



# SEPARATION OF BRANCHED ALKANE FEEDS WITH METAL-ORGANIC FRAMEWORKS

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## Novel Adsorptive Separation Process for Octane Improvement of Gasoline

The production of high-quality gasoline is currently achieved through the Total Isomerization Process [1] that separates n/iso-paraffins in the pentane (C5) and hexane (C6) range while not reaching the ultimate goal of a research octane number (RON) higher than 92. This work demonstrates two promising alternatives/strategies using metal-organic frameworks (MOF) that lead to a novel adsorptive separation process to overcome this limitation. Here, the efficient discrimination of C5/C6 alkane isomers into valuable fractions of high RON (HRON – 2,3-dimethylbutane (23DMB; RON 105), 2,2-dimethylbutane (22DMB; RON 94), and isopentane (iC5; RON 93.5)) and low RON (LRON – n-pentane (nC5; RON 61.7), (nC6; RON 30), 2-methylpentane (2MP; RON 74.5), and 3-methylpentane (3MP; RON 75.5)) compounds is achieved (Figure 1).

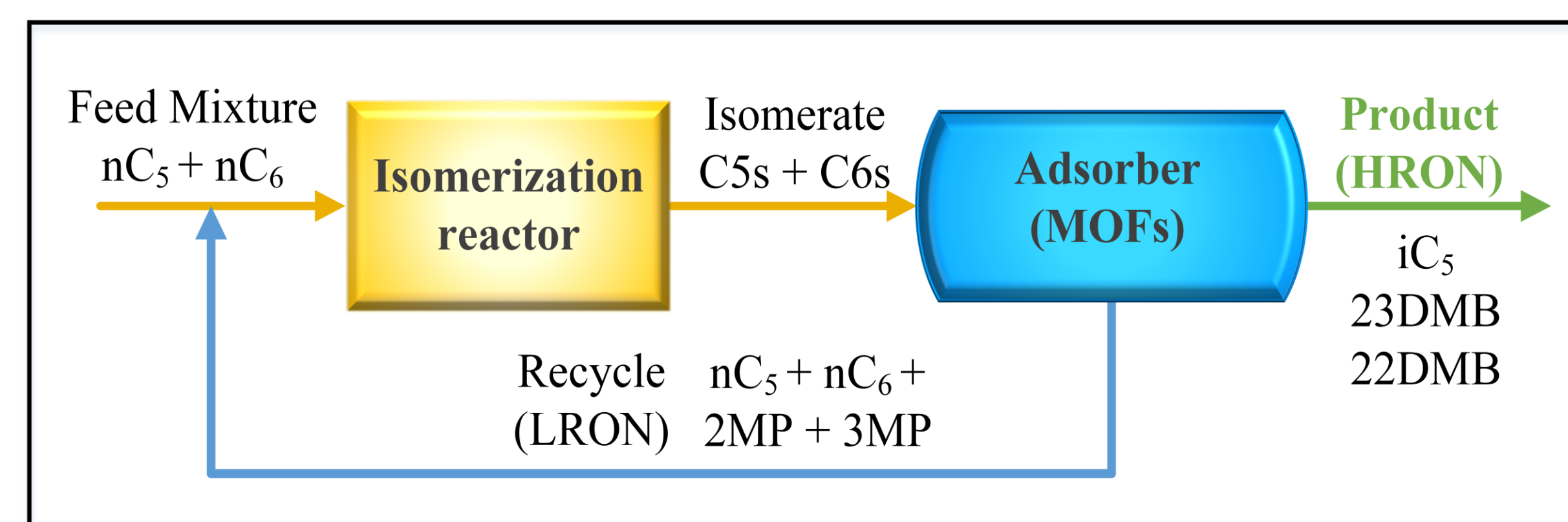
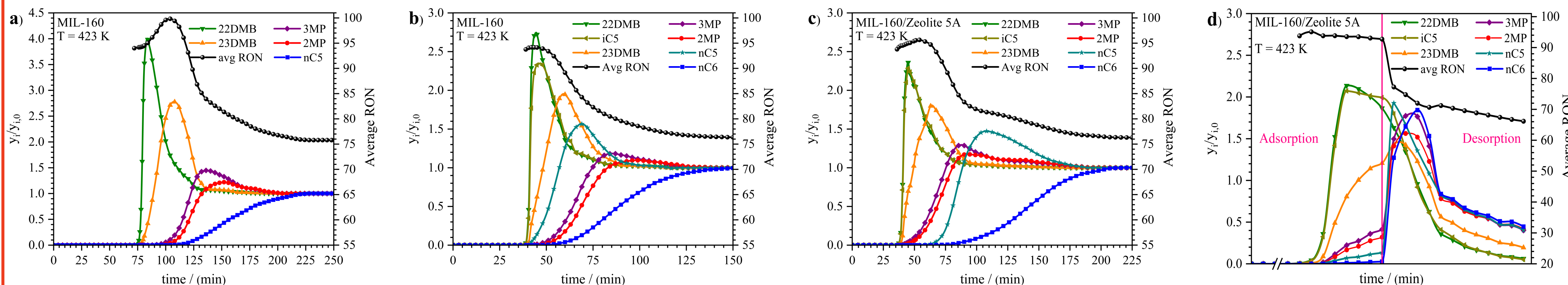


