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APCBEE Procedia 00 (2014) 000–000

APCBEE Procedia

www.elsevier.com/locate/procedia

ICBEE 2014: September 15-16, Paris, France

Pore Network Modelling of CAPRI Catalyst Using Mercury Porosimetry and Porexpert

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Abstract

The pore network modelling and simulation of THAI-CAPRI catalyst using software named Porexpert is reported. The pore network modelling and simulation method is presented for estimating the pore properties of THAI-CAPRI catalyst using a network model of void structure based on mercury intrusion porosimetry (MIP). The method is applied to the catalyst samples, and a network is derived in which mercury intrusion curve, porosity, connectivity, pore and throat size distributions are obtained. The study revealed that the network model can be applied for analysis and correlation of the pore properties of any porous media. The results suggest that the network model used to estimate the samples particle distributions and it also successfully models the permeability of the samples within similar order of magnitude.

Keywords: porenetwork,modelling,porosimetry,porexpert,catalyst,permeability

1. Introduction

The characterisation of porous materials is a difficult task and this has being a challenge for a very long time, and anybody who have worked or working in this area will testify to this fact. However, a critique of the limitations of single-technique characterisations of the void space of porous media, and a quantitative investigation of the additional information, which can be gained from a Cartesian void network model. It is convenient to categorise void space architecture into four levels. The primary structure of a porous material is

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taken to be the distribution of void sizes, the secondary structure the connectivity of these voids, the tertiary structure the relationship between the sizes of voids and the sizes of their immediate connecting neighbours, and the quaternary structure the size auto-correlations and gradations over the sample as a whole. These different levels of structure contribute to important properties of the sample, such as its filtration efficiency and capacity [1], absorption and wetting characteristics [2], and the adsorption and diffusion of pore fluids [3] . The quaternary structure determines the anisotropy of these characteristics relative to the direction of application or flow of fluids [4]. Catalyst deactivation by coke deposition has been identified as one of the main challenges suffered by THAI-CAPRI process. Where "Toe-to-Heel Air Injection", is known as THAI, and CAtalytic upgrading PRrocess In-situ (CAPRI) is way to further enhance the upgrading arising from the THAI process itself. Therefore In this study software named Porexpert will be used to characterise candidate catalyst used in the process, by modelling and simulation of the experimental data obtained from Mercury Porosimetry experiment. It is a software package which allows the study of the pore level properties of any mesoporous or macroporous solid, i.e. a solid with pore sizes greater than 2 nm. These make it most suitable since catalyst deactivation does not only depend largely on pores and pores structure, but also take place in the pores. However the defects of some of these methods are mentioned as follows, Microscopy gives a 2-dimensional view, with no information about the 3-dimensional connectivity of voids – and it is that connectivity which hugely affects properties such as the permeability, diffusion and trapping of pore fluids, and filtration characteristics. Tomography gives a 3-dimensional mapping of the voids, but not to sufficiently high resolution to give all the interconnections. Porexpert is designed to bring all this partial information together, by constructing a realistic simulation of porous material. This study attempts to characterise catalyst using a combined method of mercury porosimetry and Porexpert technique. The generated network structures created by the software are constructed under the criterion that they hold the same percolation characteristics as those derived from experimental data [5]. To simulate mercury intrusion a computational representation of fluid is applied to the top face (maximum z) of the unit cell only, and percolates in the –z direction. The throat skew, throat spread, pore skew, connectivity and short range size auto correlation are adjusted by the Boltzmann-annealed amoeboid simplex [6] to give a close fit to the entire mercury intrusion curve.

2. Materials and Methods

The catalyst samples studied in this work were Ketjenfine hydroprocessing catalysts-NiMo type (Extrudates & fragment) and CoMo type, which were refer to as sample A, B & C. Mercury porosimetry was performed on a Micrometrics Autopore IV 9500 mercury porosimeter (Micrometrics Corporation, USA) with a pressure range from 0.01 to 414 MPa, following ISO9001:2008 protocols. The standard equilibration time used for each pressure point was 30s.The sample was first evacuated to a pressure of ~50 μm Hg in order to remove physisorbed water from the interior of the sample. The raw data were analysed according to the Washburn equation the value taken for the surface tension of mercury was 0.485 Nm−1. The corresponding values for the advancing and receding contact angles were both taken as 130◦. The three catalyst samples from MIP experiment were modelled in this work using Porexpert software. 3D void networks are generated by stochastically creating unit cells comprising an array of 1000 (10×10×10) cubic pores connected by up to 3000 cylindrical throats (see Fig.1). The network model 'Pore-Cor' has been previously used to model a range of materials such as soil, sandstone, catalysts and paper coating [7],compacted mineral blocks [8] modelling diffusion in porous structure [9]. It represents the void structure of porous medium as a series of identical interconnected unit cells with periodic boundary conditions. Each unit cell comprises an array of 1000 nodes in a cubic-close-packed array equally spaced at a distance from each other in each cartesian direction.

