The Canadian Journal of Chemical Engineering

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Journal:	*The Canadian Journal of Chemical Engineering*
Manuscript ID:	CJCE-12-0551.R1
Wiley - Manuscript type:	Article
Date Submitted by the Author:	n/a
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Keywords:	Zeolite 13X, Ethane/Ethylene, Simulated Moving Bed, Molecular Simulation, Monte Carlo

From Molecules to Processes: Molecular Simulations Applied to the Design of Simulated Moving Bed for Ethane/Ethylene Separation

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Abstract

This paper presents results of a modelling study on the separation of ethane/ethylene mixture by selective adsorption on zeolite 13X in a Simulated Moving Bed (SMB) unit. Propane and *n*-butane are evaluated as desorbent candidates. The study encompasses molecular simulation calculations for determination of adsorption parameters, whose results will then be used in a mathematical model for evaluating the performance of an SMB unit. This work is entirely done *in silico*, by using available force field parameters for the molecular simulations part, and reliable mathematical models for the SMB part. Experimental data are solely used for comparison with the molecular simulation results, which are subsequently expanded to calculate adsorption properties for separating the mixtures, without further experimental work. The separation regions of an SMB unit operating with zeolite 13X for ethane/ethylene separation, using propane and *n*-butane

as desorbents, were obtained by simulation at 110 kPa and at four different temperatures: 298, 323, 348 and 373 K. For each desorbent, an operating point was selected and the size of the required unit was presented for the complete separation of the two components of the mixture.

Keywords

Zeolite 13X; Ethane; Ethylene; Simulated Moving Bed; Molecular Simulation; Monte Carlo

1. Introduction

Ethylene (ethene) is the major worldwide industrial feedstock, one of the most important raw materials for the chemical industry with an annual production of more than 25 million tons in the United States (Kirk-Othmer, 1991). Separation of paraffin/olefin mixtures, in particular ethane/ethylene and propane/propylene, requires huge distillation columns operated at a very high reflux ratio, one of the most energy consuming processes in the chemical industry (Rege *et al.*, 1998). Alternative technologies are Simulated Moving Bed (SMB) and Vacuum Swing Adsorption (VSA). The Simulated Moving Bed (SMB) technology comes from the early 1960's, with its first important industrial implementation of the Sorbex process by UOP. Since then, it has been successfully applied, first to various large petrochemical separations, including *p*-xylene separation from its C8 isomers, olefin/paraffin separation, and more recently in the pharmaceutical and fine chemical industries (Sá Gomes *et al.*, 2008). The Sorbex process operates mostly in the liquid phase by employing two separating agents: the eluent (or desorbent) and the adsorbent. The eluent can either be a gas or a liquid. The extract and the raffinate (products) are diluted with the eluent and additional separation steps, by flash or fractional distillation, are required to yield the pure products.

However, the Sorbex process can also be used for gas phase separations where a vapour or a supercritical fluid, typically CO_2, is used as eluent. Mazzotti and co-workers developed a six-port vapour phase SMB pilot plant for the separation of an *n*-pentane/iso-pentane mixture using *n*-heptane as desorbent and 5A-Zeolite as adsorbent. They reported a higher separation efficiency in a vapour-phase SMB unit compared to the liquid phase separation (Mazzotti *et al.*, 1995). Relevant references to the SMB application in the separation of propylene/propane mixtures are found in the literature (Rao *et al.*, 2005; Cheng and Wilson, 2001). Rao and collaborators reported results for this separation using silica gel as adsorbent in a moving-port system which, when embedded into a fixed bed, facilitates the continuous movement of the port along the bed for the injection and withdrawal of a fluid. The parametric study indicates that high purity products and a higher productivity by an order of magnitude can be achieved with simulated moving-beds compared to the fixed beds (Rao *et al.*, 2005).

In considering the ethane/ethylene separation by SMB, a suitable desorbent is a fundamental issue. The choice of an adequate desorbent for the separation of ethane/ethylene by gas phase SMB should consider the subsequent distillation step in order to concentrate the extract/raffinate, and to recover the desorbent. The difference between the boiling point of the desorbent and that of the raffinate (or the extract), and the presence or not of azeotropes are of key importance for the efficiency of the distillation. Propane and *n*-butane are proposed as candidate desorbents for separation of the ethane/ethylene mixture, and this is tested using predictive simulations with little input from experiment. At 101.3 kPa (1 atm), ethane has a boiling point of -89 °C, and ethylene has one of −103.7 °C. The boiling point of *n*-butane is -0.5 °C and that of propane is -42.1 °C, and thus both desorbents would be adequate for further separation by distillation.

Normally the choice of desorbent is made by trial-and-error, requiring expensive and time-consuming experimental measurements of adsorption equilibrium. A much more efficient alternative would be to choose the desorbent based on computational simulations of the SMB process, minimizing the need for experiments. However, this requires a simulation approach that can accurately predict multi-component adsorption equilibrium in the adsorbent material, and then feed this data into a large-scale simulation of the process – in other words, a simulation approach that goes from molecules to processes.

In this study, we attempt to achieve this goal by combining molecular simulation of adsorption with process simulations. Single component adsorption isotherms of all the four species herein studied, as well as binary mixtures of ethane/ethylene, ethane/propane, ethylene/propane, ethane/*n*-butane, and ethylene/*n*-butane in zeolite 13X were calculated by the configurational-bias Monte Carlo (CBMC) technique. Molecular simulations are the first prediction tool to be used here, aiming to replace expensive, time consuming and, in some cases, dangerous experiments. We adopted force fields that have been widely used to predict adsorption of hydrocarbons in zeolites (Calero *et al.*, 2004, Lamia *et al.*, 2009, Granato *et al.*, 2010), and use them to reproduce experimental data on single component adsorption of ethane and ethylene in 13X zeolite, as well as their binary mixtures with propane and *n*-butane. Subsequently, a four-section Simulated Moving Bed (SMB) unit is analyzed through simulation, in order to describe the behaviour of the unit by means of a mathematical model. This model makes use of the equilibrium adsorption data, predicted by molecular simulation, in a wide range of operating conditions. We demonstrate that this integrated approach is a powerful tool for computational design of adsorptive separation processes.

2. Computational Details

2.1 – Molecular Simulation Methods

The configurational-bias Monte Carlo (CBMC) technique in the grand-canonical (μVT) ensemble has been extensively applied for calculation of adsorption properties, such as isotherms and heats of sorption. This technique allows for accurate calculations of the adsorbed amount, since it allows the total number of molecules to vary by way of creation and deletion Monte Carlo trials. A detailed explanation of this simulation technique can be found elsewhere (Vlugt *et al.*, 1999; Smit and Krishna, 2001; Frenkel and Smit, 2002). For simple hydrocarbons, such as alkanes or alkenes, a number of 2×10^6 cycles is enough to reach equilibrium. The United Atom (UA) force field was chosen to model the adsorbates due to a good compromise between accuracy and computational effort, when compared to the All Atom (AA) or the Anisotropic United Atom (AUA) force fields. These models are widely described in the literature (Martin and Siepmann, 1998; Ungerer *et al.*, 2000). For calculations of adsorption properties, such as isotherms and heats of sorption, the UA model is advantageous because of its reduced set of parameters to represent the inter- and intra-molecular interactions between the pseudo-atoms.

The 13X zeolite framework model is the sodium form of the Faujasite (FAU) type zeolite, obtained by randomly replacing silicon by aluminium, satisfying the Löwenstein rule. This substitution generates a negatively charged framework which is compensated by inserting 88 sodium cations, yielding a composition of $Na_{88}Al_{88}Si_{104}O_{384}$ per unit cell. The cations are allowed to move inside the zeolite. Periodic boundary conditions were applied in all directions. A rigid structure was

considered for the zeolite, since framework flexibility has little influence on adsorption properties in zeolites (Vlugt and Schenk, 2002).

Non-bonded interactions are described by Lennard-Jones potentials, as shown in Equation 1. A truncated and shifted potential is applied (r_{cut} = 12 Å), and tail corrections are not used (Dubbeldam *et al.*, 2004). Electrostatic interactions are calculated by the Ewald summation which is largely described elsewhere (Frenkel and Smit, 2002; Martin and Siepmann, 1998).

$$U(r_{ij}) = \begin{cases} 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] & r_{ij} \le r_{cut} \\ 0 & r_{ij} > r_{cut} \end{cases} \quad (1)$$

Equation 2 describes the Lorentz-Berthelot mixing rules, used to calculate the cross interactions between different united atoms, except for the interactions with the non-framework cations, which requires specific parameters (Vlugt, 2000).

$$\sigma_{ij} = \frac{1}{2}\left(\sigma_{ii} + \sigma_{jj}\right), \quad \varepsilon_{ij} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}} \quad (2)$$

All adsorbate molecules were considered to be flexible, with intramolecular parameters taken from the TraPPE force-field (Martin and Siepmann, 1998). Parameters for the interactions between adsorbates and the framework were taken from our previous modelling work of propane/propylene adsorption on zeolite 13X (Granato *et al.*, 2007), which consisted of a modification of the original model by Calero *et al.* (2004). All molecular interaction parameters are given in Tables S1 and S2 of the Supporting Information File.

