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SEPARATION OF BRANCHED ALKANES FEEDS BY A SYNERGISTIC ACTION OF ZEOLITE 5A AND METAL-ORGANIC FRAMEWORK MIL-160(AL)

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A Novel Adsorption Process For Octane Improvement of Gasoline

The production of high-quality gasoline is currently achieved through the Total Isomerization Process [1] that separates pentane and hexane isomers while not reaching the ultimate goal of a research octane number (RON) higher than 92. This work demonstrates how a synergistic action of the zeolite 5A and the metal-organic framework (MOF) MIL-160(Al) leads to a novel adsorptive process for octane upgrading of gasoline through an efficient separation of isomers [2].

The innovative mixed-bed adsorbent strategy (Figure 1) achieves an efficient thermodynamic (MIL-160 (Al)) / size exclusion (zeolite 5A) separation 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.

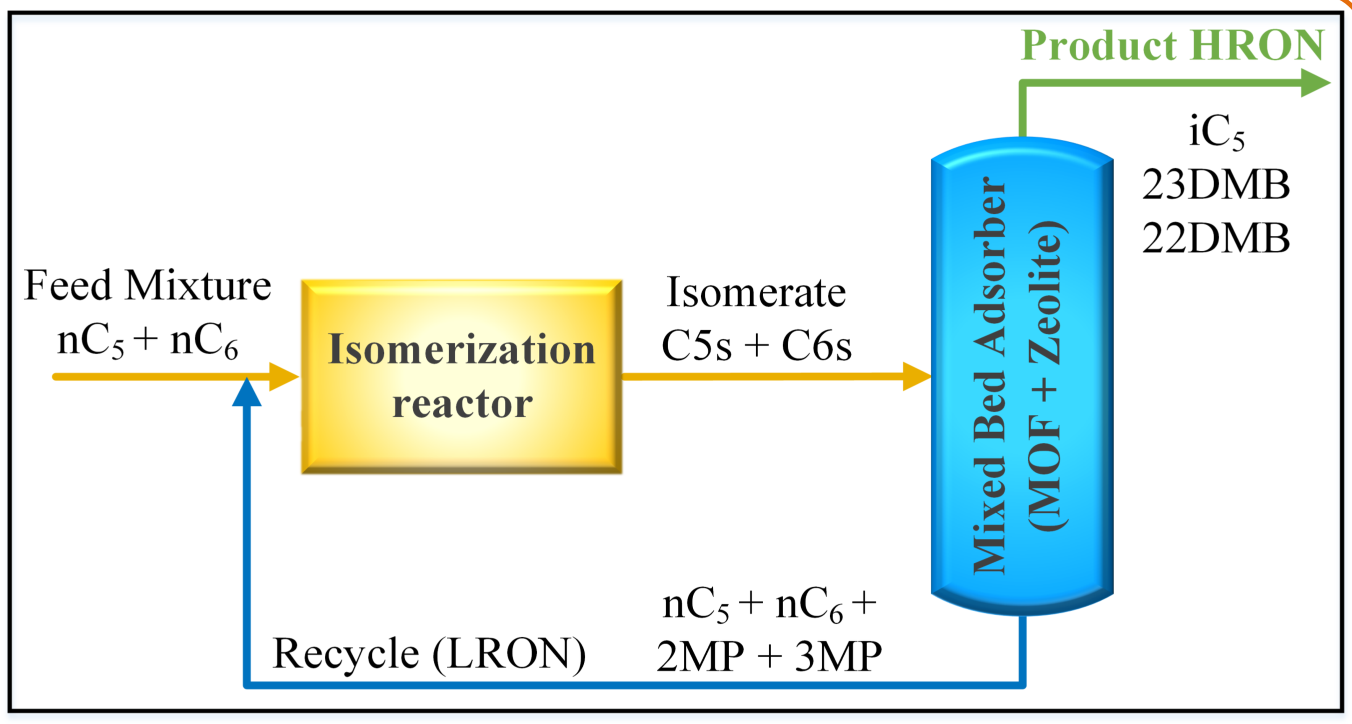
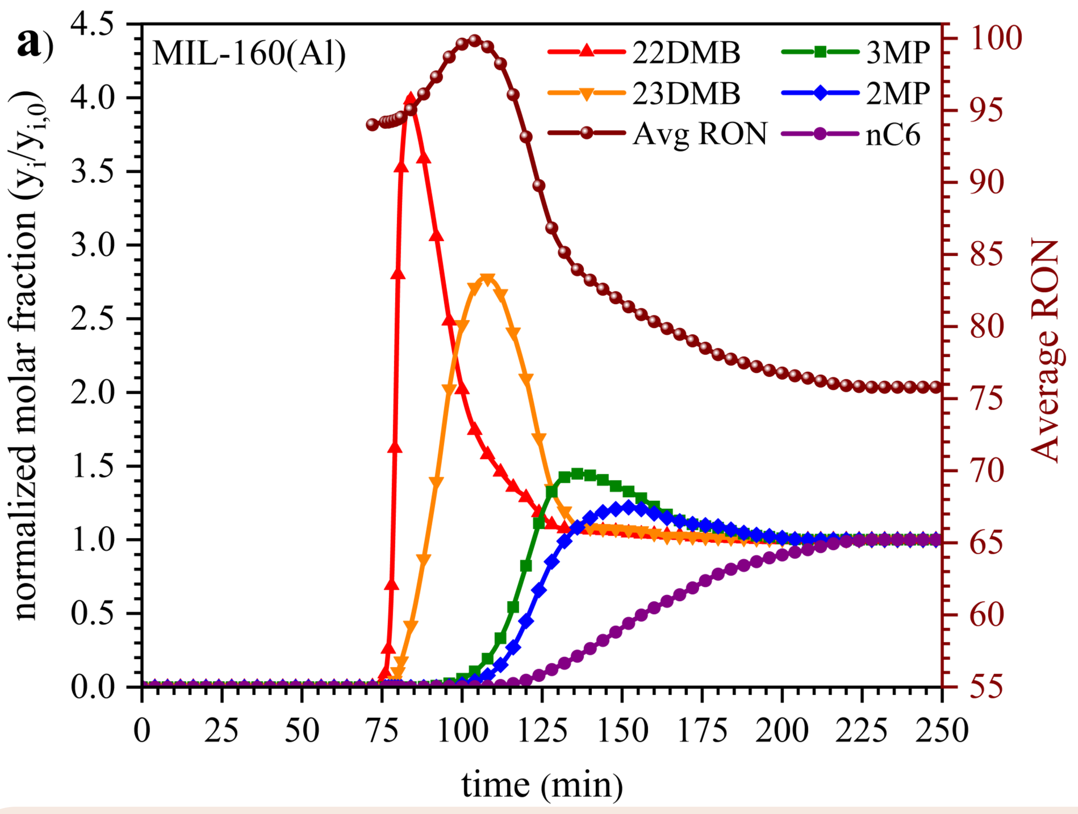


