

Separation of branched hexane isomers using zeolite BEA for the octane improvement of gasoline pool

P. S. Bárcia^a, J. A. C. Silva^a and A. E. Rodrigues^b

^aEscola Superior de Tecnologia e Gestão, Instituto Politécnico de Bragança, Apartado 1134, 5301-857 Bragança, Portugal

^bLaboratory of Separation and Reaction Engineering (LSRE), Faculdade de Engenharia, Universidade do Porto, Rua do Dr. Roberto Frias, S/N, 4200-465 Porto, Portugal

ABSTRACT

A sorption study of single, binary, ternary and quaternary mixtures of hexane (C₆) isomers n-hexane (nHEX), 3-methylpentane (3MP), 2,3-dimethylbutane (23DMB) and 2,2-dimethylbutane (22DMB) was performed in commercial pellets of zeolite BETA (BEA structure), covering the temperature range between 423 K and 523 K and partial pressures up to 0.3 bar. From these data, single and multicomponent adsorption equilibrium isotherms were collected. An extended tri-site Langmuir model (TSL) was developed to interpret accurately the equilibrium data, and a dynamic adsorption model was developed and tested predicting with a good accuracy the behaviour of multicomponent fixed bed experiments. At the partial pressures studied, the sorption hierarchy in the zeolite BETA is: nHEX > 3MP > 23DMB > 22DMB. BEA structure demonstrates a significant selectivity between C₆ isomers, especially at low coverage, giving a good perspective regarding future work.

1. INTRODUCTION

In a world aware of the end of cheap oil, it is time to research for solutions that can optimize even more the performances of the carburant, increasing the efficiency of the vehicle motors. In the case of gasoline, the combustion quality, measured by the research octane number (RON), can be improved removing low octane paraffins from the gasoline. For instance, nHEX and 3MP exhibits a RON 24.8 and 74.5, whereas 22DMB and 23DMB RON are 94.0 and 103.4, respectively. These four isomers are the major constituents of the output of Total Isomerisation Processes (TIP) [1] and their molecular kinetic diameter is similar (see Fig. 1), which makes the separation difficult. In order to improve the TIP, we start working at LSRE on the development of an adsorptive process to separate monobranched from dibranched C₆ isomers using zeolite BETA. To reach the objectives the project at LSRE consists in: *i*) performing a set of single, binary, ternary and quaternary breakthrough curves with zeolite BETA, in order to set-up adsorption equilibrium isotherms; *ii*) analysis of the influence of partial pressure and temperature in the width of mass transfer zone of breakthrough curves and determination of selectivities; *iii*) development and validation of a dynamic model to be used in the design of a cyclic adsorption process; *iv*) Selecting a proper cyclic process.

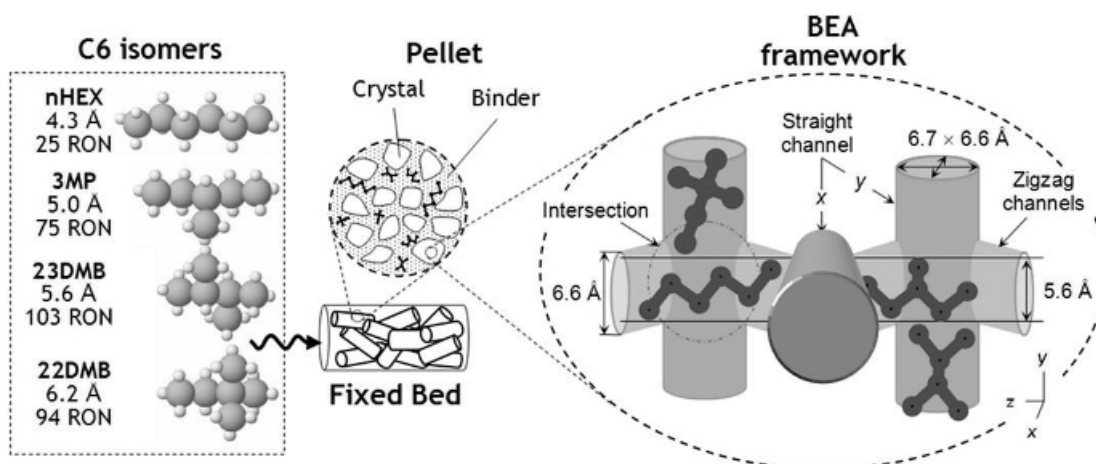


Fig. 1. Illustration of a fixed bed adsorption process showing the various scales: the fixed bed, the pellets and the zeolite framework

2. EXPERIMENTAL SECTION

2.1. Absorbent and C₆ isomers

Fig. 1 shows that the zeolite BETA structure consists of a 3-dimensional channel system composed by straight and zigzag channels with the same 12-membered rings aperture, 0.660.67 nm. However, due to the arrangement of the zigzag channel, the resulting free aperture of this type of channels is 0.560.56 nm. It is also clear from the figure that both types of channels are mutually intersecting, creating an open space that can be favourable to the adsorption of the bulkier molecules.