2.2 – SMB Process Simulations

Detailed descriptions of the gas phase SMB operation, the mathematical models, and required parameters can be found in the literature (Cheng and Wilson, 2001; Minceva *et al.*, 2003; Leão and Rodrigues, 2004; Sá Gomes *et al.*, 2008, 2009; Lamia *et al.*, 2009). In this study, a "classical" SMB mode of operation, making use of a desorbent species, as patented by Rodrigues *et al.* (2006), was chosen for the separation of a mixture of ethane–ethylene over 13X zeolite. In the mathematical model of the four-section SMB unit, a multicomponent extension of the Toth isotherm and a linear driving force (LDF) for the intra-particle mass transfer are assumed. The mathematical model further assumes plug flow with axial dispersion, no radial gradients inside the column, bed void fraction, radius and porosity of the particles are constant along the axial coordinate, negligible thermal effects, negligible pressure drop and fast rate of adsorption. The isothermal assumption for gas-phase SMB was tested by Sá Gomes *et al.* (2009) in the study of propane/propylene separation, and a temperature gradient of 4K was observed along the entire unit. More details can be found elsewhere (Cruz *et al.*, 2005; Minceva *et al.*, 2003; Leão and Rodrigues, 2004). The simulation of an SMB unit may be performed by two methods: the True Moving Bed (TMB), and the SMB approach. Both TMB and SMB model predictions of steady-state performance of the SMB unit are very close. So, the TMB model was selected to study the feasibility of this separation at different temperatures, and using the proposed desorbents – propane and *n*-butane. The Separation Volume methodology (Azevedo and Rodrigues, 1999) was used to find the operating conditions of the SMB unit.

3. Results and Discussion

3.1. Ethane, Ethylene, Propane and *n*-Butane Single Component Adsorption in Zeolite 13X

Single component isotherms of ethane and ethylene adsorption in zeolite 13X were simulated at temperatures of 305, 393 and 423 K, and pressure ranges from 1 to 200 kPa. There are many experimental studies on adsorption of ethane and ethylene over Na-Faujasites in the literature (Danner and Choi, 1978; Kaul, 1987; Dunne *et al.* 1996; Valezuela and Myers, 1989). Danner and Choi (1978) evaluated prediction models of adsorption equilibria of binary mixtures of ethane/ethylene on 13X pellets containing 20% by weight of inert clay binder and 80% percent synthetic zeolite; Dunne and co-workers made simultaneous measurements of isosteric heats of adsorption and adsorption isotherms of a series of gases, including C_2H_6, on adsorbents of varying pore structure and ion type (NaX, H-ZSM-5, Na-ZSM-5).

Figures 1 (a) and (b) show equilibrium adsorption isotherms of ethane and ethylene over zeolite 13X compared with experimental results. The shape of the isotherms is well reproduced, and there is good agreement between simulation results and the experimental data for pure gases. The slight differences between our simulations and experiments from Kaul (1987) are probably due to the use in experiments of pelletized zeolite that can present structural imperfections, pore blocking, surface adsorption, and inactivation of part of the zeolite. On the contrary, the simulations assume a perfect zeolite crystal, which can cause some differences between simulation results and experimental data. So, we also performed simulations of ethane at 305 K for comparison with experiments carried out with a commercial sample of NaX powder

(Dunne *et al.* 1996). Figure 2 shows an excellent agreement between simulations and experiments.

Equilibrium adsorption isotherms of propane and *n*-butane in zeolite 13X are equally well reproduced by our model, as shown in previous work (Granato *et al*., 2007, 2010). For completeness, the comparison between experiment and simulation for propane and *n*-butane are given in the Supporting Information. It should be noted that the ethane/ethylene data were verified with experimental measurements up to 200 kPa, while *n*-butane/propane has been validated with experimental data measured up to ~110 kPa.

3.2. Adsorption of Binary Mixtures in Zeolite 13X

The good agreement obtained for pure-component adsorption gives us confidence to use our simulations for multi-component adsorption predictions. Nevertheless, we further validate our models by simulating binary adsorption equilibrium and comparing to results estimated from experimental single-component data using the multicomponent extended Toth model (Valezuela and Myers, 1989). The experimental single component adsorption equilibrium data for ethane and ethylene on 13X presented by Danner and Choi (1978) at 298K and 323K were fit with the Toth equation, described by equation 3:

$$q_i = q_{s,i} \frac{b_i P_i}{\left(1+\left(b_i P_i\right)^{t_i}\right)^{1/t_i}} \tag{3}$$

where q_i represents the concentration of component i in the adsorbed phase, q_s is the saturation capacity, P_i is the partial pressure of component i, t_i is a parameter of the model that characterizes the system heterogeneity and b is the affinity constant that depends on the temperature, T, as follows:

$$b_i = b_{0,i} e^{\frac{-\Delta H_i}{RT}}, \quad (4)$$

where b_0 is the affinity constant at infinite temperature, ΔH is the isosteric heat of adsorption at zero loading and R is the universal gas constant. The parameters of the fit obtained are presented in Table 1. This table also presents the parameters of the Toth equation for propane taken from Da Silva and Rodrigues (1999), and the parameters for *n*-butane obtained from a fit to the experimental data presented by Tarek *et al*. (1995).

Da Silva and Rodrigues (1999) determined the adsorption isotherm data of propane from 303 to 473 K and up to 110 kPa. Tarek *et al.* (1995) determined the adsorption isotherm data of *n*-butane from 300 to 360K and up to 150 Torr (~20 kPa). The temperatures used in the SMB simulations are within the range studied by these authors. The maximum pressure used in the adsorption measurements for *n*-butane was high enough to obtain the saturation capacity. Da Silva and Rodrigues used pellets of 13X while Tarek *et al.* (1995) used powder. In a real unit, a shaped 13X would have to be used to avoid large pressure drops. Therefore the saturation capacity presented by Tarek *et al.* (1995) was reduced by 20% to represent the mass fraction of binder and to level with the data presented by Da Silva and Rodrigues (1999) and by Danner and Choi (1978) for ethane and ethylene.

The multicomponent extension of the Toth equation is described by:

$$q_i = q_{s,i} \frac{b_i P_i}{\left(1 + \left(\sum_{j=1}^{nc} b_j P_j\right)^{t_i}\right)^{1/t_i}} \quad (5)$$

The prediction of the multicomponent adsorption equilibrium obtained with this fit was compared with the binary data obtained by CBMC simulations. Excellent agreement was observed for all conditions tested. As an example, the comparison for ethane/ethylene binary adsorption equilibrium data at 323K and a total pressure of 137.8

kPa is presented in Figure 3. Results from binary adsorption experiments reported by Kaul (1987) are also included in this figure, and remarkable agreement between simulation and experiment is observed.

Additional CBMC simulations for the binary adsorption equilibria of propane and *n*-butane with ethane and ethylene, respectively, have been carried out at 373 K and several molar fractions. The simulation results are compared with data provided by the extended Toth model (Valezuela and Myers, 1989) for propane/ethane, propane/ethylene, *n*-butane/ethane, and *n*-butane/ethylene systems, using the data from pure component adsorption isotherms. The resulting x-y diagrams are shown in Figures 4a and 4b. The set of force field parameters successfully reproduce the equilibrium adsorption properties of the binary mixtures propane and *n*-butane with ethylene and ethane.

3.3 - Simulated Moving Bed Simulations

The next step in our multiscale modelling strategy is to use molecular simulation data, presented in the previous sections, directly as input into the SMB model. The separation regions of the gas phase simulating moving bed (SMB) were obtained by simulation and are presented in Figures 5 and 6. The gammas represent the ratio between the fluid velocity, v_j, in the respective section and the solid velocity, u_s, as described by

$$\gamma_j = \frac{v_j}{u_s} \tag{5}$$

where *j* is the SMB section (I, II, III, IV).

Table 2 presents the model parameters chosen to obtain the separation region. The properties of the adsorbent were taken from Da Silva and Rodrigues (1999). It should be noted that the separation region does not depend on the values of gamma 1 and gamma 4 as long as they are large enough and small enough, respectively, to ensure that

sections I and IV are cleaned. Furthermore, the advantage of representing the separation region in terms of the dimensionless variables gamma 2 and gamma 3 is that these results do not depend on the size of the columns (unless there is a strong mass transfer resistance, which is not the case here). This means that a point can be chosen from the separation region and we can either obtain the size of a unit for a given feed flow rate or obtain the feed flow rate for a given size.

Figure 7 shows the adsorption capacity of the four species at 298, 323, 373 and 423 K, obtained from the parameters presented in Table 1. Propane has an intermediate adsorption capacity, which is a desired property for a desorbent in a simulated moving bed process. Ethylene is the species with the highest adsorption capacity; therefore, a mixture of ethylene and propane will be obtained in the extract of the SMB. Ethane, as the least adsorbed species, will be obtained in the raffinate together with propane. However, *n*-butane has a strong interaction with the adsorbent, which means that it will hardly be displaced by the other species. It has a lower saturation capacity (crosses the other isotherms at a pressure bellow 100 kPa) which, depending on the temperature and feed composition, may not be able to displace the other two adsorbates.

