



Dynamics of Hydrogen Storage through Adsorption: Process Simulation and Energy Analysis

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Abstract: The mass and energy balances of a zero-dimensional model for hydrogen storage by adsorption is studied. The model is solved with an in-house MATLAB code and validated with three experimental case studies from the literature, obtained with cryogenic lab-scale reservoirs using different adsorbents and dynamic operating conditions. The results of the simulations agree well with reported measured temperature and pressure profiles. The hydrogen adsorption process is described assuming instantaneous thermodynamic equilibrium. In accordance with the potential theory, variations in the adsorbed phase volumes filling the adsorbent pores were described applying the revisited Dubinin–Astakhov (rev-D-A) equation and accounting for gas phase non-ideality. The simulation model was used to assess the energy requirements of a variety of adsorption-based hydrogen storage processes and compared with other conventional hydrogen storage modes such as compression and liquefaction. Thus, whatever different adsorbent materials are considered, this technology appears relatively energy intensive due to the reservoir cooling duty at cryogenic temperature.

Keywords: hydrogen storage; hydrogen adsorption; modeling and simulation; energy transition; adsorption application



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1. Introduction

A big proportion of the greenhouse gas emissions in the atmosphere are caused by the combustion of hydrocarbons [1]. Hydrogen has been considered as a zero-carbon fuel replacement, in particular in the transport sector for conventional vehicles, since it can be used by internal combustion engines or fuel cells [2]. Due to the low volumetric energy density of hydrogen, which is its major drawback, 5 MJ·kg⁻¹ at 700 bar and ambient temperature, compared to 32 MJ kg⁻¹ for gasoline [3], its storage is a challenge. This requires a capacity between 5 and 13 kg of hydrogen for onboard hydrogen storage to meet the driving range for the full range of light-duty vehicle platforms [3]. To store 5 kg of hydrogen at 700 bar, a type IV compressed hydrogen storage tank requires a volume of 203 L [4]. Storing hydrogen by compression at such an elevated pressure poses various issues: the high cost of the equipment, difficult maintenance operation, hydrogen contamination with lubricating oil, and embrittlement of metal components that may cause the container to fracture [5]. The alternative conventional method, which is liquefaction, offers a very high density of liquid hydrogen, namely 70 kg·m⁻³ at 20 K and 1 bar, which is far higher than the density of compressed hydrogen gas at 700 bar, 42.6 kg·m⁻³ [6]. However, the cryogenic process is technically complex and energy intensive. Moreover, it induces more potential hazards resulting from boil-off during dormancy, ice formation, and air condensation [7].

It has been recognized that storing hydrogen in a solid state by adsorption into porous materials can be a viable solution for stationary and on-board applications [8]. Hydrogen confinement in nanometer-sized pores of high-surface area materials, such as

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nanoporous carbons (activated chars, nanotubes, fullerenes, expanded graphite), metal organic frameworks (MOFs), or oxides (zeolites) results in a higher volumetric storage density than the bulk gas under the same pressure and temperature conditions [8]. The higher the difference between the densities of the adsorbed fluid and the bulk gas, the more efficient the hydrogen storage process is. However, due to hydrogen's low critical temperature ($T_c = 32$ K), reaching liquid-like densities in the adsorbed phase at ambient temperature (298 K) is particularly difficult when operating at moderate pressures, so that storage capacities do not dramatically exceed those by simple compression at the same pressure. Typically, among the best MOF materials suitable for hydrogen storage, the MOF NU-1103, synthesized by dissolving a zirconium source and organic linkers in dimethilformamide with the addition of benzoic acid, features a bulk density of 345 kg·m⁻³ and stores 8.0 gH₂·L⁻¹ (\approx 2.3 wt%) at 100 bar and 295 K, while the density of compressed hydrogen under the same conditions is 7.7 gH₂·L⁻¹ [9,10].

Consequently, in order to enhance volumetric and gravimetric adsorption capacities of hydrogen in porous materials, operation at cryogenic temperature (77 K or above) is commonly adopted. At the temperature of liquid nitrogen (77 K) and at a pressure of 100 bar, the same MOF material offers volumetric and gravimetric adsorption capacities of 44.9 gH₂·L⁻¹ and 13.0 wt%, respectively. Although carbonaceous porous materials such as activated carbons exhibit lower gravimetric adsorption capacities, reaching at best 7–10.4 wt% at 60 bar and 77 K [11], they are competitive with MOFs because they can demonstrate larger volumetric storage capacities thanks to their higher bulk density, so that a larger mass of adsorbent can be packed in the vessel. Moreover, the activated carbons are inexpensive in comparison to MOFs and commonly available on the market [5]. Furthermore, several adsorbent materials have been engineered at the simulation scale, like a titanium decorated carbon [12], exhibiting gravimetric hydrogen storage capacities up to 6.67 wt% under ambient conditions.

Most of research efforts on the application of nanoporous materials for hydrogen adsorption have been driven to meet the 5.5 wt% and 40 gH₂·L⁻¹ DoE 2025 target for onboard H₂ storage systems, including their reservoir components [13]. A great part of these studies addresses the design and characterization of porous materials and the assessment of their hydrogen adsorption—desorption capacities. But the evaluation of the energetic efficiency of the process is rarely addressed, especially in comparison to conventional methods of hydrogen storage [14]. If the overall energy consumption of the storage system can be primarily assessed by analyzing the thermodynamic path of the process between different equilibrium states, a more accurate assessment of the heat and power energy requirements should account for the dynamics of the system, and consider the transient variations in the operating parameters such as pressure, temperature, and amounts of hydrogen accumulated in the tank during the charge and discharge steps.

Simulation of the dynamic adsorption process during hydrogen loading and discharge requires the development of models relying on the formulation of mass and energy balances, combined with an equation of state to describe the gas phase behavior and temperature dependent equilibrium adsorption isotherms. Assuming the hydrogen gas phase as ideal can be considered reasonable provided that the operating adsorption pressure remains moderate [15–22]. In the pressure range of 150 bar, P. Sridhar and N. S. Kaisare [23], demonstrated that deviations computed by using either the ideal gas law or the viral equation of state are actually small, and do not exceed 0.2 bar for pressure and 1 K for temperature. However, in the case of higher working pressures, reaching about 700 bar, and cryogenic temperatures, the non-ideality of the hydrogen gas phase needs to be considered and this requires implementing a real gas equation of state [5,23,24].

In order to describe adsorption equilibrium data of hydrogen onto microporous adsorbents such as activated carbons or MOFs, different isotherm models can be applied. The modified Dubinin–Astakhov model (M-D-A) was, for instance, retained in several studies investigating hydrogen adsorption at high pressure and supercritical temperature [5,14,16,19,24–27]. Alternative models such as the Langmuir model [15,28], the

Radke–Prausnitz model [17,29] and the Unilan model [18,22,30] were also chosen. Sridhar and Kaisare [23] compared the simulation results when charging a reservoir containing MOF-5 adsorbent using three isotherm models: Unilan, M-D-A and Toth, in spite of the good fit between theoretical and experimental isotherms determined in the temperature range between 77 and 300 K, these authors showed that the predicted hydrogen up-takes in the adsorbent bed were considerably impacted by the choice of the isotherm model. The right selection of the temperature-dependent isotherm equation is therefore crucial to obtaining the good predictive ability of the process simulation model.

A comparison of models proposed in the literature in recent decades for the simulation of cryogenic hydrogen storage reservoirs operating by pressure-temperature swing adsorption is given in Table 1. Moreover, considering or not the non-ideal behavior of the hydrogen gas and describing adsorption equilibrium data according to different forms of isotherm equations, the spatial heterogeneities of the system could or not be assumed. In the case of zero-dimensional (0-D) models, also denominated as lumped models, the variables of the system are supposed to be uniform throughout the entire adsorbent vessel volume, so that overall pressure, temperature, and hydrogen amounts are computed at each time step for the whole system. In such systems, the mass and energy balance equations are derived according to Equations (1) and (2), respectively, resulting in a set of ordinary differential equations (ODEs) which are relatively easy to be solved by applying a first-order numerical method, such as Euler or Runge Kutta. One-dimensional simulation models allow computation of the system variables in the axial direction of the reservoir. The corresponding mass and energy balances (Equations (3) and (4), respectively) are then established in a cylindrical coordinate system, accounting for the shape of the tank. Taking into account the spatial variations in the radial direction of the tank, the mass and energy balance equations take the form of Equations (5) and (6), representative of a 2-D model. The great advantage of the multidimensional models is their accuracy, thanks to the local adjustment of parameters related to the mass and heat transfer kinetics, such as the intraparticle hydrogen diffusivity or heat transfer coefficients. Nevertheless, their numerical solution is much more complicated and most often relies on the spatial discretization of the set of partial differential equations (PDEs), using a finite difference method performed either by in-house codes [29] or by commercial solvers [5,16,19,23,25].

