MACEIÓ - ALAGOAS
EBA 15
15° ENCONTRO BRASILEIRO SOBRE ADSORÇÃO
15th Brazilian Meeting about Adsorption

Predictive modeling of natural gas adsorption with activated carbons in vehicle fuel tanks using artificial neural networks

Marcos A. Q. Machado [a], Daniel V. Gonçalves [a], José C. A. Oliveira [a], Andréa S. Pereira [a], Sebastião M. P. Lucena[a]

[a]*Laboratory of modeling and 3D visualization, GPSA, Dept. Eng. Química, Universidade Federal do Ceará, Campus do Pici, Bl. 709, 60455-760, Fortaleza, CE.*

Abstract

This study addresses the application of artificial intelligence models to predict the energy deactivation curves of adsorption beds composed of 17 different types of activated carbons, throughout the operating cycles of a vehicle fuel tank. Using simulated data from the adsorption of methane, ethane, propane and butane, the pore size distribution (PSD) was used as a way to characterize the activated carbons. The charge/discharge tank model, together with the Ideal Adsorbed Solution Theory (IAST), was solved iteratively in the gPROMS software to obtain data over 200 operating cycles. The Latin Hypercube Sampling (LHS) technique was used to determine efficient combinations of the molar fractions of the natural gas components, used in the calculations. Subsequently, artificial neural networks (ANNs) were trained and evaluated to predict the energy deactivation curves of the adsorption beds, whose architectures were optimized using the Particle Swarm Optimization (PSO) methodology. The results indicate that the ANN trained with the characterization data of PSD presented satisfactory performance, standing out as an effective approach in predicting this phenomenon. Therefore, the proposed model is capable of predicting the energetic deactivation curves for a wide range of activated carbons, when the PSD is known.

Keywords: Adsorption; Activated Carbons; Natural Gas; Artificial Neural Networks.

1. Introduction

Recently, there has been a significant increase in the search for more efficient and sustainable alternatives for storing gases, such as hydrogen and natural gas, in the global energy context. The use of porous media, such as adsorption beds, to store these gases has emerged as a promising and viable option [1]. Among the porous materials used, activated carbons deserve special mention, as they have demonstrated significant efficiency in gas adsorption capacity [2].

Activated carbons are extremely porous materials, obtained through the activation of carbon-rich precursors. Their porous structure provides a considerable internal surface area, enabling effective selective adsorption of gases and molecules [3].

Adsorption is influenced by several variables, including temperature, pressure, physicochemical properties of the adsorbent, and characteristics of the fluid to be stored [4]. Modeling and predicting the behavior of these variables pose persistent challenges, given their nonlinear nature and the interdependence between them. The inherent complexity of activated carbon systems demands the continuous development of more sophisticated mathematical models and prediction algorithms capable of accurately capturing the nuances of molecular interactions.

Artificial Neural Networks (ANNs), which are inspired by the neural structure of the human brain, have proven to be powerful tools for modeling complex systems and predicting variables in large, multidimensional data sets [5]. Through machine learning algorithms, these networks have the ability to recognize patterns and establish nonlinear relationships between the input and output variables of the adsorption process. This ability allows ANNs to extract valuable information from data sets from experimentation or computational simulation, resulting in accurate, reliable predictions with lower computational cost when faced with the need to solve highly complex systems of equations [6].

The application of ANNs to predict gas adsorption on activated carbons considerably expands this approach. The combination of the learning capacity of ANNs with the adjustable properties of activated carbons enables the creation of advanced and accurate prediction models.

This work presents an innovative approach in the field of gas storage for vehicular applications, highlighting the use of artificial neural networks optimized by PSO (Particle Swarm Optimization). From the models obtained, it is possible to make predictions of the energy delivered at the fuel tank outlet for different types of activated carbons, in addition to those used in this work, characterized from the PSD.

2. Models and methods

2.1 Molecular models

The activated carbons were represented using the slit-pore model, as illustrated in Figure 1. In this representation, each pore consists of two graphene layers, each with an area of 40 × 40 Å². The Lennard-Jones (LJ) parameters assigned to the carbon atoms were σ = 3.4 Å and ε/k_B = 24.6 K, where k_B represents the Boltzmann's constant. This combination of parameters has previously been used by our group to simulate the adsorption of heavy alkanes from natural gas on carbonaceous materials, as mentioned in previous works [3,7,2].

Adsorption isotherms were calculated using the Grand Canonical Monte Carlo (GCMC) method. A truncated Lennard-Jones potential without tail correction was applied. A cutoff radius of 12.8 Å was considered. The Lorentz-Berthelot mixing rule was used to calculate the solid-fluid force field parameters. At least 10^5 cycles were performed, each consisting of N steps, where N is the number of molecules in the system, with $N \geq 20$. All simulations incorporated random insertion, deletion, rotation, and translation movements of selected molecules, with equal probabilities. Peng-Robinson equation of state was employed to convert pressure to fugacity and to calculate the excess adsorbed amount from the absolute amount.