It is worth mentioning that at 323 K the equilibrium adsorption isotherm of propane is between the ones of ethane and ethylene while at 373 K, the propane isotherm crosses the ethylene adsorption isotherm at around 40 kPa.

The separation region for a feed of 80% ethylene and 20% ethane at 110 kPa and 298, 323, 348 and 373 K, using 13X as adsorbent and propane as desorbent, and a switching time of 76.5s is presented in Figure 5. The separation region for the case where *n*-butane is used as desorbent is presented in Figure 6. These regions represent the production of both ethane and ethylene with purities above 99.5%. As mentioned by Gleich (US Patent 3921411 - 1975), the composition of the feed of a C2-splitter can widely change

upon the choice of the feedstock and of the sequence selected upstream the splitter. Typical feed compositions have an ethane/ethylene ratio from about 1:3 to 3:1. The feed composition chosen in this work is similar to the one presented in Example II of that patent.

As it can be seen from the simulation results, the separation is feasible. When propane is used as desorbent it can be clearly observed that the separation region increases with the decrease of the temperature. This is due to the increase of the adsorption capacity (as shown in Figure 7), and to the increase of the selectivity. Figure 8 presents the adsorption capacity of different mixtures of ethane/ethylene at a total pressure of 110 kPa and at 323 and 373 K obtained from the parameters presented in Table 1 and with Equation 5. As it can be seen, the increase of the temperature decreases the selectivity of the adsorbent towards each species. As mentioned before, this decrease of the selectivity decreases the separation region. When *n*-butane is used at desorbent this effect of the selectivity in the separation region is not so clear. This is due to the strong interaction of *n*-butane with the adsorbent, which makes it hard to be displaced by ethane and by ethylene.

Additionally, the heights of the "triangle" that represents the separation region are much smaller when *n*-butane is used. This indicates a smaller productivity when using this desorbent. The dimensionless velocity in zone IV, however, is much smaller when *n*-butane is used. For the same time switch this is translated in a lower flow rate of the recycle pump and thus, in a smaller energy consumption of the SMB unit. However, the overall energy consumption, i.e., the energy consumption of the SMB and the energy consumption of the units to separate ethane and ethylene from the desorbent, rather than the energy consumption of the SMB unit alone, is the one that must be taken into account.

Although the separation region at 298 K when using propane as desorbent is the largest, from an industrial point of view, the operation at 323 K is more favourable. Additionally, economical aspects should be taken into consideration for selecting the best operating temperature. At 298 K the adsorption isotherms of ethane and ethylene are very steep (see Figure 7). As a consequence, the desorbent consumption will be equally large.

An operation point was selected in the separation region (black dot in Figures 5 and 6), at 323 K. The operating conditions of these points are presented in Table 3. The concentration profiles along the unit for the chosen operation point are presented in Figure 9, for propane as desorbent and in Figure 10, for *n*-butane as desorbent. The performance parameters of the unit, i.e., purity (Pur) of the streams, and recovery (Rec), are all 100%. The desorbent consumption (DC) is 0,803 m^3 of propane / kg of ethylene in the extract, and 0,798 m^3 of *n*-butane / kg of ethylene in the extract. Productivity (Prod) of ethylene is 3.64 $mol.kg^{(-1)}.h^{(-1)}$, using propane as desorbent. On the other hand, when *n*-butane is used as desorbent, the calculated productivity of ethylene is 0.20 $mol.kg^{(-1)}.h^{(-1)}$. As it can be seen, at these operating conditions, a large productivity may potentially be obtained for ethane/ethylene separation by SMB using 13X as adsorbent and propane as desorbent. As expected from the separation regions, the productivity when *n*-butane is used as desorbent is much lower.

For these operating points, if we consider a feed flow rate of 1.35 m^3/s, we need columns with 7.71 m^3, when using propane as desorbent, and columns with 140.30 m^3, when using *n*-butane as desorbent. For propane as desorbent the extract flow rate would be 1.77 m^3/s, the raffinate flow rate 1.83 m^3/s, and the desorbent flow rate 2.25 m^3/s. For *n*-butane as desorbent the extract flow rate would be 2.03 m^3/s, the raffinate flow rate 1.88 m^3/s, and the desorbent flow rate 2.56 m^3/s.

4. Conclusions

In this paper we present a multiscale *in silico* strategy to design an SMB separation unit that combines molecular simulation with process modelling, and applied it to the challenging separation of ethane and ethylene using zeolite 13X. The molecular model was validated first by comparing simulated single-component adsorption isotherms for ethane and ethylene on 13X with experimental data from several literature sources, and subsequently by comparing binary Monte Carlo simulations to estimates from the extended Toth model based on experimental single-component data. In all cases studied, there was very good agreement between simulation and experiment, giving us confidence to use our model as an adsorption prediction tool.

The results from molecular simulation were then directly used as input to the process simulation of an SMB unit to accomplish the separation of ethane and ethylene. Two candidate desorbents were evaluated, namely propane and *n*-butane. Overall, propane was found to be the most advantageous of the two candidates for this particular separation. Our results thus show that the complete separation of an ethane/ethylene mixture is feasible by SMB with a large productivity, using 13X as adsorbent and propane as desorbent. At this stage, we have not attempted to optimize the SMB unit, but it is likely that doing so will lead to even better separation performance.

The strategy presented here gives a good understanding on how molecular simulations can be coupled with a model for industrial applications. The results obtained from well established techniques provide a solid tool for an integrated approach from the molecular scale to process design. The choice of a good system sorbent/desorbent can be made more efficient by applying simulation techniques, provided there is an adequate combination of knowledge of these two scientific fields: molecules and processes.

5. Nomenclature

b	Affinity constant that depends on the temperature.
D_{ax}	Axial dispersion.
ΔH	Heat of adsorption.
k_s	Intraparticle mass transfer coefficient in the LDF model.
$k_{1,2}$	Constants related to the bonded interactions: bond stretching and bond bending, respectively.
q	In Table S1, refers to the partial charges of the cations and framework atoms.
q_i	Adsorbed phase concentration.
q_{max}	Maximum adsorbed phase concentration.
r	Bond length.
r_{cut}	Cut-off radius.
P, P_i	Pressure, partial pressure of component *i*.
T	Absolute temperature.
t_i	System heterogeneity parameter
t^*	Switching time.
u_s	Solid velocity
$U_{(r)}$	Van der Waals potential energy
V	Volume.

Greek letters

ε	Characteristic energy in pair potential.
ε_b	Particle porosity.
γ	The ratio between the fluid velocity, v_j, in the respective section and the solid velocity, u_s, where j is the SMB section.

ϕ	Torsion angle.
v_j	Fluid velocity.
η	Constants related to torsional configurations.
μ	Chemical potential.
ρ	Particle density.
θ	Bending angle.
σ	Characteristic distance in pair potential.

Acknowledgements

MAG thanks financial support from Fundação para a Ciência e a Tecnologia (FCT) under the post-doctoral grant SFRH-BPD-47432-2008. VMS acknowledges a scholarship from project PTDC-EQU-ERQ-104413-2008. This work is partially supported by projects PTDC-EQU-ERQ-104413-2008 and PEst-C/EQB/LA0020/2011, financed by FEDER through COMPETE - Programa Operacional Factores de Competitividade and by FCT - Fundação para a Ciência e a Tecnologia.

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Table 1 - Parameters of the Toth Equation.

Parameter	Ethane	Ethylene	Propane [a]	n-Butane [b]
q_s[mol/kg]	2.21	2.72	2.68	1.57
b_0[kPa^{-1}l]	5.22×10^{-6}	1.13×10^{-7}	3.50×10^{-7}	1.37×10^{-6}
-ΔH [kJ/mol)	21.4	36.3	35.8	41.2
t[-]	1.75	0.97	0.58	0.94

[a] Data from da Silva (1999)[25].

[b] Data from Tarek et al (1995)[26].

Table 2 – SMB Model Parameters.

Parameter	Value		Units
D_{ax}	3.76×10^{-4}		m^2/s
ε_b	0.4		-
ρ_p	1357		kg/m^3
$k_{s,i}$	1		s^{-1}
T	323		K
P	110		kPa
t^*	76.5		s
	Propane	*n*-Butane	
γ_I	100	150	-
γ_{IV}	0.05	0.01	-
Feed Composition (molar fraction)			Units
Ethylene	0.8		-
Ethane	0.2		-
Configuration	2-2-2-2		-

Table 3 – Operating Conditions of the Selected Point for the unit using Propane and n-Butane as desorbents.

