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Book of Abstracts

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(CHEMPOR-2023)

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Edited by:

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Separation of n/iso-paraffins in a hierarchically structured 3D-printed porous carbon monolith

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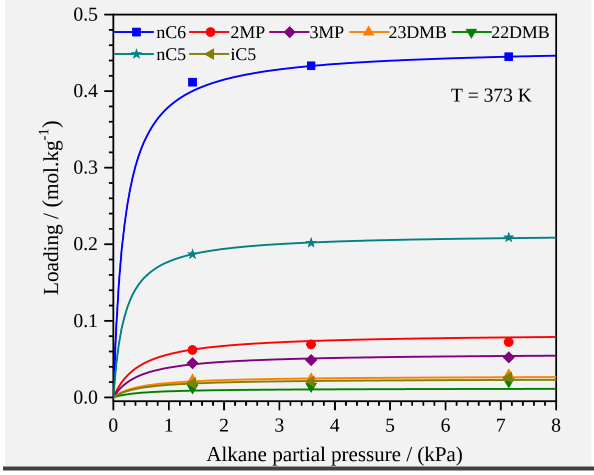

Hierarchically structured 3D-printed porous carbons monoliths were investigated for their applicability in adsorptive n/iso-paraffin separation. Three materials of the same macroscopic shape were employed, which varied in the micro- and mesoporosity by altering the final CO_2 activation step: non-activated and activated at 1133 K for 6 and 12 h, respectively. Chromatographic breakthrough experiments were conducted for pentane and hexane isomer mixtures at industrially relevant separation conditions. Results demonstrated that the initial porosity for the non-activated monolith enables the complete separation of linear paraffins from their branched isomers (slightly adsorbed) via a near molecular sieving effect. The Langmuir isotherm conveniently fitted the adsorption equilibrium data, and a dynamic mathematical model suitably predicted the breakthrough curves. Regarding the CO_2 activated monoliths, both showed adsorption towards all alkanes with practically no selectivity between them.

Introduction

The separation of mixed feedstocks containing pentane and hexane isomers for improving the octane rating of gasoline is a critical topic in the petrochemical industry. The value of a particular paraffin as a component in the gasoline pool is related to its research octane number (RON) assigned. The higher the RON is, the higher the fuel's resistance to auto-ignition [1]. As a general remark, branched alkanes have a superior RON content than their corresponding normal isomers. For example, iso-pentane (iC5; 93.5) has a RON value of nearly 30 numbers above n-pentane (nC5; 61.7). Similarly, the di-branched hexanes 2,2-dimethylbutane (22DMB; 94) and 2,3-dimethylbutane (23DMB; 105) show values at least 64 numbers higher than n-hexane (nC6; 30). The mono-branched hexanes 2-methylpentane (2MP; 74.5) and 3-methylpentane (2MP; 75.5) isomers have similar RON, whose values are about 40 numbers higher than nC6 [1]. Thus, the linear paraffins must be separated from their branched counterparts to achieve high RON blends. Therefore, developing adsorbent materials for optimal process efficiency and easy implementation in large-scale processes is critically important.

Objectives

This work aims to evaluate a series of 3D-printed carbon-based monoliths as adsorbents for the pentane and hexane isomer separation through fixed bed adsorption experiments.

Methods

The monolithic materials, exhibiting cylinder structures composed of tetragonal cubic centred unit cells, were prepared following four main steps [2]: i) resin preparation; ii) photopolymerisation (stereolithographic 3D print); iii) porogen extraction, and iv) thermal treatment. For this study, three monoliths with different degrees of CO_2 activation were evaluated: 1) non-activated (M1-pristine), 2) activated at 1133 K for 6 h (M2-CO_2_6h), and 3) activated at 1133 K for 12 h (M3-CO_2_12h). To assess the materials separation performance, experimental fixed bed breakthrough curves with an equimolar septenary mixture of all C5/C6 alkane isomers were measured with a chromatographic system [3] (373-473 K and total alkane pressure up to 50 kPa). Also, a general mathematical model, considering the kinetics of mass transfer by the linear driving force model [4], was developed to simulate and analyse the transient adsorption behaviour experimentally observed.

Results

Figure 1 shows the breakthrough curves for the temperature of 373 K and total alkane pressure of 50.0 kPa. The 3D-printed monoliths are expressed in the panels: a) M1-pristine, b) M2-CO_2_6h, and c) M3-CO_2_12h. The real time RON of the product mixture leaving the column is also plotted in the figure.

For the monolith M1-pristine (Figure 1a), the results indicate an adsorption hierarchy order as follows: nC6 > nC5 >>> 2MP > 3MP > 23DMB ≈ iC5 > 22DMB. One can equally observe the ability of the material to separate the linear paraffins from its branched isomers via a near molecular sieving mechanism. All the branched paraffins practically reach the saturation at a total molar amount fed of 0.5 mol.kg^{-1}. This size-selective separation of n/iso-paraffins arises due to the micropore morphology and connectivity of the monolith, where two types of micropores can be present in the material, being defined as open and restricted access [5]. Consequently, the entrance to the restricted pores is narrow enough to allow the passage of the linear molecules, apparently under some diffusional limitations, while getting impassable by their branched counterparts, ultimately resulting in the molecular sieving effect. Regarding the RON values, a plateau at 89 is reached when all branched paraffins leave the column separated from the linear alkanes.