An approximate three dimensional structure of C₆ isomers is also shown in Fig. 1. The kinetic diameter of the molecules is also indicated, since it plays an important role in the sorption events conditioning the access of the bulkier molecules to the zigzag channels of the zeolite BETA. According to the values of the kinetic diameters of the C₆ isomers and the channels aperture of zeolite BETA, the bulkier 22DMB and 23DMB can only access in principle the straight channels, while 3MP and nHEX can access both type of channels.

2.2. Experimental set-up and procedure

Single and multicomponent adsorption equilibrium isotherms were obtained from breakthrough experiments in the apparatus shown in Fig. 2. The adsorption column consists in a bed packed with 1/16" pellets of zeolite BETA (Si/Al = 150) operated by introducing a feed containing a C₆ isomers mixture diluted in helium at a fixed partial pressure.

A typical experiment consists in measuring continuously the concentration profile at the outlet of the bed in order to collect samples during the breakthrough curve. When the saturation is reached, the composition of each loop is evaluated by chromatography. The equilibrium loading was obtained by integrating the outlet concentration profiles.

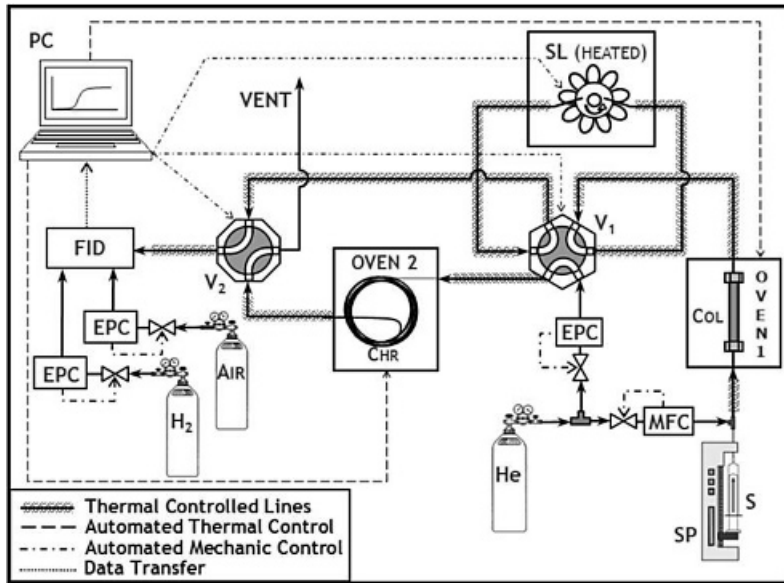


Fig. 2. Schema of the multicomponent breakthrough apparatus. (Chr) chromat. column; (Col) packed column; (EPC) elect. press. controller; (FID) flame ionization detector; (IP) injection port; (MFC) mass flow controller; (PC) computer; (S) microliter syringe; (SL) sample loops; (SP) syringe pump; (V1) and (V2) 4-way and 6-way crossover valve

2.3. Adsorption equilibrium model

For the development of an adsorptive process, it is important to obtain a good analytical description of the experimental sorption data. In order to correlate all the experimental data of sorption equilibrium of the C₆ isomers on zeolite BETA, we assume that zeolite BETA possesses three different sites for adsorption of hexane isomers (see Fig. 1 and ref [2]). Accordingly, the well known Langmuir isotherm model is expanded to describe the sorption behaviour in three different categories of active sites resulting in the following tri-site Langmuir (TSL) model isotherm,

$$q(p, T) = q_m^S(T) \cdot \frac{b^S(T) \cdot p}{1 + b^S(T) \cdot p} + q_m^Z(T) \cdot \frac{b^Z(T) \cdot p}{1 + b^Z(T) \cdot p} + q_m^I(T) \cdot \frac{b^I(T) \cdot p}{1 + b^I(T) \cdot p} \quad (1)$$

where q is the amount adsorbed, p is the pressure of sorbate, b and q_m are the adsorption affinity constant and the saturation loading in each type of sites, respectively. The superscripts S , Z and I indicate whether the adsorption sites are in a straight or zigzag channel or in an intersection, respectively.

Using the parameters given by the single component adsorption equilibrium fitting, the mixture sorption data can be predicted by an extended TSL isotherm model. Accordingly, the amount adsorbed of component i , q_i , in a mixture is given by:

$$q_i(p, T) = q_{m,i}^S(T) \cdot \frac{b_i^S(T) \cdot p_i}{1 + \sum_{k=1}^n b_k^S(T) \cdot p_k} + q_{m,i}^Z(T) \cdot \frac{b_i^Z(T) \cdot p_i}{1 + \sum_{k=1}^n b_k^Z(T) \cdot p_k} + q_{m,i}^I(T) \cdot \frac{b_i^I(T) \cdot p_i}{1 + \sum_{k=1}^n b_k^I(T) \cdot p_k} \quad (2)$$

where n is the number of C_6 isomers in the mixture.