Parameter	Propane	n-Butane	Units
t^*	76.5	76.5	s
γ_I	80	4	-
γ_{II}	21	0.85	-
γ_{III}	66	2.95	-
γ_{IV}	5	0.02	-

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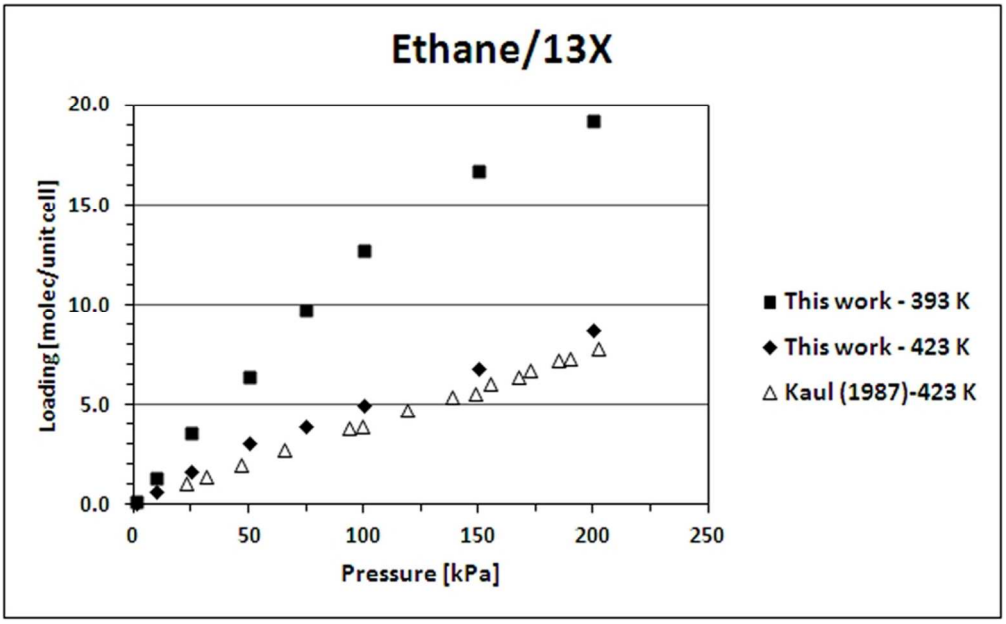

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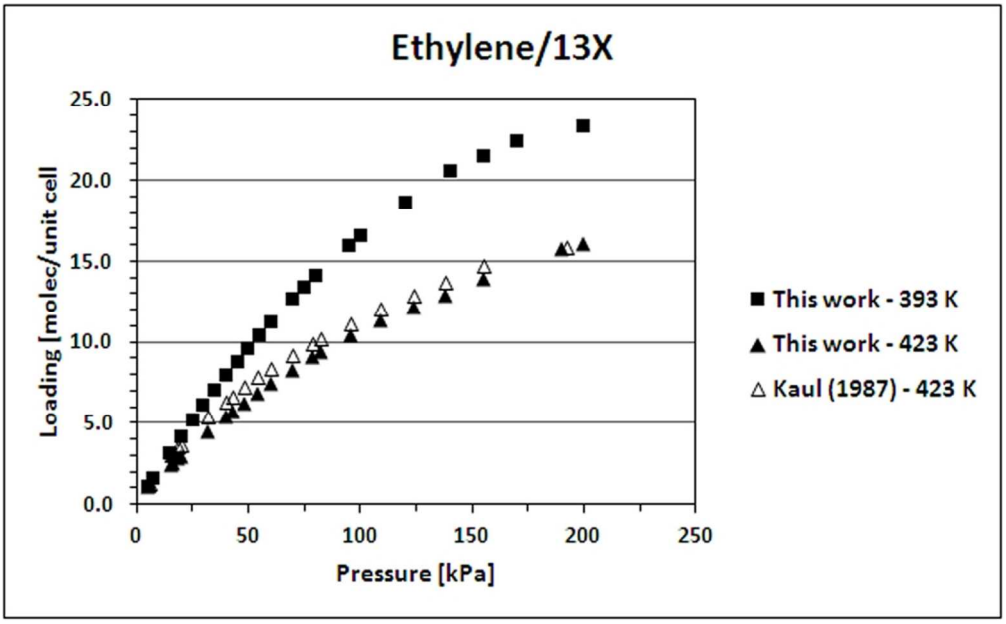

Figure 1 – Isotherms on 13X zeolite at 393 and 423 K: (a) Ethane; (b) Ethylene. Open symbols are experimental data from Kaul, (1987). Closed symbols are our simulations, which account for the presence of 20% of binder in the experimental sample.
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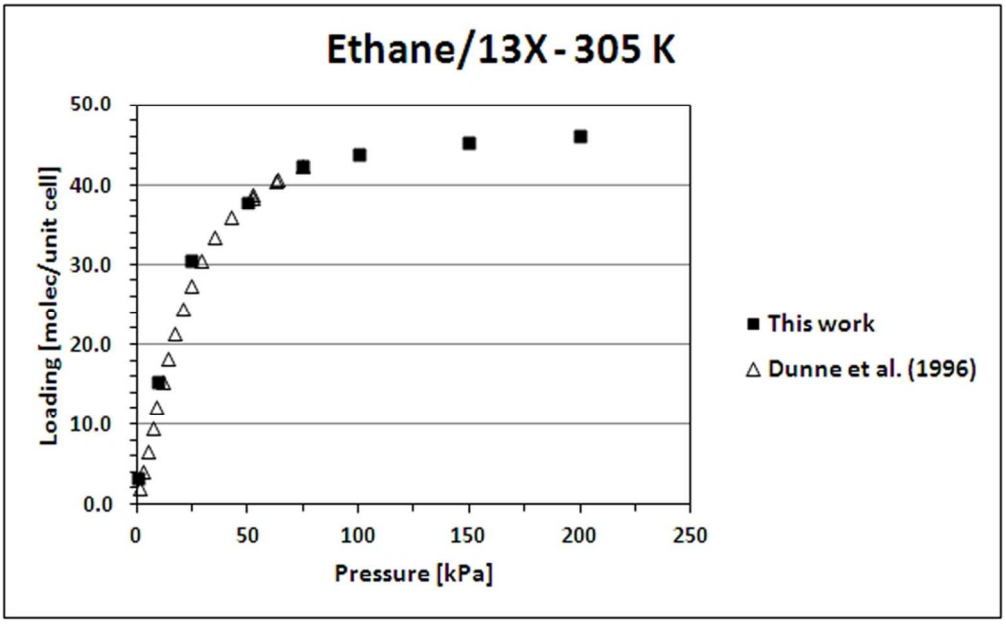

Figure 2 – Isotherms of Ethane on 13X zeolite at 305 K. Open symbols are experimental data from Dunne et al., (1996). Closed symbols are our simulations.
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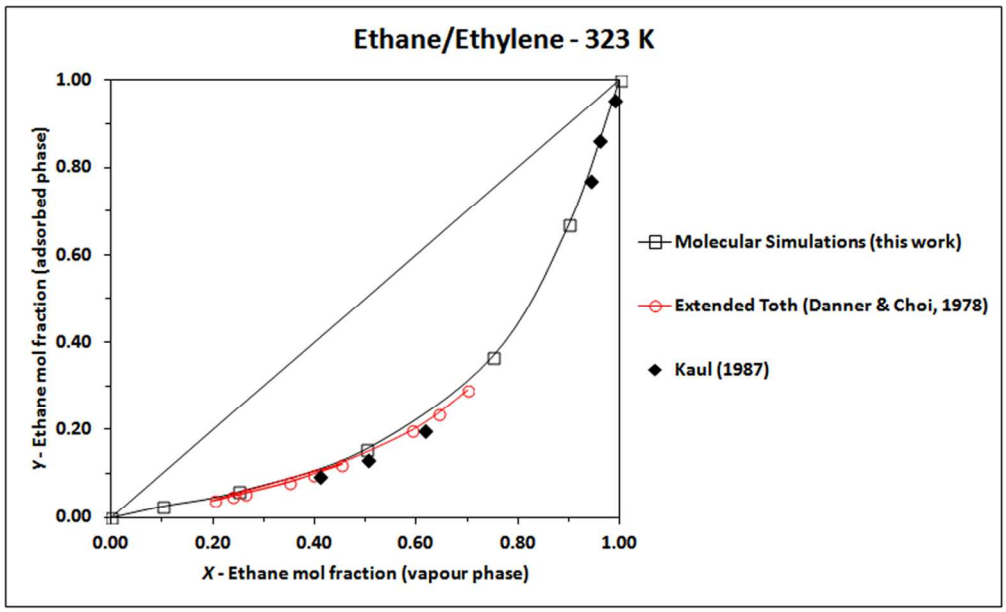