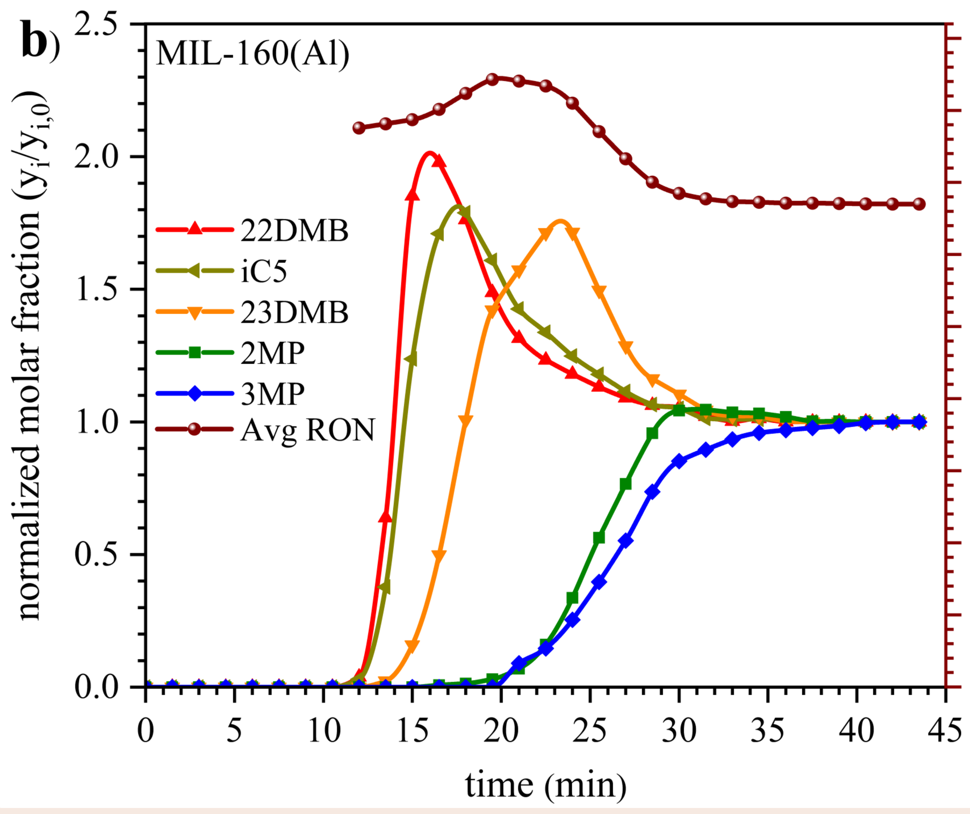
Figure 1. Advanced process for separating HRON and LRON isomers.

