16th European Symposium on Computer Aided Process Engineering
and 9th International Symposium on Process Systems Engineering
W. Marquardt, C. Pantelides (Editors)

Multi-scale modelling and optimization of hydrogen storage systems using advanced solid materials

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Abstract

The aim of the present study is the development of a multi-scale modeling and optimization framework for hydrogen storage in carbon-based nanoporous adsorbents. The outlined methodology is generic and can be easily adapted to the storage of several gases of relevant importance and/or different physisorbing nanoporous materials. The results indicate clearly how operating constraints (e.g. temperature limitations due to safety considerations) can affect the material design in terms of its pore size distribution and how material design constraints (e.g. due to manufacturing limitations) can effect the operation and efficiency of the process.

Keywords: multi-scale modelling; dynamic optimization; hydrogen storage

1. Introduction

Environmental and energy problems related to the emission of greenhouse gases and to the depletion of fossil-fuel natural resources, have led to significant research effort on alternative and cleaner fuels (Agrawal et al. 2005). During the coming century, gasoline is expected to be replaced by a cleaner, renewable motor-fuel such as hydrogen while fuel cells should take the place of the internal combustion engine. One of the main barriers towards widespread usage of hydrogen energy in automotive industry is the storage problem. Conventional storage methods such as gas compression and liquefaction are impractical since the former requires very heavy gas tanks and the latter is too expensive to be employed in public vehicles. Storing hydrogen in advanced solid materials, such as carbon-based porous adsorbents and metal hydrides, appears to be a promising, cost effective and safe method of hydrogen storage in the near future. The operation of hydrogen storage tanks packed with these materials presents distinct challenges in process modeling and optimization. In the literature very little attention has been paid on exploring the synergetic benefits between material design and process

operation/design in a view of deriving a process which, on the one hand, can operate safely and on the other in the most economically attractive way. This work presents an integrated approach that formally exploits the synergistic benefits between material and process design.

2. Microscopic Simulation of Hydrogen Storage in Carbon-Based Materials

The grand canonical Monte Carlo method is employed in this work in which the chemical potential (or gas fugacity), volume and temperature of the system are fixed and the simulation calculates the number of particles (gas molecules) in the system and the configurational energy corresponding to a particular choice of *n, V* and *T*. The method is discussed in detail in a number of books (Nicholson and Parsonage, 2001). In the present study, the system is considered to be a classical one (i.e. the quantum mechanical character of hydrogen is ignored) (Cracknell, 2001). Hydrogen-hydrogen interactions were modelled using Lennard- Jones potential.

$$u_{HH} = 4\varepsilon_{HH}\left[\left(\frac{\sigma_{HH}}{r}\right)^{6} - \left(\frac{\sigma_{HH}}{r}\right)^{12}\right] \tag{1}$$

where u_{HH} is the energy of the (pairwise) interaction between Lennard- Jones sites and ε_{HH} and σ_{HH} are the well depth energy and hard sphere diameter parameters for the interaction, respectively. A two-site Lennard- Jones model is employed, with the interactions summed over all site-site interactions. The parameters for the two-site model were devised in full accordance with similar recent studies (Cracknell, 2001). Pore walls are treated as stacked layers of carbon atoms separated by a distance Δ=0.335 nm, and having a number density ρ_w=114 atoms/nm^3 per layer. The theoretical surface area of this idealized adsorbent is 2620 m^2/g The slit- pore width, *H*, is defined as the carbon to carbon distance on opposing pore walls (Cracknell, 2001). The simulation does not therefore model any edge effects. The interaction between hydrogen and each wall of the micropore is given by the '10-4-3' potential of Steele (Steele, 1974).

$$u_w(z) = 2\pi\rho_w\varepsilon_{CH}\sigma_{CH}^2\Delta\left[\frac{2}{5}\left(\frac{\sigma_{CH}}{z}\right)^{10} - \left(\frac{\sigma_{CH}}{z}\right)^{4} - \frac{\sigma_{CH}^4}{3\Delta(0.61\Delta + z)^3}\right] \tag{2}$$

The Lennard-Jones parameters for the hydrogen-wall interaction were found from the parameters given in (Cracknell, 2001).

3. Macroscopic modelling of hydrogen storage in the tank

A two-dimensional pseudo-homogeneous macroscopic model is developed based on mass, momentum and energy balances assuming a cylindrical bed packed with a carbon-based adsorbent (Delahaye et al. 2002). Due to space limitations the details of

the model are not presented here. The Langmuir isotherm is described by the following equation:

$$q^* = \frac{q_s bP}{1+bP} = \frac{q_s b_0 \exp[-\Delta H / RT]P}{1+b_0 \exp[-\Delta H / RT]P} \quad (3)$$

where q_s and b_0 are parameters depending on the selected material and P the total pressure. Parameter (-*ΔH*) is the heat of adsorption and in the present study is considered to be identical to the isosteric heat of adsorption obtained from the microscopic model, in accord with the considerations imbedded in the Langmuir isotherm. Proper boundary and initial conditions complement the model.

