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P36: Separation of Branched Alkanes Feeds by a Synergistic Action of Zeolite 5A and Metal-Organic Framework MIL-160(Al)

A. Henrique [1,2], P. F. Brântuas [1,2], L. F. A. S. Zafanelli [1,2,3,4], E. Aly [1,2,5], A. E. Rodrigues [3,4], G. Maurin [6], C. Serre [7], J. A. C. Silva [1,2]

[1] *Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, 5300-253 Bragança, Portugal.*

[2] *Laboratório Associado para a Sustentabilidade e Tecnologia em Regiões de Montanha (SUSTEC), Instituto Politécnico de Bragança, 5300-253 Bragança, Portugal.*

adriano_henrique@ipb.pt

[3] *LSRE-LCM – Laboratory of Separation and Reaction Engineering – Laboratory of Catalysis and Materials, Faculty of Engineering, University of Porto, 4200-465 Porto, Portugal*

[4] *Alice – Associate Laboratory in Chemical Engineering, Faculty of Engineering, University of Porto, 4200-465 Porto, Portugal*

[5] *Aveiro Institute of Materials, CICECO, Department of Chemical Engineering, University of Aveiro, Campus Universitario de Santiago, 3810-193 Aveiro, Portugal*

[6] *ICGM – Univ. Montpellier, CNRS, ENSCM 34293 Montpellier, France*

[7] *Institut des Matériaux Poreux de Paris, ESPCI Paris, Ecole Normale Supérieure, CNRS, PSL University, 75000, Paris, France*

pedro.brantuas@umontpellier.fr; zafanelli@ipb.pt; ezzeldin@ipb.pt; arodrig@fe.up.pt; guilaume.maurin1@umontpellier.fr; christian.serre@espci.psl.eu; jsilva@ipb.pt

1. Introduction – The total isomerisation process (TIP) developed by the universal oil products (UOP) for upgrading the octane rating of light hydrocarbon fractions, especially mixed feedstocks containing pentane (C5) and hexane (C6) isomers, is among the first and most successful adsorption processes applied in the industry [1]. Typically, the light naphtha, characterised by a low research octane number (RON, ≈70), undergoes an incomplete catalytic isomerisation that generates an effluent containing unconverted linear paraffins, mostly n-pentane (nC5; RON 61.7) and n-hexane (nC6; RON 30), mixed with their respective branched isomers, i.e., isopentane (iC5; RON 93.5), 2-methylpentane (2MP; RON 74.5), 3-methylpentane (3MP; RON 75.5), 2,2-dimethylbutane (22DMB; RON 94), and 2,3-dimethylbutane (23DMB; RON 105). After that, the output of the isomerisation reactor is fed into an adsorber packed with zeolite (LTA type) that behaves as a molecular sieve, adsorbing only the linear paraffins (which are then recycled to the catalytic reactor for further processing). This results in a final branched isomerate product with an average RON ≈87–90. However, with the actual TIP process, the monobranched hexanes 2MP and 3MP represent up to 30% of the final product composition, which is detrimental to the octane improvement of gasoline for RON values higher than 90 [1]. Accordingly, this work shows a novel adsorptive separation process, based on the synergistic action of the zeolite 5A and the MIL-160(Al) metal-organic framework (MOF), to efficiently fractionate C5/C6 alkane isomers according to classes of high RON (HRON – 22DMB, 23DMB, and iC5) and low RON (LRON – nC5, nC6, 2MP, and 3MP) compounds.

2. Experimental - The robust, easily scalable with a predicted low-cost industrial production, and bio-derived Al-dicarboxylate MIL-160(Al) MOF is in the shaped form of beads (inorganic binder (silica sol solution 10 wt.%)) with a diameter ranging from 2.0 to 3.35 mm [2]. The zeolite 5A, with the commercial name *KÖSTROLITH® 5A BFK*, is in the shape of binder-free beads with a 1.2 to 2.0 mm diameter.

3. Results and Discussion - The core of the proposed technology is based on the outstanding property of MIL-160(Al) to separate C6 mixtures according to the degree of branching [3]. Image 1a shows the breakthrough curves measured on a fixed bed of MIL-160(Al) at 423 K and a total alkane pressure of 50.0 kPa. The HRON di-branched 22DMB and 23DMB elute first, and they are completely separated from the LRON mono-branched 3MP and 2MP, while the LRON linear nC6 elutes much later. The shape of the breakthrough curves for each isomer indicates that this excellent mixture segregation in MIL-160(Al) is primarily based on thermodynamically equilibrium competition due to their steepness and overshoot phenomenon. Moreover, the calculated ideal productivity for an accumulated RON of 92 is 1.02 $mol.dm^{-3}$, which outperforms all current adsorbent materials.

