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Deep Learning Surrogate Models for High-Pressure CO_2 Adsorption: A Bayesian Approach with Extended Peng-Robinson Equation

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Abstract

Accurate modeling for the removal of carbon dioxide (CO_2) by adsorption entails the integration of principles of mass, energy, and momentum conservation with adsorption models. In this context, the thermodynamic description of adsorption equilibrium can be approached at various levels of detail. However, incorporating highly detailed isotherms presents a significant challenge for adsorption column solvers, as it requires solutions at each time step and position, leading to a substantial increase in computation time. To address this challenge, we developed a Deep Neural Network to train a surrogate model using adsorption data obtained through the solution of an extended Peng-Robinson model for confined fluids. These equilibrium data for CO_2 adsorption were obtained by a Magnetic Suspension Balance (MSB), which enables sorption measurements at elevated pressures. We evaluated the extended Peng-Robinson model within a Bayesian framework to generate a collection of pseudo-experimental points, aiming to be used as inputs to train a model based on pattern identification techniques. The Bayesian structure is advantageous as it incorporates information from experimental data and prior assumptions of general knowledge (a priori knowledge) to generate posterior distributions of parameters and models. Finally, the output from the surrogate model is integrated into the mass balance equations while solving the partial differential equations that describe an adsorption column for CO_2 removal. This approach results in a model for the evolution of the mass front in a fixed bed, facilitating enhanced accuracy in predicting system behavior.

Keywords: Carbon dioxide removal, Multiscale model, Confined fluids, Deep Neural Network, Bayesian statistics;

1. Introduction

The adsorption process is widely used in industries to separate different fluids, including CO_2 capture. Developing adsorption models is essential for this process's optimization, design, and operation. Generally, mass and energy balances are necessary to model separation and purification in fixed bed columns. The axial dispersion term and a mass transfer model in the film using the linear drive force (LDF) equation are expected for a rupture simulation. In other words, the kinetic terms are consolidated in the literature. The bottleneck occurs when choosing predictive and accurate models for determining the adsorption isotherm, which is necessary information for the modeling. For pure substances and mixtures, it is expected to estimate the isotherm parameters, ignoring the nature of the molecules and the fundamentals of molecule-surface interactions. Although it serves the purpose, this approach limits the range of application of the model.

Travalloni *et al.* (2014) [1] and Barbosa *et al.* (2016) [2] propose an extension of the Peng-Robinson equation of state for confined fluids (PR-C) based on Grand-Canonical Monte Carlo simulations. It is applied as a hypothesis that the particles are hard spheres, confined in slit-like pores and interacting with each other by square-well potential. PR-C was able to make good correlations of type IV isotherms and present excellent predictions when compared with experimental results for the adsorption of $CH_4/CO_2/N_2$ mixtures on activated carbon at high pressures.

The main objective of this work is based, in particular, on scale integration. First, the PR-C equation of state is applied to calculate the absolute adsorption of CO_2 isotherms at high pressures. Then, a Bayesian statistical analysis is applied to make inferences about the parameters and output variables of the PR-C model.

For coupling the equation of state with the fixed-bed model, a model was trained based on machine learning to perform fast calculations of the adsorbed CO_2 concentration under multiple temperature and pressure conditions.

2. Methodology

2.1. Experimental Data

The adsorption equilibrium isotherms of CO_2 were obtained at the ATOMS Laboratory (Applied Thermodynamics and Molecular Simulation) of the Federal University of Rio de Janeiro (UFRJ), Brazil. A Rubotherm IsoSORP magnetic suspension balance (MSB) was used to conduct adsorption measurements on zeolite 4A within the 1 to 50 bar pressure range.

2.2. Modeling of confined fluids via extended equations of state

The development of statistical mechanics improved the connection between macroscopic thermodynamic properties and physical phenomena described at the microscopic level. For cylindrical pores, the PR-C model [1,2] is given by Eq. 1 and 2,

$$P = \frac{RT}{v-b_p} - \frac{a_p}{v(v+b_p)(v-b_p)} - \Psi \tag{1}$$

$$\Psi = \theta \frac{b_p}{v^2}\left(1-\frac{b_p}{v}\right)^{\theta-1}\left(1-F_{pa}\right) \times \left(RT\left(1-\exp\left(-\frac{N_{av}\varepsilon_p}{RT}\right)\right)-N_{av}\varepsilon_p\right) \tag{2}$$

in which the parameters a_p and b_p are modifications to the original Peng-Robinson parameters, v is the molar volume, θ is a parameter relative to the pore geometry, F_{pa} is a function of the fraction of particles interacting with the pore wall, N_{av} is the Avogadro number, R is the universal ideal gas constant and ε_p is the molecule-wall interaction potential.