0-D Model

$$V_{tank}\left(\varnothing \cdot \frac{\partial \rho_g}{\partial t} + \rho_s \cdot M \cdot \frac{\partial n_a^{ads}}{\partial t}\right) = \dot{m_{in}} - \dot{m_{out}}$$
(1)

$$V_{tank} \cdot T\left(\varnothing \cdot \frac{\partial(\rho_g U_g)}{\partial t} + \rho_s \cdot M \cdot \frac{\partial(n_a^{ads} U_a)}{\partial t} + \rho_s \cdot \frac{\partial U_s}{\partial t} + \rho_w \cdot \frac{\partial U_w}{\partial t}\right) = \dot{H_{in}} - \dot{H_{out}} + \dot{H_{ads}}$$
(2)

• 1-D Model

$$\varnothing \frac{\partial \rho_g}{\partial t} + \rho_s \cdot M \cdot \frac{\partial n_a^{ads}}{\partial t} = -\frac{\partial}{\partial X} (\vec{V} \cdot \rho_g)$$
(3)

$$T\left(\frac{\partial(\rho_g \cdot U_g)}{\partial t} + \rho_s \cdot M \cdot \frac{\partial(n_a^{ads} \cdot U_a)}{\partial t} + \rho_s \cdot \frac{\partial U_s}{\partial t} + \rho_w \cdot \frac{\partial U_w}{\partial t}\right) = -\frac{\partial}{\partial X} \left(\vec{V} \cdot \rho_g \cdot H_g \cdot T\right) - \frac{\partial}{\partial X} \left(\vec{V} \cdot \rho_s \cdot n_a^{ads} \cdot H_{ads}\right)$$
(4)

• 2-D Model

$$\varnothing \cdot \frac{\partial \rho_g}{\partial t} + \rho_s \cdot M \cdot \frac{\partial n_a^{ads}}{\partial t} = -\frac{\partial}{\partial X} \left(\overrightarrow{V} \cdot \rho_g \right) - \frac{1}{r} \cdot \frac{\partial}{\partial r} (r \cdot \overrightarrow{V} \cdot \rho_g)$$
(5)

$$\Gamma\left(\varnothing \cdot \frac{\partial(\rho_{g} \cdot U_{g})}{\partial t} + \rho_{s} \cdot M \frac{\partial(n_{a}^{ads} \cdot U_{a})}{\partial t} + \rho_{s} \cdot \frac{\partial U_{s}}{\partial t} + \rho_{w} \cdot \frac{\partial U_{w}}{\partial t}\right) \\
= T\left(-\frac{\partial}{\partial X}\left(\overrightarrow{V} \cdot \rho_{g} \cdot H_{g}\right)\right) - \frac{\partial}{\partial X}\left(\overrightarrow{V} \cdot \rho_{s} \cdot n_{a}^{ads} \cdot H_{ads}\right) - T\left(\frac{1}{r} \cdot \frac{\partial}{\partial r}\left(r \cdot \overrightarrow{V} \cdot \rho_{g} \cdot H_{g}\right)\right) - \frac{1}{r} \tag{6}$$

$$\cdot \frac{\partial}{\partial r}\left(r \cdot \overrightarrow{V} \cdot \rho_{s} \cdot n_{a}^{ads} \cdot H_{ads}\right)$$

Experimental validation of these models has been evaluated both at ambient temperature [17,29,31] and at cryogenic temperature [5,14,25]. Experimental tests at cryogenic temperature, which is the process that most concerns us, generally use a tank filled with the adsorbent material, submerged in a liquid nitrogen Dewar. Under these conditions, charging and discharging processes are operated, including steps of cooling, compression, storage, heating, pressure release, and dormancy of the system. Regardless of the use of sophisticated 1-D or 2-D models implemented in Multiphysics software, the simplified approach of the 0-D models can efficiently be employed to simulate reservoirs operating adsorbent masses at g-kg scales [14,24,26]. In most works, simulation models aim to reproduce temperature and pressure profiles in the system in order to determine optimal operating conditions and to upscale the process. Parameter sensitivity studies are also performed in order to evaluate experimental data that are difficult to directly measure, such as heat transfer coefficients and specific heat of the adsorbed phase. Moreover, as introduced earlier, the process simulation can enable accurate assessment of the energy efficiency of the adsorbed hydrogen storage system, which, to the best of our knowledge, has only been carried out in a limited number of works [14].

Considering the good compromise obtained from the numerical simplification of zero-dimensional mathematical models, implying a limited number of adjusted lumped parameters together with fast computation times to obtain rather good predictive ability of time-dependent profiles of pressure, temperature, and hydrogen storage capacities, this work focuses on the development of a 0-D model applicable to the pressure–temperature swing adsorption for hydrogen storage. This model is based on earlier works [24,32], but has been substantially improved: 1. by considering an isotherm model derived from the Dubinin–Astakhov (DA) isotherm equation, that we have modified in order to adapt it for supercritical temperatures and high pressures; 2. by introducing the compressibility factor of hydrogen to account for deviation from ideal gas behavior, that was computed after the equations of state implemented within the NIST Reference Fluid Thermodynamic and Transport Properties Database (REFPROP-version 8) [33]; and 3. by taking into account variation in the isosteric heat of adsorption with the amount of hydrogen adsorbed.

The validity of the model so developed was assessed for a variety of adsorption storage systems for which experimental data were reported in the literature. The results obtained so far show the capability of the new developed 0-D model to properly describe temperature and pressure profiles with time, for a variety of adsorbent materials, reservoir configurations, and operating conditions. Furthermore, the process simulation model was completed with the computation of the energy consumptions associated with the pressure-temperature swing adsorption storage system, so that a comparative analysis could be carried out with other conventional technologies, such as H₂ compression and liquefaction.

Ref	System	Isotherm	Heat of Adsorption (J/mol)	T (K)	P (Bar)	Gas Equation of State	Solver	Validation
[28]	235-L Tank: MOF5	Langmuir	4000	80 to 140	20	-	3-D and 1-D: COMSOL software	No
[25]	3-L Tank: MOF5	M-D-A	-	80 to 170	70	-	3-D: COMSOL Multiphysics v4.2 Software	Own experimental data
[15]	Natural gas: 50-L Tank: G216 Carbon	Langmuir	16,700 (natural gas)	233 to 363	35	Ideal gas law	2-D: In-house code	No
[29]	1.85-L Tank: Incinerated activated coconut coal	Radke-Prausnitz	3300	295 to 360	150	-	2-D: In-house code, developed with Fortran 77	Own experimental data
[31]	1.85-L Tank: Activated IRH3 carbon	D-A with modifications by the authors	-	295 to 340	100	-	2-D: Fluent software	Own experimental data
[5]	0.5-L Tank: Activated carbon MSC30	M-D-A	6000	77 to 300	700	Van der Waals	2-D: COMSOL [™] software	Own experimental data
[16]	2.5-L Tank: activated carbon	M-D-A	Clausius-Clapeyron equation	50 to 250	90	Ideal gas law	2-D: COMSOL Multiphysics Version 3.5a software	Own experimental data
[19]	2.5-L Tank: MOF5 and Activated carbon	M-D-A	Clausius-Clapeyron equation	250 to 350	160	Ideal gas law	2-D: COMSOL Multiphysics software and MATLAB/Simu-link.	Own experimental data
[23]	3.4-L Tank: MOF5	Unilan-Tóth-M-D-A	Clausius-Clapeyron equation	80 to 160	20	Ideal gas and virial equation	2-D: COMSOL Multiphysics 5.2a software	No
[27]	0.5-L Tank AC MSC-30	M-D-A	6000	77 to 400	700	Van der Waals	2-D: COMSOL [™] software	Own experimental data
[30]	MOF-5 Pellets	Unilan	Clausius-Clapeyron equation	80 to 300	30	Polynomial from Refprop	2-D: COMSOL [®] Multiphysics 4.2	No
[20]	50-L Tank: AC "Busofit"	Dubinin– Radushkevich	Clausius-Clapeyron equation	77 to 270	60	Ideal	2-D: -	Own experimental data
[21]	60-L Tank IRH3 AC	Extended D-A	-	77 to 400	250	Ideal	2-D: LSODE-like	Experimental data from the literature
[22]	61.5-L Tank: MOF-5 Pellets	Unilan	-	80 to 280	50	Ideal	1-D: COMSOL Multiphysics 5.2a	-
[17]	2-L Tank: Activated Carbon 35	Radke-Prausnitz	Clausius-Clapeyron equation	255 to 330	150	Ideal gas law	1-D: In-house code	Own experimental data
[18]	235-L Tank: MOF5 pellets	Unilan	4000	80 to 140	20	Ideal gas law	1-D: COMSOL Multiphysics®	No
[14]	Experimental: 2.5- L Tank-Simulation 150-L Tank: Activated carbon AX-21	M-D-A	-	60 to 300	350	-	0-D: In-house code	Own experimental data
[24]	0.5-L Tank: activated carbon MAXSORB 30	M-D-A	6000	77 to 298	700	Van der Waals	0-D: In-house code	Experimental data from the literature
[26]	2.5-L Tank: activated carbon	M-D-A	Clausius-Clapeyron equation	270 to 298	90	Ideal gas law	0-D: MATLAB/Simulink platform	Own experimental data
this work	2.5-L Tank: Activated carbon	rev-D-A	Clausius-Clapeyron equation	77 to 300	700	Compressi-bility factor	0-D: In-house code, developed with MATLAB	Experimental data from the literature

Table 1. Summary of hydrogen adsorption models.