Figure 3 - Binary adsorption equilibrium for ethane/ethylene at a total pressure of 137.8 kPa, calculated from the extended Toth model with experimental single component data from Danner and Choi (1978), predicted from CBMC simulations, and compared with experimental binary adsorption data form Kaul (1987).
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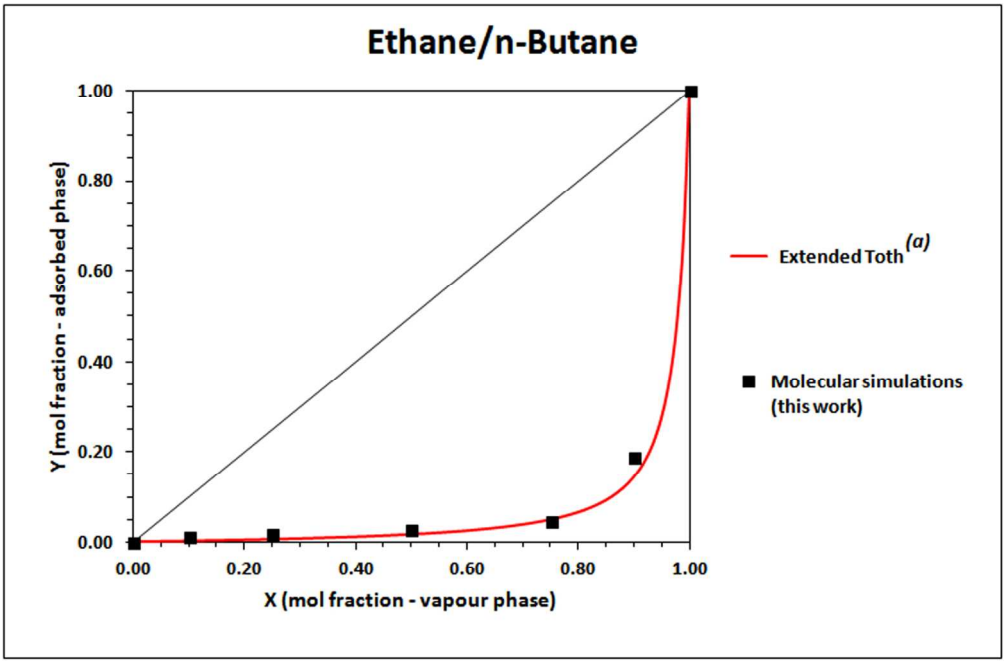

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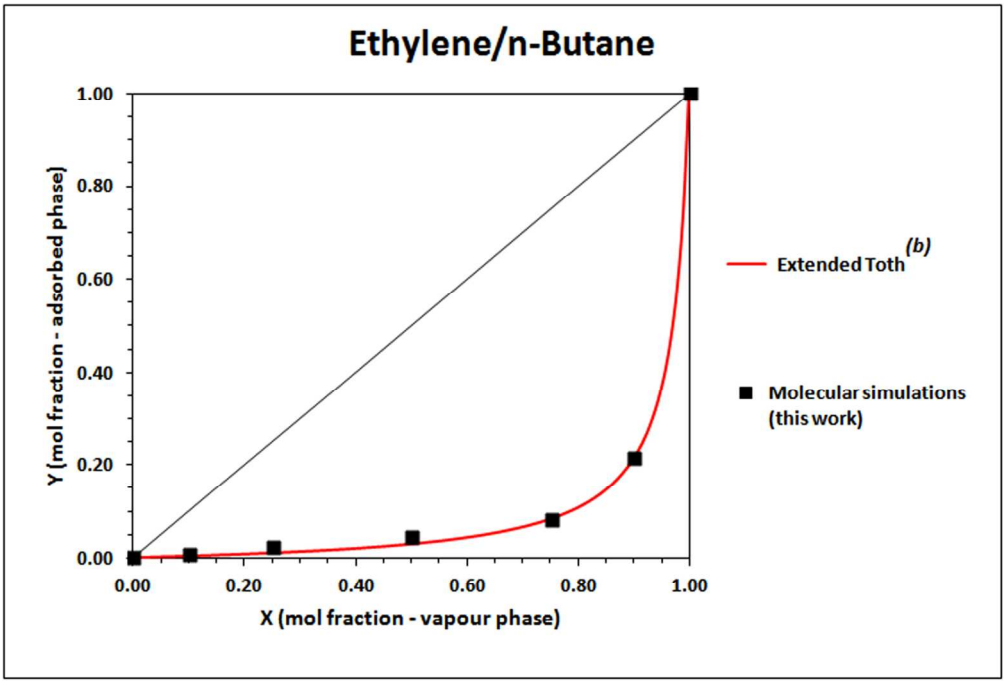

Figure 4a - Binary adsorption equilibrium at 373 K and total pressure of 110 kPa. (a,b)Experimental single component data used in the extended Toth model were taken from Danner and Choi (1978) for ethane and ethylene, and from Tarek et al. (1995) for n-butane.
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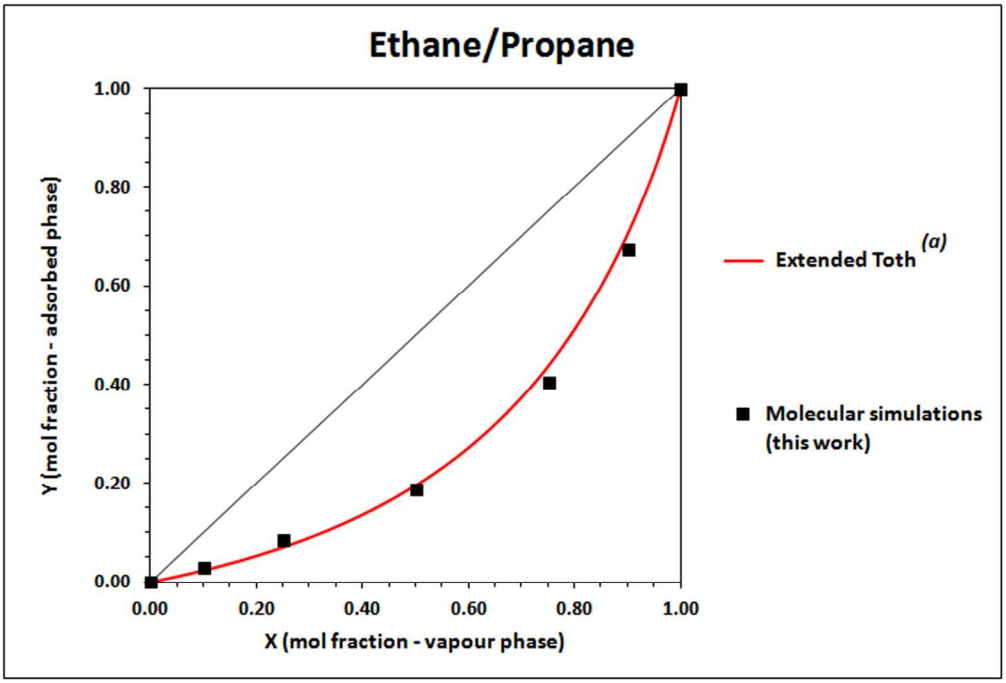

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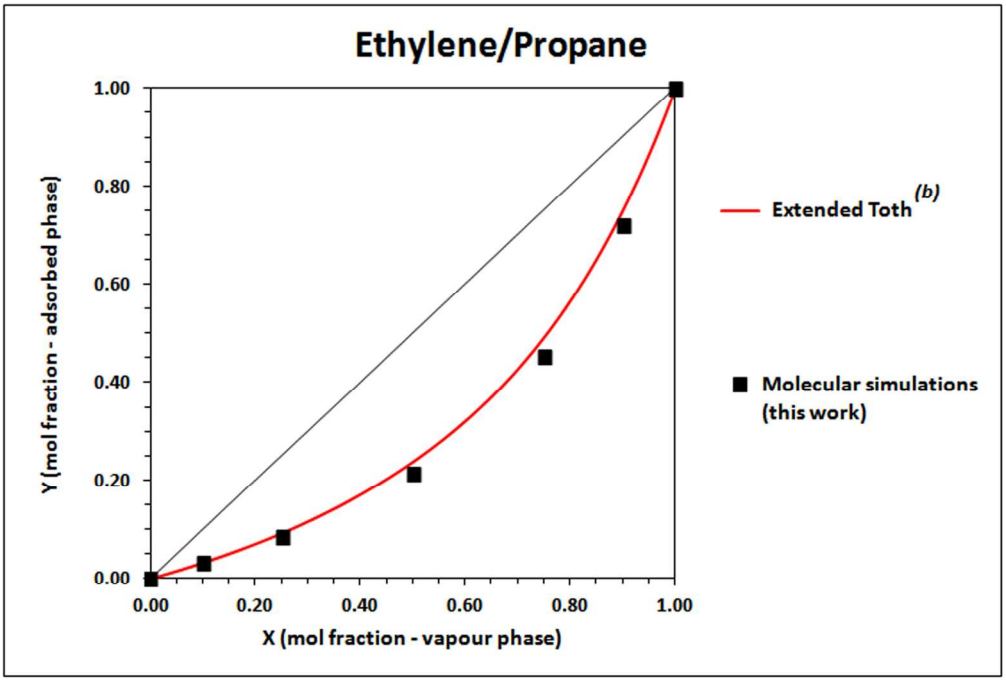

