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PART A

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Edited by

Ruren Xu
Jilin University, Changchun, P. R. China

Zi Gao
Fudan University, Shanghai, P. R. China

Jiesheng Chen
Jilin University, Changchun, P. R. China

Wenfu Yan
Jilin University, Changchun, P. R. China

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From Zeolites to Porous MOF Materials – the 40th Anniversary
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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]

[a]Escola Superior de Tecnologia e Gestão, Instituto Politécnico de Bragança, Apartado 1134, 5301-857 Bragança, Portugal

[b]Laboratory 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 (C_6) 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 C_6 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 C_6 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.

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 C_6 isomers. These data are now being used in the development of a cyclic process by an appropriate technology.

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