

SIMULATION OF A PRESSURE SWING ADSORPTION SYSTEM: MODELING A MODULAR ADSORPTION UNIT

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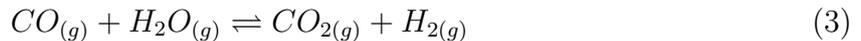
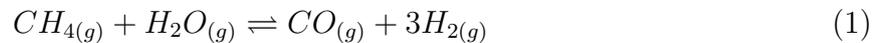
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Abstract. *Hydrogen High Purity Grade is an important compound in oil refineries due to its capability of withdrawing sulfur impurities in gasoline and diesel. This valuable feedstock is commonly produced in large scale by a Steam Methane Reforming process and is purified in batteries of adsorption columns. This work deals with numerically solving the model of a pressure-swing adsorption (PSA) column used for hydrogen purification. Five different numerical techniques were employed: Finite Differences, Method of Lines with Finite Differences, Method of Lines with Orthogonal Collocation, Fourier Transform and Method of Characteristics. The goal of this study was to develop a quick and robust application to simulate a single bed PSA unit and be incorporated in dynamic simulators. This model had been previously validated by comparison with data available in literature. The Method of Lines was considered to be the best numerical technique to solve a typical PSA column.*

1 INTRODUCTION

1.1 Pressure swing adsorption

Hydrogen gas plays a fundamental role in sulfur impurities removal processes in oil derivate products, such as gasoline and diesel. Steam reforming of natural gas, or steam methane reforming (SMR), is the most common method of hydrogen production on a large scale in oil refineries [7]. In this process, a mixture of steam and natural gas [9], (or in certain situations, nafta which substitutes methane [5]), reacts at a high temperature in the presence of a catalyst to form a mixture of carbon dioxide and hydrogen, according to the following equations [4]:



Before the hydrogen produced by this reforming process is delivered to the consumers, it must be sent to a purification unit that removes any unconverted methane and steam along with carbon monoxide and carbon dioxide [4], [3].

Pressure swing adsorption (PSA) is widely used for hydrogen purification. The impurities are desorbed by charging a column containing the adsorbent with the gas mixture and then pressurizing the column to a pressure sufficient to cause the adsorption of the gases. Hydrogen is not adsorbed when the impurities are pulled from the gas stream. When the column pressure is reduced to about atmospheric pressure, the column is evacuated in a countercurrent direction to withdraw the impurities from the column. The present operation is particularly advantageous to achieve a very high level of purified hydrogen [5], [13].

1.2 Operation and modelling of a PSA column

The PSA adsorption process is based on internal pressure modulation in the vessel where greater or lesser pressure during an operation cycle determines the degree of gases retained by the adsorption bed inside the column as well the level of impurities inside the column. In general, a single PSA vessel passes through five elementary steps along an operation cycle: adsorption; concurrent depressurization; countercurrent depressurization or blowdown; light-product purge and repressurization. On average, a single adsorption operation takes 10 to 20 minutes per PSA. These steps and the streams are shown in the Figure 1, adapted from [5].

Being a batch process, the regeneration step of the adsorption bed after its saturation is always essential. In order to ensure that the processes of hydrogen purification occurs

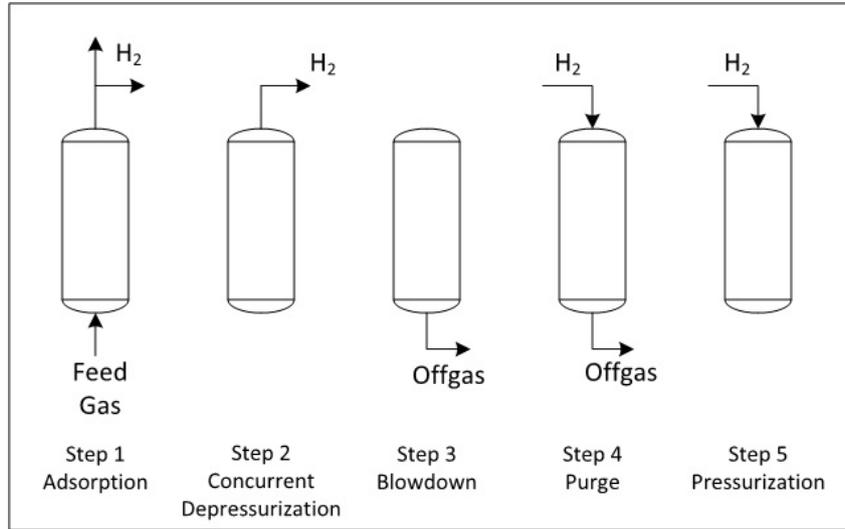


Figure 1: Elementary steps of a PSA cycle operation.

continuously, a set of at least four columns are needed. The vessels in a PSA unit operate simultaneously under different pressures and other conditions depending on which step each column is at the moment [5].