Figure 4b – Binary adsorption equilibrium at 373 K and total pressure of 110 kPa. (a,b)Experimental single component data used in the extended Toth model were taken from Danner and Choi (1978) for ethane and ethylene, and from Da Silva and Rodrigues (1999) for propane.
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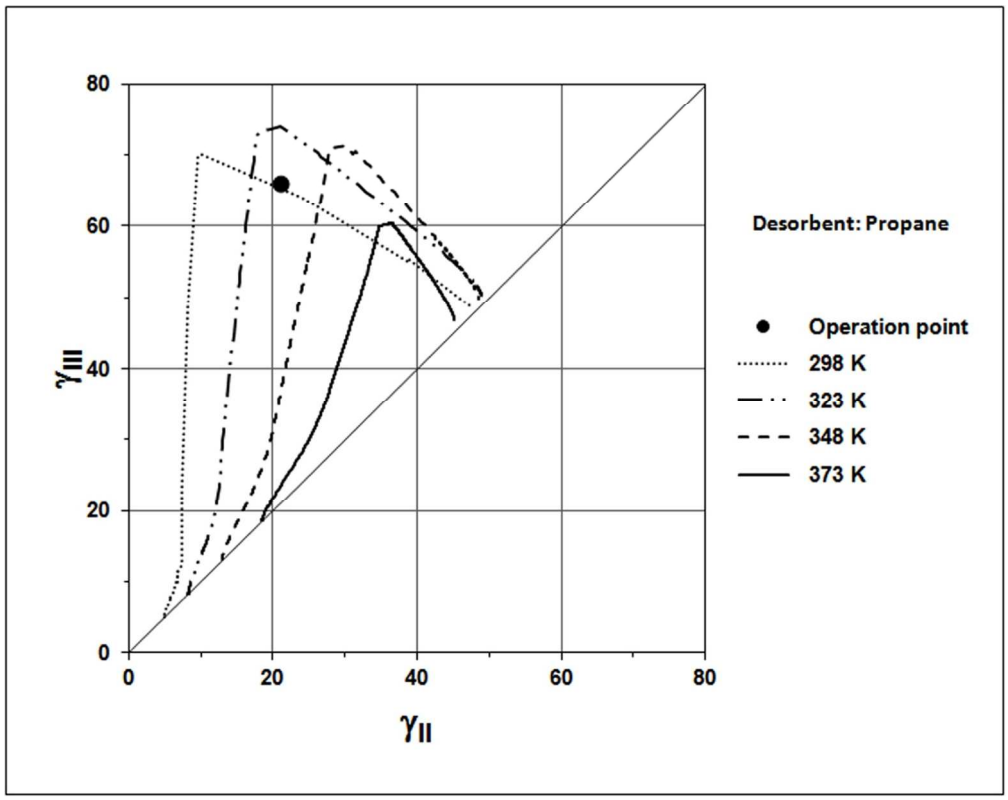

Figure 5 – Separation regions obtained by simulation using propane as desorbent at four different temperatures, and at P=110 kPa. The selected operating point is shown as a black circle.

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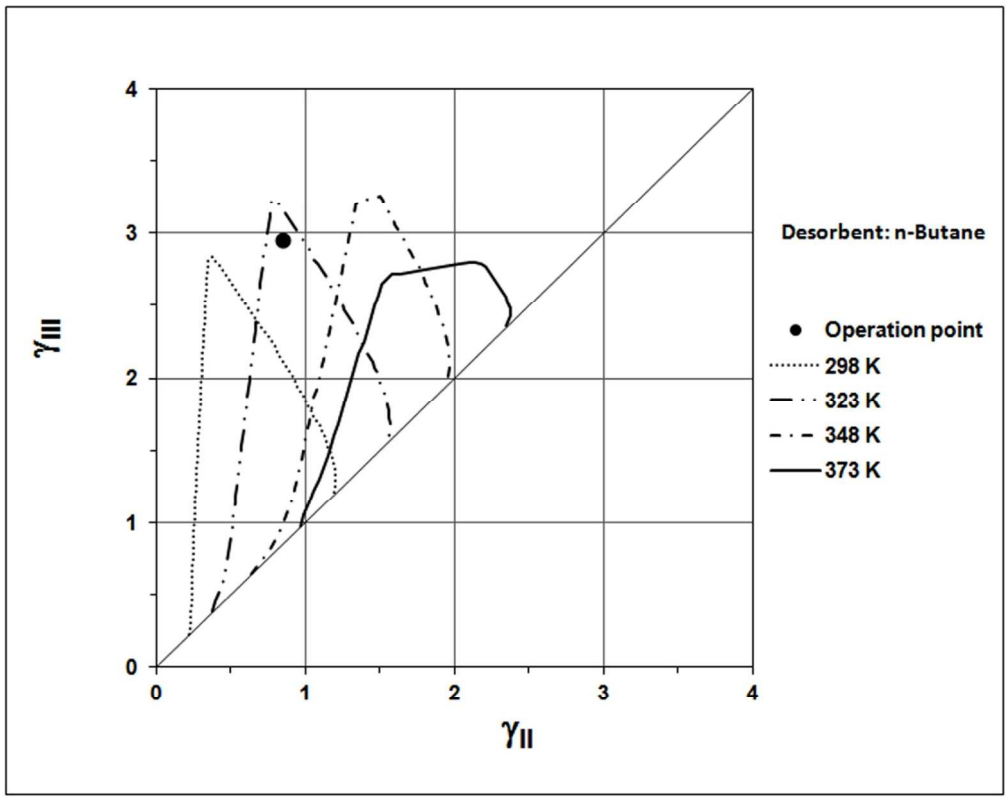

Figure 6 – Separation regions obtained by simulation using n-butane as desorbent at four different temperatures, and at P=110 kPa. The selected operating point is shown as a black circle.
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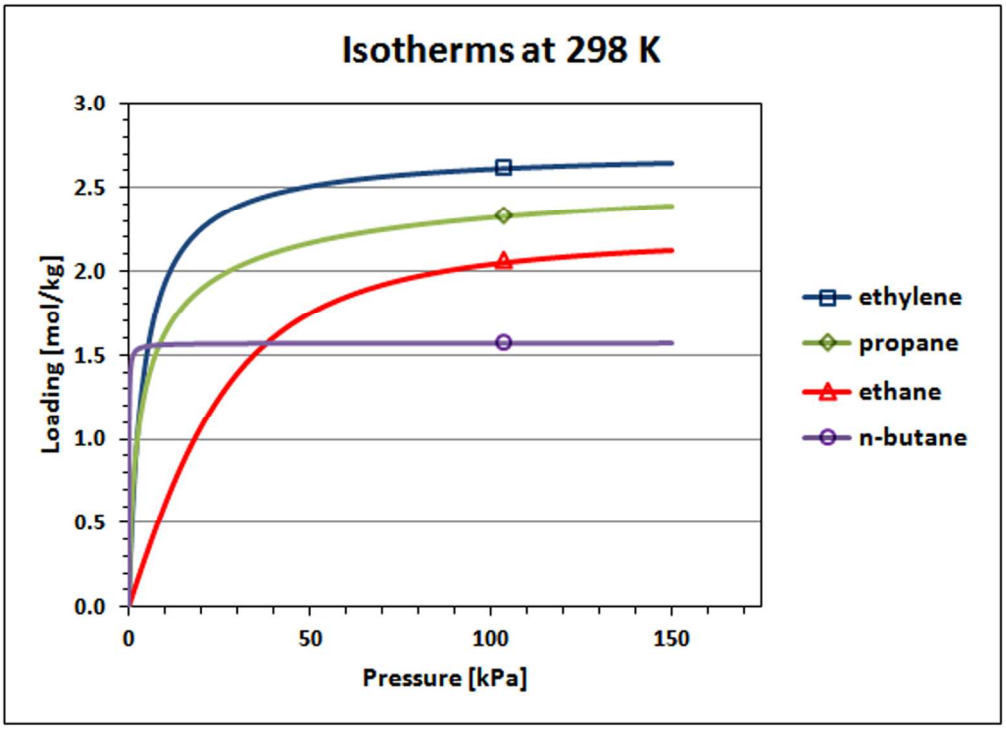

