Computational Characterization of a Pore Network Model by Using a Fast Nitrogen Porosimetry Simulation

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Abstract

Nitrogen porosimetry is a characterization technique used to obtain qualitative and quantitative information about the textural properties of porous materials. The physical phenomena exploited in the technique is related to thermodynamic equilibrium and conditioned by pore blocking. The latter phenomenon becomes relevant in highly disordered solids with a wide pore size distribution and a multilevel organization. The aforementioned technique encloses topological information associated with the trend of sorption isotherm. In this work, it is shown how a pore network model can be used to simulate nitrogen sorption process by using an efficient algorithm that combines equilibrium conditions and invasion percolation considerations. Such simulation tool will be the basis for a more comprehensive treatment of experimental characteristic curves and characterization of porous material properties.

Keywords: Digital characterization, Porosimetry, Pore Network Model, Catalyst support, Percolation algorithm, Simulation.

1. Methodology for the Simulation of the Characterization Techniques

The objective of the model is to simulate the evolution of the measured variables during the nitrogen porosimetry characterization experiment. Such an experiment measures, at various nitrogen pressures, the quantity of nitrogen that is present within the porous medium, either adsorbed on the pore walls or filling the pore volume as a liquid phase. An adsorption branch is obtained by increasing the pressure from zero to saturation pressure, and a desorption branch by decreasing the pressure from saturation pressure to zero. If during adsorption, pressure is decreased before reaching saturation pressure, a so-called scanning curve is obtained.

Since the system is equilibrated at every pressure step, a thermodynamic equilibrium model (see 1.1) has to be used to relate the pore size to the volume measured during the sorption process. After generating a geometrical model of the porous medium, it is scanned using an algorithm that determines the desorption sequence of the nitrogen contained in the network pores (see 1.2). The nitrogen sorption simulations can now be performed, both for adsorption and desorption, solving the thermodynamic model equations (see *Algorithm 1*).

```
Read Pore Network Model
Find desorption triggering diameter for each pore
FOR P_relative = 0 to 1
   FOR pore = 1,N_pores
      Calculate the quantity of nitrogen inside the pore (Eq.1
      and Eq.2) using the actual diameter (adsorption) or the
      triggering diameter (desorption)
   END FOR
END FOR
Print isotherm branch
```

Algorithm 1. Pseudo-code for the sorption algorithm

The main characteristics of the pore network generation algorithm used in this work were described by Ferreira (Ferreira et al., 2017; Ferreira, 2018). The hypotheses for the sorption simulations are:

- All pores are cylindrical and rigid.
- The adsorption mechanism starts with the adsorption of the nitrogen on the walls followed by sudden condensation.
- The phase change pressure is governed by capillary forces and pore blocking phenomena.
- The meniscus shape is cylindrical for adsorption and hemispherical for desorption.
- The condensed nitrogen needs to be in contact with the vapor phase to evaporate.
- The pore-blocking phenomenon is only dependent on the topology of the system.
- The pore size distribution is within the mesopore range and over 5 nm.
- The system is in equilibrium.
- No other cooperative effects are considered.

1.1. Thermodynamic Model

To model the vapor-liquid equilibrium in a confined medium, the Kelvin-Cohan equation is used, (Equation 1) (Zhang et al., 2006).

$$\frac{p}{p_0} = exp\left(\frac{-\sigma_{lg} \cdot V_{lm}}{RT} \cdot \left(\frac{1}{r_1(t)} + \frac{1}{r_2(t)}\right)\right)$$

Equation 1. Kelvin-Cohan equation as a function of the two curvature radii of the liquid-gas interface.

In order to calculate the thickness of adsorbed nitrogen, *t*, we have chosen the Harkins-Jura statistical thickness equation, (Equation 2) (Šolcová et al., 2006).

$$t[\text{Å}] = \left(\frac{13.99}{0.034 - log_{10}\left(\frac{p}{p_0}\right)}\right)^{\frac{1}{2}}$$

Equation 2. Harkins-Jura statistical thickness equation.

1.2. Pore Blocking Phenomena: Triggering diameter assignment.

Nitrogen adsorption is not supposed to be constrained by the topology of the structure, but nitrogen desorption can be delayed creating a metastable state. Even if the desorption pressure in a given pore is reached, the liquid phase needs to be in contact with the gaseous phase to be able to vaporize. This condition can generate a pore-blocking phenomenon. Indeed, during the desorption step, nitrogen condensed in small pores can constrain the nitrogen in bigger pores to evaporate at a lower pressure than the

one dictated by its vapor-liquid equilibrium condition. Algorithmically, the pore-blocking phenomenon is approached from the external boundary of the pore network as a simultaneous advancing or receding problem. We will define as external pores to those located at this external boundary harboring the liquid-vapor interphase. The pore-blocking is modeled as a sequence of events, each of which corresponds to a given pore. Once the equilibrium constraints are set with Equation 1, the sequence of the events will depend on the pore size and its position within the network. A pore's triggering diameter represents the pressure at which the change of state (vaporization) will happen within the pore. Since the value of the pore's triggering diameter is not necessarily equal to the actual pore diameter, two diameters have to be assigned to each pore: its actual diameter and a triggering diameter for desorption. The actual diameter is used to calculate the quantity of nitrogen subject to the change of state that occurs at the pressure corresponding to the triggering diameter during the desorption process.