The PR-C model establishes the modeling of the molecule-pore interaction through a square-well potential described in terms of radial coordinate in relation to the pore center. Finally, using the textural properties of the adsorbent solid (V_p and r_p) and the thermodynamically stable root, the number of moles of the adsorbed species (n_{ads}) is obtained through Equation 3 [6]:

$$n_{ads} = n_{exc} + V_{ads}\,\rho_{bulk} \tag{3}$$

In which n_{exc} is the excess adsorbed concentration given by the gravimetric apparatus, V_{ads} is the volume of the adsorbed phase and ρ_{bulk} is the density of the gas phase (bulk).

2.3. Bayesian general framework

Current literature points out the Markov Chain Monte Carlo (MCMC) method as a well-established solution to perform the sampling of the posterior distribution, according to Bayes' theorem [3,5]:

$$P(\theta|\mathrm{D}) = \frac{P(\mathrm{D}|\theta)\,P(\theta)}{P(\mathrm{D})} \tag{4}$$

in which $P(\theta|\mathrm{D})$ is the *a posteriori* probability of the parameters θ given a data set D; P(D |θ) is the likelihood term, described as the probability of the data against the set of parameters; P(θ) is the *a priori* probability of the parameters and P(D) is known as evidence and difficult to compute, being often treated as a normalizing constant. Therefore, attention focused on the numerator of Equation 4, so the posterior probability can be considered as proportional to the likelihood multiplied by the a priori probability [3,4].

The main advantage of the Bayesian approach is the possibility of including additional external information, the *a priori* distributions of the parameters, in addition to the experimental data. Such information can improve the accuracy and credibility of estimates. In the present work, all calculations were performed using the *emcee* package for Python language [4]. In order to obtain an adequate approximation of the posterior distribution of the parameters, 32 walkers were used in a total of 10000 Markov chain steps.

2.4. Deep Neural Network

The hyperparameters were determined using an optimization in Python using the Keras [7] and TensorFlow [8] platforms as tools. The optimal architecture was evaluated by minimizing the mean absolute percentage error.

We used the MCMC data with the following separation: 90% for training, 5% for validation, and 5% for testing. The hyperparameters were determined following the criteria: The network was optimized with mixed activation functions. The ReLU, GeLU, Sigmoid, and Tanh functions were tested for each layer. The Number of neurons: search ranges from 20 to 400; for the Number of mini-batches, the search ranges between 128 to 1024; and for the adaptive learning rate, the search ranges from $1 \cdot 10^{-3}$ to $1 \cdot 10^{-5}$.

3. Results and Discussion

3.1. Bayesian Inference applied to the calculation of absolute adsorption isotherms via PR-C model

Figure 1 presents the experimentally obtained excess adsorption isotherms for five different temperatures up to pressures of 50 bar. In general, good reproducibility is observed for the reported gravimetric technique.

Subsequently, using the excess information and the MCMC method, the absolute adsorption isotherms were calculated according to Eq. 3. Based on the experimental fluctuations, the Bayesian structure allows for the inference of uncertainties related to the parameters of the PR-C confined fluid model (confinement and textural parameters). These uncertainties are then propagated to the model's output variable (n_{ads}), enabling the construction of confidence bands for the absolute adsorption isotherms, as shown in Figure 2.

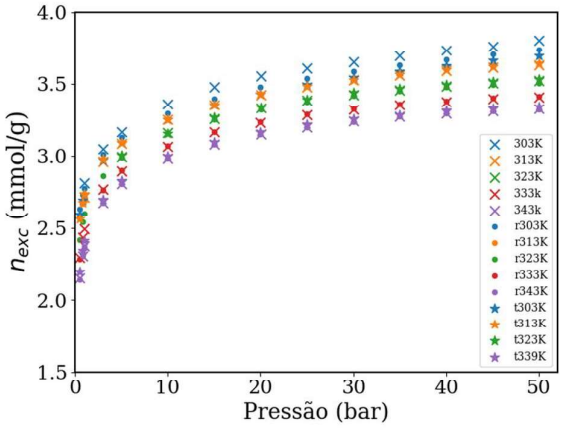

Fig. 1. Excess isotherms for CO_2 on zeolite 4A at different tempearatures.