2. Description of Hydrogen Adsorption Equilibria

When simulating hydrogen adsorption systems, the isotherm model, which describes the amount of hydrogen adsorbed at equilibrium under given (P, T) conditions, is crucial for proper evaluation of the storage capacities of the system. The Dubinin equation is based on the potential theory developed by Polányi in 1932 [34], which introduced the notion of a characteristic curve. The characteristic curve describes the relationship between the state of compression of the adsorbed fluid and the forces prevailing at the surface of the adsorbent, represented by the adsorption potential.

For a couple of given adsorbate–adsorbents, a single curve independent of temperature so describes the volume of the adsorbate in the adsorbed phase V_a^{ads} (m³·kg⁻¹) as a function of the adsorption potential *A*. Dubinin and co-workers proposed to describe the fraction of micropore volume filling occupied by the adsorbed phase according to the functional form of the Weibull distribution [34]:

$$V_a^{ads} = V_{sat}^{ads} \cdot exp\left(-\left(\frac{A}{\varepsilon}\right)^n\right)$$
(7)

where V_{sat}^{ads} (m³·kg⁻¹) is the maximum volume that the adsorbate can occupy, usually estimated as the total volume of the micropores, ε (J·mol⁻¹) is a characteristic energy representative of the adsorbent–adsorbate system, and *n* is a constant which characterizes the pore heterogeneities.

As initially proposed by Dubinin and Radushkevich (1947) [35], *n* equals 2 for carbonaceous solids with low degree of burn-off (Dubinin Radushkevich model, DR). According to

later works by Dubinin and Astakhov (1971), it ranges between 1.2 and 1.8 for carbons with high burn-off (DA model). For solids having narrow micropore size distributions, such as carbon molecular sieves or zeolites, the parameter *n* may be found to lie between 3 and 6. The predictive ability of the DR and DA equations was illustrated in the original works of Dubinin and his co-workers for a variety of fluids below their critical temperature [34]. In comparison with other classical isotherm models applicable to microporous materials, such as Langmuir, Langmuir–Freundlich, Toth, etc., these models have the advantage of being directly derived from physically meaningful data, both representative of the adsorbent microporosity and of adsorbate properties.

In Equation (7), the differential molar work of adsorption can be expressed as [34]:

$$A = R \cdot T \cdot ln\left(\frac{f_s(T, P_s(T))}{f(T, P)}\right)$$
(8)

where P_s (Pa) is the saturated vapor pressure of the adsorbate, f and f_s are the adsorbate fugacities at temperature T. Furthermore, assuming that for any adsorbate, at a same fraction of the micropore filling volume the ratio A over ε is constant, a similarity coefficient is defined according to a reference adsorbate [36]:

$$\beta = \frac{\varepsilon}{\varepsilon^0} = \frac{A}{A^0} \tag{9}$$

where (ε^0, A^0) are, respectively the characteristic energy and adsorption potential of the reference adsorbate. For activated carbons, the reference adsorbate chosen is benzene. A variety of correlations were proposed to estimate β , the affinity coefficient. According to Dubinin [36], this coefficient can be expressed as the ratio of the parachors of the adsorbate and benzene molecules: Π , Π^0 (cm³·g^{1/4}·s^{-1/2}·mol⁻¹):

$$\beta = \frac{\varepsilon}{\varepsilon^0} = \frac{\Pi}{\Pi^0} \tag{10}$$

For hydrogen β equals 0.165. ε^0 is a reverse function of the micropore half-width x (nm) and can be determined according to Equation (11) [37], obtained empirically for carbonaceous microporous solids.

$$\varepsilon^0 = \frac{13}{x} \tag{11}$$

The characteristic free energy can then be calculated as follows:

п

$$\varepsilon = \varepsilon^0 \cdot \beta = 0.165 \cdot \frac{13}{x} \tag{12}$$

Knowing the fraction of micropore volume V_a^{ads} occupied by the adsorbed phase, the molar adsorption capacity n_a^{ads} (mol·kg⁻¹) is given as a function of the density of the adsorbed phase ρ_a (kg·m⁻³).

$${}^{ads}_{a} = V_{a}^{ads} \cdot \frac{\rho_{a}}{M} \tag{13}$$

where M (kg·mol⁻¹) is the molar mass of the adsorbate.

At boiling temperature (T_b) or below, ρ_a can be assumed to be equal to the density of the bulk liquid. For the range of temperatures from the boiling point to the critical temperature T_{cr} (K), the density of the adsorbed phase is determined as a function of the thermal coefficient of limiting adsorption α (K⁻¹) and can be calculated according to the Dubinin–Nikolaev equation [34]:

$$\rho_a = \rho_b \cdot exp[-\alpha \cdot (T - T_b)] \tag{14}$$

where ρ_b (mol·kg⁻¹) is the density of the liquid at boiling temperature T_b (K). The thermal coefficient α being a constant, it can be derived from the ratio of the density of the bulk liquid

at boiling temperature ρ_b to the density of the fluid at critical temperature ρ_{cr} (m³·kg⁻¹), according to Equation (15) [34]:

$$\alpha = \frac{ln\left(\frac{p_b}{\rho_{cr}}\right)}{(T_{cr} - T_b)} \tag{15}$$

Assuming that the density of the adsorbate at the critical temperature corresponds to maximal compression, ρ_{cr} is derived from the constant *b* in the van der Waals equation of state and is expressed as [34]:

$$\rho_{cr} = \frac{M}{1000 \cdot b} \tag{16}$$

The constant b (L·mol⁻¹) is then calculated by the familiar formula:

$$b = \frac{1}{8} \cdot \frac{R.T_{cr}}{P_{cr}} \tag{17}$$

and for hydrogen it equals 0.026 L·mol⁻¹. Above the critical temperature, the density of the adsorbed phase may be considered as not dependent upon temperature and equals ρ_{cr} (77.3 kg·m⁻³) as given by Equation (16).

In order to compute the adsorption potential in Equation (8), it is necessary to derive the fugacities f and f_s of the adsorbate. For the adsorbate in the gaseous phase, its fugacity at temperature T and pressure P is simply given by:

$$f = P \cdot exp\left(\int_{0}^{P} \left(\frac{z(T,P) - 1}{P}\right) dP\right)$$
(18)

where *z* is the compressibility factor of the gaseous adsorbate.

The computation of the adsorbate fugacity at saturation f_s differs whether the temperature T is below or above the critical temperature. Under the critical temperature, the fugacity at saturation f_s is derived from Equation (18), replacing P with P_s (T). The saturated vapor pressure P_s is then estimated from Antoine equation:

$$ln(P_s) = K - N \cdot \frac{1}{T} \tag{19}$$

where coefficients *K* and *N* are determined according to the critical pressure and temperature of the adsorbate, and from its normal boiling point at 1 atm. As illustrated by numerous works [5,14,16,19,24-27], the classical DA equation can be satisfactorily employed to describe the adsorption process of gases onto microporous adsorbents under supercritical conditions, provided that parametric adjustment is performed for proper fitting of the isotherm curves.

When *T* does not significantly differ from T_{cr} , the linearity of adsorption isosthers during the transition from sub-critical to super-critical conditions suggests that this model is still valid outside the super-critical temperature domain. But for temperature largely above the critical point, it is not only the assessment of f_s that becomes difficult, but also the thermal invariance of both the characteristic energy ε and the heterogenetity parameter n, as originally postulated by Dubinin, can no longer be considered.

M.A. Richard et al. [38], therefore, proposed an empirical modification of the DA equation to describe the adsorption of supercritical gases in large temperature intervals. Assuming a linear temperature dependence of the characteristic energy of adsorption ε expressed as the sum of two contributions, the enthalpic factor *a* (J·mol⁻¹) and trhe entropic factor *B* (J·mol⁻¹·K⁻¹), the equation proposed takes the form:

$$n_a^{ads} = n_{sat}^{ads} \cdot exp\left[-\left(\frac{A}{a+B\cdot T}\right)^n\right]$$
(20)

where n_a^{ads} (mol·kg⁻¹) is the absolute molar adsorption capacity in equilibrium with the gas phase, and n_{sat}^{ads} (mol·kg⁻¹) is the maximal molar amount adsorbed at saturation of the micropore volume. According to Equation (20), the density of the adsorbed phase is then assumed constant along the micropore volume filling until saturation.

With these assumptions, this model was employed in several works [24–26,39,40] to describe adsorption–desorption capacities in hydrogen storage reservoirs with quasiperfect fitting of hydrogen adsorption isotherms between 77 and 298. K. Ramirez-Vidal et al. [41] derived experimental correlations between the isotherm parameters and textural properties of activated carbons for hydrogen adsorption: the accessible micropore volume V_p and the limiting adsorption capacity n_{sat}^{ads} where thus found to be linearly correlated with the BET surface area, while "a" and "B" coefficients were related to the average micropore size and total pore volume, respectively. The saturation pressure P_s , considered as a fitting constant parameter to compute the adsorption potential A was found to be lower for activated carbons with smaller micropores [42].