Complete information about the experimental conditions of single and multicomponent experiments performed and the optimization procedure of the TSL model parameters is reported elsewhere [2].

2.4. Modelling breakthrough experiments

Breakthrough experiments were modelled with simple LDF model for mass transfer. The following additional assumptions are made: (1) ideal gas law applies; (2) the pressure drop through the bed is negligible; (3) the flow pattern is described by the axial dispersed plug flow model; (4) the main resistances to mass transfer for adsorbable species are external fluid film resistance and macropore diffusion as pointed out by Bácia *et al.* [3] in ZLC studies of the hexane isomers in pellets of zeolite BETA. External resistance and macropore diffusion can be combined in a global resistance according to a lumped model for the adsorbent particle as suggested by Morbidelli *et al.* [4]; (5) the column is isothermal. Taking into account the previous assumptions, the dynamic mathematical model equations required to describe the fixed bed adsorption phenomena are summarized in Table 1.

Table 1

Dynamic mathematical model equations for fixed bed adsorption.

	Equations	Eq.
Mass balance to sorbate species	$\varepsilon_b D_L \frac{\partial^2 c_i}{\partial z^2} = \frac{\partial(uc_i)}{\partial z} + \varepsilon_b \frac{\partial c_i}{\partial t} + (1 - \varepsilon_b) \rho_a \frac{\partial \bar{q}_i}{\partial t}$	(3)
Overall mass balance	$C \frac{\partial u}{\partial z} + \varepsilon_b \frac{\partial C}{\partial t} + \sum_{i=1}^N (1 - \varepsilon_b) \rho_a \frac{\partial \bar{q}_i}{\partial t} = 0$	(4)
Mass transfer rate	$\rho_a \frac{\partial \bar{q}_i}{\partial t} = k(q_i - \bar{q}_i)$	(5)
Axial dispersion (Langer <i>et al.</i> , 1978)	$\frac{1}{Pe} = \frac{D_L}{uL} = \gamma \frac{D_m}{uL} + \frac{d_p}{LPe'_\infty \left(1 + \beta \frac{\gamma D_m}{ud_p}\right)}$	(6)
	being, $\gamma = 0.45 + 0.55\varepsilon_b$, $Pe'_\infty = 670 \cdot d_p$ and $\beta = 10$	

This LDF model has been used in previous studies [2, 5-6] with success. The numerical solution of the model equations was obtained by orthogonal collocation [7].

3. RESULTS AND DISCUSSION

Fig. 3(a) shows a typical binary breakthrough curve, where it can be seen a significant separation degree for an equimolar mixture of 22DMB/3MP. In case of an equimolar mixture of 23DMB/3MP, the separation degree is smaller as can be seen in Fig. 3(b); however, it is of importance since mass transfer zones do not overlap.

Fig. 4 shows an equimolar quaternary breakthrough experiment, which reveal that the retention times are in the following order: nHEX>3MP>23DMB>22DMB. This experiment also shows a complete separation between the isomers, which indicates that the separation of the hexane isomers in zeolite BETA is feasible.

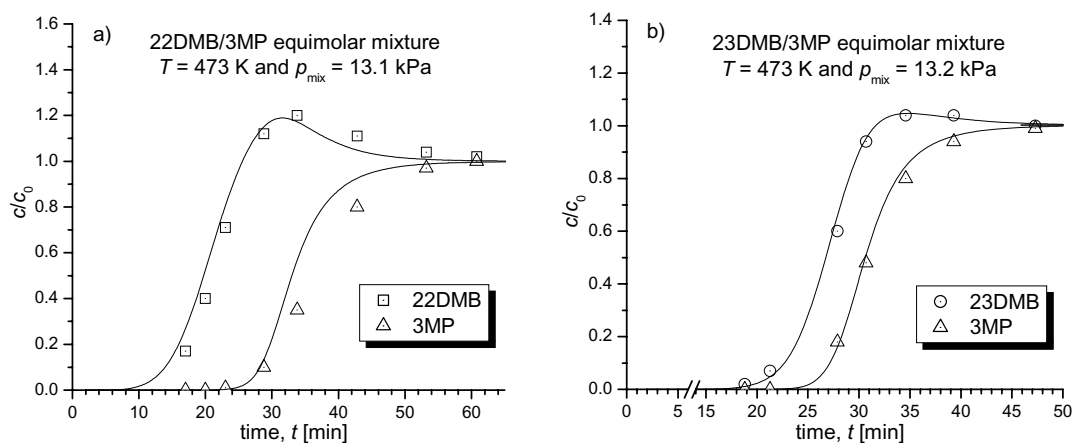


Fig. 3. Binary breakthrough curve for an equimolar mixture of (a) 22DMB/3MP and (b) 23DMB/3MP in zeolite BETA at temperature, $T = 473$ K and total isomers pressure, $p_{\text{isom}} = 13$ kPa. Lines are model predictions with TSL isotherms

