for which the temperature and pressure may both vary.

The AAE is applied in two ways. One application employs the DOE technical targets for Year 2020 and for Year 2025 [2] to determine the required range of geometrical and adsorbent parameters, which are not known a priori. In the second application, the chemical and physical characteristics of the most promising existing adsorbents are used as baseline data for the AAE.

Their performance is assessed and compared with the DOE technical targets, also identifying the enhancements required to meet the targets. In all cases the AAE is applied for a range of different geometries and operating conditions.

2. Model description

The acceptability envelope (AAE) analysis employs lumped parameters global mass and energy balances for the storage system. At present the AAE employs the Dubinin-Astakhov-Radushkevich (DAR) isotherms as discussed in [4,5]. Isotherms parameters are input functions with their associated parameters.

The conservation equations are applied to the storage vessel which is treated as a control volume having uniform properties. The overall system includes the adsorbent material and the coupled finned heat transfer system (modeled using either rectangular coordinate or cylindrical coordinate approaches), insulation system and pressure vessel. At a given time, the values of properties transported out of the control volume are assumed to be the same as those within the control volume. The gas compressibility factor and enthalpy are obtained from the NIST REFPROP database [18].

2.1 Mass Conservation

The global mass conservation equation is:

$$m_{ads}M_{H_2} \frac{dn_{total}}{dt} = \dot{m}_{in} - \dot{m}_{out} \quad 1$$

For the DAR isotherm model

$$n_{total} = n_a + c_{H_2}(V_v - V_a) \quad 2$$

Here, the total porosity is

$$\epsilon = \rho_{ads}(V_v - V_a) \quad 3$$

so that

$$\epsilon V = \rho_{ads} V (V_v - V_a) = m_{ads} (V_v - V_a) \quad 4$$

Substitute Equations 2 and 4 into Equation 1.

$$m_{ads} \frac{\partial n_a}{\partial t} + \epsilon V \frac{\partial c_{H_2}}{\partial t} = \frac{\dot{m}_{in} - \dot{m}_{out}}{M_{H_2}} \quad 5$$

Rearrange terms in Equation 5 and use the chain rule to write $\frac{dc_{H_2}}{dt}$ and $\frac{dn_a}{dt}$ in terms of $\frac{dP}{dt}$ and $\frac{dT}{dt}$.

$$\left[\epsilon V \frac{\partial c_{H_2}}{\partial T} + m_{ads} \frac{\partial n_a}{\partial T} \right] \frac{dT}{dt} + \left[\epsilon V \frac{\partial c_{H_2}}{\partial P} + m_{ads} \frac{\partial n_a}{\partial P} \right] \frac{dP}{dt} = \frac{\dot{m}_{in} - \dot{m}_{out}}{M_{H_2}} \quad 6$$

2.2 Energy Conservation

For DAR isotherms, the global energy conservation equation is [4, 5, 19]:

$$\begin{aligned} \sum_{HX \text{ Surfaces}} \tau_{Tank \text{ and } i} (m_i C_{P_i}) \frac{dT}{dt} + \epsilon V \left[h \frac{dc_{H_2}}{dt} + c_{H_2} \frac{dh}{dt} \right] - \epsilon V \frac{dP}{dt} \\ + m_{ads} \left[\frac{d\Delta U_a}{dt} + \frac{d(n_a u_0)}{dt} + C_{P_{ads}} \frac{dT}{dt} \right] = \frac{\dot{m}_{in}}{M_{H_2}} h(T_{in}, P_{in}) - \frac{\dot{m}_{out}}{M_{H_2}} h(T_{out}, P_{out}) + \frac{\delta Q}{\delta t} + \frac{\delta W}{\delta t} \end{aligned} \quad 7$$

No work, other than that due to increasing pressure, is done on the system. Therefore, the term

$\frac{\delta W}{\delta t}$ is 0. From Equation 5 for mass conservation

$$\epsilon V h \frac{\partial c_{H_2}}{\partial t} = \frac{(\dot{m}_{in} - \dot{m}_{out})}{M_{H_2}} h - m_{ads} h \frac{\partial n_a}{\partial t} \quad 8$$

Substitute Equation 8 into Equation 7, using $h = h(T_{out}, P_{out})$ for a lumped homogenized system.

$$\begin{aligned} \sum_{HX \text{ Surfaces}} \tau_{Tank \text{ and } i} (m_i C_{P_i}) \frac{dT}{dt} + \epsilon V c_{H_2} \frac{dh}{dt} + (\dot{m}_{in} - \dot{m}_{out}) h - m_{ads} h \frac{\partial n_a}{\partial t} - \epsilon V \frac{dP}{dt} + m_{ads} \left[\frac{d\Delta U_a}{dt} + \right. \\ \left. \frac{d(n_a u_0)}{dt} + C_{P_{ads}} \frac{dT}{dt} \right] = \frac{\dot{m}_{in}}{M_{H_2}} h(T_{in}(t), P_{in}(t)) - \frac{\dot{m}_{out}}{M_{H_2}} h + \frac{\delta Q}{\delta t} \end{aligned} \quad 9$$

Rearrange terms

$$\sum_{HX \text{ Surfaces}} \tau_{Tank \text{ and}} (m_i C_{P_i}) \frac{dT}{dt} + \epsilon V c_{H_2} \frac{dh}{dt} - m_{ads} h \frac{\partial n_a}{\partial t} - \epsilon V \frac{dP}{dt} + m_{ads} \left[\frac{d\Delta U_a}{dt} + \frac{d(n_a u_0)}{dt} + C_{P_{ads}} \frac{dT}{dt} \right] = \frac{\dot{m}_{in}}{M_{H_2}} [h(T_{in}(t), P_{in}(t)) - h(T_{out}, P_{out})] + \frac{\delta Q}{\delta t} \quad 10$$

If the pressure is approximately uniform throughout the vessel, as would be the case for powder-form or moderately compacted adsorbents, then $P_{out} \approx P(t)$, where $P(t)$ is the calculated vessel pressure. T_{in} is a function of time and T_{out} is the homogenized temperature within the vessel, so that it is the dependent variable and is written as $T_{out} = T(t)$.