In our study, we still consider the linear temperature dependence of the characteristic energy as proposed by Richard et al. [38], but we further propose to account for the saturation fugacity f_s instead of the saturation pressure as derived from the NIST standard reference database [33]. Moreover, in accordance with the fundamental of the potential theory, we also propose to account for the variations of the adsorbed phase volume as a function of the number of moles adsorbed and the density of the adsorbate:

$$V_a^{ads} = \frac{M \cdot n_a^{ads}}{\rho_a} \tag{21}$$

 ρ_a may be computed from Equation (14) assuming the state of the adsorbed phase is close to a liquid, or from Equation (16), considering it closer to the critical state. By combining Equations (7), (8), and (13) and expanding the term *A*, the revisited Dubinin–Astakhov (rev-D-A) equation is obtained, which takes into account the temperature dependence of the molar adsorption capacity:

I

$$n_a^{ads} = \left(V_{sat}^{ads} \cdot \frac{\rho_a}{M} \cdot exp\left[-\left(\frac{R \cdot T}{a + B \cdot T}\right)^n \cdot ln^n\left(\frac{f_s}{P}\right)\right]$$
(22)

The characteristic free energy was estimated from the micropore width *x* (nm) according to Equation (12) whilst the term *B* (J·mol⁻¹·K⁻¹), was considered as a best fit parameter:

$$\varepsilon = a + B \cdot T = 0.165 \cdot \frac{13}{x} + B \cdot T \tag{23}$$

2.1. Hydrogen Density in the Adsorbed Phase

In order to determine which assumption to retain to describe the hydrogen density in the adsorbed phase, we preliminary reviewed some data from the literature.

Numerous works attempted to determine the density of adsorbed hydrogen at saturation under different (*P*, *T*) conditions. The density data were derived either from molecular simulation studies or from in situ measurements by small-angle neutron scattering [43–46]. Figure 1 compares hydrogen adsorbed densities determined by various authors under saturation conditions at different temperatures onto different adsorbents, including activated carbons and MOFs, with the density of the liquid computed by Equation 14 and Equation 15 for different values of α . From data from the literature, significant variations of the adsorbed phase density are so reported, spreading in the range from 8 up to 72 kg·m⁻³, below the critical density. These variations do not appear solely explained by temperature effect, so that the determination of the density of the adsorbed phase at saturation conditions appears uncertain whatever the temperature domain considered.

Given such deviations, we tested one or the other assumption in the simulation of an experimental process [14], considering either the adsorbed phase density as a liquid,

dependent on temperature and on α in the range 5×10^{-4} up to 5×10^{-3} , or as a constant equal to the critical density. Figure 2 shows that pressure and temperature profiles do not significantly differ by varying the adsorbed phase density between the lower and upper limits. Note that reference [19], in line with our observation, also pointed out the low sensitivity of the hydrogen adsorbed phase density parameter on simulation data derived from a 2-D model. A better fit was obtained assuming the critical state of the adsorbed phase density, so that this assumption was retained in the coming parts of the study.



Figure 1. Variation of hydrogen adsorbed density with temperature at saturation conditions for different adsorbent materials. • [43], • [44], • [45], • [46].



Figure 2. Pressure (**a**) and temperature (**b**) fit of experimental data [14] for ρ_a calculated with Equation (14) and $\rho_a = \rho_{cr}$.

2.2. Hydrogen in the Gas Phase

Accounting for the non-ideal gas behavior through the computation of its compressibility factor, the molar amount of H_2 in the gas phase (n_g) was derived according to Equation (24):

$$P \cdot V_g = n_g \cdot R \cdot T \cdot z \tag{24}$$

Figure 3 summarizes the deviations in the compressibility factor *z* computed from both the van der Waals (VDW) and from the NIST Reference Fluid Thermodynamic and Transport Properties Database (REFPROP-version 10.0). At low pressures, deviations in the compressibility factor *z* either computed from the two methods are quite small, less than 6% at 10 MPa, but become significant at higher pressure and low temperature, reaching 26% at 20 MPa, 80 K. The NIST-REFPROP database was thus retained for the determination of the compressibility factor *z* [33]. In Equation 24, V_g is the volume of hydrogen in the bulk phase and is determined as follows:

$$V_g = V_{tank} - V_s - V_a \tag{25}$$

where V_{tank} (m³) is the internal volume of tank, V_s (m³) is the volume occupied by the solid adsorbent, which can be calculated as the ratio between the mass of the adsorbent and the skeletal density of the adsorbent (m_s/ρ_s).





3. Mass Balance

The mass balances are derived in order to account for the temporal variations in the molar quantities of hydrogen in both the adsorbed phase (n_a) and in the gas phase (n_g) , with pressure (*P*) and temperature (*T*), when the reservoir is submitted to the different steps of cooling, pressurization, gas charging, discharging, and heating. The mass balance equations are formulated according to the following assumptions:

- 1. Pressure, temperature, and phase composition inside the tank are assumed to be uniform in the entire volume of the system (0-D model);
- 2. At each time, equilibrium between the adsorbed and gas phases is assumed to be established (no mass transfer resistance is considered);
- 3. The hydrogen adsorption equilibrium is described according to the temperature dependent rev-D-A model (Equation (22));
- 4. The normal hydrogen thermodynamic data (compressibility factor *z*, fugacity at saturation f_s, enthalpiy h) were derived from the NIST REFPROP database;
- 5. The isosteric adsorption enthalpies Q_a were estimated using the Clausius–Clapeyron equation applied to the rev D-A isotherms.

The accumulation of hydrogen in the storage tank in both the gas and adsorbed phases results from the net hydrogen flow rate at the boundaries of the tank. The mass conservation equation is expressed as:

$$\frac{dn_{tot}}{dt} = n_{in} - n_{out} = \frac{dn_g}{dt} + \frac{dn_a}{dt}$$
(26)

where n_{tot} (mol) is the total mass of hydrogen in the tank and n_{in} (mol·s⁻¹) and n_{out} (mol·s⁻¹) are the inlet and outlet molar flow rate, respectively. The amount of hydrogen in the gas phase refers to the hydrogen molecules that are not adsorbed, existing instead in the gaseous or supercritical states.

Equation (22) is derived with respect to time to obtain the differential equation that expresses the variations in the amount of adsorbed H_2 in the system:

$$\frac{dn_a}{dt} = m_{ads} \cdot \left(\left(\frac{\partial n_a^{ads}}{\partial P} \right) \left(\frac{dP}{dt} \right) + \left(\frac{\partial n_a^{ads}}{\partial T} \right) \left(\frac{dT}{dt} \right) + \left(\frac{\partial n_a^{ads}}{\partial f_s} \right) \left(\frac{df_s}{dt} \right) \right)$$
(27)

$$\frac{\partial n_a^{ads}}{\partial P} = n_a^{ads} \left(\frac{R \cdot T}{a + B \cdot T}\right)^n \cdot \frac{n \cdot l n^{n-1} \left(\frac{f_s}{P}\right)}{P} \tag{28}$$

$$\frac{\partial n_a^{ads}}{\partial T} = n_a^{ads} \cdot n \cdot ln\left(\frac{n_a^{ads}}{n_{sat}^{ads}}\right) \cdot \frac{a}{T(a+B \cdot T)}$$
(29)

$$\frac{\partial n_a^{ads}}{\partial f_s} = n_a^{ads} \left(-\frac{R \cdot T}{a + B \cdot T} \right)^n \cdot \frac{n \cdot l n^{n-1} \left(\frac{f_s}{P}\right)}{f_s}$$
(30)

Finally, all the partial derivatives are replaced in Equation (27):

$$\frac{1}{m_{ads} \cdot n_a^{ads}} \cdot \frac{dn_a}{dt} = \left(\left(\frac{RT}{a + B \cdot T} \right)^n \cdot \frac{n \cdot ln^{n-1} \left(\frac{f_s}{P} \right)}{P} \right) \left(\frac{dP}{dt} \right) + \left(n \cdot ln \left(\frac{n_a^{ads}}{n_{sat}^{ads}} \right) \cdot \frac{a}{T(a + B \cdot T)} \right) \left(\frac{dT}{dt} \right) - \left(\left(\frac{RT}{a + B \cdot T} \right)^n \cdot \frac{n \cdot ln^{n-1} \left(\frac{f_s}{P} \right)}{f_s} \right) \left(\frac{df_s}{dt} \right)$$
(31)

By differentiating Equation (24) with respect to time and solving for $\frac{dn_g}{dt}$, the differential equation for the H₂ evolution in the gas phase is obtained:

$$\frac{dn_g}{dt} = n_g \left(\frac{1}{P} \cdot \frac{dP}{dt} - \frac{1}{T} \cdot \frac{dT}{dt} + \frac{1}{V_g} \cdot \frac{dV_g}{dt} - \frac{1}{Z} \cdot \frac{dz}{dt} \right)$$
(32)

