

Separation of branched hexane isomers on zeolite BETA

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The main goal of this research focuses on the development of an adsorptive process to separate branched hexane isomers in order to improve the quality of gasoline measured by the octane number (RON). In this investigation, studies of sorption equilibrium and kinetics of hexane isomers: n-hexane (RON 25), 3-methylpentane (RON 75), 2,3-dimethylbutane (RON 103) and 2,2-dimethylbutane (RON 94) on BETA zeolite pellets are addressed. These four isomers were selected since they are the major constituents of the output of Total Isomerisation Processes (TIP) and their molecular kinetic diameter is similar, which makes the separation very challenging.

Sorption equilibrium (breakthrough curves) and kinetics (ZLC) of hexane isomers, were studied in commercial pellets of zeolite BETA in the form HBEA with a Si/Al ratio of 150 (see Figure 1), between temperatures of 423 K and 523 K and partial pressures up to 0.30 bar. Figure 2 shows a schematic diagram of the breakthrough and ZLC experimental apparatus.

Four different models were used to interpret the equilibrium data, named: Langmuir, Multi-site Langmuir (MSL), Dual-site Langmuir (DSL) and Toth. Figure 3 shows a comparison of adsorption equilibrium data of the isomers at 473K. The figure shows different amounts adsorbed for all the isomers. The best model to fit the di-branched isomers is the MSL, and for nHEX and 3MP the DSL. The affinity to the adsorbent measured by the Henry's constants decreases with the degree of branching, with selectivities that can reach a value of 8.8 between nHEX and 22DMB. The heats of adsorption at zero coverage decrease with the degree of branching, being: 63.4 kJ/mol for nHEX, 59.7 kJ/mol for 3MP, 57.1 kJ/mol for 23DMB and 53.6 kJ/mol for 22DMB. However, the isosteric heat of sorption changes with coverage with a different behavior for the three isomers.

Sorption kinetics studied by Zero Length Chromatography (ZLC) technique allowed us to find the nature of controlling diffusion mechanism (macropore or micropore); for nHEX and 3MP macropore diffusion is controlling with activation energies similar to the heats of sorption at zero coverage. For 23DMB and 22DMB, the controlling mechanism changes, being the system governed apparently by both macropore and micropore diffusion. Figure 4 shows the effect of the degree of branching on ZLC desorption curves at 473K. Data from this work are also compared with those reported in literature for both zeolite BETA and silicalite.

A set of multi-component experiments were also performed in order to study the behavior of the hexane isomers on BETA zeolite. Figure 5 shows a binary breakthrough curve. It is clear from this figure that the selectivity between mono- and di-branched isomers is significant. The results of this study are now being used in the development of a cyclic process for the separation of di-branched and mono-branched hexane isomers.

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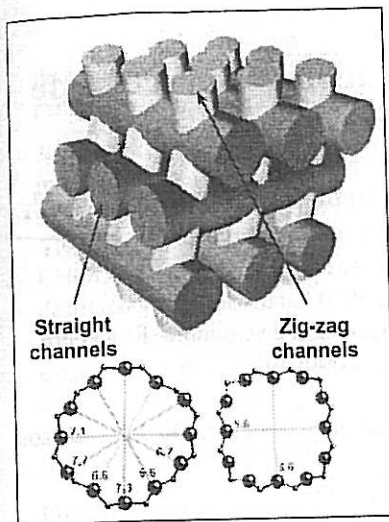


Figure 1. Perspective view show the straight and zigzag channels of zeolite beta. This representation facilitates the visualization of the intersections between the channels. The 12-membered ring free pore apertures of straight and zig-zag channels were also shown for a good visualization of its structure.

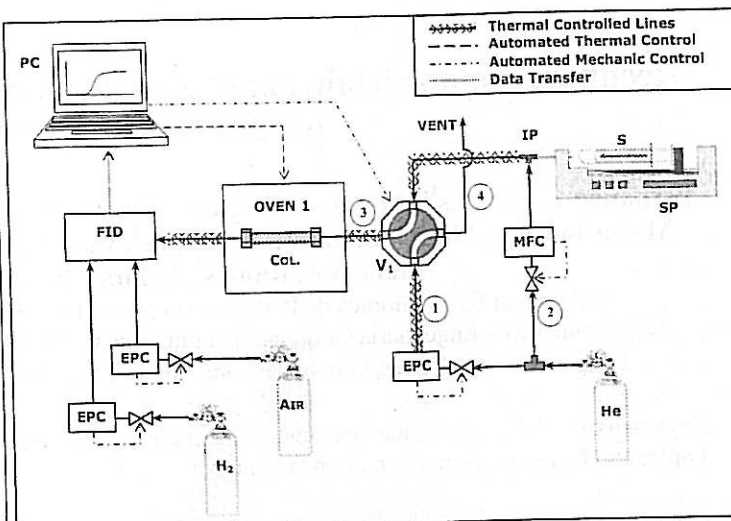


Figure 2. Schematic diagram of the ZLC experiment apparatus used to measure adsorption equilibrium and ZLC data: (Col.) packed column; (EPC) electronic pressure controller; (FID) detector of chromatograph; (IP) injection port; (MFC) mass flow controller; (PC) computer; (S) microliter syringe; (SP) syringe pump; (V_1) 4-way crossover valve; (1, 2, 3, 4) streams.

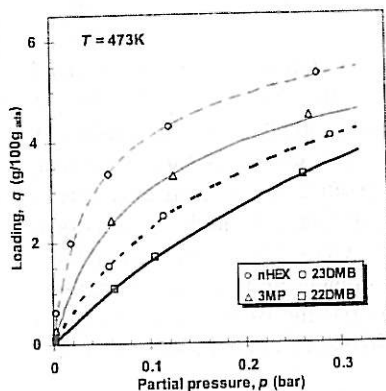


Figure 3. Adsorption equilibrium isotherms. The lines represent model fitting. (MSL for the di-branched isomers and DSL for 3MP and nHEX) of hexane isomers at 473K.

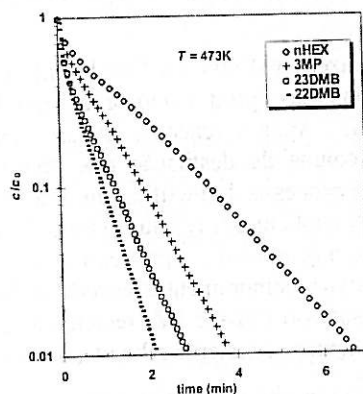


Figure 4. Effect of degree of branching on ZLC desorption curves at 473K. Semilog plot of c/c_0 vs time t .

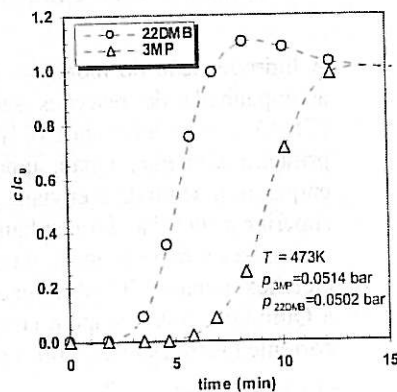


Figure 5. Binary breakthrough curve for an equimolar mixture of 22DMB and 3MP at 473K.

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