CHEMICAL ENGINEERING TRANSACTIONS

VOL. 57, 2017

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Sauro Pierucci, Jiří Jaromír Klemeš, Laura Piazza, Serafim Bakalis

ISBN 978-88-95608- 48-8; **ISSN** 2283-9216

Evaluation of a Simplified Model of Adsorption used to Separate Ethanol-Water

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With the increasing demand for high quality anhydrous ethanol the production process by adsorption cycle is gaining more space among dehydration conventional processes, since the adsorption process does not leave traces of solvent in the final product and when compared with other dehydration processes (extractive and azeotropic distillations) has lower power consumption. However, the design of an adsorptive separation process is complicated and expensive when done in experimental and pilot scale, so a simulation tool is used to assist the design. To make the simulation of the adsorption process, it was chosen GAMS/CONOPT3 software since it presents great robustness in solving mathematical models. However, before the simulation of the pressure swing cycle, it is necessary to assess whether the chosen software is effective to solve the adsorption step. The objective of this work is the simplified simulation of an adsorption column for separation of ethanol-water mixture to evaluate the reliability of GAMS software to simulate the adsorption process. The present results were compared with EMSO software results using the same adsorption model removed from the work of SIMO et. al. (2008), which made the separation of ethanol-water mixture using experimental data.

1. Introduction

Conventionally the techniques employed for the production of anhydrous ethanol are azeotropic distillation and extractive distillation, although the relative importance of adsorption has increased in recent years as a consequence of the increase in energy costs, which favours processes of higher thermal efficiency, and with the development of the adsorption processes and the invention of the molecular sieves. In this way, the PSA (Pressure Swing Adsorption) processes became an alternative to the conventional distillation processes (Carmo and Gubulin, 2002).

The PSA process is highly used in gas separation, which it consists of the passage of a gaseous mixture under high pressure, through a porous bed filled with a specific high surface adsorbent that has the function of imprisoning a certain component of the mixture. This process generally operates in cycles with two beds, one bed of adsorption and one of desorption, which the bed that is performing the adsorption always works at a pressure higher than the desorption one. Adsorption is a process of low energy consumption and has become an attractive option in recent years (Jacques et al., 2003).

The main advantages of the PSA process for ethanol dehydration are: high-quality alcohol production (without solvent contamination) and lower energy consumption when compared to distillation-based processes (only one vaporization step is required) (Huang et al., 2008).

The precise design of PSA processes is a difficult task, since many operational parameters affect this separation process and, in addition, pilot experiments are expensive and economically expensive. This leads to the interest of using the computational simulation of the process to assist the optimization and initial evaluation of a PSA process.

To carry out the simulation it is necessary to choose a robust software, so that the answers are as close as possible to a real process. The simulation of this work will be performed in GAMS 24.3.1 software.

GAMS (General Algebraic Model System) is a software that was developed at the World Bank’s Research and Development Center in Washington to allow models with varying degrees of complexity and size to be solved on different types of computers, GAMS can be used to solving mathematical optimization problems (Brooke et al., 1998). The solver that was used to solving the mathematical model was CONOPT3.

GAMS consists of its own compilation language, a highly stable and highly integrated problem solving method, which can be used to develop and solve liner programming (LP) or nonlinear programming (NLP) problems.
The results of this work were compared with the results of a simulated adsorption column in the EMSO (Environment for Modeling, Simulation and Optimization) software.
EMSO is a free and full graphical environment where the user can model dynamic processes or stady state by simply selecting and connecting the template blocks. Where they can be used models already made for EMSO models library (EML) or you can create new models using appropriate language (Soares, 2007).
EMSO software was created with the intention of being a tool that aims to give users more flexibility to use the resources available in the program, this can be used for simulations of dynamic and stationary processes or can perform an optimization using their internal solvers (Soares and Secchi, 2003).
This work aims to evaluate the reliability of the simulation of a PSA cycle in GAMS, simulating a simplified adsorption model and comparing with the results of the EMSO software, where the same modelling of the adsorption model was made by Stinguel et al. (2016) comparing with results from Simo et al. (2008).

2. Methodology

To perform the GAMS evaluation, an adsorption bed was simulated in its simplified version (Figure 1), comprised only by an adsorption column, a feed stream and an outlet stream.