Use the chain rule to write Equation 10 in terms of $\frac{dP}{dt}$ and $\frac{dT}{dt}$.

$$\left[\sum_{HX \text{ Surfaces}} \tau_{Tank \text{ and}} (m_i C_{P_i}) + \epsilon V c_{H_2} \frac{\partial h}{\partial T} - m_{ads} h \frac{\partial n_a}{\partial T} + m_{ads} \left(\frac{\partial \Delta U_a}{\partial T} + \frac{\partial (n_a u_0)}{\partial T} + C_{P_{ads}} \right) \right] \frac{\partial T}{\partial t} + \left[\epsilon V c_{H_2} \frac{\partial h}{\partial P} - m_{ads} h \frac{\partial n_a}{\partial P} + m_{ads} \left(\frac{\partial \Delta U_a}{\partial P} + \frac{\partial (n_a u_0)}{\partial P} \right) - \epsilon V \right] \frac{dP}{dt} = \frac{\dot{m}_{in}}{M_{H_2}} [h(T_{in}(t), P_{in}(t)) - h] + \frac{\delta Q}{\delta t} \quad 11$$

where, $h = h(T_{out}, P_{out}) = h(T(t), P(t))$.

2.3 Ancillary equations

The partial derivatives, $\frac{\partial c_{H_2}}{\partial T}$ and $\frac{\partial c_{H_2}}{\partial P}$ are obtained from the relation

$$c_{H_2} = \frac{P}{Z(T,P)RT} \quad 12$$

where: $Z(T,P) =$ The compressibility factor for hydrogen

$$R = \text{Gas constant} = 8.314 \text{ (J/mol-K)}$$

Hence,

$$\left. \frac{\partial c_{H_2}}{\partial T} \right|_P = -\frac{P}{R[Z(T,P)T]^2} \left[T \frac{\partial Z(T,P)}{\partial T} + Z(T,P) \right] \quad 13$$

and

$$\left. \frac{\partial c_{H_2}}{\partial P} \right|_T = \frac{1}{RZ(T,P)T} - \frac{P}{RT[Z(T,P)]^2} \left[\frac{\partial Z(T,P)}{\partial P} \right] \quad 14$$

The expression for the absolute adsorbed hydrogen (n_a) and the adsorbed phase internal energy

(ΔU_a) for DAR isotherms [4, 5] are expressed as follows:

$$n_a = n_{max} \exp \left[-\left(\frac{RT}{E_a} \right)^2 \ln^2 \left(\frac{P_0}{P} \right) \right] \quad 15$$

and

$$\Delta U_a = \frac{-n_{max} \alpha \sqrt{\pi}}{2} \left[1 - \operatorname{erf} \left(\sqrt{-\ln \left(\frac{n_a}{n_{max}} \right)} \right) \right] + n_a \left[RT - \alpha \sqrt{-\ln \left(\frac{n_a}{n_{max}} \right)} \right] \quad 16$$

The parameters in the DAR model as applied to MOF-5[®] are listed in Table 1.

Table 1

The partial derivatives of n_a and ΔU_a with respect to T and P are [4,5]:

$$\left. \frac{\partial n_a}{\partial T} \right|_P = \frac{2\alpha n_a \ln \left(\frac{n_a}{n_{max}} \right)}{T(\alpha + \beta T)} \quad 17$$

$$\left. \frac{\partial n_a}{\partial P} \right|_T = \frac{2n_a RT \sqrt{-\ln \left(\frac{n_a}{n_{max}} \right)}}{P(\alpha + \beta T)} \quad 18$$

$$\left. \frac{\partial \Delta U_a}{\partial T} \right|_P = n_a R + \frac{2\alpha n_a}{T(\alpha + \beta T)} \left[RT - \alpha \sqrt{-\ln \left(\frac{n_a}{n_{max}} \right)} \right] \ln \left(\frac{n_a}{n_{max}} \right) \quad 19$$

$$\left. \frac{\partial \Delta U_a}{\partial P} \right|_T = \frac{2n_a RT}{P(\alpha + \beta T)} \sqrt{-\ln \left(\frac{n_a}{n_{max}} \right)} \left[RT - \alpha \sqrt{-\ln \left(\frac{n_a}{n_{max}} \right)} \right] \quad 20$$

3. Applications

Equations 6 and 11 comprise a system of ordinary differential equations with P and T as the dependent variables, to be solved given the initial conditions. Equations 12-20 define terms within equations 6 and 11. Input parameters, defined by the user, are: \dot{m}_{in} , \dot{m}_{out} , m_{ads} , $P_{in}(t)$, $T_{in}(t)$ and the DAR parameters for the particular adsorbent. Initial conditions are the initial temperature and initial pressure of the vessel and its contents. The hydrogen enthalpy and compressibility factor are obtained from the NIST REFPROP database [18].

The total available, or the deliverable, amount of hydrogen is defined as

$$N_{available} = m_{ads} M_{H_2} \left(n_{total}(T_f, P_f) - n_{total}(T_0, P_0) \right) \quad 21$$

Equation 21 together with the required mass of deliverable hydrogen is used to calculate the mass of adsorbent. For this analysis it is assumed that all stored hydrogen is within the adsorbent bed volume, which includes the void space within the adsorbent (e.g. intra- and inter-particle void volume).