The dynamic mathematical models of a single adsorbent bed are required to simulate an H₂-PSA unit. The simulation may be used to train operators by embedding it in Operator Training Simulator (OTS) systems, as well as to optimize the hydrogen purification process. Different models for a single adsorbent bed have been studied and proposed in literature. This paper deals with numerical issues involved in the Partial Differential Equation (PDE) solution of a single bed model of a H₂-PSA unit [15], [12]. For these simulations, five different numerical techniques were employed: Finite Differences (FD), Method of Lines with Finite Differences (MOL-FD), Fast Fourier Transform (FFT), Method of Lines with Orthogonal Collocation (MOL-OC), and Method of Characteristics (MOC). This study aims at developing a dynamical model for a PSA column that can be embedded into existing simulators. It is not required that the model be extremely precise, as it is intended to assist in operators training. It is, however, necessary that its running time be low, in order to prevent communication delays between the simulator and the model. Too high a running time would compromise the concept of real-time dynamic simulation which is central to any operators training software.

1.3 Mathematical modelling

The dynamic behavior of PSA columns results from the interaction of fluid dynamics, adsorption equilibrium and mass transfer. For that reason, the mathematical modeling of such systems requires that appropriate models for each of these components be selected.

The mass transfer model chosen was the linear driving-force model, also known as LDF. It assumes that the rate of mass transfer is directly proportional to the mass transfer driving-force, namely the difference between the actual concentration of adsorbed gas in the solid phase and the theoretical concentration that would exist under equilibrium conditions [16], [2] [3], [6], [15].

$$\frac{\partial q_i}{\partial t} = k_i (q_i^* - q_i) \quad (4)$$

When in contact with a gas mixture for enough time, an adsorbent material will adsorb a certain amount of each component of the mixture and reach equilibrium [8]. The relation between the amount adsorbed of a given compound and the total pressure at a fixed temperature is called an adsorption isotherm. There are many isotherm models, one of the most common being the Langmuir single-site model [15], which is the model chosen for this paper:

$$q_i^* = \frac{q_i^{sat} b_i P_i}{1 + \sum_j b_j P_j} \quad (5)$$

$$q_i^{sat} = a_{1,i} + \frac{a_{2,i}}{T} \quad (6)$$

$$b_i = b_{0,i} \exp\left(\frac{b_{1,i}}{T}\right) \quad (7)$$

The mass balance for the one-dimensional flow of PSA systems can be written as follows [1]:

$$\epsilon \frac{\partial C_i}{\partial t} + (1 - \epsilon) \rho_s \frac{\partial q_i}{\partial t} + \frac{\partial vC}{\partial x} = D_L \frac{\partial^2 C_i}{\partial t^2} \quad (8)$$

If we were to omit the axial dispersion term (which is a reasonable assumption that greatly simplifies the model), the resulting mass balance would be reduced to [1]:

$$\epsilon \frac{\partial C_i}{\partial t} + (1 - \epsilon) \rho_s \frac{\partial q_i}{\partial t} + \frac{\partial vC}{\partial x} = 0 \quad (9)$$

We will assume throughout this paper that the PSA column operates under isothermal conditions. For that reason, no explicit energy balance equations are required. This assumption was made due to the fact that by dropping PDEs, the model becomes less

complex an, therefore, gains speed. As in any viscous flow through porous media, there occurs pressure drops due to the viscous energy losses and to the drop of kinetic energy. A fairly common equation used to model these effects is the Ergun equation [1]:

$$-\frac{dP}{dz} = \frac{150\mu(1-\epsilon^2)}{d_p^2\epsilon^3}v + \frac{1.75}{d_p}\frac{1-\epsilon}{\epsilon^3}\left(\sum_i M_{w,i}C_i\right)v|v| \quad (10)$$

1.4 Numerical methods

Five techniques were employed for solving the model. A brief description of each of them follows.