The variation with time of the H_2 gas phase is obtained by differentiating Equation (25) with respect to time:

$$\frac{dV_g}{dt} = -\frac{M}{\rho_a} \cdot \frac{dn_a}{dt}$$
(33)

By replacing the differential equation of the amount of hydrogen both in the gas and adsorbed phase, Equation (31) and Equation (32), respectively, in Equation (26) and rearranging for $\frac{dP}{dt}$, the differential equation for the pressure in the system is obtained:

$$\frac{dP}{dt} = \frac{n \dot{r}_{in} - n \dot{r}_{out} + \left(\frac{n_g}{T} - m_{ads} \cdot \frac{\partial n_a^{ads}}{\partial T}\right) \frac{dT}{dt} + \frac{n_g}{z} \cdot \frac{dz}{dt} - \left(m_{ads} \cdot \frac{\partial n_a^{ads}}{\partial f_s}\right) \frac{df_s}{dt} + \left(\frac{n_g}{V_g} \cdot \frac{M}{\rho_a}\right) \cdot \frac{dn_a}{dt}}{\frac{n_g}{P} + m_{ads} \cdot \frac{\partial n_a^{ads}}{\partial P}}$$
(34)

The values of $\frac{df_s}{dt}$, $\frac{dZ}{dt}$ are approximated by numerical differentiation over every step size:

$$\frac{df_s}{dt} = \frac{f_{s\ i} - f_{s\ i-1}}{t_i - t_{i-1}} \tag{35}$$

$$\frac{dz}{dt} = \frac{z_i - z_{i-1}}{t_i - t_{i-1}} \tag{36}$$

The NIST REFPROP database makes it possible to compute at each step the gas compressibility factor z_i and the fugacity at saturation fs_i as functions of temperature T_i and pressure P_i .

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4. Energy Balance

The total internal energy of the system U (J), which includes the storage tank, the adsorbent material, the amount of hydrogen contained in both the adsorbed and gas phases, is expressed at temperature T as:

$$U = \left(m_{ads} \cdot C_s + m_a \cdot C_{v,a} + m_g \cdot C_{v,g} + m_w \cdot C_w\right) \cdot T \tag{37}$$

where m_{ads} (kg) and m_w (kg) are, respectively, the mass of the adsorbent and of the tank, and their corresponding specific heat capacities are C_s (J·kg⁻¹K⁻¹) and C_w (J·kg⁻¹·K⁻¹), m_a (kg) and m_g (kg) are, respectively the mass of hydrogen in the adsorbed and gas phases, their specific heats are $C_{v,a}$ (J·kg⁻¹·K⁻¹) and $C_{v,g}$ (J·kg⁻¹·K⁻¹), obtained with the reference fluid thermodynamic and transport properties database (REFPROP) software version 10.0 [33]. For the calculation of $C_{v,g}$ the conditions of pressure and temperature of the system were applied. $C_{v,a}$, was computed at the same temperature accounting for the adsorbed phase density (ρ_{cr}).

With the changes in both kinetic and potential energies ignored, the rate of change in the internal energy of the system is derived from the difference in the enthalpy of the fluid streams at the inlet and the outlet and accounts for the heat fluxes either generated or absorbed by the internal sources during the adsorption and desorption steps and exchanged throughout the tank walls with the surroundings. It can be expressed as:

$$\frac{dU}{dt} = \dot{H_{in}} - \dot{H_{out}} + \dot{Q}$$
(38)

These terms are calculated with the following equations:

$$\dot{H}_{in} = \dot{m}_{in} \cdot h_{in} \tag{39}$$

$$H_{out} = \dot{m}_{out} \cdot h_{out} \tag{40}$$

where \dot{m}_{in} (kg·s⁻¹) and \dot{m}_{out} (kg·s⁻¹) are the inlet and outlet mass flowrates of hydrogen. The specific enthalpy, h, (J·kg⁻¹) is derived from the REFPROP software version 10.0, for h_{in} , and h_{out} , respectively, the temperature of inlet H₂ flow and the temperature of the tank are used. Both internal and external heat sources are accounted for throughout the variable \dot{Q} :

$$Q = Q_e + Q_a \tag{41}$$

 Q_e (J·s⁻¹) is the rate of heat transferred between the tank and the environment, which is calculated using a global heat transfer coefficient, H_c (W·m⁻²·K⁻¹):

$$Q_e = H_c \cdot S \cdot (T_a - T) \tag{42}$$

S (m²) is the wall surface area of the tank, T_a (K) is the temperature of the surroundings and T (K) is the temperature of the system. \dot{Q}_a (J·s⁻¹) is the rate of adsorption heat, which represents the flux of heat released when adsorption takes place or the flux of heat adsorbed when desorption occurs. To determine the isosteric heat of adsorption, Q_a (J·mol⁻¹), the Clausius–Clapeyron equation (Equation (43)) is applied to the isotherm model (Equation (22)).

$$Q_a = -R \cdot \left(\frac{\partial ln(P)}{\partial \left(\frac{1}{T}\right)}\right) \tag{43}$$

Its temporal variation can be expressed as:

$$\dot{Q}_a = Q_a \cdot \frac{dn_a}{dt} = \left((a + B \cdot T) \cdot \left(\frac{T}{n \cdot n_a} \cdot \left(-ln \frac{n_a^{ads}}{n_{sat}^{ads}} \right)^{\frac{1}{n}-1} \cdot \left(\frac{dn_a}{dT} + n_a \cdot \alpha \right) \right) - a \cdot \left(-ln \frac{n_a^{ads}}{n_{sat}^{ads}} \right)^{\frac{1}{n}} \right) \cdot \frac{dn_a}{dt}$$
(44)

The application of the Clausius–Clapeyron equation to the rev-D-A isotherm of adsorption considers the ideal gas behavior. A study conducted by A. F. Kloutse et al. [47] investigated the hydrogen isosteric heats on five representative metal–organic frameworks using both experimental methods and the model's predictions with the Clausius– Clapeyron method applied to three different adsorption isotherms (M-D-A, Unilan, and Toth). The results demonstrated good agreement between the model's predictions and the experimental method.

Accounting for the terms described above, the energy balance as given by Equation (38) takes the form of the following differential equation:

$$\frac{d}{dt}\left(\left(m_{ads}\cdot C_s + m_a\cdot C_{v,a} + m_g\cdot C_{v,g} + m_w\cdot C_w\right)\cdot T\right) = m_{in}\cdot C_{pg}\cdot T_{in} - m_{out}\cdot C_{pg}\cdot T + \dot{Q}_a + H_c\cdot S\cdot (T_a - T)$$
(45)

Developing and rearranging Equation (45), the temperature derivative of the system is given as:

$$\frac{dT}{dt} = \frac{\dot{m_{in}} \cdot h_{in} - \dot{m_{out}} \cdot h_{out} + (Q_a - M \cdot C_{v,a} \cdot T) \frac{\partial n_a}{\partial t} - M \cdot C_{v,g} \cdot T \cdot \frac{\partial n_g}{\partial t} + H_c \cdot S \cdot (T_a - T)}{m_{ads} \cdot C_s + m_a \cdot C_{v,a} + m_g \cdot C_{v,g} + m_w \cdot C_w}$$
(46)

The system consists of four ordinary differential equations (ODEs) that describe the behavior of four unknown variables over time: hydrogen adsorbed (n_a , Equation (27)), hydrogen in the gas phase (n_g , Equation (32)), pressure (P, Equation (34)), and temperature (T, Equation (46)). To solve the system, the fourth order Runge–Kutta (RK4) method is employed, setting initial values to each variable. The mathematical model is implemented using an in-house MATLAB code, which incorporates a link to the REFPROP software version 10.0 for computing hydrogen properties. Throughout the simulation, a time step of 0.1 s was selected based on a balance between result accuracy and computational time. Although smaller step sizes are possible, they do not significantly enhance result accuracy and considerably prolong the computation time.

5. Results and Discussion

5.1. Isotherm Fit

In order to validate the proposed approach for isotherm modeling, we simulated the experimental data of hydrogen adsorption equilibria for different nanoporous materials available in the literature [38,42,47]. The excess adsorption data, n_{ex}^{ads} (mol·kg⁻¹) were converted to absolute adsorption capacities by applying Equation (47), where V_{sat}^{ads} is assumed to be the micropore volume accessible for hydrogen.

$$n_a^{ads} = n_{ex}^{ads} + \frac{\rho_g \cdot V_{sat}^{ads}}{M} \tag{47}$$

Note that due to small size of the H₂ molecule and possibly its adsorption in the narrowest micropores, V_{sat}^{ads} can be higher than the micropore volume determined from N₂ physisorption data at 77 K, so V_{sat}^{ads} was obtained by fitting the experimental hydrogen adsorption data. The factor "a" of the characteristic free energy is calculated with Equation (23), according to the pore size of the adsorbent.