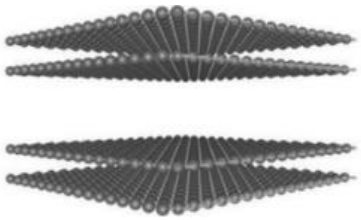

Fig. 1. Graphene slit-pore model.

To properly perform the adsorption isotherm calculations, we adopted an approach using the pore size distribution (PSD), calculated from experimental and simulated N_2 isotherms at 77 K. Our PSD consists of 22 pore sizes as applied in previous works [8,3,7].

2.2 Experimental planning

The Latin Hypercube Sampling (LHS) technique was used to determine the combinations of molar fraction values of the four natural gas components. These combinations were used in the calculations of the energy delivered at the fuel tank outlet in each operating cycle, which is the variable of interest in this study, representing the adsorbent capacity of the beds over successive loading and unloading cycles. This statistical approach is frequently used in experiments and computational simulations to efficiently sample the parameter space of a mathematical model.

2.3 Loading and unloading tank model

The system proposed for the tank operates in an iterative manner, alternating between high pressure levels during the injection of natural gas into the fuel tank, which has a defined composition, and reduced pressure during depressurization throughout the operation of the vehicle's engine, where there is variation in composition.

Tank operating pressure ranges have previously been reported by the United States Department of Energy (DOE) [10] to be between 1 and 35 bar and by the United States Advanced Research Projects Agency for Energy [11] between 5.8 and 65 bar, taking into account a reasonable practical application. The operating temperature of the tank was kept constant at room temperature (298 K), and data from the curves representing the energetic deactivation of the adsorption bed were collected over 200 operating cycles.

According to the Ideal Adsorbed Solution Theory (IAST), the phase equilibrium in the adsorption process is characterized by the equality of fugacity between the adsorbed phase and the gas phase. This can be compared to the liquid-vapor equilibrium, as expressed in Raoult's Law, represented in Eq. 1.

$$f_i = P.\varphi_i.y_i = f_i^0.x_i \quad (1)$$

The simplifications adopted for the development of the tank model included the following assumptions:

• It is feasible to assume isothermal operation of the tank, since the loading (adsorption) and unloading (desorption) processes occur at a speed that allows disregarding thermal effects.
• The model is defined by lumped parameters, which means that it does not consider spatial variations in its properties, such as pressure and concentration.
• The equality between adsorption and desorption in the gaseous and adsorbed phases occurs instantaneously, that is, the presence of an infinite mass transfer coefficient is assumed.

The set of equations related to the loading and unloading tank model, as well as to IAST, was solved iteratively in the gPROMS software.

2.4 Artificial Neural Network (ANN)

The input variables in the ANN include descriptors related to the tank operating cycles, such as the loading and unloading pressure ranges, the molar fractions of the natural gas components, and the PSD. The output variable is the values related to the energy deactivation of the adsorption bed. All data were normalized using the min-max function.

A total of 14 activated carbons were used in the neural network training process, with another 3 reserved to evaluate its predictive capacity: NORIT, DESOREX, and PRA50.

The metrics selected to evaluate the accuracy of the ANN models during training were the coefficient of determination (R^2), the mean square error (MSE) and the mean relative error (MRE). The approach adopted consisted of applying the cross-validation methodology with 5 folds (k-folds), in which the total set of 336 curves is divided into 5 permuted subsets, with 80% and 20% of the curves allocated for training and testing, respectively. Thus, the criterion for optimizing the ANN parameters was established to increase the average of the 5 R^2 values obtained for the training set and the R^2 value obtained for the test set, in addition to reducing the standard deviation between these values, in order to avoid overfitting. This approach aims to ensure the generalization of the model and avoid excessive adjustments to the training data. Due to the significant presence of outliers in the first 10 cycles of the curves calculated by gPROMS, these data were excluded from the training/validation sets in the data processing stage. Consequently, the predictions were directed exclusively to cycles 11 to 200.

The training algorithm used was backpropagation and the optimization of the hyperparameters of the ANN models was conducted using the Particle Swarm Optimization (PSO) methodology. The essence of PSO lies in the simulation of a set of particles moving through the search space in an optimization problem. Each particle represents a possible solution, and its movement is influenced by the individual performance history and the best global solution found by the set [12].

3. Results

Table 2 presents the average values obtained for the performance evaluation metrics of the models for the training curves and for the validation curves.

Table 2. Performance evaluation metrics.

	R^2	MRE
Training	0.959	0.46%
Validation	0.983	0.51%

It can be observed that the performance metrics agree with each other, demonstrating high R^2 values and low MRE values.

Figure 2 presents the parity graph obtained for the total set of validation points and their respective predictions. Figure 3 shows the predicted energy delivered at the tank outlet curve (dashed orange) for NORIT in the pressure range 1-35bar and the simulated curve (blue).