4. Determination of Optimal Sorption Properties from the Macroscopic Model

The process model along with the boundary and initial conditions involve certain parameters that must be optimally selected in order to achieve an economic and safe process performance. Such parameters are the macroscopic Langmuir constants q_s and b_0 whose values affect the maximum amount of hydrogen that can be stored in the bed for a specific charging time. There are two main issues, which must be taken into consideration when establishing optimal control strategies for this system. The first is to ensure that the maximum process storage efficiency is achieved. The second is to ensure satisfaction of all operating and design constraints. This can be expressed by imposing an upper bound on the average bed temperature in order to account for potential safety concerns. The problem is posed as a dynamic optimization problem and solved using gPROMS dynamic optimization capabilities (Process Systems Enterprise Ltd 2004).

5. Determination of Optimal Pore Size Distribution from the Microscopic Model

In this work the micropore range (from 0.5 to 2.0 nm) was subdivided in *N* equidistant intervals (classes of pores) with 0.1 nm spacing between them. The fraction of the total pore volume associated with each interval, is calculated on the basis of an assumed Particle Size Distribution (PSD) and keeping the total pore volume equal to the measured one. Thus, the amount of gas adsorbed in every class at a certain pressure is evaluated by the simulation, and consequently, a computed isotherm is constructed. This, after comparison to its experimental counterpart, results in the optimum micropore size distribution provided by the best fit. In the present study the "experimental" isotherm that is used to derive the optimal pore size distribution is obtained from the Langmuir equation where the parameters b_0, q_s , have been optimally determined from the macroscopic simulations described in section 4.

The procedure for the determination of the optimum PSD involves the numerical solution of a minimization problem under certain constraints. In practice, the problem consists of minimizing the function:

$$q_i - \sum_{j=1}^{N} d_{ij} w_j \qquad i=1..,M, \quad j=1\ldots,N \qquad (4)$$

for M different pressure values P_i; where q_i (gr/m^3) is the "experimentally" adsorbed amount determined at pressure P_i from the Langmuir isotherm (eq. 3) with the optimally determined parameters b_0, q_s , (section 4). Variable d_{ij} is the calculated density of H_2 in a pore of width H_j at pressure P_i, and w_j represents the fraction of pores with size H_j .

6. Integration of microscopic and macroscopic models

The macroscopic model determines the optimum isotherm parameters that should be used further in the microscopic model to determine the optimum pore size distribution of the material. On the other hand, both the heat of adsorption, $|\Delta H|$, and the bulk density of the material, ρ_s, that are input parameters in the macroscopic model, depend on the pore size distribution, which is determined by the microscopic model. It is therefore clear that the macroscopic model depends on the results of the microscopic model, and particularly on the pore size distribution which determines the values of ΔH and ρ_s. Therefore the following iterative procedure is employed for different bounds on the temperature.

- From the macroscopic model the optimum sorption isotherm parameters are determined, given initial guess of the heat of adsorption, $|\Delta H^{(0)}|$, and bulk density of the material, $\rho_s^{(0)}$.
- From the microscopic model the optimum pore size distribution is determined corresponding to the Langmuir isotherm data based on the above parameters.
- From the optimum pore size distribution the "new" values of $|\Delta H|$ and ρ_s are computed.
- The above steps are repeated until convergence is achieved.

7. Results and Discussion

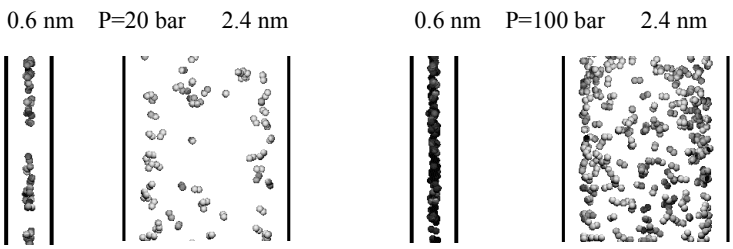

Figure 1: Visual representation of H_2 physisorption in the graphite nanopores (T=298 K)

Molecular simulation results regarding hydrogen adsorption on different carbon slit sizes are shown in Figures 1. It is seen that strong confinement effects are present at small pore sizes (0.6 nm) resulting in close packing structures of the adsorbed hydrogen, which once formed, no longer change significantly with pressure. On the other hand at large pore sizes (2.4 nm) there is significant space for the storage of hydrogen molecules resulting in a continuous increase of sorption capacity as pressure increases further. However, even at pressures of 100 bar, there is a lot of empty space in the pore except from regions in the vicinity of the pore walls. Typical results from the iterative process are shown in Figure 2. It is seen that after 4-5 iterations no significant change is observed in the values of ΔH and essentially the iterative procedure has converged. The same is true for the values of the optimized Langmuir parameters, q_s and b_0, and for the resulting pore size distribution as seen in Figure 2.