Figure 4 shows the experimental fit of isotherms for six different materials and the corresponding parameters used in the rev-D-A model are presented in Table 2. The model thus proved to be a good analytical tool for simulation of hydrogen adsorption equilibria under supercritical conditions.



Figure 4. rev-D-A model fit (solid lines) to experimental absolute adsorption isotherms of hydrogen on activated carbon and MOF: (a) AX-21 [14]; (b) MSC30 [42]; (c) MSP20X [42]; (d) Cu-BTC [44]; (e) MOF-5 [44]; (f) MOF-177 [47].

Table 2. Model parameters for isotherm fit. References for micropore half-width: AX-21: [48–51]; MSC-30 and MSP-20X [42]; Cu-BTC [52]; MOF-5 [53]; and MOF-177 [54].

Rev-D-A Equation Parameters	AX-21	MSC-30	MSP-20X	Cu-BTC	MOF-5	MOF-177
a (J·mol ^{−1})—Characteristic free energy factor	2600	3093	3807	3168	2540	3118
B (J·mol ⁻¹ ·K ⁻¹)—Characteristic free energy factor	19.0	14.2	15.2	19.5	16.0	13.5
V_{sat}^{ads} (m ³ ·kg ⁻¹)—Pore volume	0.0012	0.0017	0.0010	0.0007	0.0010	0.0011
<i>n</i> —Exponential coefficient	2.0	1.5	1.9	2.2	2.3	3.1
x (nm)—Micropore half-width	0.825	0.640	0.525	0.625	0.75	0.635

5.2. Validation (Case 1)

The work of Richard et al. [14] is one of the reference studies addressing the evaluation of a lab-scale reservoir for adsorbed hydrogen storage. Figure 5a shows the test bench,

which consists of a tank filled with activated carbon AX-21 submerged in a liquid nitrogen Dewar, completed with an inlet and outlet hydrogen flow control system, pressure transducers, and thermocouples located inside the reservoir to measure temperature evolution during the different phases of the charge–discharge cycle. The hydrogen and nitrogen lines are equipped with heat exchangers submerged in water to warm the exhaust line and hydrogen to allow the measurement of hydrogen flow rate and pressure during the discharge with instruments that are not rated for cryogenic temperatures.



Figure 5. (a) Schematic representation of the test bench [14]. (b) Pressure fit experimental data. (c) Temperature fit experimental data. Experimental data [14], Simulation 0-D model 1 [14], Simulation 0-D model 2 [24].

The tank initially at 80 K and 0.14 MPa was filled with hydrogen at 295 K at a rate of $1.44 \text{ g} \cdot \text{min}^{-1}$ for 27 min. The tank average temperature initially rose up to 103 K before returning to the initial value within 80 min. The final pressure in the tank was 3.23 MPa. The model is validated with the experimental data obtained, parameters used for the simulation are summarized in Table 3. Figure 5b,c compares the simulated pressure and temperature profiles predicted by different modelling approaches for the same experimental case. The predictive ability of the model proposed in this study is shown to be very satisfactory along the whole cycle. Both pressure and temperature profiles match the experimental data well, whilst a better fit is observed compared with reference models.

Table 3. Parameter specification for the simulation of case 1 [14].

Rev-D-A Equation Parameters	Value	Reference
<i>a</i> (J·mol ^{-1})—Characteristic free energy factor	2600	
B (J·mol ^{-1} ·K ^{-1})—Characteristic free energy factor	19.0	This second.
V_{sat}^{ads} (m ³ ·kg ⁻¹)—Pore volume	0.0012	This work
n	2.0	

AX-21 Bed and Tank Properties	Value	Reference
$ ho_s$ (kg·m ⁻³)—Skeletal density m_{ads} (kg)—M ass of adsorbent V_{tank} (L)—Volume of the tank C_w (J·kg ⁻¹ ·K ⁻¹)—Specific heat of tank walls	2200 0.67 2.5 38 + 3·T	[14]
m_w (kg)—Mass of steel tank S (m ²)—Heat transfer area	1.15 0.12	[24]

Table 3. Cont.

While most of parameters required for simulation are well-known (physical characteristics of the fluids or materials employed), several parameters remain uncertain, in particular the heat transfer coefficient and the specific heat of the adsorbent. Two parameters are evaluated to determine their influence on the final result of the simulation; the heat transfer coefficient H_c , which is expected to range from 20 W·m⁻²·K⁻¹ to 100 W·m⁻²·K⁻¹ in water cooling systems [26] and the specific heat of the adsorbent (C_s), which can vary between 600 J·kg⁻¹·K⁻¹ and 1100 J·kg⁻¹·K⁻¹ with respect to the temperature of the activated carbon [55]. A sensitivity analysis is performed to examine the more accurate set of values, this was carried out by determining the coefficient of determination for both charging and cooling and the difference between the pressure and temperature at the end of the charging. Figures 6–9 show the results obtained, each step of the test (charging and cooling) was studied separately; it is evident that H_c has a much higher influence than C_s , when charging H₂ in the temperature-controlled vessel with N₂, 37 W·m⁻²·K⁻¹ has been determined as the best optimal value. When cooling the vessel, the optimal H_c value was 20 W·m⁻²·K⁻¹. The results agree with the values of H_c usually found in the literature, since the charging represents forced flow convection conditions, H_c is higher than during cooling, which is carried out under natural flow convection conditions. Sdanghi et al. obtained 40 and 15 $W \cdot m^{-2} \cdot K^{-1}$ for the charging and the cooling stages of H₂, respectively [24], and Xiao et al. obtained 36 W·m⁻²·K⁻¹ for the charging phase [26].



Figure 6. Comparison between experimental and numerical data: pressure sensitivity analysis during the charging phase: (a) Deviations observed for different H_c . (b) Deviations observed in the coefficients of determination and (c) in the final pressure data according to H_c and C_s . Experimental data [14].



Figure 7. Comparison between experimental and numerical data: temperature sensitivity analysis during charging phase: (a) Deviations observed for different H_c . (b) Deviations observed in the coefficients of determination and (c) in the final temperature data according to H_c and C_s . Experimental data [14].



Figure 8. Comparison between experimental and numerical data: pressure sensitivity analysis during dormancy phase: (a) Deviations observed for different H_c . (b) Deviations observed in the coefficients of determination according to H_c and C_s . Experimental data [14].



Figure 9. Comparison between experimental and numerical data: temperature sensitivity analysis during dormancy phase: (a) Deviations observed for different H_c . (b) Deviations observed in the coefficients of determination according to H_c and C_s . Experimental data [14].

Figure 10a–c presents the evolution of the saturation fugacity over the adsorption film (f_s), the adsorbed phase volume (V_a), and the gas phase volume (V_g). According to M.A. Richard et al. [38], these variables were assumed as constant which appears to be in contradiction with the fundamental assumptions of Dubinin theory. From our model, it is shown that assuming a constant density of the adsorbed phase, both volumes of the adsorbed and gas phases may vary significantly in the system, and the saturation fugacity is also affected by temperature variations.



Figure 10. M-D-A and rev-D-A parameters for experimental test [14]: (**a**) Saturation pressure. (**b**) Adsorbed phase volume. (**c**) Gas phase volume. Reference value [14].

5.3. Validation (Case 2)

In the work of Sdanghi, Nicolas et al. [5], hydrogen is compressed up to 70 MPa based on hydrogen adsorption/desorption on activated carbon. The experimental setup (Figure 11a) consists of a tank filled with activated carbon and pressurized with hydrogen and placed a in liquid nitrogen bath to maintain cryogenic temperature. During the compression step the tank is removed from the Dewar and placed at ambient temperature to let heat exchange with environment (a ventilation system is used to force convection). A series of tests were conducted to evaluate the performance of different amounts of adsorbent in the tank and the initial pressure of desorption. We carried out the simulation of the desorption phase of hydrogen in a closed reservoir containing a mass of activated carbon of 0.135 kg at an initial pressure of 8 MPa. Table 4 summarizes the parameters used for the simulation.

Table 4. Parameter specification for the validation of model (case 2) [5].

Rev-D-A Equation Parameters	Value	Reference
a (J·mol ^{-1})—Characteristic free energy factor	3093	
<i>B</i> (J·mol ^{-1} ·K ^{-1})—Characteristic free energy factor	6.2	This work
V_{sat}^{ads} (m ³ ·kg ⁻¹)—Pore volume	0.002	THIS WORK
n	1.3	

Table 4. Cont.