1. Finite Differences (FD) - from explicit algebraic approximations of the derivatives in a rectangular grid, a linear system is obtained, from which the PDEs are solved.
2. Method of Lines with Finite Differences (MOL-FD) - the domain is spatially discretized and the PDEs are thus transformed into a system of ODEs. The so obtained system is solved by any time-stepping scheme such as the explicit Euler's method, as was the case with our system.
3. Fast Fourier Transform (FFT) - upon taking the Fourier transform of the original set of PDEs, a new set of differential equations is obtained. The dependent variables of these new equations are the Fourier transforms of the original variables. A time-stepping scheme (Euler) is then used to calculate the time evolution of the transformed PDEs. After each iteration, the inverse Fourier transform is applied to the transformed values, thus recovering the meaningful values. On the next iteration, Fourier transform is applied again, Euler's method evaluates the new values for the transformed variables and, again, the inverse transform is applied, recovering the original variables. The process is repeated for as many times as necessary. The main advantages of the Fourier Transform is its spectral accuracy and its relatively low running times - $O(n \log n)$. It does, however, impose tight restrictions on the types of functions on which it may be applied, namely, the functions must be periodic. The PSA differential equations do not yield, in general, periodic results. This problem may be circumvented, however, by using their periodic extensions.
4. Method of Lines with Orthogonal collocation (MOL-OC) - much like the MOL-FD, the original set of PDEs is thought of as a system of ODEs. However, instead of replacing the space derivatives for finite difference approximations, the derivatives are calculated by fitting a Lagrange polynomial to the function at each iteration. It is a very widespread technique for solving adsorption-related problems.
5. Method of Characteristics (MOC) - It is very popular in fluid mechanics related fields. In order to solve the PDE, the Method of Characteristics analytically seeks

the characteristic curves of the PDE (a reparametrization which allows for direct integration) and solve it over these characteristics.

The finite difference approximations used were of the form:

$$\left[\frac{\partial f}{\partial x} \right]_i = \frac{f_{i-1} - f_i}{\Delta x} \quad (11)$$

A more comprehensive discussion on FD, MOL-FD and MOL-OC can be found in [11]. As for the MOC, a good description can be found in [14]

2 METHODOLOGY

2.1 Hardware and software

The model applied to simulate the single unit evaluated in this study was developed using the software MATLAB[®] version R2013a, and installed on a machine with the following hardware configurations:

Item	Configuration
Processor	Intel [®] Core [™] i7, 2.00 GHz
Memory (RAM)	6,00 GB
System type	64 bits
Operational system	Windows 8

Table 1: System hardware and operating system characteristics.

As previously mentioned, five numerical methods for solving the set of partial differential equations were evaluated (FD, MOL-FD, FFT, MOL-OC, and MOC). In order to compare the performance of each one, the number of points used and the time spent to perform the calculations and data processing were the main variables investigated. The method that is to be used as the default in the PSA unit simulations is the one that yields the best relationship between accuracy and running time. The dynamic model was developed to operate with several commercial dynamic process simulators. At the moment, the model is being embedded in an Excel[™] spreadsheet which can be used to exchange data with our current simulator. We restricted ourselves to only simulating the adsorption stage, as it is the most significant step in the overall operation.

2.2 Case of study

In this work the adsorption of hydrogen impurities through a pressure swing operation was simulated. The adsorption column studied is equipped with three different adjacent zeolite layers, whose heights are ΔZ_1 , ΔZ_2 and ΔZ_3 respectively. The specifications for this column are displayed in Figure 2 and in Table 2.

Symbol	Meaning	Value
ΔZ_c	Total column height	4800 mm
D_c	Inner diameter	2000 mm
ΔP	Total pressure drop	0.5 kgf/cm ²
ΔZ_1	Height of Zeolite H-1 layer	1600 mm
ΔZ_2	Height of Zeolite H-1-4 layer	1600 mm
ΔZ_3	Height of Zeolite H-2-10 layer	1600 mm

Table 2: Specifications of the PSA column to be simulated.

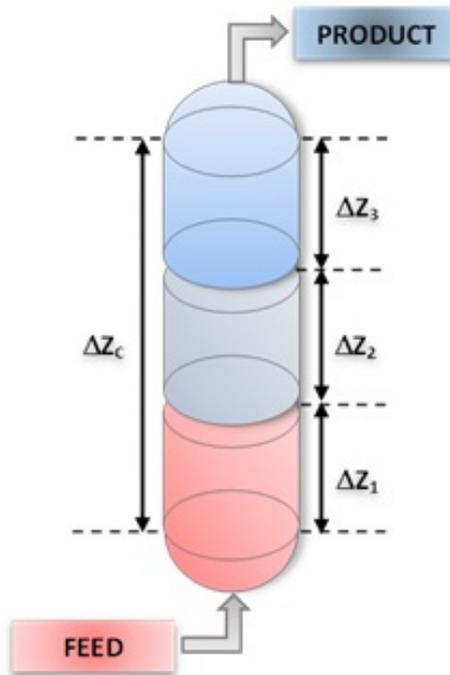


Figure 2: Schematic diagram of the PSA column to be simulated.

