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Separation of Branched Alkane Feeds with Metal-Organic Frameworks

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Purifying hydrocarbons is of great importance in petrochemical chemistry and will remain one of the most challenging and energy-intensive separation processes in the coming decades until a complete shift towards renewable carbon pathways is found.[1] The production of gasoline is currently achieved through the conventional Total Isomerization Process (TIP) from Universal Oil Products (UOP)[2,3] that separates mixed feedstocks containing pentane (C5) and hexane (C6) isomers while not reaching the ultimate goal of a research octane number (RON) higher than 92. Typically, the light straight-run (LSR) naphtha undergoes an incomplete catalytic isomerization 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 (i-C5; RON 93.5), 2-methylpentane (2MP; RON 74.5), 3-methylpentane (3MP; RON 75.5), 2,3-dimethylbutane (23DMB; RON 105) and 2,2-dimethylbutane (22DMB; RON 94). These remaining linear paraffins are commonly separated from their branched isomers in an adsorption unit packed with zeolite 5A, resulting in a final branched isomerate product with an average RON ~ 87-90. However, the presence of a large amount of mono-branched C6 isomers, 2MP and 3MP (ca. 30%) on the product, is detrimental to the octane upgrading of gasoline for RON values up to 92. Therefore, it is crucial to develop new advanced adsorption separation processes that efficiently discriminate the TIP reactor effluent into fractions of high RON (HRON – 22DMB, 23DMB, and iC5) and low RON (LRON – nC5, nC6, 2MP, and 3MP) compounds (Figure 1a).

Accordingly, we report two potential strategies using metal-organic frameworks (MOFs) for reaching such an ambitious task. The first is based on the aluminium-dicarboxylate MIL-160(Al), a highly stable, bioderived, and easily scalable MOF. The breakthrough curves for an equimolar mixture of C6 isomers (Figure 1b) revealed the outstanding property of the material to separate them into valuable fractions according to the degree of branching through a thermodynamically controlled process. The HRON di-branched hexanes 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 associated ideal productivity for an accumulated RON of 92 is 1.02 mol.dm^{-3}, which outperforms all current adsorbent materials. A screening test with a feed mixture of all C5/C6 alkane isomers was also performed. In this case, an additional adsorbent, zeolite 5A, was used to form a mixed-bed (70 wt% MIL-160(Al) and 30 wt% zeolite 5A) to improve the separation performance. The corresponding breakthrough data collected at the industrially relevant temperature of 423 K (Figure 1c) revealed the desired sorption hierarchy of LRON over HRON alkanes, nC6 > nC5 >> 2MP > 3MP >> 23DMB > iC5 ≈ 22DMB, with an excellent 92 RON ideal productivity of 1.14 mol.dm^{-3}, which is a major achievement reported so far. Through a preliminary two-step Pressure Swing Adsorption (PSA) experiment, i.e., i) pressurization and adsorption with feed and ii) vacuum countercurrent depressurization with inert purge (desorption), this MOF/zeolite duo was proven to operate under cyclic operating conditions. The cyclic steady state (CSS) (Figure 1d) shows that 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.[4]

The second process relies on the new Fe(III)-MOF (referred to as MIP-214), which is also easily synthesized and scalable under mild conditions. MIP-214 has the unprecedented property to enable not only a thermodynamically controlled separation of all the C6 isomers, but also the discrimination of all C5/C6 alkanes into valuable HRON and LRON fractions. The breakthrough experiment measured at 373 K (Figure 1f), revealed an adsorption hierarchy order of nC6 >> nC5 ≈ 2MP > 3MP > 23DMB ≈ iC5 ≈ 22DMB, where the high-octane di-branched 22DMB and 23DMB and mono-branched iC5 elute nearly together, much earlier than the elution of the other four LRON components, leading to an ideal 92 RON productivity of 0.67 mol.dm^{-3}. Exceptionally, to the best of our knowledge, this is the first evidence that a single porous adsorbent can perform this highly challenging task under practical operating conditions (gas phase).[5] Although MIP-214 shows lower 92 RON ideal productivity than the mixed-bed duo (MIL-160/zeolite 5A), its unique separation property may decrease the complexity of designing adsorption industrial processes using two adsorbent materials.

As main conclusions, we presented two promising alternatives/strategies with considerable potential to be exploited in current TIP processes for the octane improvement of gasoline pools (RON > 92), eliminating/reducing the need for additives in the petrochemical industry, which usually significantly increases the final product price. Both MOFs' easy scalability gives the building block for further testing them at a pilot scale. 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.

