CONFERENCE PROGRAM

Octane Upgrading of TIP Processes by Recycling in a Layered Zeolite 5A/BETA 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 at 523 K 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.

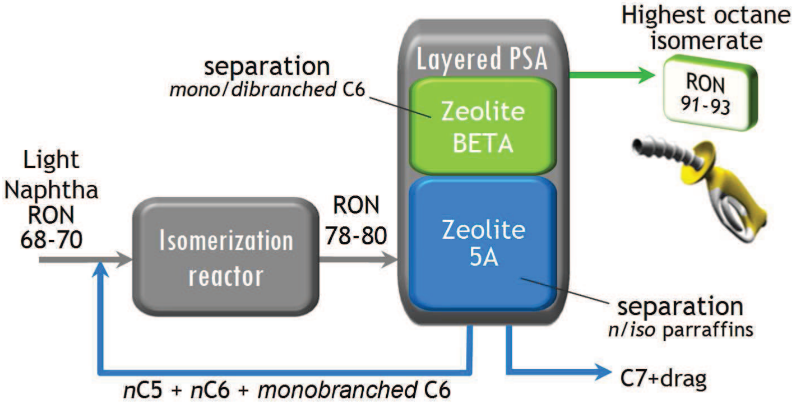

Figure 1. Improvement of TIP process in a layered 5A/BETA PSA.

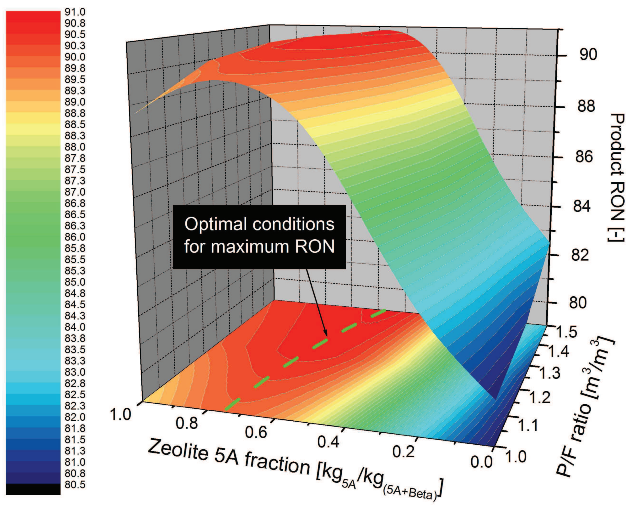

Figure 2. RON product as a function of zeolite 5A mass fraction and purge-to-feed volumetric ratio in a layered 5A/BEA PSA. T = 523K; P_{Feed}/P_{Purge}= 5/1 bar; pressurization with feed; co-current depressurization; pure H_2 purge; t_{cycle} = 200 s.

References:

[1] José A. C. Silva, *Separation of n/iso-Paraffins by Adsorption Process*. Ph.D. Thesis, University of Porto, Portugal, **1998**.

[2] 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**.

[3] N.A. Cusher, in *Handbook of petroleum refining processes*, R.A. Meyers (ed.), 3rd ed., McGraw-Hill, New York **2004**, Chapter 9.4.