MSC-30 Bed and Tank Properties	Value	Reference
<i>m_{ads}</i> (kg)—Mass of adsorbent	0.135	
V_{tank} (L)—Volume of the tank	0.5	[5]
C_w (J·kg ⁻¹ ·K ⁻¹)—Specific heat of tank walls	460	[5]
ρ_s (kg·m ⁻³)—Skeletal density	2200	
m_w (kg)—Mass of steel tank	0.23	Estimated
S (m ²)—Heat transfer area	0.12	Estimated
H_c (W·m ⁻² K ⁻¹)—Heat transfer coefficient	30	TT1 · 1
$C_s (J \cdot kg^{-1} \cdot K^{-1})$	800	This work

 $H_{c} (W \cdot m^{-2} K^{-1}) - Heat transfer coefficient 30$ $C_{s} (J \cdot kg^{-1} \cdot K^{-1}) 800 This work$ Figure 11b,c shows the resulting pressure and temperature computed profiles. The final 65 Mpa reached after 100 min of desorption is well simulated, on the contrary, the simulation implemented by the reference authors overestimates the final pressure by 5 Mpa. The likely explanation is the use of the van der Waals equation of state in the model retained by the authors using the COMSOL simulator, which as demonstrated previously, can present significant differences when compared with more accurate equations of state, especially at such a high operating pressure. The temperature profile does not exactly

match the experimental data, which can be attributed to deviations due to local temperature measurement whereas temperature uniformity is assumed in the 0-dimensional model. Nevertheless after 50 min, when the whole system reaches equilibrium with ambient surroundings, temperature data are accurately predicted.



Figure 11. (a) Schematic representation of the test bench for the validation case 3 [5]. (b) Pressure fit experimental data. (c) Temperature fit experimental data. Experimental data [5]. Simulation 2-D model with COMSOL [5].

5.4. Validation (Case 3)

The flow-through cooling process consisting of charging and discharging the tank at the same time was studied by Hou et al. [25]. The impacts of different parameters such as mass flow rate, outlet opening time, bed density and heating power were investigated. For the purpose of model validation, we simulated the process of the effect of outlet mass flow rate in the charging process. In their setup, illustrated in Figure 12a, the inlet mass flow rate was fixed at $0.65 \text{ g} \cdot \text{s}^{-1}$, after 23 s, the outlet mass flow rate was fixed at $0.52 \text{ g} \cdot \text{s}^{-1}$. The experimental isotherm data were not available, so the model isotherm parameters reported in the reference were used to fit the rev-D-A parameters. Table 5 summarizes the parameters used for the simulation.

Rev-D-A Equation ParametersValueReferencea (J·mol⁻¹)—Characteristic free energy factor1400B (J·mol⁻¹·K⁻¹)—Characteristic free energy factor19

Table 5. Parameter specification for the validation of model (case 3) [25].

<i>u</i> ()·.	mor <i>j</i> —Characteristic nee energy factor	1400	
<i>B</i> (J·mol ^{-1} ·K ^{-1})—Characteristic free energy factor		19	TTL
	V_{sat}^{ads} (m ³ ·kg ⁻¹)—Pore volume	0.0018	I his work
	n	2.5	
	MOF-5 Bed and Tank Properties	Value	Reference
	<i>m_{ads}</i> (kg)—Mass of adsorbent	0.526	[05]
V_{tank} (L)—Volume of the tank		3	[23]
C_w	$(J \cdot kg^{-1} \cdot K^{-1})$ —Specific heat of tank walls	$38 + 3 \cdot T$	[14]
	ρ_s (kg·m ⁻³)—Skeletal density	1920	[56]
m_w (kg)—Mass of steel tank S (m ²)—Heat transfer area		1.38	Father to 1
		0.144	Estimated
H_c (W·m ⁻² ·K ⁻¹)—Heat transfer coefficient C_s (J·kg ⁻¹ ·K ⁻¹)		37	TTI · 1
		800	This work



Figure 12. (a) Schematic representation of the test bench for the validation of case 3 [25]. (b) Pressure fit experimental data. (c) Temperature fit experimental data. (d) Pressure fit experimental data with an increase of discharge flow to $0.54 \text{ g} \cdot \text{s}^{-1}$. (e) Temperature fit experimental data with increase of discharge flow to $0.54 \text{ g} \cdot \text{s}^{-1}$. (e) Temperature fit experimental data with COMSOL [25].

Figure 12b,c show the computed pressure and temperature profiles. In order to obtain a better simulation profile, the discharge flow was increased to $0.54 \text{ g} \cdot \text{s}^{-1}$ (Figure 12d,e), which represents less than 4% the original value and that can be within the uncertainty of the measurement equipment. Additionally, whilst the initial temperature rise also appears well predicted as well as the shape of the curve during its decline, an underestimation of

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the temperature peak by around 5 K is noticed, which is due to the average temperature calculation with several sensors in a medium that is in dynamic conditions, as was also the case with the simulation with COMSOL by the authors.

6. Energy Analysis of the H₂ Storage System

The process energy requirements highly rely on the amount of heat exchanged between the reservoir and the cryogenic bath. To the best of our knowledge, the heat exchanges during hydrogen loading in the cryogenic process were only determined in the work of Richard et al. [14]. Two computation methods can be considered to estimate the cooling requirements of the cryogenic process during hydrogen loading: Method 1, by determining the amounts of heat absorbed by the hydrogen feeding flow to be cooled at cryogenic temperature, and that absorbed by the adsorbent bed to compensate the heat released by the exothermal adsorption process, or Method 2, by determining the total amount of heat exchanges throughout the reservoir walls between the adsorbent bed and the cryogenic bath.

According to [14], the net amount of heat evacuated at the reservoir walls was experimentally reported to be 139 kJ \pm 35 KJ (0.99 \pm 0.25 KWh·kg⁻¹·H₂), which supports the results obtained by this work, according to both methods, Method 1: 157 kJ (1.13 KWh·kg⁻¹·H₂) and Method 2: 180 kJ (1.29 KWh·kg⁻¹·H₂), as shown in Figure 13. According to the data obtained, the heat of adsorption contributes close to one third of the reservoir cooling duty.



Figure 13. Comparison of the computed and experimental [14] amount of heat exchanged between the tank and the cryogenic bath.

To compare the adsorbents for H₂ storage, we applied the simulation conditions of the experience of Richard et al. [14] evaluated at 20 bar and 50 bar, in terms of amount of H₂ stored and energy consumption. The materials evaluated include activated carbons: AX-21 [14], MSC-30, and MSP-20X [42] and metal–organic frameworks: Cu-BTC, MOF-5, and MOF-177 [44]. The process cooling duty allows to determine the amount of liquid nitrogen (L-N₂) to keep the system at cryogenic conditions, which was derived from its heat of vaporization, that is $5.632 \text{ kJ} \cdot \text{mol}^{-1}$ [57]. The results are presented in Tables 6 and 7, as well as in Figure 14. The adsorbent showing the best performance for maximizing H₂ storage with lowest L-N₂ requirement is the AC AX-21.

The energy consumption of the process operating hydrogen loading should include the mechanical energy required to feed the tank (H_2 compression) in addition to the heat transferred for cooling the hydrogen inlet gas flow and the heat exchanged to compensate the H_2 adsorption exothermicity (internal source). Assuming a cyclic process, the heat required for initial cooling of the tank from ambient to cryogenic temperature was not considered.

Adsorbent	Heating by H ₂ Inlet Flow, Cooling from 298 K to 80 K (KWh·kg ⁻¹)	Heating by H ₂ Adsorption (KWh·kg ⁻¹)	Cooling Duty to Maintain Isothermal Conditions (KWh·kg ⁻¹)	L-N ₂ Required (L·kg ⁻¹)
AX-21	0.74	0.54	1.28	28.6
MSC-30	0.75	0.74	1.49	25.0
MSP-20	0.75	0.54	1.29	33.2
MOF-5	0.74	0.54	1.28	29.4
MOF1-77	0.74	0.74	1.48	28.7
Cu-BTC	0.75	0.42	1.17	24.9

Table 6. Heat released during the adsorption process at 20 bar computed with method 1 for the experimental study of Richard et al. [14].

Table 7. Heat released during the adsorption process at 50 bar computed with method 1 for the experimental study of Richard et al. [14].

Adsorbent	Heating by H ₂ Inlet Flow, Cooling from 298 K to 80 K (KWh·kg ⁻¹)	Heating by H ₂ Adsorption (KWh·kg ⁻¹)	Cooling Duty to Maintain Isothermal Conditions (KWh·kg ⁻¹)	L-N ₂ Required (L.kg ⁻¹)
AX-21	0.74	0.38	1.12	25.0
MSC-30	0.74	0.58	1.32	29.4
MSP-20	0.73	0.37	1.10	24.9



Figure 14. (a) H₂ storage capacity at 20 and 50 bar, (b) LN₂ required at 20 and 50 bar.

Usually, gas compression is carried out in several stages, because this reduces the required energy. However no significant energy reduction is obtained beyond three stages [58]. Thus, the mechanical energy required to compress the hydrogen flow feeding the process was estimated assuming a 3-stage set of compressors, with an isothermal efficiency of 70% [14]. The power consumption for the adiabatic compression can be computed from [58]:

$$W_s = \dot{n}_{in} \cdot R \cdot T \cdot \left(\frac{3k}{k-1}\right) \cdot \left(\left(\frac{P_2}{P_1}\right)^{\frac{k-1}{3k}} - 1\right) \times \frac{1}{\eta}$$
(48)

where \dot{n}_{in} is the inlet flow (mol·s⁻¹), *k* is the H₂ heat capacity ratio (1.31), η is the isothermal efficiency of the compressor, P_2 is the final pressure and P_1 is the initial pressure. As presented in Figure 15, the compression energy can represent around 10% of the total energy consumption.