Several approaches can be adopted to provide the cooling/heating power required to adsorb-desorb hydrogen in the material. One of the most effective and easiest approaches sees the adoption of a flow-through cooling system to provide the required cooling power to adsorb the hydrogen. Cold hydrogen, flowing through the adsorbent tank, provides the cooling power that maintains the material at the required cryogenic temperatures. The hydrogen not adsorbed in the material is recirculated and reused to cool the system. Several examples of successful application of the flow-through cooling approach are documented in the literature with both modeling and experimental results showing effective hydrogen adsorption [19,20,21]. The heating power required to desorb hydrogen can be provided in several ways. Within the DOE HSECoE, the baseline approach saw the adoption of a resistive heater, placed in the central axial position of a honeycomb finned heat exchanger. The heat is exchanged with the adsorbent

material mainly through conduction, with the finned structure spreading the heat from the heater through the absorbent structure. The concept has been recently demonstrated for a 0.5 L tank, filled with MOF-5® material and achieving effective discharge rates at relatively low heating power [23]. The combined flow-through cooling and conductive discharge approach represents the baseline system for the AAE analysis application described in the current paper.

3.1 *Flow-through cooling adsorption and conductive desorption*

When the storage vessel arrives at the fueling station, it will be in a state of hydrogen depletion with a reduced pressure and elevated temperature. During the charging process heat is generated due to pressure work and the enthalpy of adsorption [19]. One proposed method for reducing the vessel temperature is flow through cooling, by which heat is removed convectively by circulating cold hydrogen through the adsorbent bed [19]. Flow-through cooling may be coupled with cooling of the exterior of the storage vessel.

If flow-through cooling alone is used to remove heat during the charging process, then $\frac{\delta Q}{\delta t} = 0$ in Equation 11. If the external cylindrical surface of the vessel is cooled during the charging process, $\frac{\delta Q}{\delta t}$, is approximated in a way that represents heat transfer at the surface.

In summary, for given combinations of \dot{m}_{in} , \dot{m}_{out} , m_{ads} , $P_{in}(t)$, $T_{in}(t)$, $C_{P\ ads}$, $m_{Tank\ \&\ Hx}$, $C_{P\ Tank\ \&\ Hx}$, V , ϵ , and isotherm parameters, the flow-through cooling model simultaneously solves Equations 6 and 11 to calculate $T(t)$, $P(t)$, $N_{available}(t)$, $H_{exhaust}$, $M_{H2\ exhaust}$. The term $H_{exhaust}$ represents the total enthalpy of the exhaust hydrogen used to cool the vessel and $M_{H2\ exhaust}$ is the mass of the hydrogen. These parameters determine the energy required to return the exhaust hydrogen to the state at which it entered the storage vessel. The functions $T(t)$ and $P(t)$ are the lumped vessel temperature and pressure and consequently, the exit temperature and pressure as functions of time. By varying the inputs a range of values is obtained for the calculated parameters. By constraining the dependent and independent

variables to values satisfying the technical targets a range of acceptable design and operating parameters are obtained.

In the charging or discharging process, the adsorbent might be cooled or heated via conduction to heat exchangers, having surfaces in contact with the adsorbent. Due to the low thermal conductivity of the adsorbent, heat transfer through the adsorbent bed is the limiting process for this configuration. Therefore, the cell size, which is a measure of the thermal diffusion length, is the dominant factor in heat transfer process.

As discussed in the section on flow-through cooling, there is a need to remove heat from the storage vessel during the charging process. This requirement applies to heat removal by conduction as well, and the concepts that applied to charging using flow-through cooling also hold for conduction.

While either flow-through cooling or conduction may be used during the charging of the vessel, conduction heat transfer is alone suitable for discharge. To discharge hydrogen, which is an endothermic process, it is apparent that heat must be added to efficiently recover the adsorbed gas. However, the thermodynamic path followed during the discharge process will impact dormancy – the amount of time required for heat transfer from the ambient environment to raise the temperature of the cryogenically cooled tank while the vehicle is idle. To optimize dormancy, the scheme for discharging hydrogen is to first depressurize the vessel and then heat the adsorbent as required to recover the pressure [23]. Therefore, to determine the required characteristics of the heat exchanger for the discharge process, it is assumed that the adsorbent is heated with the vessel acting as a closed control volume, for which there is no gas flowing into or out of the vessel. Heating will continue from the initial state until the pressure reaches a specified value. The accompanying temperature rise is determined by the equation for conservation of mass as shown in Equation 23 below. The equations for mass and energy conservation, together with the known final pressure, are used to determine the final mean

temperature and the amount of heat required. With appropriately defined terms, the equations apply to both heating and cooling and can be used for discharging and charging.

From Equation 1 for mass conservation

$$m_{ads} M_{H_2} \frac{dn_{total}}{dt} = \dot{m}_{in} - \dot{m}_{out} \quad 22$$

Integrate Equation 22 from initial to final state

$$n_{total}(T_f, P_f) - n_{total}(T_0, P_0) = \Delta m_{in} - \Delta m_{out} \quad 23$$

Use Equation 23, together with P_f to calculate T_f .