On the other hand, both CO_2 activated monoliths (M2-CO_2_6h and M3-CO_2_12h) do not exhibited such a size-exclusion separation. Figure 1b and 1c reveals that all paraffin isomers were adsorbed, with most of them practically showing a simultaneous elution at a total molar amount fed of 2.0 and 3.0 mol.kg^{-1}, respectively. Moreover, there is a change in the elution order of the components, with the pentane isomers leaving the column first being followed by the hexane isomers (iC5 < nC5 < 22DMB < 23DMB < 2MP < 3MP < nC6). Another interesting remark seen in their breakthrough curves is the high overshoots in concentration, a typical characteristic of adsorption based on thermodynamically equilibrium competition.

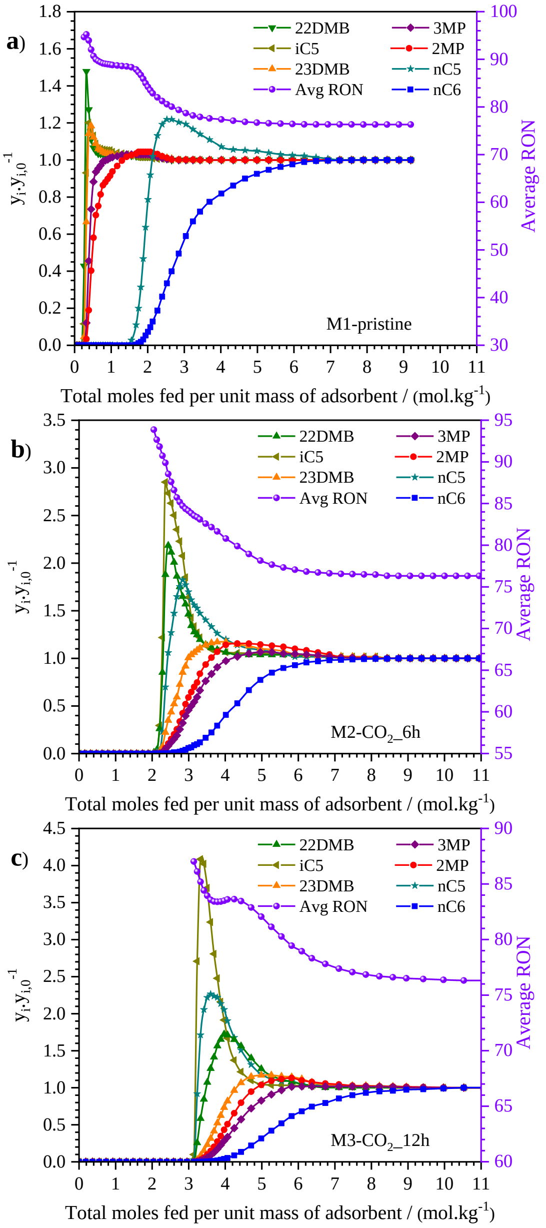

Figure 1. Experimental breakthrough curves for a septenary equimolar mixture of pentane and hexane isomers in 3D-printed monoliths at 373 K and 50.0 kPa: a) M1-pristine, b) M2-CO$_2$_6h, and c) M3-CO$_2$_12h.

Comparing the mixture loadings from each material, the adsorption uptake achieved by the monolith M1-pristine (0.85 mol.kg^{-1}) is around three and four times lower than the ones obtained on the monoliths M2-CO$_2$_6h (2.24 mol.kg^{-1}) and M3-CO$_2$_12h (3.20 mol.kg^{-1}), respectively. Despite creating additional microporosity, in the CO$_2$ activation process, there are also pore widening and joining of close pores (caused by the removal of the separating walls between them due to mass loss), being these effects more pronounced as temperature and/or activation time increases.

Practically, it can be stated that the monolith M1-pristine represents the most suitable material considering applications for pentane and hexane isomer separation. Thus, the measured data were numerically modulated to gain insights into the governing sorption mechanisms. The Langmuir isotherm was used (continuous lines in the Graphical Abstract), in which the sorption competition of the isomers was divided into two groups: one for the small amounts of branched paraffins in the open pores and the other for the adsorption of linear ones on the pores with restricted access. Then, the obtained parameters were inserted in the mathematical model, and the results are shown in Figure 2. The mass transfer coefficients found to obtain the best fit of the experimental data is around 0.0018 s^{-1} for the linear paraffins and 0.018 s^{-1} for their branched counterparts.

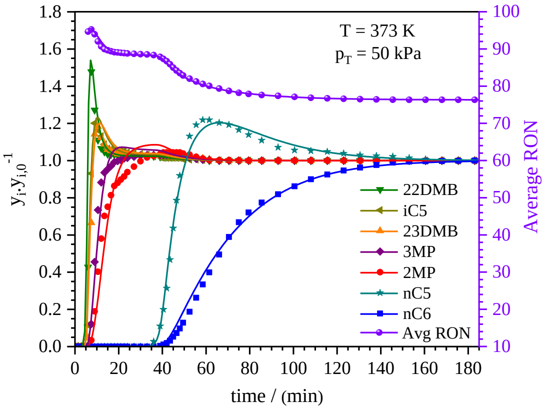

Figure 2. Experimental and numerical breakthrough curves for a septenary equimolar mixture of pentane and hexane isomers in monolith M1-pristine at 373 K and 50 kPa. The continuous lines represent the numerical simulations.

Conclusions

This is the first experimental study on the sorption of pentane and hexane isomers on a series of hierarchically structured 3D-printed porous carbons monoliths. Among the materials, monolith M1-pristine can completely separate linear from iso-paraffins through a near molecular sieving effect, which arises from its micropore morphology and connectivity. To the best of our knowledge, these outcomes have never been reported to such an extent before in any porous solid carbonaceous materials. Concerning the CO$_2$ activated monoliths, the oxidation and, thus, widening of the pore mouths resulted from the thermal treatment is very likely the main reason for the loss of molecular sieving properties seen in the untreated M1-pristine.

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