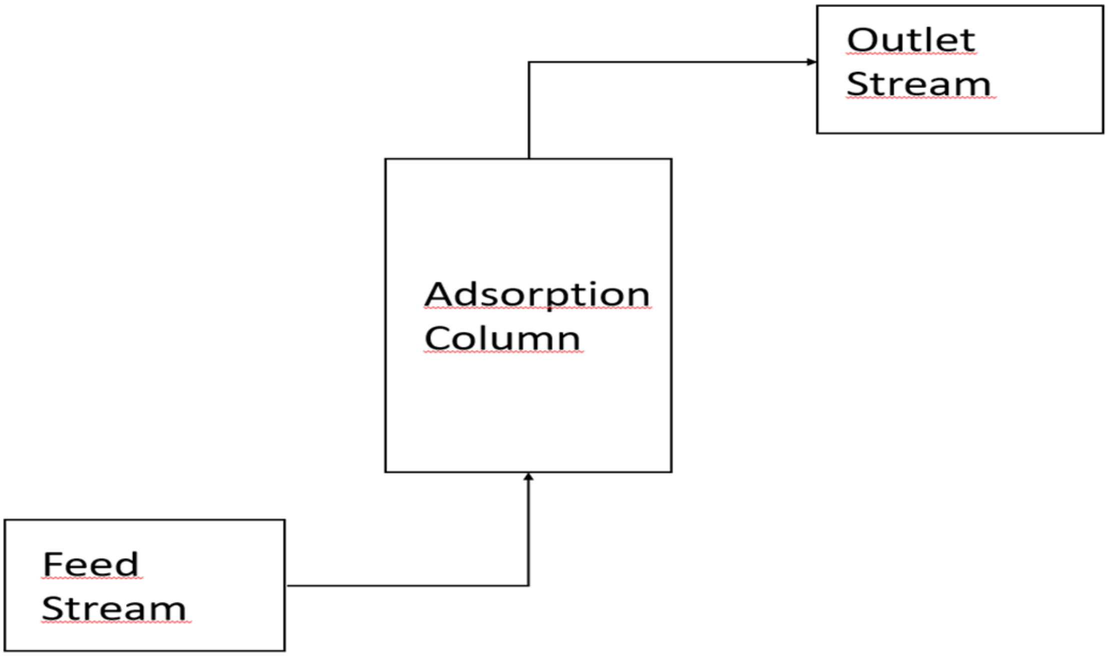

Figure 1: Flowchart of the simplified adsorption process.

For ran the scheme described in the Figure 1 only material balance equation was use, this equation was taken from the work of Simo et al. (2008). The material balance assumes that radial gradients are negligible and do not exhibit chemical reactions.
The mass balance in the gas phase considers the effects of axial dispersion, the convection term, the accumulation of the gas phase, and the adsorbent flow rate. Thus for a given component i the material balance is given by:

$$\frac{\partial c_i}{\partial t} = D_{ax}\frac{\partial^2 c_i}{\partial z^2} - \frac{1}{\varepsilon}\frac{\partial}{\partial z}(uc_i) - \frac{(1-\varepsilon)}{\varepsilon}\rho_S\frac{\partial q_i}{\partial t} \tag{1}$$

where c_i is the molar concentration in the fluid phase of the adsorbed component, t is the time, D_{ax} is the effective dispersion axial coefficient, z is the axial position of the column, ε is the bed porosity, u is the surface velocity of the fluid, ρ_S is the density of the solid and q_i is the molar concentration of water in the adsorbent phase.

To remove the term ∂u/∂z, Eq(1) is combined with the global material balance, generating:

$$\frac{\partial c_i}{\partial t} = D_{ax}\frac{\partial^2 c_i}{\partial z^2} - \frac{u}{\varepsilon}\frac{\partial c_i}{\partial z} + c_i\frac{1}{C}\frac{\partial C}{\partial t} - \frac{(1-\varepsilon)}{\varepsilon}\rho_S\left(\frac{\partial q_i}{\partial t} - Y_i\sum_{i=1}^{n}\frac{\partial q_i}{\partial t}\right) \tag{2}$$

where Y_i is the molar fraction of the adsorbed component in the fluid phase.
For the model in its simplified form, the following considerations must be obeyed:

- Ideal gas behaviour;
- Water is the only adsorbed component;
- The transfer of mass, energy and momentum in the radial direction of the column are negligible, and only the axial coordinate is considered;
- The process is considered isothermal;
- Constant pressure in adsorbent bed;
- Constant fluid surface velocity;
- Concentration of adsorbate in the adsorbent is equal to the concentration of adsorbate in the adsorbent in the equilibrium condition;

