CHEMICAL ENGINEERING TRANSACTIONS
VOL. 50, 2016

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

Guest Editors: Katharina Kohse-Höinghaus, Eliseo Ranzi

ISBN 978-88-95608-41-9; **ISSN** 2283-9216
DOI: 10.3303/CET1650024

Implementation of an Adsorption Model in EMSO Software for Ethanol-Water Mixture Separation

Lucas Stinguel*, Maria Regina Wolf-Maciel, Reginaldo Guirardello

School of Chemical Enginnering, State University of Campinas, Av. Albert Einstein 500, 13083-852, Campinas-SP, Brazil.
lucastinguel@hotmail.com;

The main form of bioethanol production is fermentation of sugar cane juice which is proven to be the best raw material for bioethanol production. A major problem in ethanol production is the high energy cost associated with their separation because of water excess and the existence of an azeotrope in the ethanol-water mixture which through the conventional distillation can be separated to a maximum of 95% by weight. In order to produce anhydrous ethanol another distillation type is required, called dehydration, which the most used are the azeotropic and extractive distillation. However the production by adsorption has increased greatly in recent years because of the need for a purer product. Although the adsorption project to separate ethanol from water is very laborious as it must operate in cycles, this leads to the use of simulation as an outlet for the design of an adsorption process. Among the simulators available in the market there is EMSO (Environment of Modeling, Simulation and Optimization), which is an easily accessible and free simulator, but EMSO has no adsorption model in its library. Thus the main objective of this work is the implementation of an adsorption model in EMSO software to separate the ethanol-water mixture. The mathematical model used in this study was taken from the literature, which was used for ethanol dehydration in a complete adsorption cycle. This simplified model is based on material balance and the variation of the superficial velocity of the fluid equations. The adsorption simulations were performed with the total time of 345s, as this is the time taken for a column to be saturated in an adsorption cycle. The water mole fraction profile satisfactorily in the simulations, which leads to the conclusion that the EMSO software may well be used for the simulation of a process of separation of ethanol-water mixture by adsorption has been reached.

1. Introduction

Ethanol is a fuel typically produced by crops such as sugarcane, corn, beet, among others. In Brazil it is produced from sugarcane, which today is proven to be the best raw material for ethanol production (RAIZEN, 2011).

The most commonly used raw material for alcohol production in Brazil is sugar cane, which contains in its fermentation broth 6-10% by weight of ethanol. However, the ethanol-water mixture from sugarcane juice has an azeotrope that prevents complete separation of the mixture by conventional distillation, obtaining at most 95% by weight of ethanol, which can be marketed as hydrous ethanol. Nevertheless, if the intention is to sell anhydrous ethanol another purification process is required.

Conventionally the techniques employed for final purification are azeotropic distillation and extractive distillation, although the relative importance of adsorption has increased in recent years as a result of rising energy costs, which favors the higher thermal efficiency processes, and the development of adsorption processes and the invention of molecular sieves. Thus, the PSA process (Pressure Swing Adsorption) has become an alternative to azeotropic distillation (CARMO e GUBULIN, 2002).

The PSA process is widely used in gas separation processes where a gaseous mixture under pressure percolates through a porous bed filled with high specific surface adsorbent in order to retain a given component of the mixture, while the others continue through the bed (JACQUES, LYONS e KELSALL, 2003).

The main advantages of the PSA process for ethanol dehydration are High-quality production of alcohol (no solvent contamination) and lower energy consumption when compared to the distillation-based processes (only one vaporization step is required) (HUANG, RAMASWAMY, *et al.*, 2008).

Please cite this article as: Stinguel L., Wolf-Maciel M.R., Guirardello R., 2016, Implementation of an adsorption model in emso software for separation of ethanol-water mixture, Chemical Engineering Transactions, 50, 139-144 DOI: 10.3303/CET1650024

The design of a PSA process is not simple, as it involves many operating parameters. The simulation can be used in order to facilitate the implementation of such a process, with the purpose of helping baseline. Among the various software that can be used for the simulation process, there is EMSO (Environment for Modeling, Simulation and Optimization) which is a free and easily accessible software. This work is part of a thematic project and it aims to build a virtual bio refinery in EMSO therefore this software was chosen to run simulations.

EMSO is a free and full graphical environment where the user can model dynamic processes or steady state by simply selecting and connecting the template blocks. This environment allows the use of models already made for EMSO models Library (EML) or new models using appropriate language (SOARES, 2007).

