BOOK OF ABSTRACTS

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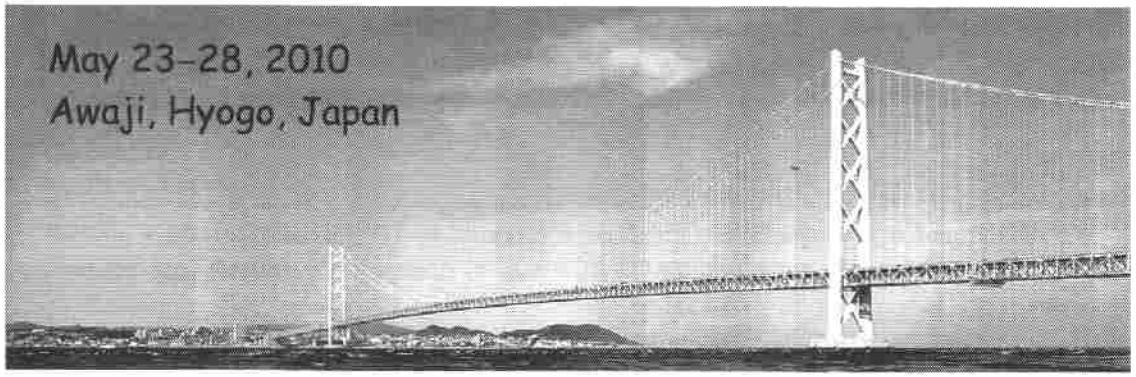

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Improvement of the recycle technologies for C5/C6 isomerization by layered PSA

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With the increasing regulation of gasoline composition, paraffin isomerization has grown rapidly in importance as a means to boost light naphtha research octane number (RON). Isomerization of light naphtha fractions rich in *n*C5 and *n*C6 is achieved by catalytic reaction on either chlorinated alumina or zeolite based Pt-containing catalysts which convert the low octane linear paraffins into branched ones. Several variations of the *n*C5/*n*C6 isomerization process are commercially available. In once-through isomerization, i.e. without recycle of the isomerate product, a product RON up to 80 can be achieved. If the normal paraffins in the reactor product are separated and recycled the product RON can be improved up to 88-89. For such recycle units the octane quality of the final isomerate product depends on the separation technique applied. The octane gain from pentanes and hexanes can be controlled by the Deisopentanizer (DIP) and Deisohexanizer (DIH) distillation columns, respectively. The separation between *n*- and *iso*-parraffins is also possible by selectively adsorbing the normal paraffins on a molecular sieve bed of zeolite 5A (e.g., the *Ipsorb* process from *Axens* and the *Total Isomerization Process* (*TIP*) from *UOP*). The second option is from afar the less energy consuming recycle technology available.

The objective of this work consists in studying the separation mono/dibranched paraffins by cyclic adsorption process using a layered bed of zeolites 5A and Beta (Figure 1). Aspen ADSIM 2006.5 (AspenTech Inc.) was used for numerically solving an adiabatic dynamic model incorporating mass, energy and momentum balance. Model parameters were taken from experimental data reported in the literature [1, 2]. Parametric studies were simulated to determine how process performance is affected by purge quantity, 5A-*to*-Beta ratio, repressurization/blowdown schemes and operating temperature. Figure 2 shows that a combination of zeolites 5A and Beta can produce an octane gain of 1 RON comparatively to the conventional TIP [3] by reducing the monobranched C6 fraction in the product. Another advantage of this configuration is the possibility to increase the penetration distance because zeolite Beta acts like a "*barrier*" to the linear alkanes desorbed from zeolite 5A during the co-current depressurization step. It was also demonstrated that a slight increase in temperature (20 K) results in a RON benefit of 0.2 points. Several alternatives are provided to improve the performance of the existing TIP processes with this combination of adsorbents.

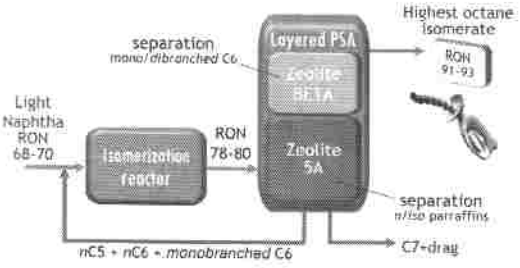

Figure 1. Improvement of the TIP process by layered PSA.

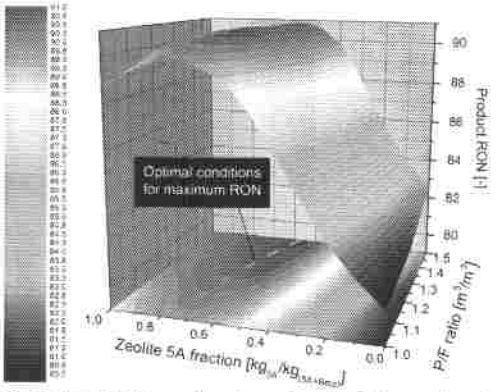

Figure 2. Product RON as a function of zeolite 5A mass fraction and purge-to-feed volumetric ratio. T = 523K; P_{Feed}/P_{Purge}= 5/1 bar; pressurization with feed; co-current depressurization; pure H_2 purge; t_{cycle}= 200 s.