From Equation 7 for energy conservation with $\frac{\delta W}{\delta t} = 0$

$$\sum_{HX\ Surfaces} (m_i C_{P_i}) \frac{dT}{dt} + \epsilon V \frac{dc_{H_2} h}{dt} - \epsilon V \frac{dP}{dt} + m_{ads} \left[\frac{d\Delta U_a}{dt} + \frac{d(n_a u_0)}{dt} + C_{P_{ads}} \frac{dT}{dt} \right] - \frac{\delta Q}{\delta t} = \frac{\dot{m}_{in}}{M_{H_2}} h(T_{in}, P_{in}) - \frac{\dot{m}_{out}}{M_{H_2}} h(T_{out}, P_{out}) \quad 24$$

Apply $\int_{t_0}^{t_f} dt$ to Equation 24

$$\Delta Q = \frac{\Delta m_{out}}{M_{H_2}} h(T_{out}, P_{out}) - \frac{\Delta m_{in}}{M_{H_2}} h(T_{in}, P_{in}) + \epsilon V [c_{H_2} h]_{T_0, P_0}^{T_f, P_f} - \epsilon V [P]_{P_0}^{P_f} + \sum_{HX\ Surfaces} (m_i C_{P_i}) (T_f - T_0) + m_{ads} [\Delta U_a + n_a u_0]_{T_0, P_0}^{T_f, P_f} + m_{ads} \int_{T_0}^{T_f} C_{P_{ads}} dT \quad 25$$

For inflow, as would occur during charging, it is reasonable to assume that the incoming gas properties are fixed. However, for outflow the properties of the exiting gas are representative of the gas within the vessel, which change in time. Therefore, Equations 23 and 25 is best applied for no outflow ($\dot{m}_{out} = 0$ and $\Delta m_{out} = 0$) which, as discussed above, applies to the discharge scheme for the storage vessel.

If τ_{disch} is the required time for discharge (pressurization) to occur and if heat transferred to the adsorbent is constant, then the heat transfer rate is

$$\dot{Q} = \text{Heat Transfer Rate} = \frac{\Delta Q}{\tau_{disch}} \quad 26$$

The rate of heat transfer per volume of adsorbent is

$$q''' = \text{Heat Transfer Rate per Volume of Adsorbent} = \frac{\dot{Q}}{V_{ads}} \quad 27$$

The geometric forms of the heat exchangers are approximated as:

- Rectangular configurations, which include tube-and-fin heat exchangers and microchannel heat exchangers, which act as fins with internal flow channels.
- Cylindrical configurations which approximate hex-cell lattice heat exchangers.

During discharge, the goal of the analysis is to determine a range of characteristic lengths for the heat exchanger geometries that enable sufficient heat transfer without the surfaces of the heat exchangers exceeding the temperature limits of the adsorbents. The characteristic length for rectangular configurations would be the spacing between the fins, while for cylindrical configurations the characteristic length would be the radius of the cylinder.

3.1.1 Rectangular cell configuration

The contact area of each of the 2 surfaces is

$$A_{rhx} = \frac{V}{L_{bed}}$$

The number of cells is

$$n_{rhx} = \frac{L_{bed}}{L}$$

where: L = The spacing between the rectangular fins

For a wall heat flux given by $q'' = \frac{Q/2}{A_{rhx}n_{rhx}}$, the temperature distribution within the cell is [20]

$$T(x, t) = T_0 + \frac{q''t}{\rho C_P L/2} + \frac{q''L/2}{k} \left\{ \frac{3x^2 - (L/2)^2}{6(L/2)^2} - \frac{2}{\pi^2} \sum_{n=1}^{\infty} \left[\frac{(-1)^n}{n^2} e^{-\alpha \left(\frac{n\pi}{L/2}\right)^2 t} \cos\left(\frac{n\pi x}{L/2}\right) \right] \right\} \quad 28$$

where: $\alpha = \text{Thermal diffusivity} = k/\rho C_P$

Note that Equation 28 applies to the half-cell, from a heat transfer surface to the symmetric (zero heat flux) boundary at half the distance between the surfaces. For *heating* with a rectangular configuration during the discharge process, the maximum temperature at time t occurs at the heat transfer surface where $x = 0$. That is,

$$T_{max}(t) = T(0, t)$$

The maximum temperature during heating is important because some adsorbents may become damaged or suffer a loss of capacity at elevated temperatures.

3.1.2 Cylindrical cell configuration

The number of hexagonal cells within the vessel is calculated by superposing an array of cells onto a circle, as shown in Figures 1 and 2.

Figure 1 shows the arrangement of cells in a cross-section of the vessel with numbers assigned to the offset rows of cells. From Figure 2, which shows the geometry of the cells, it can be clearly seen that

$$a = \frac{R_{cell}}{\sqrt{3}} \quad \text{and} \quad \ell_{cell} = \frac{2R_{cell}}{\sqrt{3}}$$

where: $R_{cell} =$ Radius of the cylindrical cell (m) which is the flat-to-flat distance within a hex-cell

$$\ell_{cell} = \text{Half of the diagonal distance across the hex-cell}$$

The periodic length of the cell structure, λ_{cell} , is

$$\lambda_{cell} = 2(a + a) + 2(\ell_{cell} - a) = 2\sqrt{3}R_{cell}$$

From Figure 1 the cell rows range from 0 to $nrows$, where

$$nrows = \begin{cases} \left\lfloor \frac{R_{bed} - R_{cell}}{R_{cell}} \right\rfloor + 1 & \text{if } \left[\left(\frac{R_{bed} - R_{cell}}{R_{cell}} \right) - \left\lfloor \frac{R_{bed} - R_{cell}}{R_{cell}} \right\rfloor \right] > Ctol \\ \left\lfloor \frac{R_{bed} - R_{cell}}{R_{cell}} \right\rfloor & \text{if } \left[\left(\frac{R_{bed} - R_{cell}}{R_{cell}} \right) - \left\lfloor \frac{R_{bed} - R_{cell}}{R_{cell}} \right\rfloor \right] \leq Ctol \end{cases}$$

where: $\text{floor}(x) =$ Is the integer obtained by removing the decimal places in x . If x and integer $\text{floor}(x)$ is x otherwise $\text{floor}(x)$ is the greatest integer that is less than x .