The thermodynamic parameters used are displayed in Table 3. The composition of the gas mixture fed to the PSA column is shown in Table 4 and it was taken from historical data.

3 RESULTS AND DISCUSSION

The results are presented as follows: a comparison of each numerical method with all the others with respect to its accuracy and its computational time is presented and, afterwards, the concentration profiles of each component (CO, H₂, CO₂, N₂ and CH₄) along the reactor length is shown as calculated through the numerical method considered best. An error measure was defined as follows:

Layer	Component	$a_{i,1} \times 10^3$ (mol/g)	$a_{i,2}$ (K)	$b_{i,0}$ (mmHg)	k (s ⁻¹)	ϵ (-)	d_p (m)
H-1	H ₂	1.24	0.36	2.2	1	0.4	0.027
	CO	-0.58	0.84	2.53	0.3		
	N ₂	-0.23	1.015	6.38	0.15		
	CO ₂	2.09	0.63	0.67	0.1		
	CH ₄	-0.29	1.04	6.44	0.4		
H-1-4	H ₂	1.23	0.357	2.19	1	0.4	0.027
	CO	-0.56	0.81	2.57	0.15		
	N ₂	-0.198	1.017	6.37	0.2		
	CO ₂	2.075	0.624	0.659	0.05		
	CH ₄	-0.28	1.036	6.53	0.4		
H-2-10	H ₂	4.32	0.0	6.72	1	0.4	0.027
	CO	0.92	0.52	7.86	0.147		
	N ₂	-1.75	1.95	25.9	0.19		
	CO ₂	-14.2	6.63	33.03	0.046		
	CH ₄	-1.78	1.98	26.6	0.42		

Table 3: Mass transfer and porous flow data for the model [?].

Component	Molar fraction
H ₂	0.0400
CO	0.0243
N ₂	0.3000
CO ₂	0.1709
CH ₄	0.4648
Total	1.000

Table 4: PSA feed composition.

$$e = \int_0^{t_{max}} \int_0^L |y_{CO_2}^{MOL}(z, t) - y_{CO_2}(z, t)| dz dt \quad (12)$$

In this equation $y_{CO_2}^{MOL}(z, t)$ denotes the CO₂ concentration profile over time calculated through the MOL-FD using a 400-point discretization over the z-axis and a 10000-point discretization over the t-axis. This MOL-FD solution was considered to be sufficiently close to the real solution, so that it could be used as a reference. The $y_{CO_2}(z, t)$ term denotes the concentration profile of CO₂ over time obtained through the method being considered. The simulation was for all methods for $t_{max} = 55$ s. Figure 3 shows a graph comparing the accuracy (the error measure) of different methods versus the number of

Method	Number of x-points yielding $\log(e) = 0.724$
MOL-FD	13
MOL-OC	22
FFT	64
FD	13
MOC	137

Table 5: Number of spatial discretization points for each method necessary to achieve $\log(e) = 0.724$.

discretization points on the z-axis. It is clear that the error diminishes as the number of points increases, as it would be expected. The curve corresponding to orthogonal collocation stops at about 35 points due to numerical instability. It can be seen that the most precise methods overall were MOL-FD and FD. Following these two methods were MOL-OC (for less than 35 points) and FFT. The MOC was the least accurate method.

In order to compare the running time of each method, a benchmark error was chosen and each algorithm was run with a number of points which would yield that same error. The choice was carefully made in such a way that the number of points corresponding to it was a power of 2. This is necessary for the FFT algorithm to function correctly. The chosen value was such that $\log(e) = 0.724$ (represented by the black horizontal line in Figure 3). Table 5 shows the number of points that each method requires to achieve such precision.

By running each of the methods 30 times with the number of points shown in Table 5, it is possible to calculate the mean running time of each one of them and its corresponding standard deviances. The values so obtained are shown both in Table 6 and in Figure 4. By ensuring that the errors associated to each method are roughly the same, it is now possible to make a fair comparison of their running times.