As the adsorption stage is the major step to be considered to make the simulation of a PSA process, along with the lack of an adsorption model in EMSO library, this study aims to implement an adsorption model to carry out the separation of ethanol-water mixture in EMSO software.

2. Methodology

The equations that make up the mathematical model used in this work were taken from Simo et. al. (2008) who performed the simulation of a PSA cycle to separate the ethanol-water mixture.

The following simplifications have been applied to facilitate the implementation of the model in EMSO software:

- Ideal gas behavior;
- Water is the only adsorbed component;
- The mass transfer, 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 the adsorbent bed;
- The adsorbate concentration in the adsorbent is equal to the concentration of adsorbate on the adsorbent in balance;

Considering the simplifications listed above, only the material balance equations and variation of the superficial velocity of the fluid are considered in calculating the adsorption model.

2.1 Material Balance

The mass balance assumes that radial gradients are negligible, do not have chemical reactions and mass transfer follows the Linear Driving Force model (LDF). The mass balance in the gas phase considers the effects of axial dispersion, the term of convection, the accumulation of the gas phase, and the adsorbent flow rate.

For any given i component, 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 fluid phase molar concentration of water, t is the time variable, D_{ax} is the axial effective dispersion coefficient, z is the spatial coordinate, ε is the gas void fraction, u is the superficial fluid velocity, ρ_S is the density of the solid e q_i is the molar concentration of water in the adsorbed phase.

The overall mass balance is:

$$\frac{\partial C}{\partial t} = -\frac{C}{\varepsilon}\frac{\partial u}{\partial z} - \frac{(1-\varepsilon)}{\varepsilon}\rho_S\sum_{i=1}^{n}\frac{\partial q_i}{\partial t} \tag{2}$$

Where C is the fluid phase molar concentration of the mixture.

Eq(1) can be substituted in Eq(2) to remove the term $\partial u/\partial z$:

$$\frac{\partial c_i}{\partial t} = D_{ax}\frac{\partial^2 c_i}{\partial z^2} - \frac{u}{\varepsilon}\frac{\partial c_i}{\partial z} + c_i\frac{1}{C}\frac{\partial C}{\partial t} - \frac{(1-\varepsilon)}{\varepsilon}\rho_S\left(\frac{\partial q_i}{\partial t} - Y_i\sum_{i=1}^{n}\frac{\partial q_i}{\partial t}\right) \tag{3}$$

Where Y_i is the fluid phase molar fraction of water.

Applying the ideal gas law and assuming that only one component is adsorbed Eq(3) becomes:

$$\frac{\partial Y_i}{\partial t} = D_{ax}\frac{\partial^2 Y_i}{\partial z^2} - \frac{u}{\varepsilon}\frac{\partial Y_i}{\partial z} + Y_i\frac{1}{P}\frac{\partial P}{\partial t} - \frac{(1-\varepsilon)}{\varepsilon}\rho_S\frac{RT}{P}\frac{\partial q_i}{\partial t}(1-Y_i) \tag{4}$$

Where P is the bed pressure, R is the universal gas constant and T is the operation temperature.
The term containing the derivate of P as a function of time can be considered equal to zero, since its contribution is very small, thus obtained:

$$\frac{\partial Y_i}{\partial t} = D_{ax}\frac{\partial^2 Y_i}{\partial z^2} - \frac{u}{\varepsilon}\frac{\partial Y_i}{\partial z} - \frac{(1-\varepsilon)}{\varepsilon}\rho_S\frac{RT}{P}\frac{\partial q_i}{\partial t}(1-Y_i) \tag{5}$$

Whereas the surface velocity varies in the direction of z and the concentration of adsorbate on the adsorbent is equal to the concentration of adsorbate on the adsorbent in the equilibrium condition Eq(5) becomes:

$$\left(\varepsilon + \left((1-\varepsilon)\rho_S\frac{RT}{P}\left(q_S\frac{KP}{(1+KPY_i)^2}\right)\right)\right)\frac{\partial Y_i}{\partial t} = \varepsilon D_{ax}\frac{\partial^2 Y_i}{\partial z^2} - u(z)\frac{\partial Y_i}{\partial z} \tag{6}$$

Where q_S is the concentration of adsorbent saturation, K is the Langmuir isotherm constant.
Since K is calculated by:

$$\ln\frac{K}{K_0} = \frac{Q}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right) \tag{7}$$

Where K_0 is the Langmuir isotherm constant at the reference temperature, Q is the heat of adsorption and T_0 is the reference temperature.