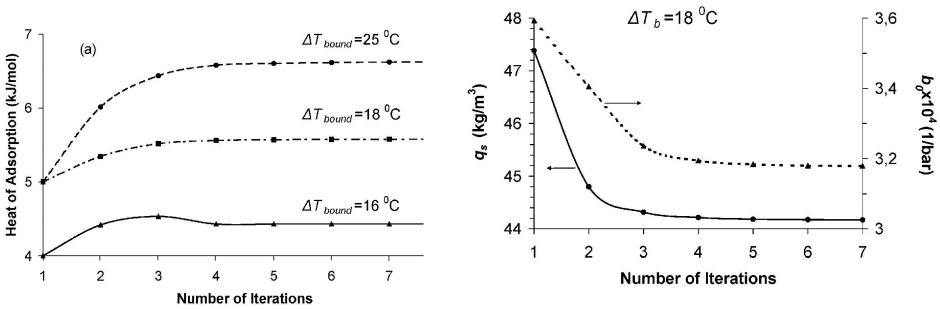

Figure 2: Convergence of the heat of adsorption and the Langmuir parameters through the multi-scale iterative procedure.

Figure 4 illustrates the resulting densities of H_2 stored in the carbon-based optimized materials on a per volume and per weight basis. It is interesting to observe that the two densities show a completely opposite trend as the temperature constraint changes. In particular, as ΔT_b (mean aeverage temperature) decreases so does the volumetric density of H_2 while its gravimetric density increases. The apparent contradiction is easily explained since as ΔT_b decreases so does the density of the optimized material (not presented here). The optimal pore size distributions that result from the optimization procedure are depicted in Figure 5. It is evident that when loose bounds are imposed on the temperature rise in the bed (high ΔTb), the optimum pore size distribution is very narrow and it is limited in sizes of 1 nm or lower. On the other hand, as the temperature bounds are tightened, we observe a shifting of a fraction of pores towards larger sizes, where both the volumetric hydrogen density and the heat of adsorption of the material are significantly lower.

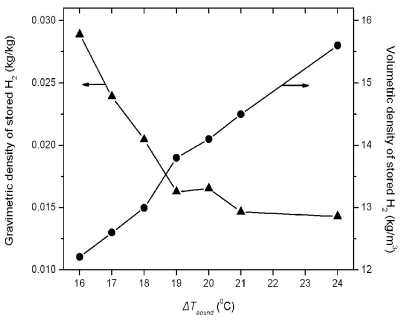

Figure 4: Effect of the imposed temperature bounds on the resulting (converged) value of the gravimetric and volumetric hydrogen density stored in the adsorbent.

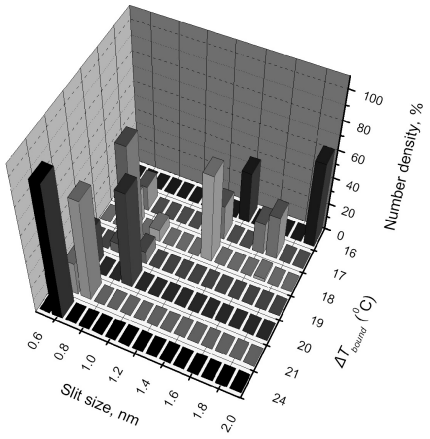

Figure 5. Effect of the imposed temperature bounds on the resulting (converged) optimal pore distributions of the adsorbent.

8. Conculsions

The present work presents a multi-scale modeling and optimization framework for hydrogen storage in carbon-based materials. The outlined methodology is generic and can be easily adapted to the storage of several gases of relevant importance (e.g. methane, carbon dioxide) and/or different nanoporous adsorbents (metal-doped carbon nanotubes, zeolites, metal-organic frameworks, etc.). The results indicate clearly the strong interactions between material and process design.

References

R. Agrawal, M. Offutt, MP. Ramage,.2005, Hydrogen Economy – An opportunity for Chemical Engineers, *AIChE Journal*, 51: 6: 1582.

R.F. Cracknell, 2001, Molecular Simulation of Hydrogen adsorption in graphic nanofibres. *Phys. Chem. Chem. Phys.*, 3, 2091.

A. Delahaye, A. Aoufi, A. Gicquel , I. Pentchev, 2002, Improvement of Hydrogen Storage by Adsorption using 2-D Modelling of Heat Effects, *AIChE Journal*, 48, 2061.

D. Nicholson , NG. Parsonage, 2001, Computer Simulations and the Statistical mechanics of Adsorption. Academic Press, New York.

Process Systems Enterprise Ltd. 2004, gPROMS Advanced Users Guide, London, UK.

W.A. Steele, 1974, The interaction of Gases with solid surfaces. Pergamon, Oxford.