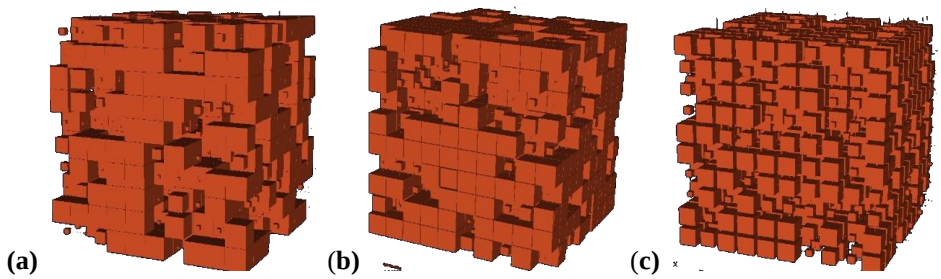

Fig. 1. (a) sample A; (b) sample B;(c) sample C

3. Results and Discussion

The experimental mercury porosimetry curve fitting process was undertaken using an annealed simplex algorithm which works to find the global minimum for a five dimensional global minimum [10]. The fits between the experimental and simulated curve matched very closely as shown in Fig. 2. Sample A structure shown in Fig. 1 has simulated porosity of 55.86 % and experimental porosity of 55.84 %. The Porexpert network simulation software also modelled correctly the trend of the experimental mercury intrusion curve for samples B and C. The fits between the experimental and simulated curve matched very closely. The sample B structure shown in Fig. 1 has simulated porosity of 60.39 % and experimental porosity of 60.40 %. While structure of sample C shown in Fig. 1, have simulated porosity of 37.87 % and experimental porosity of 37.87 %. Comparing the experimental and simulated curve of samples, it can be seen that in the mesopore size range, the pore size distributions have an overall sigma shape with relatively flat plateaus at both small and very large pore sizes. In this simulation, mercury is injected normal to the xy plane at z= 0 in the -z direction. Since the unit cell repeats in each direction, z = 0 at z =I_{cell}, the unit cell size, and the injection corresponds to intrusion downwards from the top surface (see Fig.1). Therefore the generated structures presented in this study are the result of mapping the mercury intrusion curve of the sample onto a network of pores and throats.

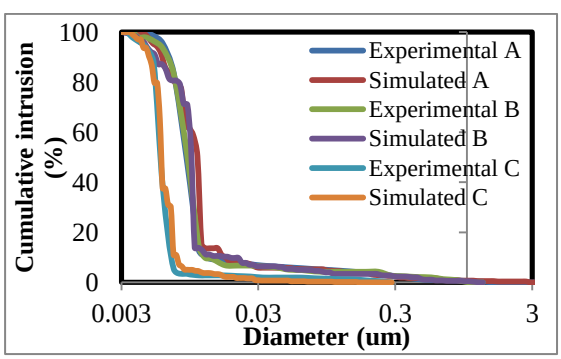

Fig. 2. Comparison of experimental and simulated mercury intrusion curve of samples

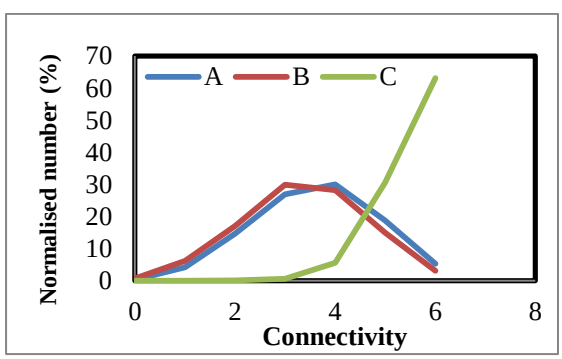

Fig. 3. Connectivity distribution of catalyst samples

As shown in Fig. 3 the connectivity distributions of all the pores within the unit cell, determines how many throats are connected to each individual pore. There is similarity in the shape of the path of A and B distribution curves. This could suggest that fragmentation of A to B (powder) had a negligible effect. All samples have highest connectivity value of six. It can be seen from Fig. 3, connectivity distribution curves for