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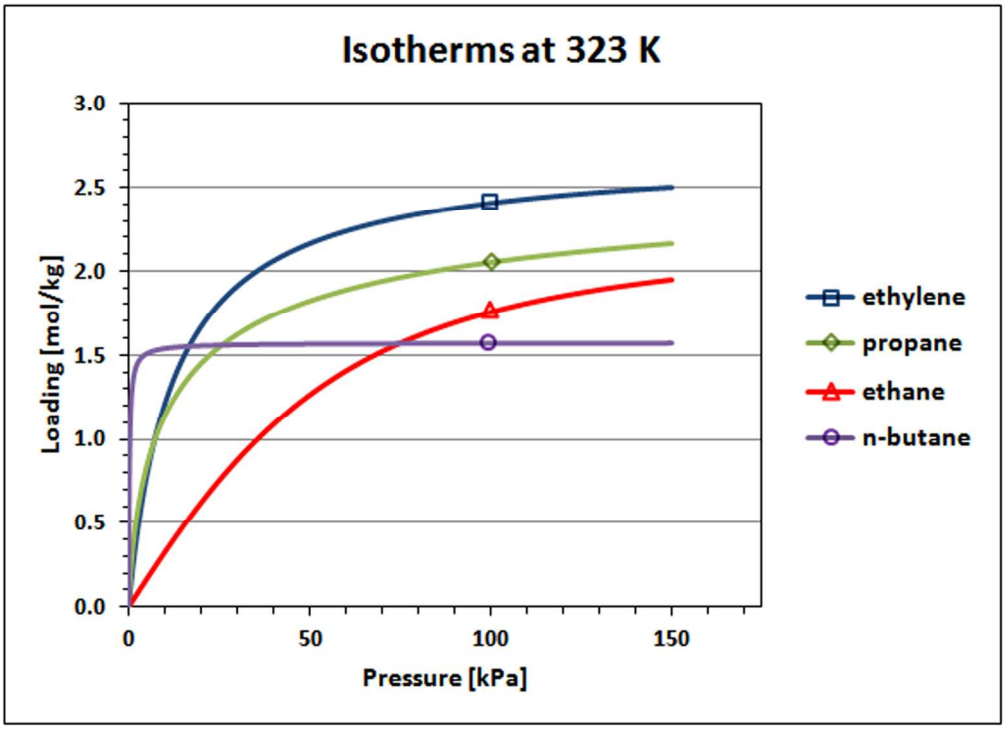

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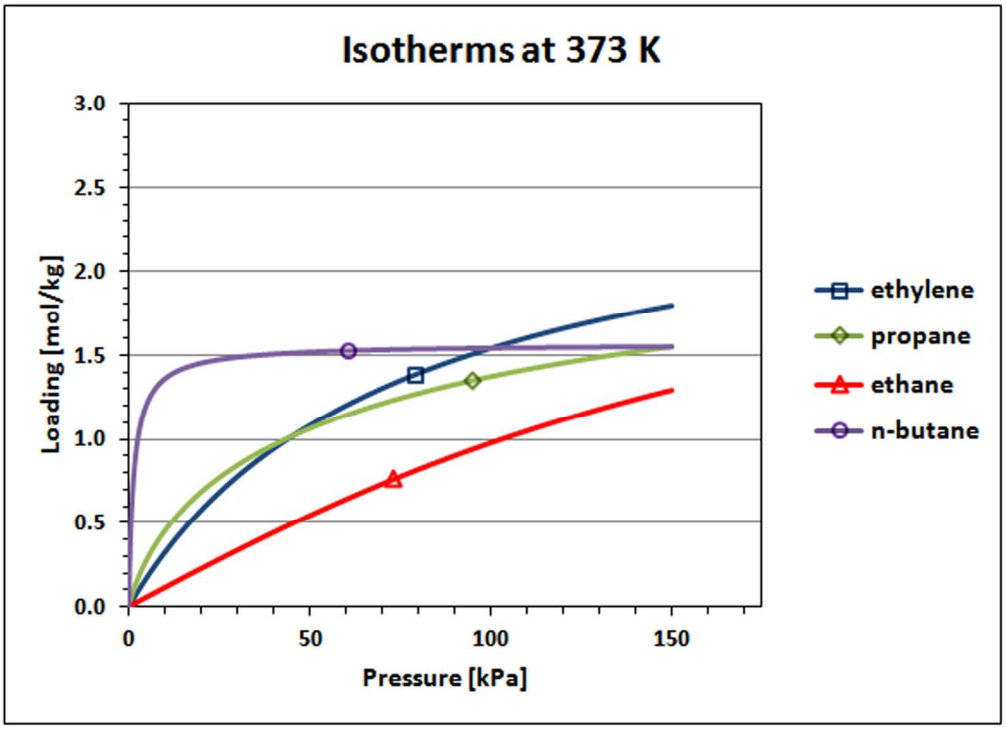

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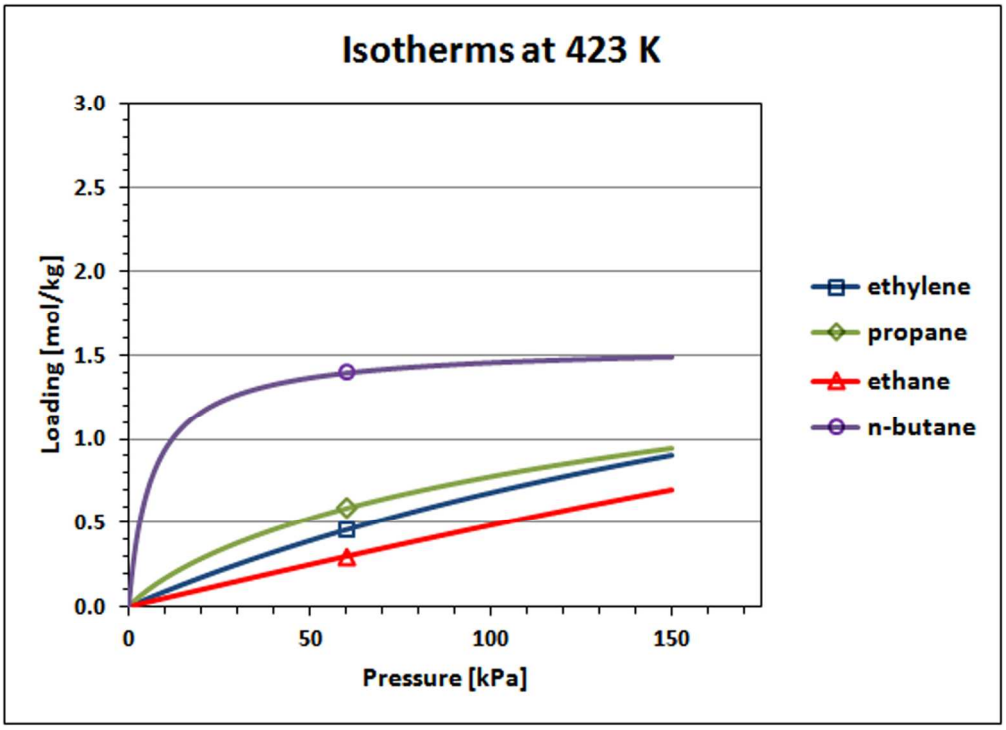

Figure 7 - Single component isotherms at different temperatures.
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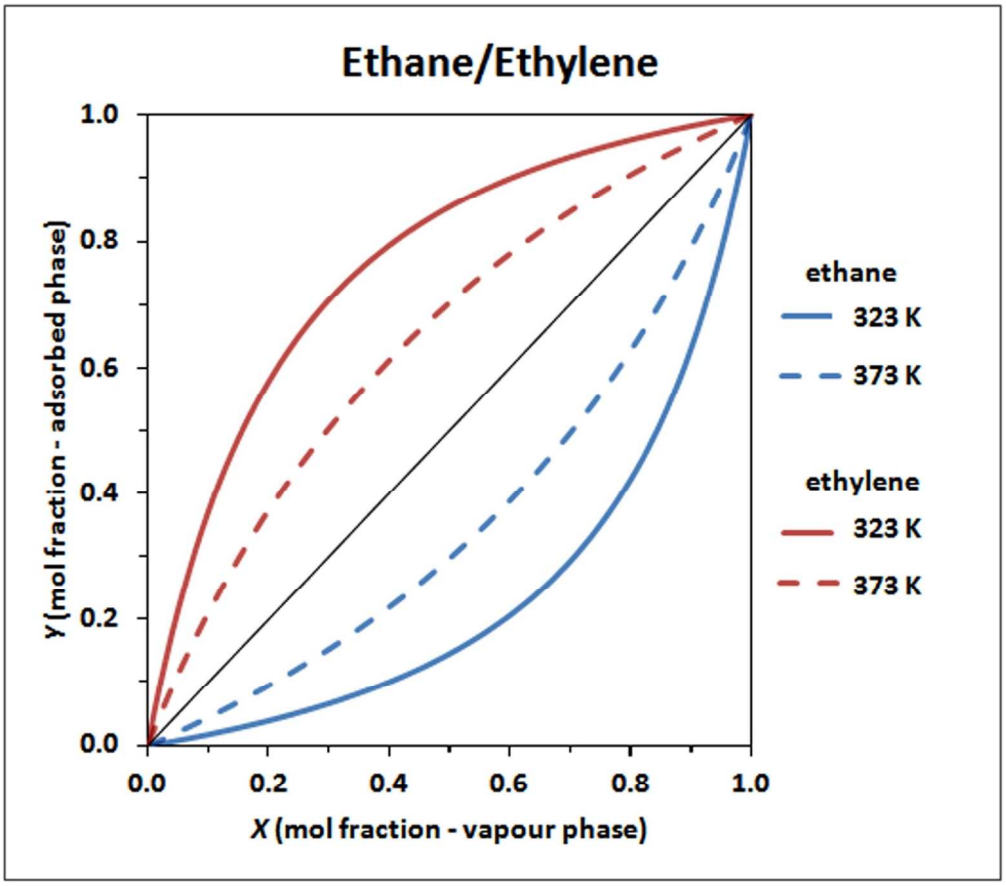