Applying the above considerations in Eq(2):

$$\left(\varepsilon + \left((1-\varepsilon)\rho_S RTq_s K\left(\frac{1+KPY^2+2Y}{(1+KPY)^2}\right)\right)\right)\frac{\partial Y}{\partial t} = \varepsilon D_{ax}\frac{\partial^2 Y}{\partial z^2} - u\frac{\partial Y}{\partial z} \tag{3}$$

where R is the universal gas constant, T is the operating temperature, P is the bed pressure, q_S is the saturation concentration of the adsorbent and K is the Langmuir isotherm constant.
The constant K is calculated by:

$$\ln\frac{K}{K_0} = \frac{Q}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right) \tag{4}$$

In order for the GAMS to solve a differential equation such as Eq(3), it is necessary to perform a discretization by numerical method. For this work the discretization was done using the finite difference method with Backward Difference Formulas (BDF), as shown in Eq(5).

$$\frac{Y_{i-2,j} - 4Y_{i-1.j} + 3Y_{i,j}}{2\Delta t} = \frac{\varepsilon D_{ax}\left(\frac{Y_{i,j-2} - 2Y_{i,j-1} + Y_{i,j}}{\Delta z^2}\right) - u\left(\frac{Y_{i,j-2} - 4Y_{i,j-1} + 3Y_{i,j}}{2\Delta z}\right)}{\varepsilon + \alpha\left(\frac{1+KPY_{i,j}^2 + 2Y_{i,j}}{(1+KPY_{i,j})^2}\right)} \tag{5}$$

where the α present in Eq(5) is a factor given by:

$$\alpha = (1-\varepsilon)\rho_S RTq_s K \tag{6}$$

Since GAMS is an optimization software, an objective function has been defined as z = 1, so that the program can be used to find a feasible solution for the model described in the equations above.

3. Results

The simulation was performed in the GAMS software using Eq(5) together with the conditions described in Table 1 and parameters in Table 2 for an operating time of 345 s, which is the time required to saturate an adsorption bed according to Simo et al. (2008). Using the discretization intervals of Δz = 0.0365 m and Δt = 34.5 s. The solver used to solve the system was CONOPT3.
The initial and boundary conditions applied for the resolution of Eq(5) are shown in Table 1.

Table 1: Initial and Boundary Conditions.

Initial Condition (t = 0)			
$Y_i = 0$	$T = T_F$	$P = P_F$	$u = u_F$
Boundary Condition 1 (z = 0)			
$Y_i = Y_F$	$T = T_F$	$P = P_F$	$u = u_F$
Boundary Condition 2 (z = L)			
It is usually used $\frac{\partial Y}{\partial z} = 0$, but in this case, because there is not much difference between both, it is used the differential equation for the output point.			

The Values of the parameters used in the simulation are found in Table 2.

Table 2: Specifications of the Adsorbent Simulation.

Description	Symbol	Value	Units
Feed			
Molar Fraction of Water	Y_F	0.182	-
Feed Temperature	T_F	440	K
Feed Pressure	P_F	379.2	kPa
Feed Superficial Fluid Velocity	u_F	0.7	m/s
Universal Constant of Gases	R	8.31	J/molK
Adsorbent Bed			
Bed Length	L	7.3	m
Gas Void Fraction	ε	0.63	-
Heat of Adsorption	Q	51.9	kJ/mol
Axial Dispersion Coefficient	D_{ax}	1.13×10^{-3}	m^2/s
Adsorbent (zeolite 3A)			
Solid Density	ρ_S	729	kg/m^3
Langmuir Isotherm Parameters			
Saturation Concentration of Water Amount on Adsorbent	q^s_i	10.6659	mol/kg
Reference Temperature	T_0	323	K
Equilibrium Constant Isotherm on Reference Temperature	K_0	0.0441765	1/Pa

From the simulation performed in the GAMS software, the main result obtained is the behaviour of the adsorbed component (in this case water) during the axial position, in an operation time of 345 s. The behaviour of the water in the column can be observed in Figure 2.

It can be seen from the breaking curves shown in Figure 2 that the behaviour of the water at several points of the axial axis of the column is satisfactory, with the final saturation of the column occurring in the expected saturation time mentioned in the literature by Simo et al. (2008) which is 345 s.

However, to be sure that this behaviour of the adsorption column is valid, the results of the breaking curves shown in Figure 2 are compared with the result of the EMSO software of a simple adsorption column presented by Stinguel et al. (2016). For ease comparison only the 7.3 m curve is used, as shown in Figure 3.

Analysing Figure 3, it can be said that the behaviour of the simulated column in the GAMS software was exactly equal to the result presented by the EMSO software.

The simulations on GAMS were performed on an Intel Core i7 3.4 GHz computer with 12 GB of RAM, and the time spent for the convergence of the model was approximately 20 seconds.