2.2 Variation of Surface Velocity Fluid

The velocity variation is given by the global mass balance (Eq(2)) in its most rigorous form:

$$\frac{\partial C}{\partial t} = -\frac{1}{\varepsilon}\frac{\partial}{\partial z}(Cu) - \frac{(1-\varepsilon)}{\varepsilon}\rho_S\sum_{i=1}^{n}\frac{\partial q_i}{\partial t} \tag{8}$$

Whereas:

$C = \frac{P}{RT}$, T fixed, $\frac{\partial P}{\partial t} \cong 0$ and only one component adsorbed, it has been.

$$\frac{\partial u}{\partial z} = -(1-\varepsilon)\rho_S\left(\frac{RT}{P}\right)\frac{\partial q_i}{\partial t} \tag{9}$$

Considering also the concentration of adsorbate on adsorbent is equal to concentration of adsorbate on adsorbent in equilibrium concentration, it has:

$$\frac{\partial u}{\partial z} = -(1-\varepsilon)\rho_S\left(\frac{RT}{P}\right)q_S\left(\frac{KP}{(1+KPY_i)^2}\right)\frac{\partial Y_i}{\partial t} \tag{10}$$

So the mathematical model becomes a system of differential equations formed by Eq(6) and Eq(10). However, EMSO only contains tool for solving differential in function of time, then the differentials in function of axial position in the present system of equations have been discretized using finite difference of 2nd order, generating the equations:

$$\frac{\partial Y_i}{\partial t} = \left(\left(\varepsilon D_{ax}\left(\frac{Y_i^{j+1} - 2Y_i^j + Y_i^{j-1}}{\Delta z^2}\right)\right) - u(z)\left(\frac{Y_i^{j+1} - Y_i^j}{2\Delta z}\right)\right) \Bigg/ \left(\varepsilon + \left((1-\varepsilon)\rho_S\frac{RT}{P}\left(q_S\frac{KP}{(1+KPY_i^j)^2}\right)\right)\right) \tag{11}$$

$$\frac{u^{j+1}-u^{j-1}}{2\Delta z}=-(1-\varepsilon)\rho_S\left(\frac{RT}{P}\right)q_S\left(\frac{KP}{(1+KPY_i)^2}\right)\frac{\partial Y_i}{\partial t} \tag{12}$$

With this government equations (Eq(11) and Eq(12)) of the mathematical model form a system of differential and algebraic equations (DAE) and to solve this system EMSO uses the solver DASSL (Differential/Algebraic System Solver).

The values of parameters used to perform the simulation are values similar to those used in industrial process and are presented in table 1.

Table 1: Specifications of Column Adsorption 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	4.0	m/s
Universal Constant of Gases	R	8.31	J/molK
Gas Density	ρ_g	4.25	kg/m^3
Adsorbent Bed			
Bed Length	L	7.3	m
Gas Void Fraction	ε	0.63	-
Bulk Void Fraction	ε_b	0.4	-
Heat of Adsorption	Q	51.9	kJ/mol
Axial Dispersion Coefficient	D_{ax}	1.13x10^{-3}	m^2/s
Adsorbent (zeolite 3A)			
Solid Density	ρ_S	729	kg/m^3
Adsorbent Particle Radius	r_p	1.5875x10^{-3}	m
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

Initial conditions and boundary conditions used in the simulation are listed in table 2.

Table 2: Initial Condition and Boundary Condition.

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 simulation of the adsorption column was performed with the mathematical model presented above, using the Δz = 0.001 m, and the total operating time was set at 345s, since according Simo et. al. (2008) this is the time required for the adsorption bed is saturated in a process of separation of ethanol-water mixture. It is interesting to note that the saturation time of the column varies according to the initial superficial velocity, so that to obtain a 345s saturation time the speed must have a value of 4.0 m/s, while in another example for an initial superficial velocity of 0.3 m/s the saturation time would be 5010s.

In order to ensure the reliability of numerical model, the simulations were performed using different time intervals (Δt) 5s and 1s.

3. Results

The results presented in this study were compared with those presented by Fonseca (2011) (Figure 1), which simulated the PSA process for separation of ethanol-water mixture in Aspen Adsim software using the model proposed by Simo et. al. (2008) as base.