Figure 8 - Binary component equilibrium diagrams at different temperatures.
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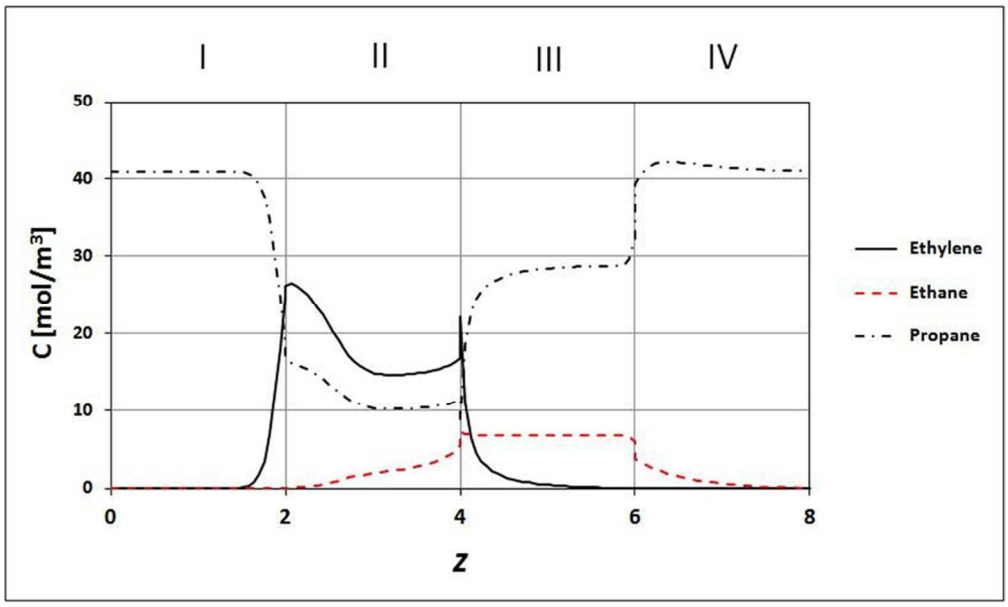

Figure 9 - Concentration profile along the unit for the selected operating point using propane as desorbent.
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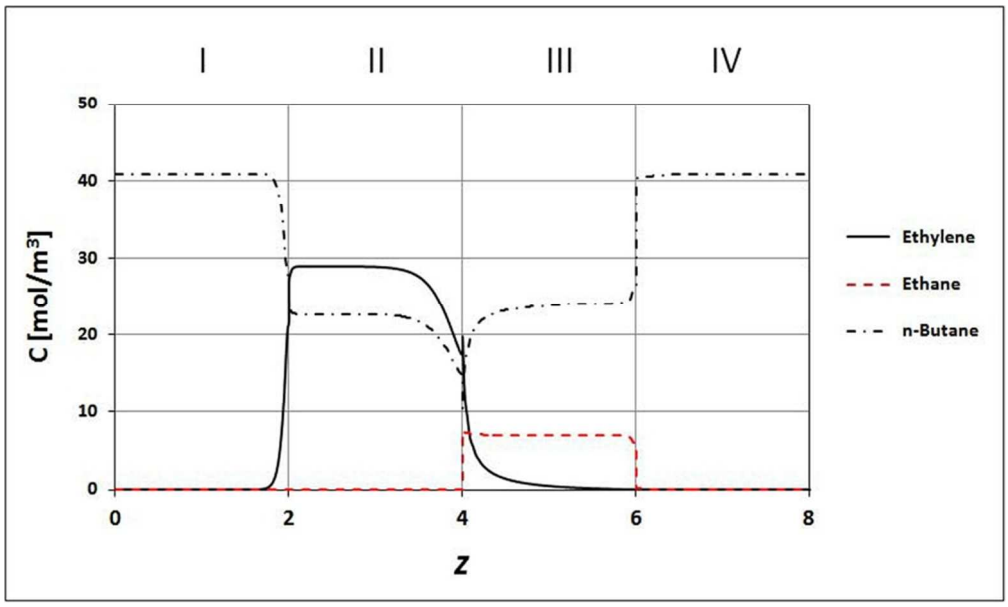

Figure 10 - Concentration profile along the unit for the selected operating point using n butane as desorbent.
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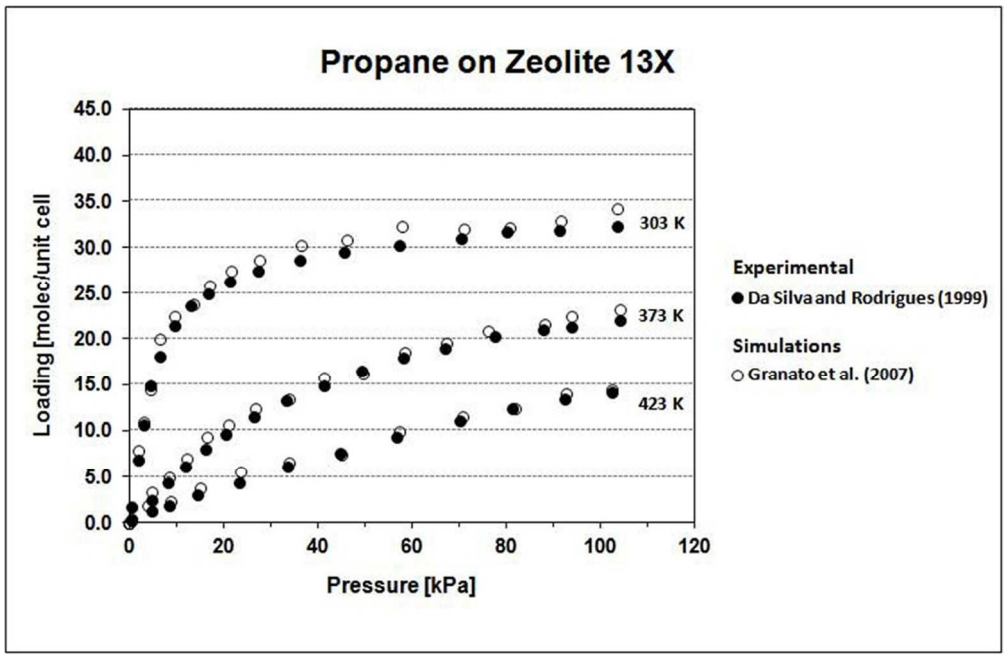

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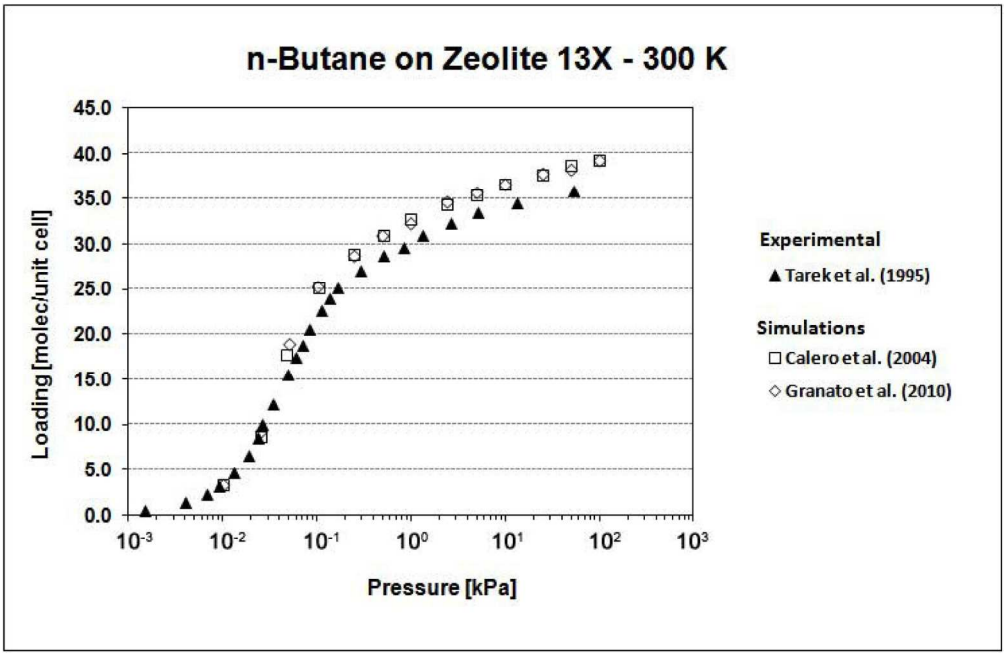

Figure S1 – Isotherms of propane(a) and n-butane(b). Taken from Granato et al. (2007, 2010).
170x110mm (300 x 300 DPI)