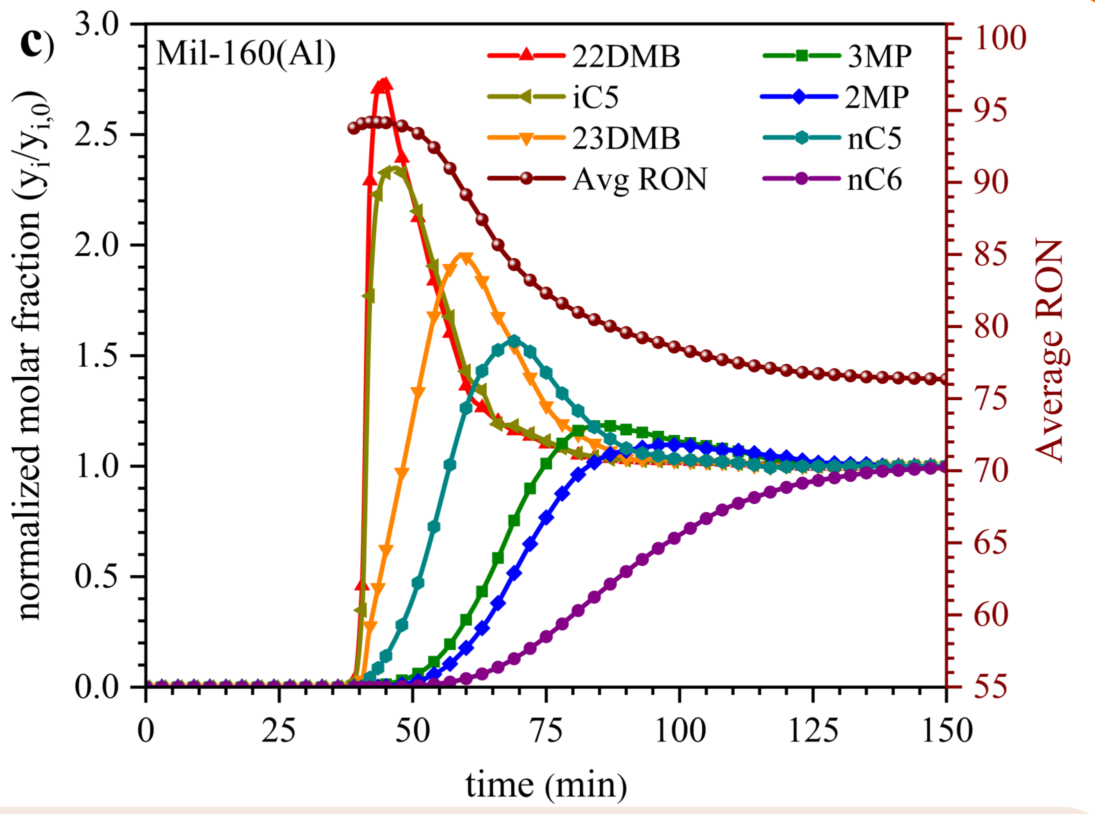
Adsorbent Materials: MIL-160(Al) and Zeolite 5A