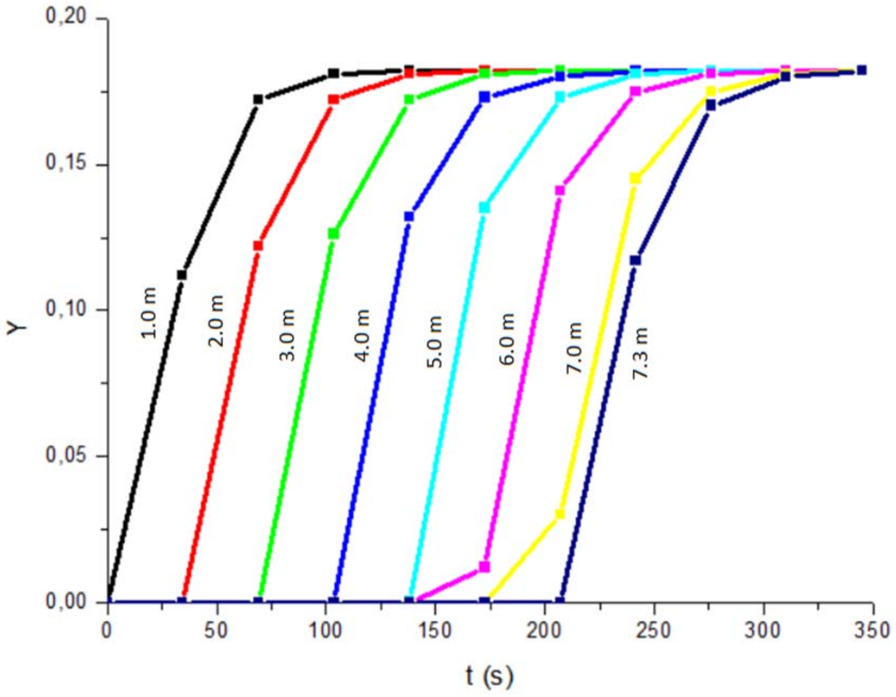

Figure 2: Breaking curves for the component adsorbed through the axial axis of the column.

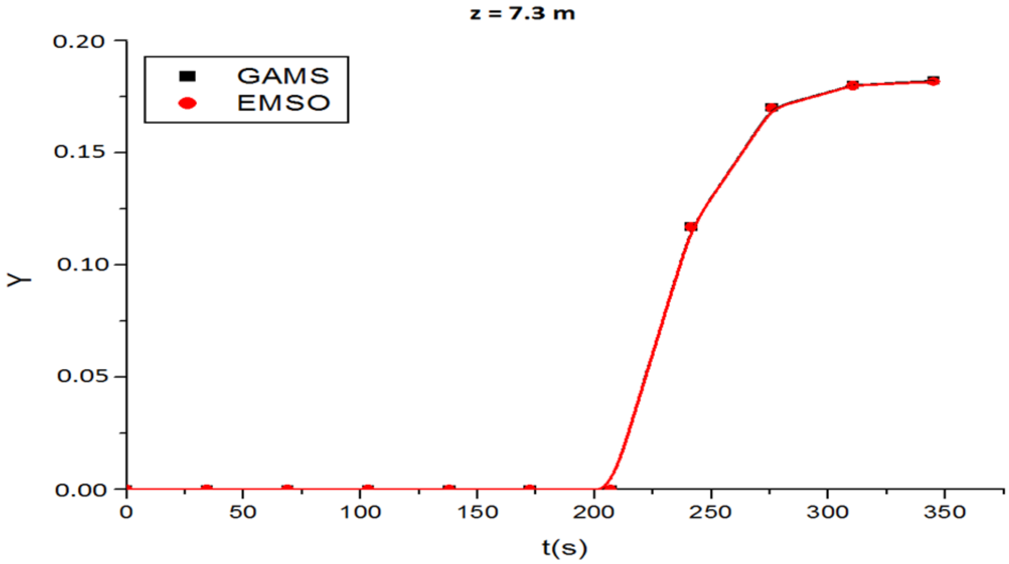

Figure 3: Comparison of GAMS and EMSO software breaking curves.

4. Conclusions

With the results observed in Figure 2, it can be said that the GAMS software can satisfactorily describe an adsorption column, and with the results of Figure 3, it is possible to notice that the GAMS software solves the adsorption column as well as the EMSO software, considering the simplified model used in the simulations.
Therefore, GAMS can be used for the optimization of the adsorption column, where a suitable objective function is maximized or minimized, while satisfying the constraints given by the model. Also, the model can

be further improved, with a more complex and detailed representation of the column. The results of this work will be used in future research, aiming to further develop the adsorption model and to optimize the full process cycle.

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