ADSORPTION EQUILIBRIUM AND KINETICS OF HIGH MOLECULAR WEIGHT N-PARAFFINS MIXTURES AND KEROSENE ON 5A ZEOLITE

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N-Paraffins have been widely used in detergent manufacture. These linear hydrocarbons can be selectively separated by adsorption from petroleum fractions using the appropriate adsorbent and the simulated moving bed technology (SMB). The development and design of adsorption processes requires equilibrium and kinetic data. These parameters are available in bibliography for light paraffins in gas phase, however, there is scarce information form liquid phase systems involving high molecular weight paraffins.

The aim of this work is the study of adsorption equilibrium and kinetics of high molecular weight paraffins on 5A zeolite. The representative paraffins studied have been: *n-decane, n-dodecane, n-tetradecane, n-hexadecane and n-octadecane*. *N-pentane* has also been studied, since this paraffin is the desorbent used in the SMB industrial process for separating paraffins. A theoretical model has been developed to describe the kinetics of adsorption of the studied systems. The model has been included in a SMB simulation program (SMBSIM), and the model prediction has been compared with the separation performance data reported for a commercial SMB unit that separates normal paraffins from a hydrotrated kerosene fraction.

N-paraffin adsorption experiments have been carried out in a fixed bed at 175ºC and 21 barg using a commercial 5A zeolite molecular sieve as adsorbent. Experimental procedure consists in the following steps: adsorbent activation at high temperature (350ºC), conditioning of the bed with a mixture of *iso-octane-n-pentane* (40-60% in weight), feeding of the adsorption mixture (*iso-octane*, used as solvent, *trimethylbenzene*, as a tracer, and paraffins in concentrations ranging between 0,1 and 10% in weight). Breakthrough curves have been obtained by gas chromatography analysis of the samples periodically collected at the outlet of the fixed bed by an automatic sampler.

First, pure paraffin isotherms and kinetics were studied. However, the pure paraffin parameters obtained cannot predict the behavior of paraffin mixtures. Paraffin mixtures experiments were carried out (*n-decane*, *n-dodecane* and *n-tetradecane* mixtures) to obtain a multicomponent isotherm and the kinetic parameters. Finally, the breakthrough curves obtained from mixture experiments have been compared to those obtained from a complex mixture, a hydrotreated kerosene fraction.

Equilibrium data have been fitted to the Langmuir model, since linear paraffins exhibit a type I isotherm behavior. Breakthrough curves have been latter fitted using a kinetic model based on conservation equations. Three resistances in series to the mass transfer have been considered. The results show that the limiting step is the mass transfer in the zeolite micropores.

Kinetic parameters and Langmuir isotherms have been used in the development of a simulated moving bed model, with the purpose of optimizing an industrial unit and predicting the effects of changes in the operational variables, such as feed composition. The model has been validated by comparison with bibliography data [1], obtaining errors lower than 10% in paraffin concentration in extract and raffinate.

[1] H.J. Bieser, Process for separating normal paraffins, U.S. Patent 4006197 (1977).