To assign a triggering diameter for desorption to each pore, a dedicated assignation algorithm was developed. There are six main rules on which our algorithm is based:

- The triggering diameter (for desorption) is assigned only once to every pore. There is no overwriting of the triggering diameter.
- A pore can be added to the search list only once.
- A node can be visited only once.
- The pore picked up from the search list must always be the pore with the biggest diameter on the list (priority rule).
- The triggering diameters of the external pores correspond to their actual pore diameters.
- The input of the search list must contain all the external pores (boundary conditions).

For the triggering diameter assignation algorithm, we employ four different lists: *visited_nodes, visited_pores, searchlist* and *connectivity_matrix.* The first two are indexed lists. The third one is a dynamic list handled through binary heaps. The last one is a matrix that contains the information of the pore network.

First, the external pores and the external nodes of the network are identified and listed in *searchlist* and *visited_nodes* respectively. *Searchlist* contains the list of pores to be analyzed. The binary heap (max heap) used to handle *searchlist* allows to rapidly find the pore with the biggest diameter, faster than using any kind of sorting algorithm (Masson and Pride, 2014). The pore with the biggest diameter is the first to be taken for analysis and will be called "guide pore". There are two nodes connected to the guide pore: one of them has already been identified and saved in *visited_nodes*, so the "new" one (not visited yet) can easily be recognized. The connectivity of the unvisited node is explored to identify the pores connected to the guide pore using the *connectivity_matrix*. The newly identified pores will be added to *searchlist*, but first, two actions are needed: a test and the triggering diameter assignation. First, it is verified that the newly identified pores have not been analyzed before by comparing their index to the *visited_pores* list. For those that have not been analyzed before, their triggering diameter is obtained using the two following assignation rules:

- If the diameter of the pore is smaller than the triggering diameter of the guide pore, the pore conserves its original diameter as triggering diameter.
- If the diameter of the pore is bigger than the triggering diameter of the guide pore, the pore adopts the guide pore's triggering diameter as its own triggering diameter.

Once the triggering diameter is assigned, the pore is added to *searchlist* and to *visited_pores*. On the other hand, the node is saved in the *visited_nodes* list. Finally, the guide pore is removed from *searchlist*. The loop starts again with a new guide pore selected from *searchlist*. The process is repeated until *searchlist* has been emptied, which means that all the non-isolated pores (pores with a pathway to the surface) have been assigned a triggering diameter. The binary heap created in *searchlist* uses a function for creating the heap, one for *adding* new elements to the heap and one for *eliminating* the guide pore from the heap once it has been treated.

2. Simulation of Nitrogen Porosimetry Curves

The simulation starts from a relative pressure equal to zero. As the adsorption process evolves in two steps, it is necessary to establish a condensation criterion for the cumulated volume of condensed nitrogen. If the diameter of the pore (D_p) is higher than the Kelvin-Cohan equilibrium diameter (D_{eq_n}-2t) for a given relative pressure, then the adsorbed volume in the pore will be equal to:

$$V_{@p_i} = \pi \cdot (D_p - t) \cdot t \cdot l$$

Equation 3. Total adsorbed volume as a function of the adsorbed layer thickness.

Otherwise, it is considered that core volume has already been filled with liquid nitrogen and the condensed volume in the pore is simply equal to:

$$V_{@p_i} = \frac{\pi}{4} \cdot {D_p}^2 \cdot l$$

Equation 4. Total liquid volume within the pore

For the desorption, as the pore blocking phenomenon exist, the procedure is the same but using the triggering diameter (D_T) of the pore instead of its actual diameter (D_p) for the comparison against the Kelvin-Cohan equilibrium diameter (D_{eq_n}-2t) for the given pressure step.

2.1. Scanning Curves

It is also possible to generate scanning curves accounting for the pore blocking phenomenon by adapting the full Nitrogen Adsorption algorithm. An easy way to do this is by changing the input provided to the invasion percolation algorithm. The initial pressure of the desorption scanning branch is fixed and the corresponding critical pore diameter is calculated. For the pores with a diameter over the calculated critical diameter, they are temporarily assigned a very large diameter.

3. Case Study

3.1. Network Parameters

Networks with zero volume spherical nodes are considered for the case study. A 3D regular cubic lattice of 50x50x50 nodes was employed along with a Pore Existence Probability (PEP) equal to 0.75. The length of the pores is considered constant and equal to 21 nm. A pore size distribution generated by a Gaussian distribution centered at 10 nm and a standard deviation of 2 nm was employed. The consistency between the input and output cumulative distribution functions for the networks with zero volume spherical nodes was verified. An average connectivity equal to 4.2 and a void fraction of 0.38 were obtained.