1. J.A.C. Silva, *Separation of n/iso-Paraffins by Adsorption Process*. Ph.D. thesis, University of Porto, Portugal, **1998**.
2. P. Bárcia, J.A.C. Silva, A.E. Rodrigues, *AIChE J.*, **2006**, 53, 1970-1981.
3. N.A. Cusher, in *Handbook of petroleum refining processes*, R.A. Meyers (ed.), 3rd ed., McGraw-Hill, New York **2004**, Chapter 9.4.

P25-11

Multicomponent adsorption of hexane isomers in MOFs

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The refining industry makes every endeavor to enhance the octane quality of the gasoline (RON) satisfying at the same time the environmental standards imposed. The recent restrictions to the use of oxygenated additives have complicated even more this hard task. The Total Isomerization Process (TIP) is commonly used to increase the RON by separating linear molecules from light naphtha, and isomerizating them on a catalytic reactor. The actual TIP produces an isomerate with about 89 RON; however the data from UOP reveal that 30% of its typical composition consists of low RON monobranched hexane isomers. The goal of this work is optimizing the actual TIP coupling an adsorber able to remove the monobranched hexane isomers from the isomerate, and recycle them to the isomerization reactor. This extra unit will permit us to obtain a final isomerate reaching about 93 RON.

To achieve the objectives, we have performed a set of screening studies for quaternary mixtures of hexane isomers *n*-hexane (nHEX), 3-methylpentane (3MP), 2,3-dimethylbutane (23DMB) and 2,2-dimethylbutane (22DMB) in two porous rigid MOFs (figure 1). First, the chromium trimesate MIL-100(Cr),[1] which possesses mesoporous cages accessible through 5-9 Å microporous windows, and secondly the zirconium terephthalate UiO-66,[2] which exhibits a 3D microporous (5-10 Å) pore system. The temperature range 323-423 K and partial pressures up to 30 kPa have been explored. Figures 2(a-b) shows typical multicomponent equimolar experiments. For all experiments, the sorption hierarchy in MIL-100 is: nHEX>>>3MP>23DMB>>22DMB while UiO-66 possesses the opposite 22DMB>23DMB>>>3MP>nHEX. The results show that both MOFs can be effective for this separation. Further studies are now being developed to increase the degree of separation.

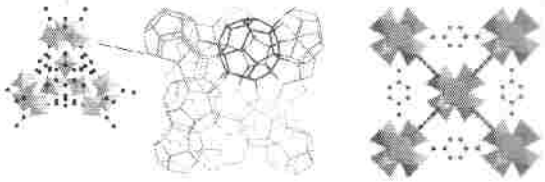

Figure 1. 3D-structures of MIL-100 and UiO-66.

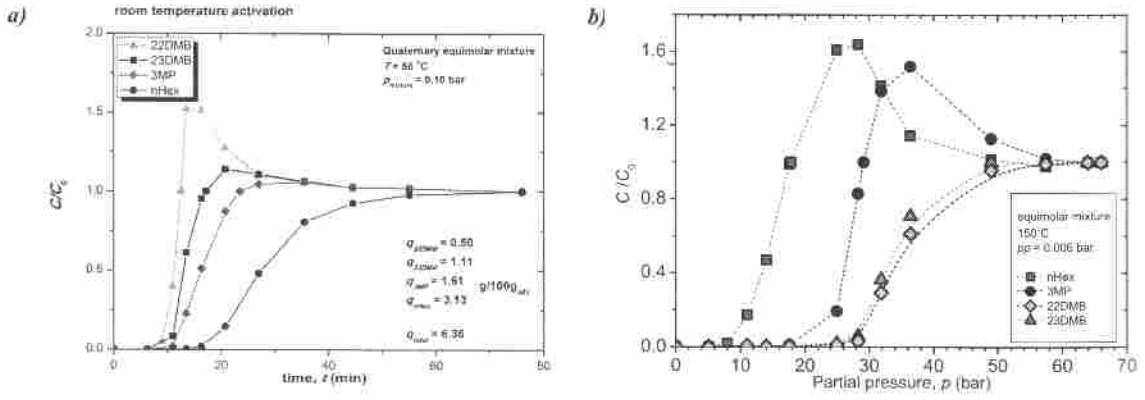

Figure 2. Breakthrough curves for equimolar mixtures. (a) MIL-100(Cr). (b) UiO-66.

[1] G. Férey et al., *Angew Chem. Int Ed.*. **2004**, *43*, 6296.

[2] J. Hafizovic Cavka et al., *J. Am. Chem. Soc.* **2008**, *130*, 13850.