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# Modeling intragranular transport in a catalytic reactor: Descriptors and representation of the porous structure

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## 1. Introduction

Understanding how transport phenomena and chemical reactions within porous catalysts are affected by the texture of the support opens the door to optimizing the catalyst performance. New and more rigorous heterogeneous models for chemical reactor design could be created by accounting explicitly for the phenomena occurring at the pore scale. To model structures of porous catalysts several approaches can be found in literature [1,2]. Generating computational structures that match structural descriptors of the real material requires information about the textural properties and the topology of the material. In this work, the impact of the porous structure of gamma-alumina catalyst supports on mass transfer phenomena in non-reactive and reactive systems is studied. The representation of the alumina support is based on Ferreira's work, in which a network of interconnected cylindrical pores is created by means of a stochastic assembly algorithm [3]. By using a hierarchical network, Ferreira [4] was able to computationally generate several pore network structures whose textural and transport properties matched those obtained experimentally in Kolitcheff's work [5]. The objective is now to further constrain the number of possible structures by generating a network that allows representing experimental results obtained from different characterization techniques. Nitrogen Porosimetry (NP), Mercury Porosimetry (MP), Nuclear Magnetic Resonance Cryo-Porometry (CP) and Thermo-Porometry (TP) are such characterization techniques that deliver quantitative and qualitative information about the porous structure by using theoretical and empirical models: pore size distribution, pore volume, and surface area are textural properties estimated by these techniques [6].

## 2. Methods

The pore networks used for the simulations were generated through a discrete reconstruction model based on a stochastic algorithm described by Ferreira [3,4]. For the models, two cases are considered: in the first case, the pores are modelled as cylinders that are connected through zero volume nodes, while in the second case the pores are cylindrical and connected to spherical nodes. The cylinders are organized in space using a 3D cubic lattice that can be regular or disordered. By using a Monte-Carlo approach, the creation process of every pore is totally random, constrained just by the pore existence probability defined as input. To characterize the digital pore network, simulation algorithms for NP, MP, CP and TP were developed. The algorithms account for percolation phenomena and confinement effects occurring within the porous network during the characterization. Selection of the right computational algorithms to model the physical

phenomena and to store and handle the network's information is quite relevant to limit the execution time. An Invasion Percolation (IP) algorithm was adapted for each modelled technique based on the work of Wilkinson and Willemsen [7] and the improvement made by Masson and Pride [8].

## 3. Results and discussion

The textural properties of the digital pore network were calculated both geometrically and by processing the results of the simulated characterization techniques. Compared to the direct calculation of the textural properties by simply counting the numbers of pores, the direct simulation of the entire characterization profiles provides a better interpretation of the experimental results by analysing the validity of the assumptions made by theoretical and/or empirical models used for the calculation of the material's textural properties from the experimental data. The pore network generation tool is based on a ***O(****log(n))* algorithm that allows to create a network with $6 \cdot 10^6$ pores in only 46 seconds on a Dell desktop computer with a 3.5 GHz Intel Xeon E5 CPU and 16GB of RAM. For the characterization techniques, the use of a dynamic priority list to handle the exploration of the network is valid for all techniques, as the phase change and/or percolation phenomena occurring in every technique are constrained by the topology of the network, The algorithms are capable of reproducing typical hysteresis behaviour observed in the experimental results for alumina catalyst supports. By versioning the IP algorithm to our needs and handling the priority list using diverse versions of binary heaps, we were able to maintain a good time performance for the different algorithms created for each characterization. The execution time for the characterization techniques corresponds to an ***O(****nlog(n))* behaviour and takes about 25 seconds for $8 \cdot 10^6$ pores. To match the textural properties of the digital pore network with that of an actual alumina support, the input variables of the network model are modified until the differences between the output textural properties and actual values are minimized. A good agreement was observed between the properties of the digital twins and the actual aluminas.

## 4. Conclusions

In this work, a pore network generation algorithm was used to represents gamma-alumina supports. To obtain the textural properties of such a digital pore network, an Invasion Percolation algorithm was adapted in order to characterize this structure by means of the computer-equivalent of nitrogen porosimetry, mercury porosimetry, NMR cryo-porometry, and thermo-porometry. Using the developed algorithms, it was possible to generate digital pore networks whose properties are in good agreement with the properties experimentally measured by different characterization techniques on actual gamma-alumina supports.

## References

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