For the chosen accuracy, the fastest methods were MOL-FD and MOL-OC. Despite being a fast algorithm, the extra work required to fit the problem to the requirements of the FFT greatly increased its running time. FD ran slower than both MOL and OC, but still faster than the FFT. The greatest running time is that of the MOC. Despite being relatively simple, many points are required for the MOC to yield a satisfactory accuracy. Figure 5 shows the concentration profiles of methane and nitrogen along the PSA bed during the adsorption stage at three different times. The profiles were obtained through a 22-point OC. The profiles do exhibit the expected behavior.

One important observation is that the choice of the fastest algorithm is heavily dependant on the implementation of the methods. For instance, MATLAB[®] solves linear systems through a heavily optimized routine for quickly handling matrices. If another routine is

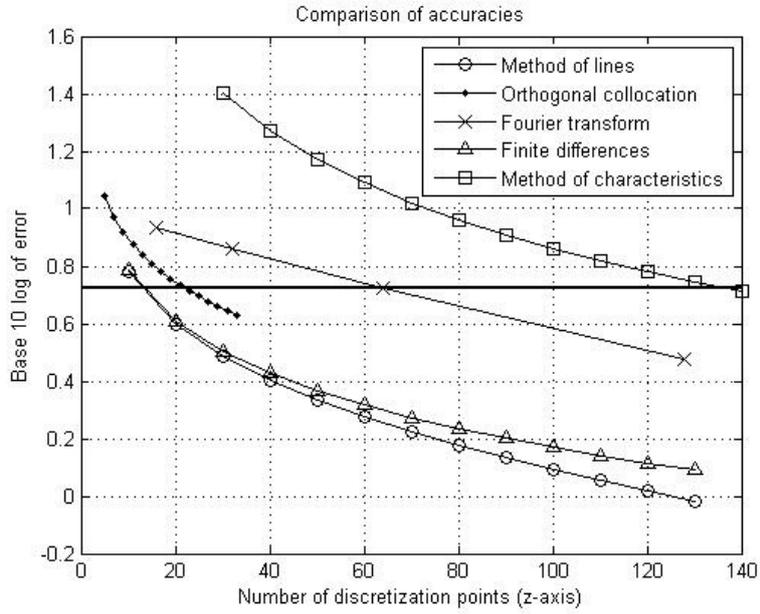


Figure 3: Error versus number of spatial discretization points for each method.

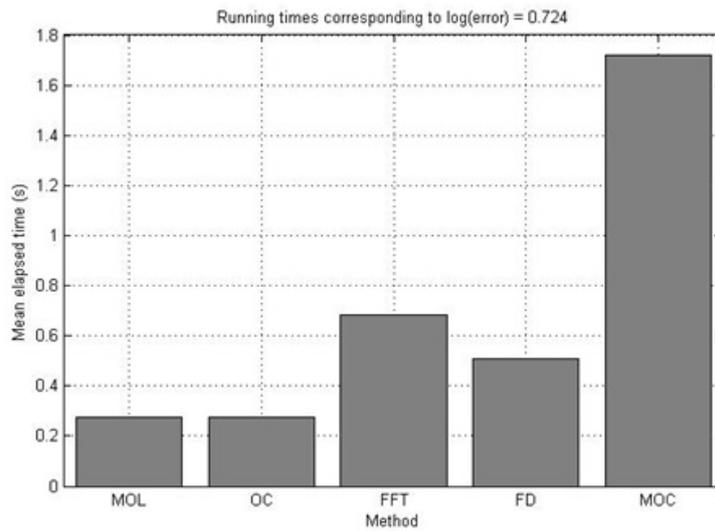


Figure 4: Comparison of the running times of each method.