The lines in the Figs. 3 and 4 represent the dynamic model simulation using a multicomponent TSL model for the prediction of adsorption equilibrium data. The model parameters are shown in Table 2. The agreement between experimental data and the mathematical model is reasonable good, and this is remarkable taken into consideration that we are using a simple LDF model in a simulation of a very non-linear multicomponent, in a complex zeolite structure. Once more we believe that these results are possible due to the good job done by the extended tri-site Langmuir model.

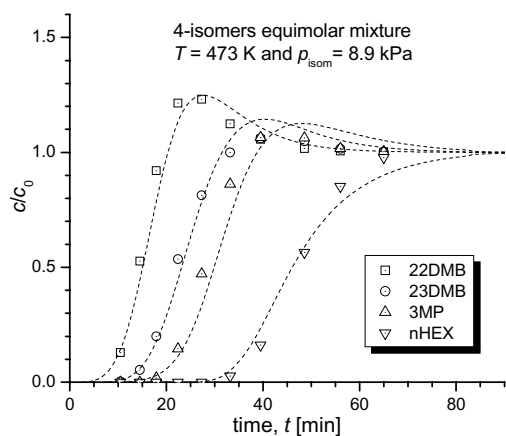


Fig. 4. Breakthrough curve for an equimolar mixture 22DMB/23DMB/3MP/nHEX in zeolite BETA. Lines are model predictions with TSL isotherms

Table 2

Experimental conditions, amount adsorbed and dynamic model parameters of the simulation for multicomponent breakthrough curves.

Run	Helium flowrate, ϕ_{He} (mL/min)	Total isomers pressure, p_{isom} (kPa)	Amount adsorbed, q (g/100g _{ads})				D_L (m ² /s)	Mass transfer coefficient, k (s ⁻¹)			
			22DMB	23DMB	3MP	nHEX		22DMB	23DMB	3MP	nHEX
22DMB/3MP	2.2	13.1	1.122	-	2.514	-	5.3×10^{-5}	0.030	-	0.015	-
23DMB/3MP	2.2	13.2	-	1.743	2.148	-	5.3×10^{-5}	-	0.030	0.015	-
4-isomers	3.3	8.9	0.355	0.708	0.895	1.622	5.3×10^{-5}	0.030	0.018	0.006	0.030

4. CONCLUSIONS

We have presented a multicomponent adsorption study with hexane isomers on zeolite BETA. Having in mind the separation of the hexane isomers by a cyclic process in a fixed bed, a simple LDF mathematical model coupled with the TSL model isotherm was tested in its capability to simulate the experimental breakthrough curves. The agreement between the dynamic model and experimental data is good, which opens a good perspective regarding future work.

In terms of the experimental data obtained, we conclude that the separation of hexane isomers in zeolite BETA is possible at low mixture loadings, and this can be achieved at high temperatures (473 K).

The results arising from this study are opening a window to solve the separation problem between monobranched and dibranched C₆ isomers. These data are now being used in the development of a cyclic process by an appropriate technology.

ACKNOWLEDGEMENT

José A. C. Silva acknowledges financial support from Fundação para a Ciência e Tecnologia under project EQU/60828/2004. Patrick S. Bácia acknowledges a FCT grant (SFRH/BD/30994/2006).

REFERENCES

- [1] T. C. Holcombe, T. C. Sager, W. K. Volles, A. Zarchy, Isomerisation Process, U.S. Patent No. 4 929 799 (1990).
- [2] P. S. Bácia; J. A. C. Silva, A. E. Rodrigues, submitted to AIChE Journal (2006).
- [3] P. S. Bácia; J. A. C. Silva, A. E. Rodrigues, Microporous Mesoporous Mater., 79 (2005) 145.
- [4] M. Morbidelli, A. Servida, G. Storti, S. Carrá Ind. Eng. Chem. Fundam., 21 (1982) 123.
- [5] F. A. Silva, J. A. C. Silva, A. E. Rodrigues, Adsorption, 5 (1999) 229.
- [6] P. S. Bácia, J. A. C. Silva, A. E. Rodrigues, Ind. Eng. Chem Res., 45 (2006) 4316.
- [7] J. V. Villadsen, M. L. Michelsen, Prentice-Hall Inc.: Englewood Cliffs, New Jersey, 1978.