3.2. Characteristic Curves

The simulated sorption isotherm is shown in Figure 1a. It corresponds qualitatively to typically observed experimental curves for mesoporous alumina. The isotherm

qualitatively corresponds to a type V isotherm (according to IUPAC classification) with a hysteresis loop closing at about 0.42 (Rouquerol et al., 2014). The hysteresis loop is a consequence of the pore blocking phenomenon and the meniscus curvature difference considered between condensation and vaporization in the Kelvin-Cohan equation. The starting and closing volume naturally coincide for both branches.
Figure 1b shows the back-calculated pore size distribution by applying the BJH method (Barrett et al., 1951)to the simulated isotherm. A good agreement was found between the pore size distribution generated from the adsorption branch and the original distribution used for the pore network generation.

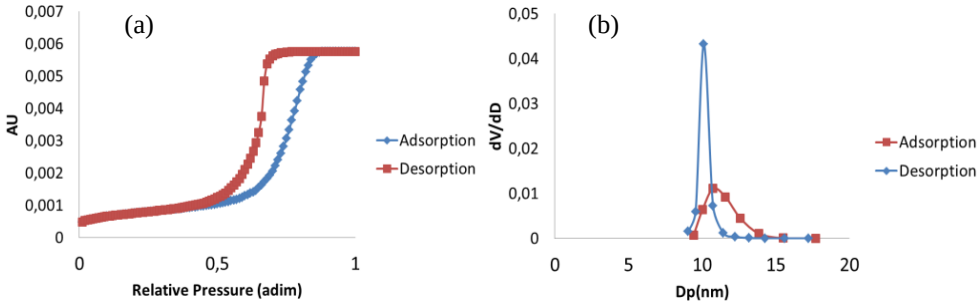


Figure 1: (a) Numerical Nitrogen Isotherm (b) Calculated BJH Pore Size Distribution (Adsorption and desorption branches)

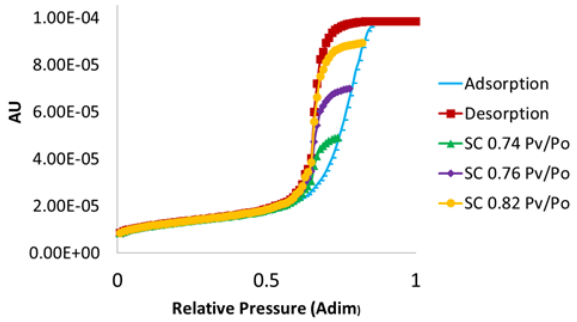


Figure 2: Digital Scanning Curves

Finally, Figure 2 provides an example of the adsorption-desorption scanning curves obtained for this sample. The hysteresis loop is of the H2 type with the scanning curves converging to the closure point of the hysteresis loop.

3.3. Algorithm's Execution Time

In order to test how the execution time of the simulations scales with the size of the network, six cubic lattice networks of different sizes were generated. The pore existence probability (PEP) was set to 1. All the other input parameters have been maintained as described in section 3.1. The results are shown in Figure 3. The execution time is plotted as a function of the total number of pores connected to the surface. As the size of the network increases, the time required for the execution increases as well. The algorithm execution time proceeds with an O(Mlog(N)) time.

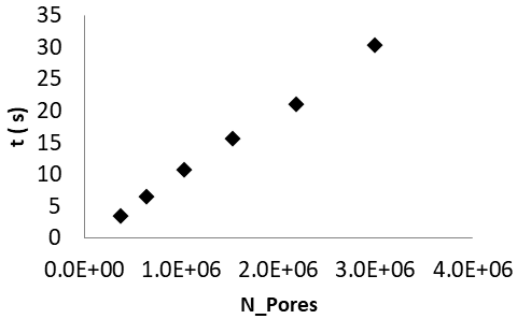


Figure 3: Effect of the number of pores on execution time of the nitrogen porosimetry algorithm.

4. Conclusions

A fast algorithm for the simulation of nitrogen porosimetry within a digital pore network was developed. The thermodynamic equilibrium conditions within the porous solid during nitrogen porosimetry and the associated pore blocking phenomena were considered. The algorithm was sped up by using a Max-Heap. A time execution test for the nitrogen porosimetry algorithm and an octahedral lattice of about 2 million pores only required 6.7 seconds for a single simulation using the binary heap in comparison to 19 hours using conventional sorting algorithms. This shows the advantage of using the binary heap for handling the search list as suggested by Masson (Masson and Pride, 2014). The size of the network is the main parameter that affects the execution time and exhibits an O(Mlog(N)) behavior.

Valuable information about the topology of the pore network is implicit in the desorption branch of the isotherm and can be exploited by using this type of simulation. Adding an optimizer to this algorithm in order to adjust the digital characteristic curves to those of an actual porous alumina sample will allow obtaining a digital structure that not only exhibits the same macroscopic properties but that could also represent statistically the topology of the material. This algorithm has also been adapted to other porosimetry characterization techniques, such as mercury porosimetry, cryo-porometry, and thermo-porometry.

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