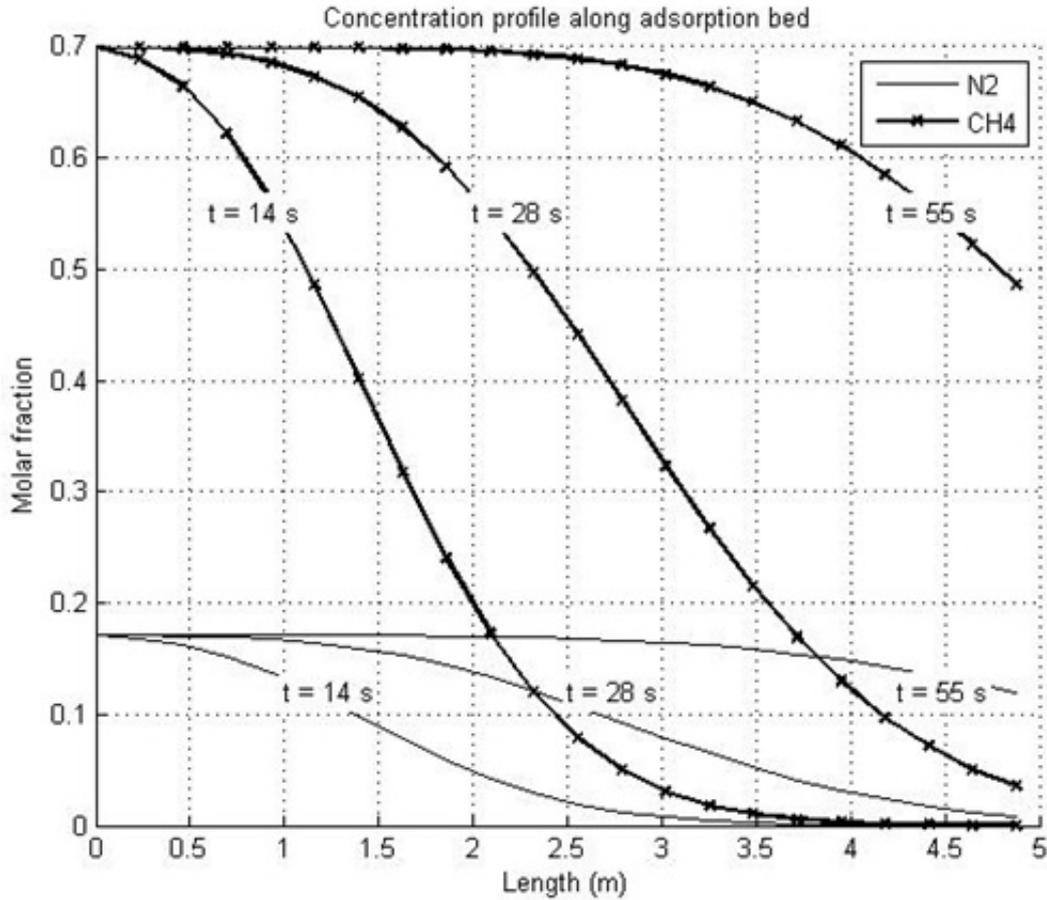


Figure 5: Concentration profiles of methane and nitrogen along the column during the adsorption phase at different times. Graphs obtained through a 22-point MOL-OC method.

used, the running time might change considerably.

4 CONCLUSIONS

The method considered best for the given PSA problem is the MOL-FD, since it demands a relatively low computational time to run, is easy to implement, is accurate and handles well varying boundary conditions. Despite the fact that the MOL-OC method required a comparable computational time, it was also less precise. The FD method displayed the third lowest running time. However, it also demands a considerable amount of computer memory, which may be a problem. Even though the FFT is a very fast algorithm, the amount of extra work required to fit the problem into its requirements made the overall running time greatly surpass that of the algorithm itself. Moreover, the FFT is highly sensitive to changing boundary conditions, which occur frequently in a common PSA unit.

Method	Mean running time (s)	Standard deviation (s)
MOL-FD	0.28	0.03
MOL-OC	0.28	0.02
FFT	0.69	0.07
FD	0.51	0.04
MOC	1.7	0.1

Table 6: Mean simulation time per method and standard deviances.

For those reasons, the FFT is not recommended. The MOC displays a relatively high running time and is not as accurate as any of the other methods. Once again, it is important to state that these results are highly dependent on how each method is implemented.

5 SYMBOLS TABLE

Symbol	Meaning
b	Langmuir equation parameter
C	Molar concentration
d_p	Particle diameter
D_c	Column inner diameter
k_i	Mass transfer coefficient of the i -th component
P_i	Partial pressure of the i -th component
ρ_s	Solid medium density
q_i	Adsorbed amount of the i -th component
q_i^*	Adsorbed amount of the i -th component at equilibrium
t	Time
t_{max}	Simulation time
T	Absolute temperature
v	Interstitial velocity
z	Axial position in an adsorption column
y	Molar fraction
ΔZ_c	Total column height
ΔZ_1	Height of the H-1 Zeolite layer
ΔZ_2	Height of the H-1-4 Zeolite layer
ΔZ_3	Height of the H-2-10 Zeolite layer
μ	Viscosity

Table 7: Symbols table.

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