$C_{tol} =$ Is a fraction of cell height (flat-to-flat distance) to accommodate a small extension of a hex-cell beyond R_{bed} . This is akin to a round-off value.

By inspection of Figure 1, the number of cells in the i^{th} row is

$$ncells_i = \begin{cases} \left\lfloor \frac{rbed_i - 2\frac{R_{cell}}{\sqrt{3}}[1+(-1)^i]}{2\sqrt{3}R_{cell}} \right\rfloor + 1 & \text{if } \left\{ \frac{rbed_i - 2\frac{R_{cell}}{\sqrt{3}}[1+(-1)^i]}{2\sqrt{3}R_{cell}} - \left\lfloor \frac{rbed_i - 2\frac{R_{cell}}{\sqrt{3}}[1+(-1)^i]}{2\sqrt{3}R_{cell}} \right\rfloor \right\} < Ctol \\ \left\lfloor \frac{rbed_i - 2\frac{R_{cell}}{\sqrt{3}}[1+(-1)^i]}{2\sqrt{3}R_{cell}} \right\rfloor & \text{if } \left\{ \frac{rbed_i - 2\frac{R_{cell}}{\sqrt{3}}[1+(-1)^i]}{2\sqrt{3}R_{cell}} - \left\lfloor \frac{rbed_i - 2\frac{R_{cell}}{\sqrt{3}}[1+(-1)^i]}{2\sqrt{3}R_{cell}} \right\rfloor \right\} \geq Ctol \end{cases}$$

where: $rbed_i = \sqrt{R_{bed}^2 - (iR_{cell})^2} =$ The horizontal distance to the edge of the cylinder wall at the vertical height of the i^{th} row of cells.

See Figure 1.

The total number of cells, n_{chx} , is then,

$$n_{chx} = 2ncells_0 + 4 \sum_{i=1}^{nrows} ncells_i$$

Figure 1.

Figure 2.

Approximate the hex-cells as cylinders of radius, R_{cell} , and length, L_{bed} . The heat transfer surface area of a given cell is

$$A_{chx} = 2\pi R_{cell} L_{bed}$$

For a wall heat flux of $q'' = \frac{\dot{Q}}{n_{chx} A_{chx}}$, the temperature distribution within the cell is [20]:

$$T(r, t) = T_0 + \frac{2q''\alpha t}{kR_{cell}} + \frac{q''R_{cell}}{k} \left\{ \frac{r^2}{2R_{cell}^2} - \frac{1}{4} - 2 \sum_{n=1}^{\infty} \left[e^{-\alpha\beta_n^2 \left(t/R_{cell}^2 \right)} \frac{J_0(r\beta_n/R_{cell})}{\beta_n^2 J_0(\beta_n)} \right] \right\} \quad 29$$

where: $\beta_n =$ Positive roots of the first order Bessel function of the first kind

$$J_1(\beta_n) = 0$$

In Equation 29 $r = R_{cell}$ is the location of the heat transfer surface and $r = 0$ is the center of the cell. Therefore, for heating with a cylindrical configuration during the discharge process, the maximum temperature at time t occurs at the heat transfer surface where $r = R_{cell}$ that is,

$$T_{max}(t) = T(R_{cell}, t)$$

3.2 Balance of tank model

The current analysis focuses on the assessment of the technical performance (weight and volume capacity) of the adsorbent system, including the pressure vessel and its internal components.

Figure 3 shows a schematic of the adsorbent tank system, including the vessel interior structure (radius R_1), pressure vessel wall (radius R_2), multilayer vacuum insulation (radius R_3) and external vacuum shell (radius R_4).

Figure 3:

The pressure vessel was conceptually designed assuming degrees of freedom, corresponding to the pressure vessel type, endcap design, length-to-diameter ratio, insulation thickness and type, and the presence or absence of a tank cooling system. Type 1 pressure vessels are composed of

metal, with aluminum and stainless steel being the two most common metals used. Type 3 and 4 vessels are composite pressure vessels with metal or plastic liners, respectively, wrapped in carbon fiber material to reduce the pressure vessel mass without compromising strength. The choice between pressure vessel types is a balance between mass and cost for a given set of operating conditions (pressure and temperature). The Type 1 pressure vessel is in general preferable at pressures ≤ 100 bar [24] due to its low cost and reasonably small mass and volume. The pressure vessel endcaps are typically hemispherical, oblate, or ellipsoid, with differences defined by the ratio of the pressure vessel cylinder radius (R_1) to the endcap depth (r). Hemispherical and oblate endcaps were set to $r = R_1$ and $r = 2/3 * R_1$, respectively, while the ellipsoid endcap can have a variety of ratios with the most common being $r = R_1/2$. Similarly, the length-to-diameter ratio ($L_{bed}/2R_1$) covers a range of pressure vessel sizes from 2:1 to 10:1 depending upon the vehicle framework. Typically, the insulation is high multilayer vacuum insulation of varying thicknesses up to 0.025 m. Three vacuum insulation layers were assumed for the current analysis based on the typical cryogenic temperatures to be achieved in the hydrogen adsorption applications. To minimize cooling needs, several pressure vessel designs can also include a LN2-based tank cooling system, but this option was not included in the current work.

Based on the parametric study in reference [24], the baseline design had Type 1 aluminum pressure vessels with 2:1 $L_{bed}:2R_1$ ratios, which minimized the cost and volume for design pressures below 100 bar. The pressure vessel is designed around the volume required for the adsorbent material and internal heat exchanger. The pressure vessel is designed based on the hoop stress and Von Mises stress necessary to maintain a 2.5 safety factor at the maximum design pressure and minimum design temperature. The additional pressure vessel balance of tank is added to the pressure vessel, including the boss, plug, support rings, 1-inch multilayer

insulation (i.e. $R_3-R_2= 0.025$ m), cooling channels, and 2-mm outer vacuum shell (i.e. $R_4-R_3= 0.002$ m).