As a next step, MIL-160(Al) was associated with the commercially available zeolite 5A to design a single adsorption bed to feed all the C5/C6 alkane isomers. The corresponding experimental breakthrough data collected for the mixed bed of 70 wt% MIL-160(Al) and 30 wt% zeolite 5A demonstrated the desired discrimination between fractions of HRON (22DMB, 23DMB, and iC5) and LRON (nC6, nC5, 2MP, and 3MP) compounds (Image 1b). An ideal sorption hierarchy: nC6 ≫ nC5 ≫ 2MP ≈ 3MP ⋙ 23DMB > iC5 ≈ 22DMB is associated with an excellent productivity of 1.14 $mol.dm^{-3}$ for an accumulated RON of 92.

Further, a preliminary cyclic experiment was conducted to see how these results could be relevant to industrial applications. Image 1c displays the cyclic steady state (CSS) of a simplified 2-step PSA experiment, i.e., (i) pressurisation and adsorption with feed and (ii) vacuum countercurrent depressurisation with inert (helium) purge (desorption). At step I (adsorption), the mass front of the HRON 22DMB and iC5 has completely left the column, while the mass transfer front of 23DMB is concentrated at the edge of the column. The other LRON molecules mostly remain inside the bed, with only a small concentration leaving the column at the end of the adsorption step I. Also, the real-time RON history shows that the product mixture has an average RON higher than 92.

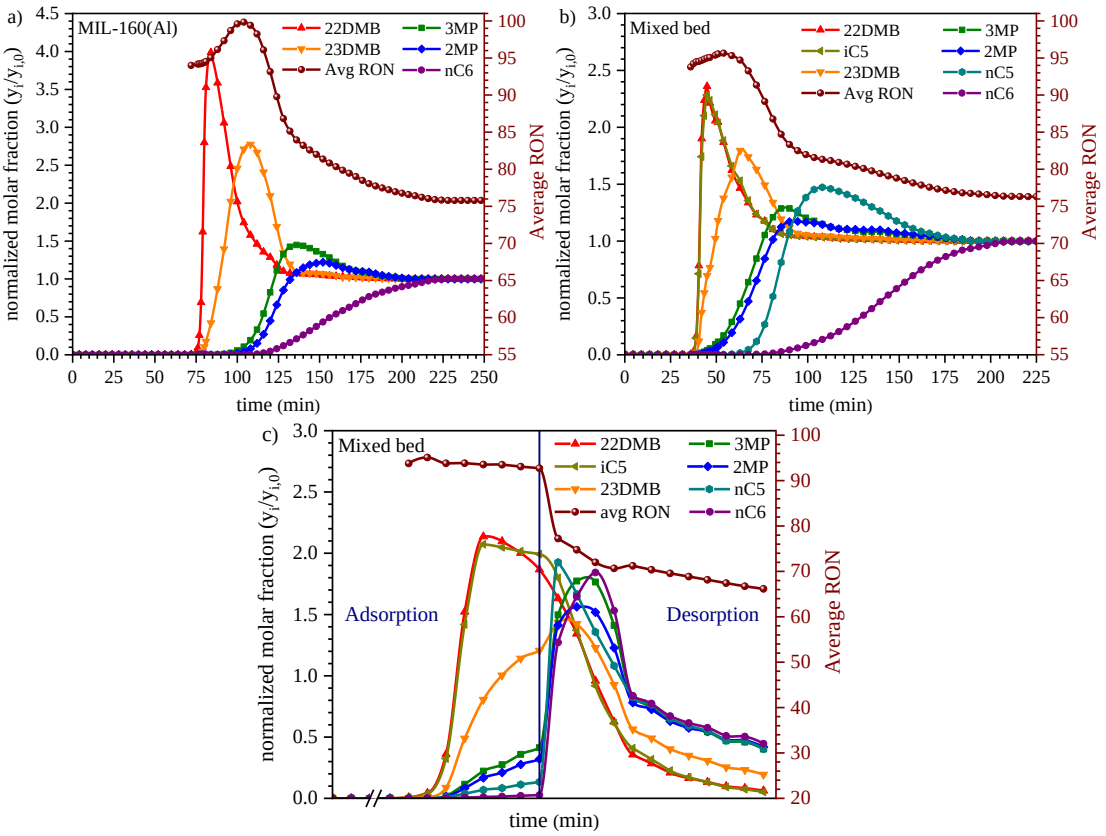

Image I. **a)** Breakthrough data for an equimolar C6 mixture fed in MIL-160(Al). **b)** Breakthrough data for an equimolar C5/C6 mixture fed in the mixed-bed adsorber of 70 wt% MIL-160(Al) and 30 wt% zeolite 5A. **c)** Cyclic steady-state data of a PSA experiment with an equimolar C5/C6 mixture fed in the mixed-bed adsorber of 70 wt% MIL-160(Al) and 30 wt% zeolite 5A.

4. Conclusions - This work reveals that the synergistic action of a mixed bed made by the MOF MIL-160(Al) together with the commercially available zeolite 5A led to the complete fractionation of light naphtha (RON < 70) into an HRON hydrocarbon final product (RON > 92) under relevant industrial operating conditions. As MIL- 160(Al) can be produced at a multi-kilogram scale, while zeolite 5A is already commercially available, this gives the building block for further pilot-scale testing before envisaging industrial commercialisation.

5. References

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