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 [3]. The zeolite 5A (commercial name: KÖSTROLITH® 5A BFK) is in the shape of binder-free beads with a 1.2 to 2.0 mm diameter. The performance of these materials was accessed using a chromatographic technique through dynamic fixed bed breakthrough experiments performed at 423 K with total isomer pressure of 50 kPa.

Fixed Bed Breakthrough Curves



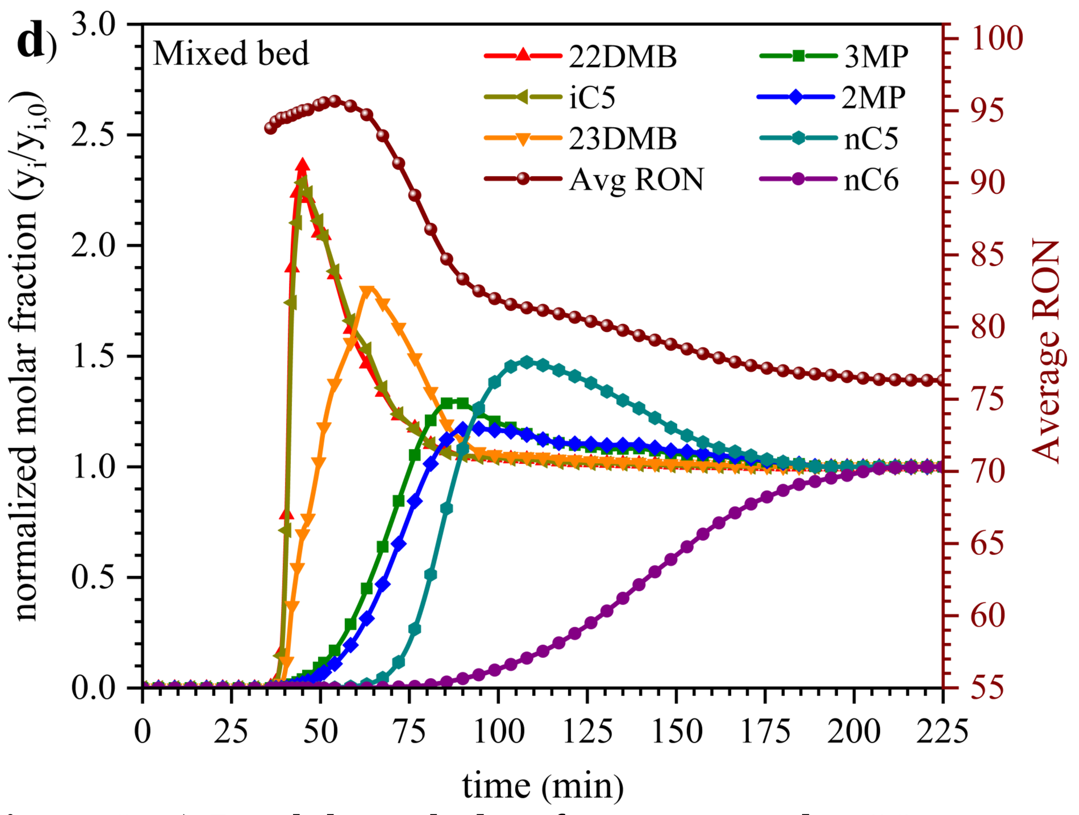




- Outstanding property to separate C6 isomers into valuable fractions according to the degree of branching;
- 92 RON ideal productivity of 1.02 mol.dm^{-3}, which outperforms all current adsorbent materials.