4. Results

The models for flow-through cooling and for charging and discharging heat transfer by heat exchangers were programmed into Mathcad® [21]. Input and application format was general to allow for a wide range of storage system evaluations. The AAE approach has been applied assuming the integrated flow-through cooling and conductive discharging as the baseline approach. Two cases were examined. The first analysis was performed for adsorbents with known thermodynamic properties and system operating conditions as variables. The aim of this analysis is to see the behavior of known materials under different operating conditions. In particular, MOF-5® has been assumed as the baseline material and its performance has been assessed under different operating conditions. The DAR model parameters for the material are shown in Table 1, interpolating data available from Ford® [22]. A bulk density (ρ_{ads}) of 150 kg/m^3 and a thermal conductivity (k) of 0.05 W/mK have been assumed based on recent data available from Ford® [22]. To evaluate the specific heat of the materials, Pyda's correlation [25] has been adopted, assuming that the specific heat MOF-5® is close to that of MaxSorb® activated carbon [19]. Recent results confirmed the validity of this hypothesis [26]. The baseline system operating conditions are shown in Table 2, based on the conditions assumed within the HSECoE.

Table 2

The profiles of gravimetric and volumetric capacities for the MOF-5® adsorbent system, under the operating conditions listed in Table 2, are shown in Figures 4 and 5. The adsorbent gravimetric capacity (wf_{ads}) and volumetric capacity (vf_{ads}) are defined as the ratio of the total weight of the hydrogen stored inside the bed to the total weight of adsorbent and adsorbed hydrogen, for wf_{ads} , or to the bulk volume, for vf_{ads} . The system gravimetric capacity (wf_{sys}) and

volumetric capacity (vf_{sys}) are defined as the ratio of the total weight of stored hydrogen and the weight, for wf_{sys} , or the volume, for vf_{sys} , of the overall system. The system weight/volume accounts for: 1) the weight/volume of the adsorbent material and of the stored hydrogen, 2) the weight/volume of the pressure vessel, 3) the weight/volume of the insulation and shell of the container, and 4) the weight/volume of the outer shell of the tank. The terms have been suitably assessed following the model described in Section 3, applied for the different operating conditions.

Figure 4:

Figure 5:

Under the operating conditions indicated in Table 2, MOF-5[®] can achieve a material gravimetric capacity that is about 2.6 times higher than the 2025 DOE system target (5.5 wf%) as shown in Figure 4. However, the additional system weight reduces the overall system gravimetric capacity to about 4 wf%, which is approximately 27% lower than the 2025 DOE system target. The MOF-5[®] volumetric capacity reaches values on the order of 25 g/L, which is approximately 63% the 2025 DOE target, namely $vf = 40$ g/L. The addition of system volumes reduces the overall system volumetric capacity to values on the order of 15 g/L, representing approximately 38% of the 2025 DOE target (Figure 5). Based on the results achieved under the conditions of Table 2, different sensitivity analyses have also been carried out for the MOF-5[®] adsorbent system. It was found that the inlet hydrogen pressure is the parameter with the highest influence on the gravimetric and volumetric capacities of the system. The hydrogen inlet pressure was varied from 40 bar to 100 bar, maintaining the inlet hydrogen temperature at 80 K. Results of the pressure sensitivity analysis are shown in Figures 6 and 7. The material weight fraction (wf_{ads}) is strongly affected by the adsorbent operating pressure. An increase of about 66% of the inlet hydrogen pressure, from 60 bar to 100 bar, results in an increase of almost 30%, from about 14

wf% to about 19 wf%, of the material-based gravimetric capacity. However, the additional system weight due to insulation, pressure vessel and the balance of plant, almost completely offsets the benefits achieved by the pressure increase. The final system gravimetric capacity of 4.3 wf%, obtained for an inlet pressure of 100 bar, is only 5.4% higher than the corresponding value achieved at 60 bar (namely 4.0 wf%) and it is still almost 22% lower than the 2025 DOE target for the system gravimetric capacity.

Figure 6:

Figure 7 shows the material and system volumetric capacity profiles for hydrogen pressures between 40 bar and 100 bar. A 66% increase in the inlet hydrogen pressure, from 60 bar to 100 bar, results in an increase in the material-based volumetric capacity of almost 36%, from about 25 g/L to about 35 g/L. However, at a pressure of 100 bar the system based volumetric capacity can reach values on the order of 20 g/L, representing 50% of the 2025 DOE target. The main effect of increasing pressure is the reduction of the system volume, resulting in a significant increase of the system volumetric capacity and material gravimetric capacity. However, the system gravimetric capacity is also strongly affected by the weight of the pressure vessel, which increases with increasing pressure. This negative effect essentially balances the positive effect due to the system size reduction.

Figure 7:

To achieve the maximum MOF-5[®] gravimetric and volumetric capacities in 200 s, the mass of recirculated hydrogen must be between 5 and 10 times the mass of stored hydrogen, as shown in Figure 8. Results of the calculations show that an inlet pressure of 60-100 bar is required to limit the amount of hydrogen to be recirculated to maintain a temperature of 80 K. The other operating conditions are shown in Table 2.