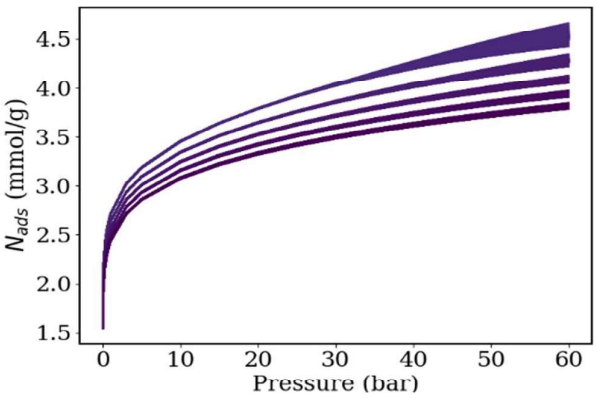

Fig. 1.. Absolute isotherms for CO_2 calculated using PR-C model and after Bayesian framework.

3.2. Surrogate model from a DNN approach

The best architecture for the model training, based on the described methodology, was using a model with two hidden layers: the input connects with the first layer by a GeLU function, the second layer has a ReLU function, and the last layer has a linear output. All hidden layers had 240 neurons. As shown in Fig. 3, the parity plot presents a good agreement between the experimental and predicted values with an R^2 of 0.9996.

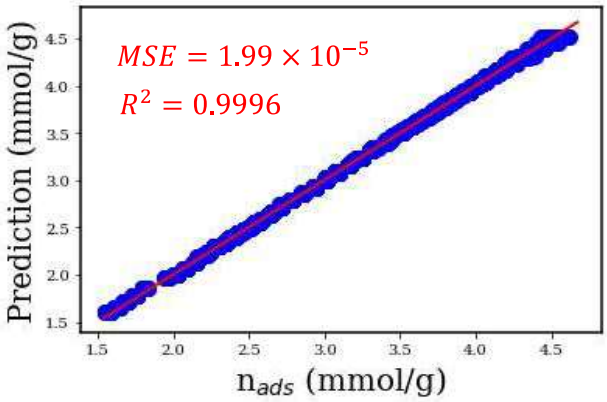

Fig. 2. Parity plot between the predicted and the experimental adsorbed CO2 on zeolite 4A.

The advantage of using a model generated by neural networks is that it reduces computational costs. Here, the prediction of the CO_2 adsorption capacity calculated by the surrogate model is calculated two times faster than by the PR-C model (Table 1).

Table 1. Comparison of methodologies

Computational cost for calculating a point (T,P) of the isotherm	
PR-C model	0.42 ms
Surrogate Model	0.19 ms

3.3. Fixed bed simulations

The surrogate model generated by DNN was coupled to the differential mass and energy balances for a fixed bed adsorption column. Initially, Figure 1 presents the simulations of the CO_2 breakthrough curves for different compositions when feeding a pilot scale column at 1 bar.

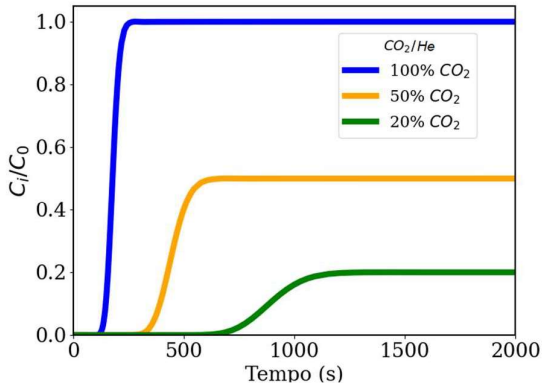

Fig. 3. CO_2 breakthrough curves for different inlet compositions at 1 bar.

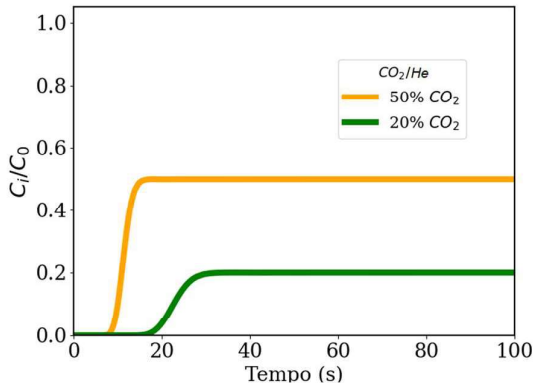

Fig. 5. CO_2 breakthrough curves for different inlet compositions at 50 bar.

Finally, Figure 5 presents the simulations of the CO_2 rupture curves for a pilot-scale column under high pressure conditions (50 bar).

4. Conclusions

The Equation of State (EoS) for confined fluids has demonstrated its suitability for calculating absolute adsorption isotherms at high pressures, showing comparability with other methodologies such as Ozawa [6]. Additionally, the development of an accurate surrogate model offers a lower computational cost alternative for isotherm calculations. Moving forward, the next steps will involve the implementation of a multicomponent approach and validation against dynamic experimental data.

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