Figure 1. Advanced process for separating HRON and LRON isomers.

## Fixed Bed Adsorption – Breakthrough Curves

Case 1: Synergistic action between the Al-dicarboxylate MIL-160(Al), a bio-derived MOF that is easily scalable with a predicted low-cost industrial production, and the benchmark zeolite 5A [1].



- Outstanding property to separate C6 isomers into valuable fractions according to the degree of branching;
- 92 RON ideal productivity of 1.02 mol.dm<sup>-3</sup>, which outperforms all current adsorbent materials.

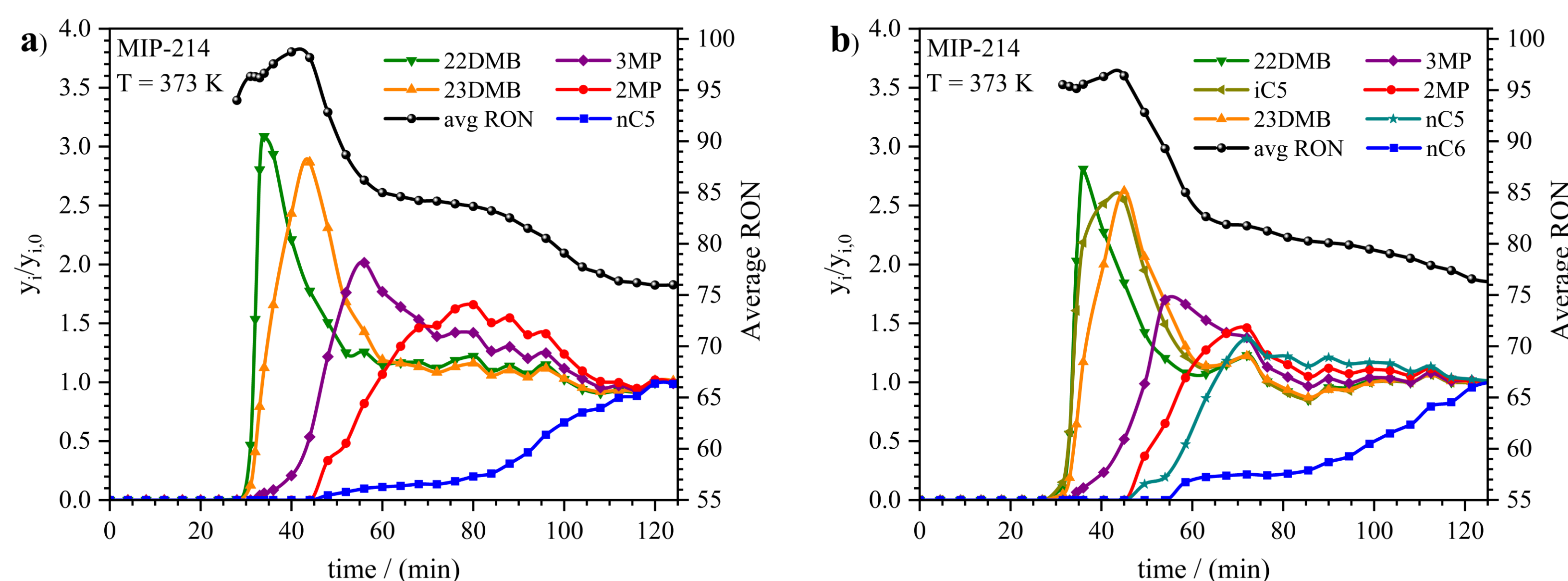
- Unwantedly, the LRON nC5 elutes almost simultaneously with the HRON 23DMB;
- Substantial drop in the 92 RON ideal productivity (0.59 mol.dm<sup>-3</sup> compared to 1.02 mol.dm<sup>-3</sup>).