Figure 15. Energy spent for hydrogen storage through adsorption compared with compressed and liquid hydrogen. (**a**) Storage at 20 bar, (**b**) Storage at 50 bar.

The specific total energy requirement of the process operating hydrogen storage in the adsorbed state was further compared with the ones estimated for both the compressed and liquefaction processes. The mechanical energy consumed to store hydrogen by compression in a system operating at elevated pressures of 300 and 700 bar was derived using Equation (48). The energy consumption for liquid nitrogen production is based on an industrial Collins-based process, 0.474 KWh·kg⁻¹ [59], which is more than twice the ideal consumption, 0.21 KWh·kg⁻¹ [60]. When comparing the energy consumption with another compound of similar boiling temperature (77 K for N₂), such as methane, whose boiling temperature is 111 K, the energy consumption is lower: 0.29 KWh·kg⁻¹ [61]; thus, the data agree with thermodynamic laws.

Figure 15 presents the results obtained, disclosed by fractions of energy for hydrogen inlet flow compression, and cryogenic cooling from 298 K to 80 K, including compensation of heat losses due to adsorption. The energy required to store hydrogen in an adsorbent-based system is around 13 KWh.kgH₂⁻¹, which is close to a H₂-liquefaction process, that has been reported to be between 7 and 13 KWh.kgLH₂⁻¹ [62–66]. It also represents around 32% of the hydrogen high heating value (HHV). The lowest energy duties were computed for storage by compression, with values of 3.52 KWh·kgH₂⁻¹ and 4.2 KWh·kgH₂⁻¹ at 300 bar and 700 bar, respectively, which agree well with data from the literature [64,65,67,68].

Hydrogen storage by adsorption under cryogenic conditions so appears energetically not better efficient than other modes of storage, by compression at elevated pressures or by liquefaction. But the application potential of that technology should also consider other factors, such as equipment compactness, capital, operation and maintenance costs, and safety concerns, which were not covered in this study.

7. Conclusions

In this work, we have developed an improved 0-D model for the description and simulation of lab-scale reservoirs for hydrogen storage by pressure swing adsorption. This model is based on the adsorption potential theory and accounts for the partial micropore volume filling by the adsorbed phase function of the adsorption potential. Adsorption equilibria were so described by the revisited Dubinin–Astakhov (rev-D-A) isotherm equation adapted to supercritical temperatures, whilst the non-ideality of the gas phase was accounted for considering the compressibility factor and the fugacity. In line with the fundamentals of the Dubinin equation [14,24,26], the model proposed assumes a variable volume of the adsorbed phase until adsorbent saturation and takes into account the variations in the amount of gas adsorbed assuming the density of the adsorbed phase equals to hydrogen critical density. The predictive ability of the proposed 0-D model was assessed

for three experimental case studies from the literature. Results show that neglecting local space variations in pressure and temperature is a reasonable assumption at the liter scale.

The validated simulation tool was finally used to quantify the energy requirement of an adsorption-based hydrogen storage process. Compared with other conventional storage modes, at equal amounts of hydrogen stored in the reservoir, the energy required to operate the cryogenic adsorption process is comparable to the one necessary to store hydrogen by liquefaction. The cooling duty necessary to compensate the heat losses at the reservoir walls and maintain the reservoir temperature at 80 K was so estimated to be one third of the produced hydrogen HHV, with little variations depending on the adsorbent used, so that the selection of that technology should rather be dictated by other possible advantages, considering the investment cost and safety criteria.

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Nomenclature and Units

H _{ads}	Adsorption heat rate, $J \cdot s^{-1}$
$\dot{H_{in}}$	Inlet flow enthalpy, J·s ⁻¹
Hout	Outflow enthalpy, J·s ⁻¹
$\dot{m_{in}}$	Hydrogen inlet flow, kg·s ⁻¹
$\dot{m_{out}}$	Hydrogen outflow, kg·s ^{-1}
n ^{ads}	Adsorbed H ₂ per mass of adsorbent, mol·kg ^{-1}
n ^{ads}	Excess hydrogen adsorbed per mass of adsorbent. $mol \cdot kg^{-1}$
n ^{ads} n _{sat}	Limiting adsorption capacity per mass of adsorbent, mol kg^{-1}
n _{in}	Hydrogen inlet flow, mol s^{-1}
n _{out}	Hydrogen outflow, mol \cdot s ⁻¹
V_a^{ads}	Hydrogen adsorbed per mass of adsorbent, $m^3 \cdot kg^{-1}$
V_{sat}^{ads}	Maximum hydrogen adsorbed per mass of adsorbent, $m^3 \cdot kg^{-1}$
Q	Total heat sources, $J \cdot s^{-1}$
Qa	Rate of adsorption heat. $J \cdot s^{-1}$
Qe	Rate of heat transfer between the tank and the environment, $J \cdot s^{-1}$
а	Characteristic free energy factor, $J \cdot mol^{-1}$
А	Adsorption potential J·mol $^{-1}$
b	Coefficient of van der Waals equation of state, 0.026 L ·mol ⁻¹
В	Characteristic free energy factor, $J \cdot mol^{-1} \cdot K^{-1}$
Cs	Specific heat of adsorbent, $J \cdot kg^{-1} \cdot K^{-1}$
C _{v,a}	Specific heat at constant volume of adsorbed phase, $J \cdot kg^{-1} \cdot K^{-1}$
C _{v,g}	Specific heat at constant volume of gas phase, $J \cdot kg^{-1} \cdot K^{-1}$
Cw	Specific heat of wall tank, $J \cdot kg^{-1} \cdot K^{-1}$
f	Fugacity of equilibrium pressure, Pa
fs	Fugacity of saturated pressure, Pa
h _{in}	Inlet H_2 specific enthalpy, J.kg ⁻¹
h _{out}	Outlet H_2 specific enthalpy, J.kg ⁻¹
H _{ads}	Adsorption heat, $J \cdot mol^{-1}$
Hg	Bulk gas Enthalpy, J·kg $^{-1}$ ·K $^{-1}$
H _c	Global heat transfer coefficient, $W \cdot m^{-2} \cdot K^{-1}$

- k H₂ heat capacity ratio, 1.31
- K Antoine equation coefficient
- $m_a \qquad H_2 \text{ adsorbed mass, } kg$
- m_g H₂ bulk mass, kg
- m_{ads} Adsorbent mass, kg
- m_w Tank mass, kg
- M Molecular weight of hydrogen, 0.00216 kg \cdot mol⁻¹
- n Distribution parameter
- N Antoine equation coefficient
- n_a Adsorbed hydrogen amount, mol
- n_{ex} Excess hydrogen adsorbed, mol
- ng Gas hydrogen amount, mol
- n_{tot} Total H₂ amount, mol
- P Equilibrium pressure, Pa
- P_{cr} Critical pressure, Pa
- P_s Saturated vapor pressure, Pa
- Q_a Heat of adsorption, J·mol⁻¹
- r Tank radial length, m
- R Gas constant, 8.314 J·mol⁻¹·K⁻¹
- S Wall surface are of tank, m²
- T Temperature, K
- t Time, s
- T_a Surrounding temperature, K
- T_b Boiling temperature, K
- T_{cr} Critical temperature, K
- U Total internal energy, J
- U_a Internal energy of hydrogen adsorbed, J·kg⁻¹·K⁻¹
- U_g Internal energy of bulk gas, J·kg⁻¹·K⁻¹
- U_s Internal energy of adsorbent, J·kg⁻¹·K⁻¹
- $U_w \qquad \text{Internal energy of wall tank, } J \cdot kg^{-1} \cdot K^{-1}$
- V_a Adsorbed phase volume, m³
- V_g Gas phase volume, m³
- V_s Adsorbent volume, m³
- V_{tank} Tank volume, m³
- x Micropore half-width, nm
- X Tank axial length, m
- z H₂ compressibility factor
- ε^0 Benzene characteristic energy, J·mol⁻¹
- A^0 Benzene adsorption potential, J·mol⁻¹
- Π^0 Benzene parachor, cm³·g^{1/4}·s^{-1/2}·mol⁻¹
- η Compressor isothermal efficiency
- Ø Porosity
- α Coefficient of limiting adsorption, K⁻¹
- β Affinity coefficient, 0.165
- ho_a Adsorbed phase density, kg·m⁻³
- ρ_b H₂ density at boiling point, kg·m⁻³
- ρ_{cr} H₂ density at critical point, 77.3 kg·m⁻³
- ρ_g Bulk gas density, kg·m⁻³
- ρ_s Solid adsorbent density, kg·m⁻³
- ρ_w Wall tank density, kg·m⁻³
- ε Characteristic energy, J·mol⁻¹
- Π Parachor, cm³·g^{1/4}·s^{-1/2}·mol⁻¹
- \vec{V} Superficial velocity of gas, m·s⁻¹

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