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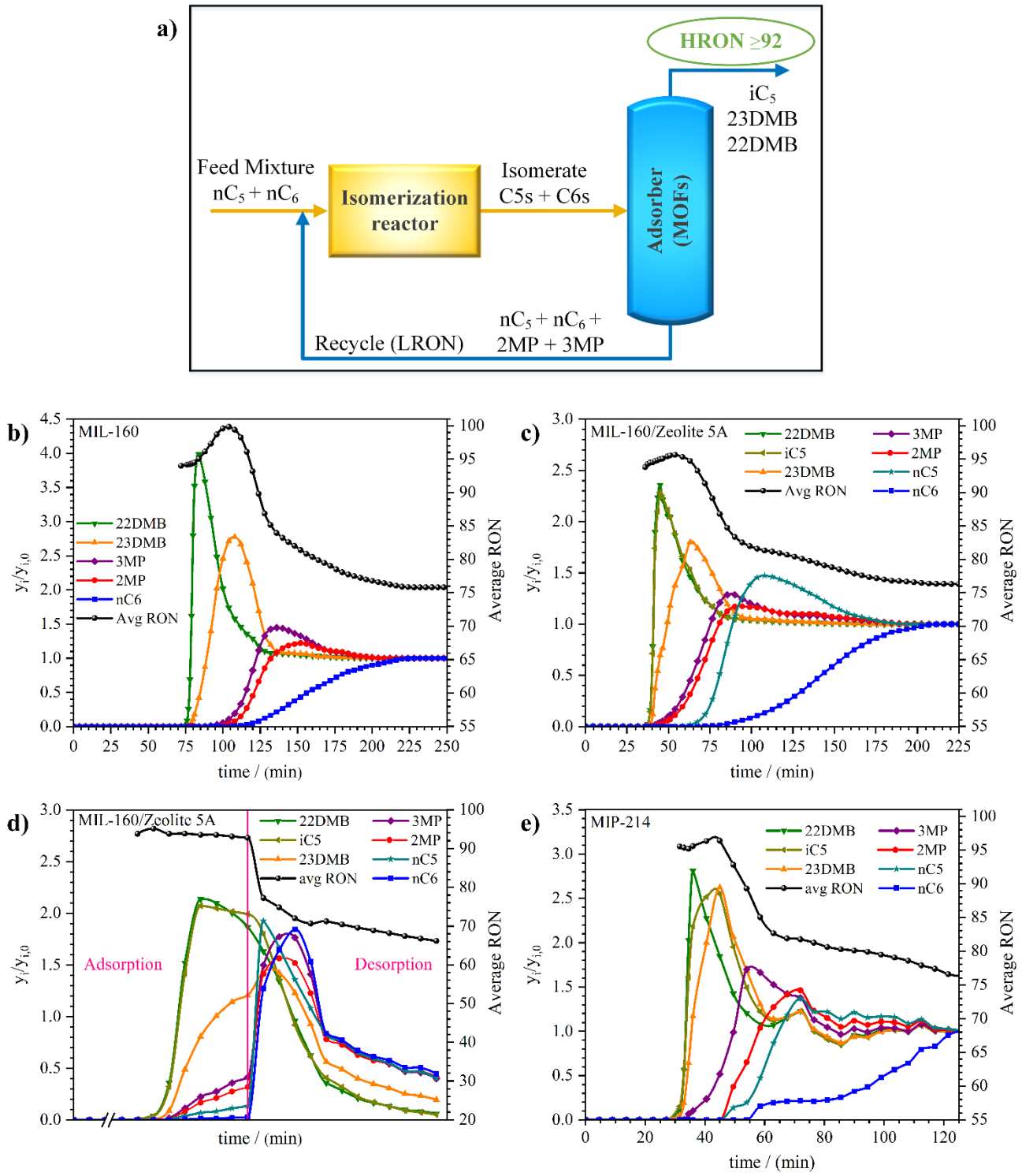

Figure 1. a) Advanced TIP process for separating HRON and LRON fractions with MOFs. **b)** Separation of a equimolar mixture of C6 isomers by fixed bed adsorption with MIL-160(Al) at 423 K. **c)** Separation of a equimolar mixture of C5/C6 alkane isomers by fixed bed adsorption with 70 wt.% MIL-160(Al) and 30 wt.% zeolite 5A at 423 K. **d)** CSS conditions of a PSA experiment for an equimolar mixture of C5/C6 alkane isomers in the mixed-bed of 70 wt.% MIL-160(Al) and 30 wt.% zeolite 5A at 423 K. **e)** Separation of a equimolar mixture of C5/C6 alkane isomers by fixed bed adsorption with MIP-214 at 373 K. Breakthrough data is plotted as the normalized molar fraction of each alkane (left y-axis) and average real-time RON (right y-axis) as a function of time.