Figure 8:

The AAE model was also applied to solve inverse problems, where the operating conditions and weight and volume fraction targets are known and the material properties are the unknowns of the problem. The aim of this analysis is to assess the acceptable range of thermodynamic and physical properties of an ideal material, being able to meet the targets under selected operating conditions. The baseline conditions are those shown in Table 2. In addition, the following assumption on the material thermodynamic properties was also made. The MOF-5[®] material DAR model parameters have been assumed for the ideal material as well, except for the variable n_{\max} . This implies that the ideal material can adsorb the maximum amount of hydrogen (i.e. maximum of the function $n_a = n_a(P, T)$) under the same operating conditions as for the MOF-5[®] material, but the actual adsorption value can vary. A more complete sensitivity analysis, including the other DAR parameters, would require the inclusion of a multivariable optimization procedure, accounting for the material physical and chemical intrinsic property relationships, which is beyond the scope of this work. Several sensitivity analyses were carried out, showing that the gravimetric and volumetric capacities were mainly affected by the adsorbent density and by the n_{\max} quantity. Results showing the influence of n_{\max} on the gravimetric and volumetric capacities are shown in Figures 9 and 10[†]. The ideal material, being able to meet the 2025 DOE targets for both the gravimetric and volumetric capacities, under the conditions and assumptions described above, needs to achieve a maximum hydrogen adsorption capacity (n_{\max}) of about 400 mol_{H2}/kg_{ads}. This value is approximately 4.5 times higher than that of MOF-5[®], namely $n_{\max} = 88.1$ mol_{H2}/kg_{ads}. The ideal material system, with $n_{\max} = 400$ mol_{H2}/kg, can achieve the 2025 DOE volumetric capacity and can also reach a gravimetric capacity approximately 1.8 times higher than the corresponding 2025 DOE target, see Figure 9. To reach the 2020 DOE target of a volumetric capacity of 30 g_{H2}/L, a material with $n_{\max} \approx 275$ mol_{H2}/kg is required, representing about 3.1 times the corresponding maximum capacity of MOF-5[®] material.

[†] The other thermal, chemical and physical properties (i.e. density, thermal conductivity, specific heat, etc.) of the ideal material were assumed equal to the values for MOF-5[®].

Figure 9:

Figure 10:

The same sensitivity analysis was carried out to analyze the influence of the material density (ρ_{ads}) on the material and system gravimetric and volumetric capacities, as shown in Figure 11 and Figure 12[‡]. Figure 11 shows the influence of the material bulk density on the material and system gravimetric capacity. Figure 12 shows the influence of the material bulk density on the material and system volumetric capacity. The system gravimetric capacity data are fitted through a polynomial regression (Figure 11), while a linear regression is used fit the system volumetric capacity (Figure 12). With increasing adsorbent bulk density, the material gravimetric capacity decreases as shown in Figure 11. However, the system gravimetric capacity increases, due to the reduced size and correspondingly the weight of the vessel and insulation. The ideal material, being able to meet the 2025 DOE targets for gravimetric and volumetric capacity, under the conditions and assumptions described above, needs to have a material bulk density of about 700 kg/m³, approximately 3-4.5 times higher than the MOF-5[®] material densities[§]. This “ideal” material can fully meet the 2025 DOE system volumetric capacity target and very closely approach the system gravimetric capacity target. However, to meet the 2020 DOE targets a material with a bulk density on the order of 450 kg/m³ needs to be identified. This value is about 2-3 times the typical density of powder MOF-5[®] and is comparable with the density of pelletized MOF-5[®] [24].

Figure 11:

Figure 12:

[‡] The other thermal, chemical and physical properties (i.e. n_{max} , thermal conductivity, specific heat, etc.) of the ideal material were assumed equal to the values for MOF-5[®].

[§] The bulk density of powder MOF-5[®], in general, to the knowledge of the authors, can vary between 150 kg/m³ [22] and 220 kg/m³ [26]

5. Conclusions

The Adsorbent Acceptability Envelope (AAE) utilizes the coupled adsorbent and system characteristics to evaluate the overall performance of a gas storage system relative to operational targets, rather than simply the merit of individual material properties in isolation. The basis of the AAE is a lumped, transient mass and energy balance model. In the application considered in this paper, the AAE is applied to flow-through cooling and conduction heat exchange in rectangular and cylindrical geometries. In the present model either flow-through cooling or conduction can be used for removal of heat generated during the charging process. During the discharge process, heat addition is by conduction from heat exchanger surfaces only. In the case of flow-through cooling, the AAE can be used to determine the process efficiency based on the total enthalpy of the discharged hydrogen used as a heat transfer fluid, and the energy required to reclaim it by returning it to the state of the inlet hydrogen. Liquid nitrogen assisted flow-through cooling during the charging process can be investigated by applying an appropriate heat source in Equation 11. The model is general and can be applied to adsorbent based storage of a variety of single component gases, such as methane or hydrogen, the latter of which was used in the current study. Although the AAE utilized the Dubinin-Astakhov-Radushkevich isotherm model in this study, alternative isotherms, such as the UNILAN or dual-site models, could easily be employed. For hydrogen adsorption, results of the AAE analysis applied to flow-through cooling concept, showed that MOF-5[®], under the assumed conditions, does not have the potential to reach the gravimetric and volumetric capacity in the 2025 DOE targets. At 100 bar and 80 K charging conditions, MOF-5[®] can reach a weight capacity approximately equal to 78% of the 2025 DOE target (5.5 wf%) and a volumetric capacity about half the corresponding 2025 DOE target (40 g/L). Under conditions assumed in this paper, it is necessary to have a material with either a bulk density approximately 3-4.5 times higher than MOF-5[®] or a maximum hydrogen

storage capacity (n_{\max}) about 4.5 times higher than MOF-5[®] to meet the target 2025 DOE gravimetric and volumetric capacities. The 2020 DOE targets can be achieved with a material having a bulk density of about 2-3 times the corresponding value of powder MOF-5[®] or with a maximum storage capacity about 3 times the MOF-5[®] maximum capacity.