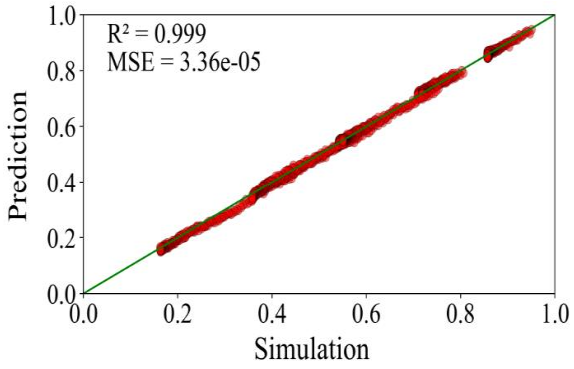

Fig. 2. Prediction results for ANN.

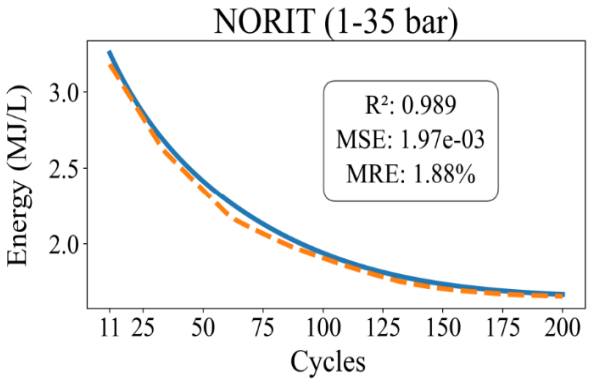

Fig. 3. Predicted curve for NORIT at 1-35 bar.

The accuracy of the models remained consistent, reinforcing the robustness of the approaches used. This is particularly important as it suggests that the models can be applied with confidence under different conditions. The low variability in the mean relative errors (< 1%) and the high R^2 values indicate not only a good fit of the models to the theoretical data, but also an excellent generalization capacity to new data and under different pressure conditions.

4. Conclusions

The use of artificial intelligence (AI) models in conjunction with the pore distribution methodology (PSD) is a pioneering step in this study. AI proved to be effective in predicting the variable of interest, emerging as an alternative to solving complex systems of differential equations that require higher computational costs. The characterization of activated carbons with the PSD for training ANN models demonstrated effectiveness in predicting the values related to the energy deactivation curves of the adsorption beds, achieving high accuracy and precision. Thus, the models obtained can predict the performance for different types of activated carbons used in adsorption beds and in different operating conditions of the fuel tank.

Acknowledgements

The authors wish to acknowledge financial support for this study from CAPES, CNPq and FUNCAP and the use of the computer cluster at National Laboratory of Scientific Computing (LNCC/MCTI, Brazil)

References

[1] Chen Z. et al. Porous materials for hydrogen storage. Chem, feb. 2022.
[2] Peixoto HR. et al. Carbon natural gas storage performance as predicted by multiscale modeling. Chemical Engineering Journal, v. 426, p. 131593–131593, 1 dec. 2021.
[3] Gonçalves DV. et al. Prediction of the monocomponent adsorption of H2S and mixtures with CO2 and CH4 on activated carbons. Colloids and Surfaces A: Physicochemical and Engineering Aspects, v. 559, p. 342–350, dec. 2018.
[4] Sreedhar I. et al. Carbon capture by absorption-Path covered and ahead. Renewable and sustainable energy reviews, v. 76, p. 1080-1107, 2017.
[5] Jo HS. et al. Path Loss Prediction Based on Machine Learning Techniques: Principal Component Analysis, Artificial Neural Network, and Gaussian Process. Sensors, v. 20, n. 7, p. 1927, 30 mar. 2020.
[6] Nelles O. Nonlinear System Identification: From Classical Approaches to Neural Networks and Fuzzy Models. [s.l.] Springer Science & Business Media, 2001.
[7] Lucena SMP. et al. Molecular simulation of the accumulation of alkanes from natural gas in carbonaceous materials. Carbon, v. 61, p. 624-632, 2013.
[8] De Oliveira JCA. et al. Predicting hydrogen storage at 298 K in activated carbons. Adsorption, 17 oct. 2023.
[9] Martin MG, Siepmann JI. Transferable Potentials for Phase Equilibria. 1. UnitedAtom Description of n-Alkanes. The Journal of Physical Chemistry B, v. 102, n. 14, p. 2569– 2577, 17 mar. 1998.
[10] Burchell T, Rogers M. Low Pressure Storage of Natural Gas for Vehicular Applications. SAE technical paper series, 19 jun. 2000.
[11] MOVE: Methane Opportunities for Vehicular Energy. Advanced Research Projects Agency - Energy, U.S. Department of Energy: Washington, DC, 2012.
[12] Pedersen MEH, Chipperfield AJ. Simplifying Particle Swarm Optimization. Applied Soft Computing, v. 10, n. 2, p. 618–628, mar. 2010.