sample C differs with no peak present. This could also suggest that sample C may have connectivity higher than 6. There is possibility that the connectivity distribution curve for C may have increased further, but stopped by what could be believed to be an artefact from the software. The connectivity distribution works out whether a pore has zero connectivity that is an isolated pore, one connection that is an ink bottle pore, two connections, three connections, four connections, five connections and six connections. It is worth mentioning that for all connectivity distribution present in the sample, the ink bottle pores, which are the pores with one connection, are the most important, because they mainly responsible for the hysteresis of mercury during a mercury porosimetry experiment. Fig. 4 shows pore and throat size distribution of the simulated catalyst samples. Their distributions are characterized by peaks. It can be seen that sample B has the highest number of pores (see Fig. 4 and Table 1), followed by A and C. Conversely sample C which has the smallest number of pores, displayed higher throat number than A and B which both have the same throat number. The effective thermal conductivity, porosity, number of pores and throat of the simulated network structures are presented in Table 1.These represents the features of the catalyst samples as simulated by the software.

Table 1. Thermal conductivity, porosity and number of pores and throat of simulated network structure

Sample	Porosity %	Pore	Throat	Pore conductivity (W/mK)	Solid Conductivity (W/mK)	Permeability (mD)
A	55.86	46	99	0.0694	0.888	2.32E-08
B	60.39	55	99	0.061	0.792	5.33E-08
C	37.87	31	97	0.25	0.758	3.67E-07

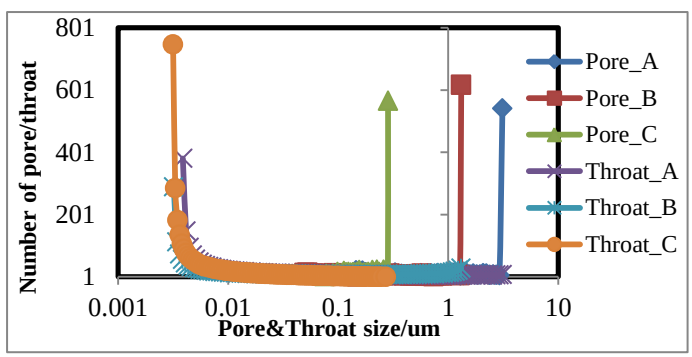

Fig. 4. Pore and throat size distribution of catalyst samples

The network simulator can also calculate the permeability of the simulated porous structures using equation (1) [10].

$$K = \frac{\pi}{8}\Omega_{cell}(F_{arcs})\frac{l_{cell}}{A_{cell}} \quad (1)$$

Where k is absolute permeability, l_{cell} is the length of the unit cell of the network model, and A_{cell} is the cell's cross-sectional area. A network analysis approach to this problem supplies the term $\Omega_{cell}(F_{arcs})$ as the maximal flow capacity through the network of pores and throats [10]. It is calculated by means of the archetypal network capacity algorithm developed by Dinic [11]. There is an overall conservation of flow, so that the entire volume of fluid entering the top of the unit cell emerges at the bottom, with no build-up through the network. The value obtained, as the maximal flow, is based on the capacities of only the channels found to carry flow. The permeability results as modelled using Porexpert are shown in Table 1. The predicted

permeability of sample A and B are of similar order of magnitude. However, sample B showed a higher permeability values than sample A. This can be seen clearly in Table 1. This could be supported by the fact that B is the fragmented form of A. Considering the entire catalyst sample in their various forms they displayed a unique features and characteristics in the pores, throat, connectivity distribution and fitting parameters. This method of permeability calculation employed in this work is a more precise approximation than the other main methods of solving the flow in void networks, namely the resistor network [12]. Conclusively all modelled network permeability of samples are within similar order of magnitude and very much more realistic than values derived from semi-empirical equations.

4. Conclusions

The pore network modelling and simulation method for estimating the pore properties of THAI-CAPRI catalyst using a network model of void structure based on mercury intrusion porosimetry (MIP) was also carried out. The study revealed that the network model has three main characteristics: a real pore space geometry; the same geometry is used to model a wide range of properties; and no property-independent fitting parameters are invoked; and thus the method can be applied for analysis and correlation of the pore properties of any porous media. The results suggest that the network model was used to estimate the samples particle distributions and it also successfully models the permeability of the samples to within similar order of magnitude.

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