- First experimental evidence that an adsorbent effectively fractionates C5 and C6 branched isomers into LRON (2MP ≈ 3MP) and HRON (23DMB > iC5 ≈ 22DMB) fractions.

- Unwantedly, the LRON **nC5** elutes almost simultaneously with the HRON 23DMB;
- Substantial drop in the 92 RON ideal productivity (0.59 mol.dm^{-3} compared to 1.02 mol.dm^{-3}).



- 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^3.

- 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.

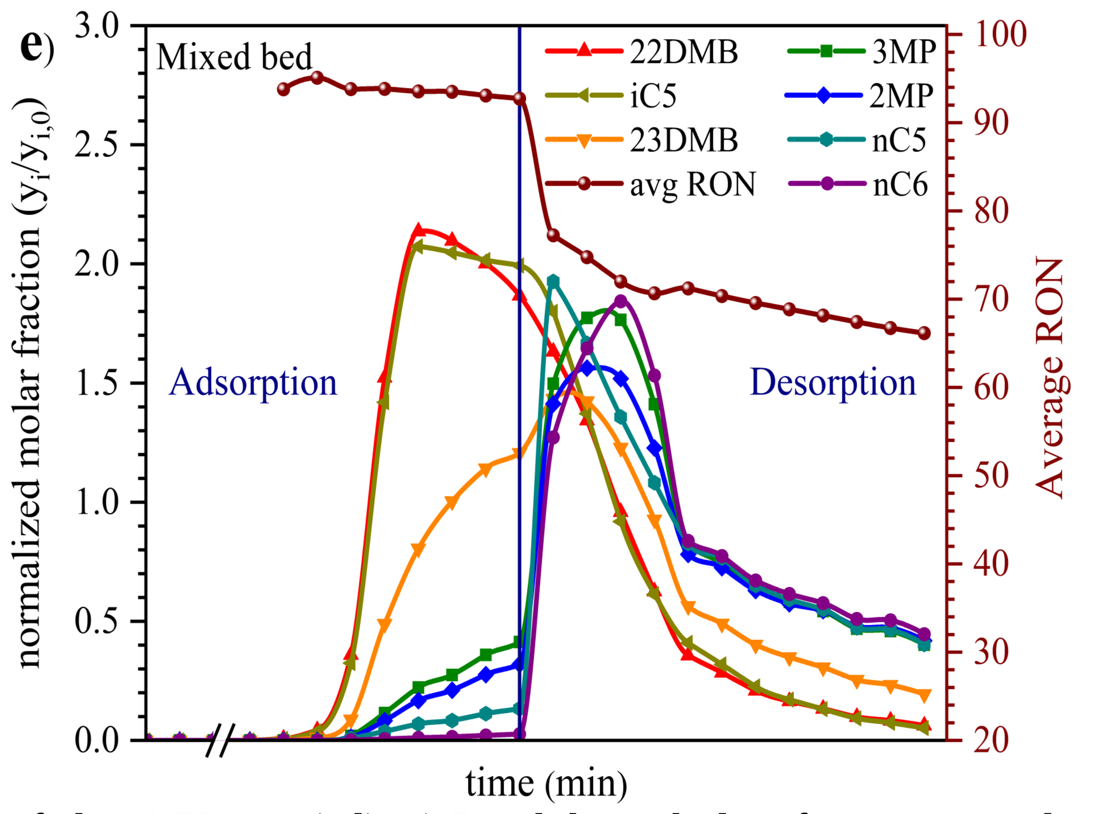


Figure 2. **a)** Breakthrough data for an equimolar C6 mixture fed in MIL-160(Al). **b)** Breakthrough data for an equimolar C5/C6 branched mixture fed in MIL-160(Al). **c)** Breakthrough data for an equimolar C5/C6 mixture fed in MIL-160(Al). **d)** Breakthrough data for an equimolar C5/C6 mixture fed in the mixed-bed adsorber of 70 wt% MIL-160(Al) and 30 wt% zeolite 5A. **e)** 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.

Remarks and Future Directions

✓ 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 (423 K);

✓ 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.

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