Acknowledgements

This work was performed as part of the US DOE-EERE's Hydrogen Storage Engineering Center of Excellence. The authors gratefully acknowledge the support, insight and assistance by Drs. Ned Stetson and Jesse Adams, who were the DOE managers for this project.

The views and opinions of the authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights.

References

- [1] Gardiner M. Energy requirements for hydrogen gas compression and liquefaction as related to vehicle storage needs. DOE Hydrogen Program Record, Record # 9013, (2009).
- [2] DOE Hydrogen Storage Website, <https://www.energy.gov/eere/fuelcells/doe-technical-targets-onboard-hydrogen-storage-light-duty-vehicles> (Accessed March 2018)

- [3] Syed MT, Sherif SA, Veziroglu TN, Sheffield JW. An economic analysis of three hydrogen liquefaction systems. *Int J Hydrogen Energy* 1998;23(7):565-576.
- [4] Richard M-A, Bénard P, Chahine R. Gas adsorption process in activated carbon over a wide temperature range above the critical point. Part 1: modified Dubinin-Astakhov model. *Adsorption* 2009;15:43-51.
- [5] Richard M.-A, Bénard P, Chahine R. Gas adsorption process in activated carbon over a wide temperature range above the critical point. Part 2: conservation of mass and energy. *Adsorption* 2009;15:53-63.
- [6] Kumar VS, Raghunathan K, Kumar S. A lumped-parameter model for cryo-adsorber hydrogen storage tank. *Int J Hydrogen Energy* 2009;34:5466-75.
- [7] Kumar VS, Kumar S. Generalized model development for a cryo-adsorber and 1-D results for the isobaric refueling period. *Int J Hydrogen Energy* 2010;35:3598-3609.
- [8] Ghosh I, Naskar S, Bandyopadhyay SS. Cryosorption storage of gaseous hydrogen for vehicular application – a conceptual design. *Int J Hydrogen Energy* 2010;35:161-8.
- [9] Hermosilla-Lara G, Momen G, Marty PH, Le Neindre B, Hassouni K. Hydrogen storage by adsorption on activated carbon: Investigation of the thermal effects during the charging process. *Int J Hydrogen Energy* 2007;32:1542-53.

- [10] Momen G, Hermosilla G, Michau A, Pons M, Firdaus M, Marty PH, et al. Experimental and numerical investigation of the thermal effects during hydrogen charging in a packed bed storage tank. *Int J Hydrogen Energy* 2009;52:1495-1503.
- [11] L. Zhan, K.X. Li, R. Zhang. Improvements of the DA equation for application in hydrogen adsorption at supercritical conditions. *J. Supercrit. Fluids* 2004;28:37-45.
- [12] Paggiaro R, Michl F, Bénard P, Polifke W. Cryo-adsorptive hydrogen storage on activated carbon, II: Investigation of the thermal effects during filling at cryogenic temperatures. *Int J Hydrogen Energy* 2010;35:648-59.
- [13] Schütz W, Michl F, Polifke W, Paggiaro R. Storage systems for storing a medium and method for loading a storage system with a storage medium and emptying the same therefrom. Patent(WO/2005/044454), <http://www.wipo.int/pctdb/en/wo.jsp?wo=2005044454>; 2005.
- [14] Xiao J, Tong I, Deng C, Bénard P, Chahine R. Simulation of heat and mass transfer in activated carbon tank for hydrogen storage. *Int J Hydrogen Energy* 2010;35:8106-116.
- [15] Vasiliev LL, Kanonchik LE. Activated carbon fibres and composites on its base for high performance hydrogen storage system. *Chem Eng Sci* 2010;65:2586-95.
- [16] Bhatia SK, Myers AL. Optimum Conditions for Adsorptive Storage. *Langmuir* 2006;22:1688-1700.

- [17] Corgnale C, Hardy BJ, Tamburello DA, Garrison SL, Anton DL. Acceptability envelope for metal hydride-based hydrogen storage systems. *Int J Hydrogen Energy* 2012;37:2182-24.
- [18] Lemmon EW, Huber ML, McLinden MO. NIST Standard Reference Database 23: Reference Fluid Thermodynamic and Transport Properties-REFPROP, Version 8.0, National Institute of Standards and Technology, Standard Reference Data Program, Gaithersburg, 2007.
- [19] Hardy B, Corgnale C, Chahine R, Richard M-A, Garrison S, Tamburello D, Cossement D, Anton D. Modeling of adsorbent based hydrogen storage systems. *Int J Hydrogen Energy* 2012;37:5691-5705.
- [20] Carslaw HS, Jaeger JC. "Conduction of Heat in Solids," Second Edition, Oxford University Press (1976).
- [21] Mathcad 15.0. Copyright © 2011 Parametric Technology Corporation
- [22] Sudik A. Personal communications. Ford, 2011.
- [23] Corgnale C, Hardy B, Chahine R, Cossement D. Hydrogen desorption using honeycomb finned heat exchangers integrated in adsorbent storage systems. *Applied Energy* 2018;213:426-434.
- [24] Tamburello D, Hardy B, Corgnale C, Sulic M, Anton D. Cryo-adsorbent hydrogen storage systems for fuel cell vehicles. *Proceedings of the ASME 2017*

Fluids Engineering Division Summer Meeting (FEDSM2017-69411), Waikoloa,
Hawaii, USA

- [25] Pyda M, Bartkowiak M, Wunderlich B. Computation of heat capacities of solids using a general Tarasov equation. *J Thermal Analysis* 2009;52(2):631-656.
- [26] Ming Y, Purewal J, Liu D, Sudik A, Xu C, Yang J et al. Thermophysical properties of MOF-5[®] powders. *Microporous and Mesoporous Materials* 2014;185:235-244.