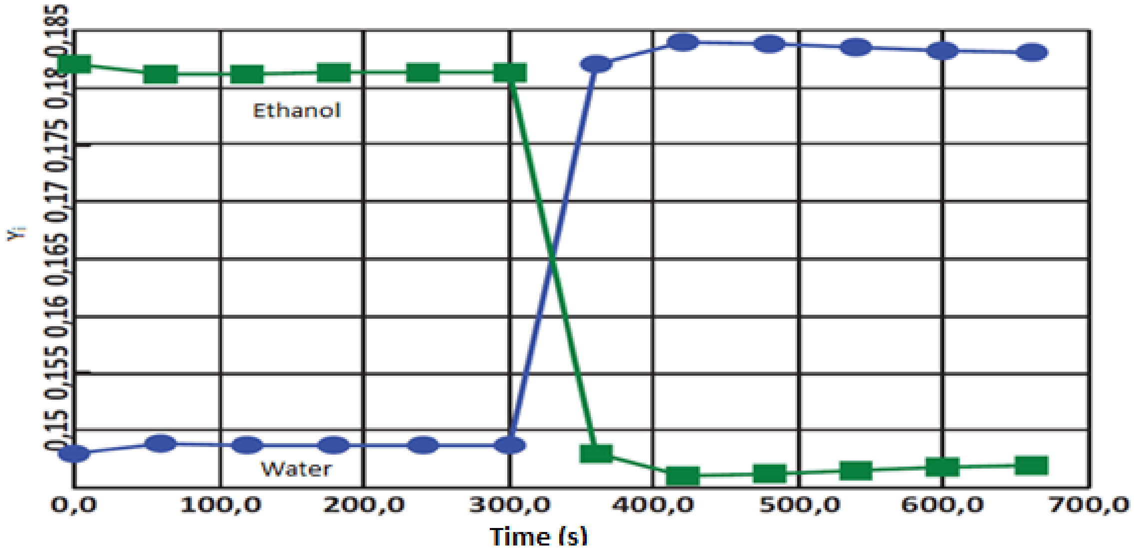

Figure 1: Data of water and ethanol concentration in the product stream to the first adsorption cycle. Obtained from Fonseca (2011).

It is noteworthy that the first cycle of the PSA process amounts to adsorption simulation that was conducted in this work.

The system of equations (Eq(11)) and (Eq(12)) was solved in EMSO software in order to generate the profile of the molar fraction of water obtained during the time of adsorption. Since the results obtained are presented in the form of breakthrough curves as shown in figures 2 and 3.

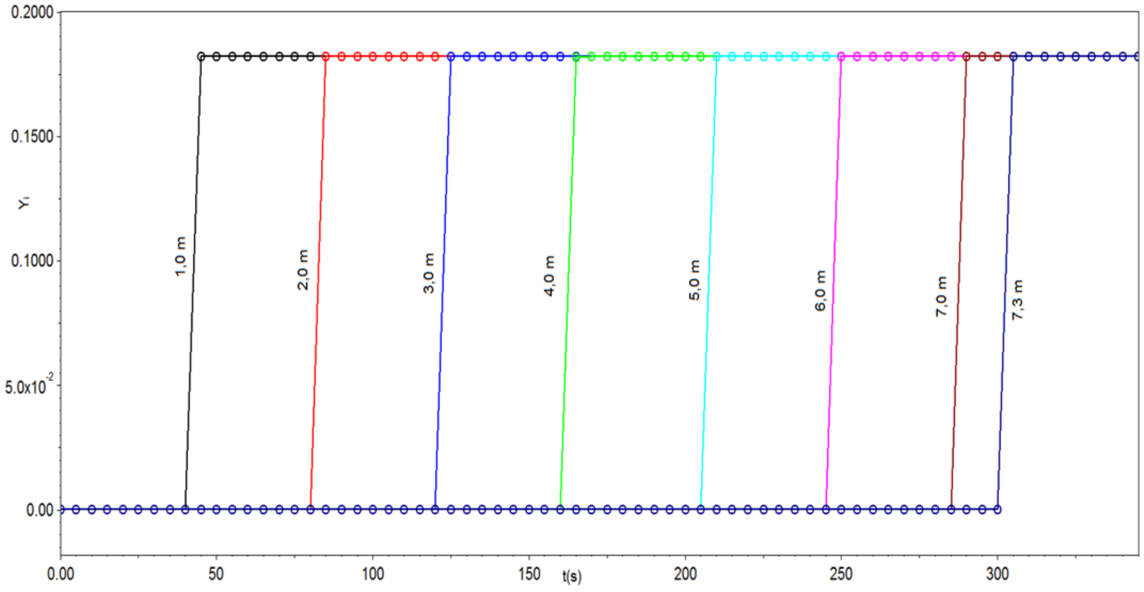

Figure 2: Breakdown curve for the mole fraction of water with a 5s time interval.

