Zeolite Beta Membranes for the Octane Upgrading of C5/C6 Light Naphta

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One of the major processes in the oil refinery is the isomerization of light parafins which increase the octane rating of low-grade linear alkanes. The conversion from linear to branched is often performed on a platinum loaded mordenite catalist (Pt-H/MOR). Separation of the non-converted linear molecules is carried out using adsorbing beds of zeolite 5A. Nevertheless, one third of the resulting isomerate consists in low octane number (RON) linear and monobranched alkanes. The oil refining market requires the development of alternative solutions which can improve the RON quality of the gasoline fulfilling at the same time the environmental standards imposed.
Recently, adsorption studies performed at *LSRE-IPB* indicate that zeolite beta can selectively adsorb the low octane C6 isomers from a vapour mixture at low partial pressure by fixed bed technique [1]. Such behaviour could be explained by both preferential adsorption and shape selectivity, being the last originated by the presence of two different types of interconnected channels.

At the same time, interest in zeolite membranes has been growing rapidly due to their capability to separate compounds in continuous operation. Since 2008, LSRE has been working in collaboration with the Catalysis Engineering group at *DelftChemTech* (Delft University of Technology, The Netherland) with the goal of exploring the use of zeolite membranes for the separation of hexane isomers. For this purpose, different synthesis methods for manufacturing zeolite beta membranes have been explored and their performance in the vapour phase separation of hexane isomer mixtures studied. This work represents, to the best of our knowledge, the first one dealing with the separation of four C6 isomers (n-hexane (nHEX), 3-methypentane (3MP), 2,3-dimethybutane (23DMB) and 2,2-dimethylbutane (22DMB)) using zeolitic membranes.

The zeolite Beta membranes were prepared by secondary growth method in asymmetric tubular α-Al_2O_3 supports (*Inocermic GmbH, Germany*), combining three different types of seeding techniques and crystallization conditions. Figure 1 show SEM micrographs of a typical non-calcined beta membrane synthesized in this work (cross section view).

The vapour permeation experiments performed in the apparatus shown in Figure 2 with mixtures of *n*HEX, 3MP, 23DMB and 22DMB show that permeate flux increase as the degree of branching decreases following the order: nHEX>>3MP>23DMB>22DMB. Approximately one third of the feed stream cross the membranes. Figure 3 shows that in the retentate stream the fractions of monobranched and normal hexane isomers (low RON compounds) decrease while the concentration of dibranched isomers (high RON compounds) is increased in relation to the equimolar feed composition. Consequently, the RON can be boosted in retentate up to 3.8 points. These results demonstrate the potential of the zeolite beta membranes for application in the production of additive-free premium gasoline.

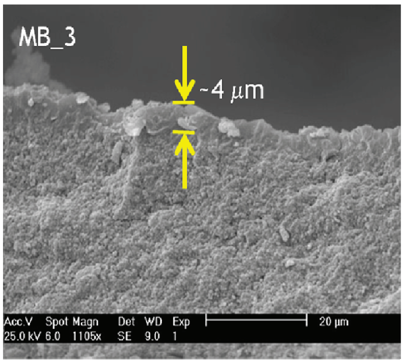

Figure 1. SEM micrographs of a typical non-calcined beta membrane (cross section view).

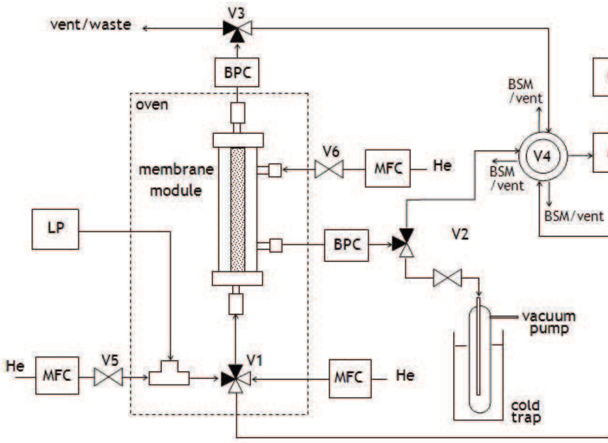

Figure 2. Schematic representation of the experimental apparatus used for vapour permeation tests.

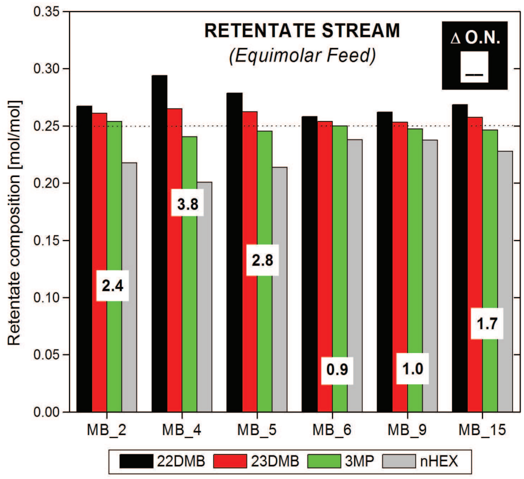

Figure 3. Composition of the retentate for a equimolar feed mixture of nHEX, 3MP, 23DMB and 22DMB at T=100 ºC and p_{mix}=1kPa in typical zeolite Beta membrane.

References:

[1] Patrick S. Bárcia, *Separation of light naphtha for the octane upgrading of gasoline: adsorption and membrane technologies and new adsorbents*, Ph.D. Thesis, University of Porto, Portugal, **2010**.