- Ideal sorption hierarchy of LRON over HRON alkanes, nC6 > nC5 >> 2MP ≈ 3MP >> 23DMB > iC5 ≈ 22DMB;
- Excellent 92 RON ideal productivity of 1.14 mol.dm<sup>-3</sup>.

- The HRON 22DMB and iC5 has completely left the column, while 23DMB is concentrated at the edge;
- The other LRON molecules mostly remain inside the bed.

Figure 2. a) Breakthrough data for an equimolar C6 mixture fed in MIL-160(Al). b) Breakthrough data for an equimolar C5/C6 mixture fed in MIL-160(Al). c) 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. d) Cyclic steady-state data of a simplified 2-step pressure swing adsorption (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.

Case 2: Fe(III)-MOF (referred to as MIP-214), easily synthesized and scalable under mild conditions [2].



- Separate C6 isomers into valuable fractions according to the degree of branching;
- 92 RON ideal productivity of 0.74 mol.dm<sup>-3</sup>

- Ideal sorption hierarchy of LRON over HRON alkanes, nC6 > nC5 >> 2MP ≈ 3MP >> 23DMB > iC5 ≈ 22DMB;
- First experimental evidence that a single porous adsorbent effectively discriminates all C5/C6 alkane isomers into LRON and HRON fractions;
- 92 RON ideal productivity of 0.67 mol.dm<sup>-3</sup>

Figure 3. a) Breakthrough data for an equimolar C6 mixture fed in MIP-214. b) Breakthrough data for an equimolar C5/C6 mixture fed in MIP-214.

## Remarks and Future Directions

- Two promising alternatives/strategies with considerable potential for the octane improvement of gasoline pools (RON > 92), which eliminate/reduce the need for additives in the petrochemical industry, are presented;
- As Both MOFs are easily scalable, while zeolite 5A is already commercially available, this gives the building block for further pilot-scale testing before envisaging industrial commercialization;
- These advanced staged recycling technologies might not only provide the production of higher quality clean gasoline but also fill the gap in the current industrial adsorption separation science.

## References

- [1] R. A. Meyers, "Handbook of petroleum refining processes"; McGraw-Hill Education, New York, 2004.
- [2] P. F. Brântuas, A. Henrique, M. Wahiduzzaman, A. Von Wedelstedt, T. Maity, A. Rodrigues, F. Nour, U.-H. Lee, K. H. Cho, G. Maurin, J. A. C. Silva, C. Serre, *Adv. Sci.* 2022, 9(22), 2201494, DOI: doi.org/10.1002/adv.202201494.
- [3] L. Zhou, P. Brântuas, A. Henrique, H. Reinsch, M. Wahiduzzaman, J.-Marc Grenèche, A. E. Rodrigues, J. A. C. Silva, G. Maurin, C. Serre, *Angew. Chem. Int. Ed.* 2024, e202320008, DOI: doi.org/10.1002/anie.202320008.

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