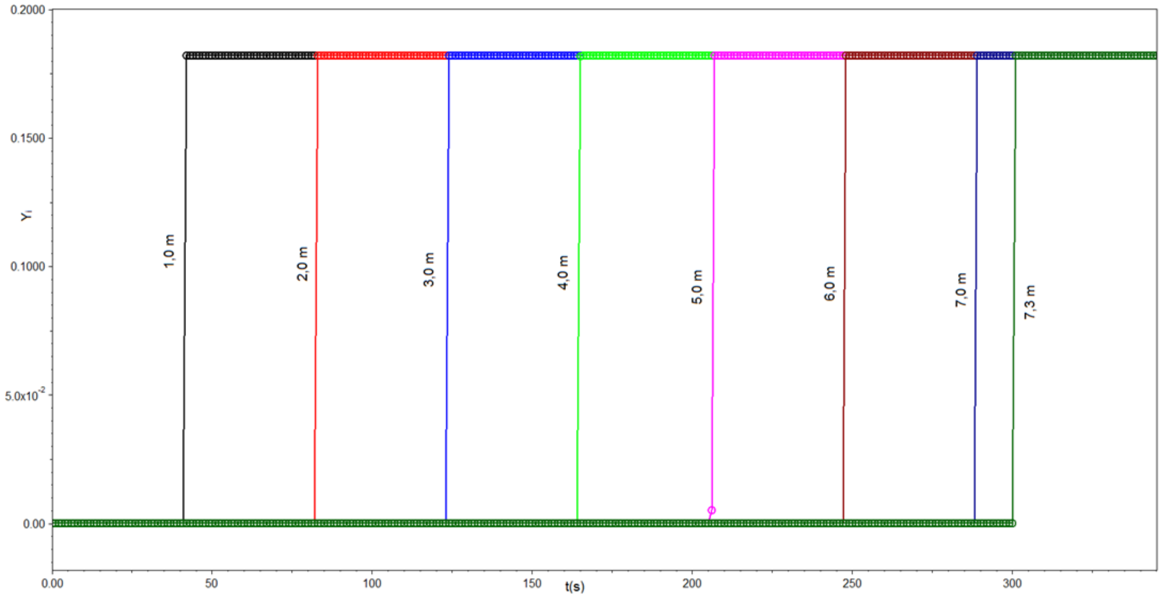

Figure 3: Breakdown curve for the mole fraction of water with a 1s time interval.

In an analysis of Figures 2 and 3, it can be seen that for various time intervals the model was stable, thus proving their numerical reliability. It is also possible to say that all the curves at the point 7.3 m (which is the output of column) had saturation happening in approximately 300s operation, that is a very close result to that obtained by Aspem (figure 1, water curve). Being able to say the EMSO performed the simulation satisfactorily of an adsorption column for separation of ethanol-water mixture.

The simulations 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 5-7 hours. As the simulation time was very high, the equations were discretized using a BDF method (Backward Differentiation Formula), so that the value of Δz could be increased to 0.037 m and the time of calculation was reduced to 14 seconds.

4. Conclusion

Based on the simulation results of the adsorption, it was observed that EMSO was able to solve the mathematical model and represent the process properly, using industrial scale data adsorption. It was concluded that the implementation of the adsorption model was successful and that same model can now be used to simulate a PSA adsorption cycle.

References

Carmo, M. J., & Gubulin, J. C. (2002). Ethanol-water separation in the PSA process. *Adsorption*, *8*(3), 235-248.

Fonseca, N. A. A. (2011). *Simulação do Processo de Adsorção PSA para Separação da Mistura Etanol-Água* (Dissertação de Mestrado, UNICAMP, Campinas).

Huang, H. J., Ramaswamy, S., Tschirner, U. W., & Ramarao, B. V. (2008). A review of separation technologies in current and future biorefineries.*Separation and Purification Technology*, *62*(1), 1-21.

Jacques, K. A., Lyons, T. P., & Kelsall, D. R. (2003). *The alcohol textbook: A reference for the beverage, fuel and industrial alcohol industries*. Nottingham University Press.

Raizen (2011), “Etanol: Fatos e Mitos. Tecnologia na produção de etanol”, avaliable at: http://www.raizen.com (accessed 10 May 2013).

Simo, M., Brown, C. J., & Hlavacek, V. (2008). Simulation of pressure swing adsorption in fuel ethanol production process. *Computers & Chemical Engineering*, *32*(7), 1635-1649.

Soares, R. P. (2007), “EMSO Manual”, avaliable at: http://www.enq.ufrgs.br/alsoc (accessed 05 October 2013).