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Using transient breakthrough experiments for screening of adsorbents for separation of C\textsubscript{2}H\textsubscript{4}/CO\textsubscript{2} mixtures

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ABSTRACT

The recovery of C\textsubscript{2}H\textsubscript{4} from gaseous reactor effluents from processes such as oxidative coupling of methane (OCM), and biomass gasification (at relatively low temperatures (770–880 °C)) is becoming of increasing industrial and economic importance. The reactor effluents are N\textsubscript{2}/H\textsubscript{2}/CO/CO\textsubscript{2}/CH\textsubscript{4}/C\textsubscript{2}H\textsubscript{6}/C\textsubscript{2}H\textsubscript{4} mixtures, typically containing less than 15% C\textsubscript{2}H\textsubscript{4}. For recovery of C\textsubscript{2}H\textsubscript{4}, pressure swing adsorption (PSA) technology using a selective adsorbent offers an energy-efficient alternative to the more conventional separation schemes such as amine absorption and cryogenic distillation. The major objective of this investigation is to screen commercially available cation exchanged zeolites (13X, CaX, NaY, 5A, 4A) and activated carbon (AC) to determine the most suitable adsorbent. For all these materials, the adsorption strengths of CO\textsubscript{2}, and C\textsubscript{2}H\textsubscript{4} are significantly higher than that of other gaseous constituents; consequently, the C\textsubscript{2}H\textsubscript{4}/CO\textsubscript{2} separation selectivity is the key to the efficacy of any adsorbent. The variety of adsorbents were screened using transient breakthrough experiments with feed mixtures using different C\textsubscript{2}H\textsubscript{4}/CO\textsubscript{2} ratios. On the basis of the breakthroughs, the adsorbents could be distinguished in three different categories: (i) 13X and 4A are selective to CO\textsubscript{2}, (ii) CaX, NaY, and 5A are virtually non-selective, and (iii) AC is selective to C\textsubscript{2}H\textsubscript{4} over the entire range of feed compositions and is therefore the adsorbent of choice.

The experimental breakthrough results are also compared with simulations using published unary isotherm data, along with the Ideal Adsorbed Solution Theory (IAST) for determination of mixture adsorption equilibrium. This comparison demonstrates that screening adsorbents solely on the basis of IAST calculations is likely to be misleading. This article underscores the need for performing transient breakthrough experiments with realistic feed gas mixtures for process modelling and development purposes.

1. Introduction

Ethene (C\textsubscript{2}H\textsubscript{4}, commonly referred to as ethylene) is a valuable petrochemical feedstock that is primarily produced on a large scale by naphtha cracking. Due to increasing demand and the desire to replace fossil fuels, alternative sources of C\textsubscript{2}H\textsubscript{4} have received increased attention in recent years; two such alternatives are discussed below.

The oxidative coupling of methane (OCM) process involves reaction of CH\textsubscript{4} with oxygen under high temperatures (973–1173 K) to produce C\textsubscript{2}H\textsubscript{4}, followed by in-situ oxidation to C\textsubscript{2}H\textsubscript{4} [1]. The partial or total combustion to CO or CO\textsubscript{2} are the main side reactions. Typically, the conversion of methane < 40%, and the selectivity to C\textsubscript{2}H\textsubscript{4} and to C\textsubscript{2}H\textsubscript{6} is less than 50% and the reactor effluent consists of H\textsubscript{2}/CO/CO\textsubscript{2}/CH\textsubscript{4}/C\textsubcript{2}H\textsubscript{6}/C\textsubscript{2}H\textsubscript{4} mixtures typically containing < 10% C\textsubscript{2}H\textsubscript{4}. The conventional schemes for recovery of C\textsubscript{2}H\textsubscript{4}, involving amine absorption followed by cryogenic distillation at high pressure, are energy intensive [2,3]. Use of pressure swing adsorption (PSA) technology for C\textsubscript{2}H\textsubscript{4} recovery offers the potential for development of an energy-efficient OCM process [1,4–6]. The optimal process scheme for implementation of PSA technology requires use of a C\textsubscript{2}H\textsubscript{4}-selective sorbent in which the C\textsubscript{2}H\textsubscript{4}-free raffinate is recycled back to the reaction train [5]; see Fig. 1. CO\textsubscript{2} is removed from the C\textsubscript{2}H\textsubscript{4}-rich extract stream and subsequently distilled to obtain C\textsubscript{2}H\textsubscript{4} of the required purity. C\textsubscript{2}H\textsubscript{4} the bottoms product from the distillation tower, is used as purge gas in the PSA section and recycled to the OCM reaction unit.

Biomass gasification at temperatures in the range 770–880 °C results in a syngas mixture, which also contains CO\textsubscript{2}, C\textsubscript{2}H\textsubscript{6}, along with the valuable C\textsubscript{2}H\textsubscript{4} in concentrations up to 16% [7]. Recovery of C\textsubscript{2}H\textsubscript{4} by selective adsorption could significantly contribute to the economic viability of syngas production from biomass.

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For most available adsorbents, CO$_2$ and C$_2$H$_4$ are more strongly adsorbed than H$_2$, CH$_4$, CO, and C$_2$H$_6$; consequently, the efficacy of any PSA process, such as that shown in Fig. 1, requires the sorbent to have a high C$_2$H$_4$/CO$_2$ separation selectivity. Bachman et al. [4] have recently reported that Mn$_2$(m-dobdc) (m-dobdc$^-$ = 4,6-dioxido-1,3-benzenedicarboxylate), a metal-organic framework (MOF) featuring a high density of unsaturated Mn$^{2+}$ sites, offers a C$_2$H$_4$/CO$_2$ separation selectivity of about 10. In the context of the OCM process scheme (cf. Fig. 1), Bachman et al. [4] conclude “unique metal-adsorbate interactions facilitated by Mn$_2$(m-dobdc) render this material an outstanding adsorbent for the capture of ethylene from the product mixture, enabling this potentially disruptive alternative process for ethylene production”.

The primary objective of this article is examine whether any commercially available adsorbents could offer comparable C$_2$H$_4$/CO$_2$ separation (disruptive?) capabilities, obviating the need for development of novel MOFs. Prior to embarking on an extensive experimental campaign, we use literature data on unary isotherms, along with the Ideal Adsorbed Solution Theory (IAST) of Myers and Prausnitz [8] to compare the performance of Mn$_2$(m-dobdc) with different commercially available sorbents such as cation exchanged zeolites (13X, CaX, NaY, SA, 4A) and activated carbon (AC). For this purpose, the required unary isotherm data are culled from literature sources; the isotherm data, along with the details of IAST methodology, are provided in the Supplementary material accompanying this publication. It must be noted that the unary isotherm data for CO$_2$ and C$_2$H$_4$ in AC, used in the IAST calculations are for heterogeneous microporous activated carbon (Type BPL, 6/16 mesh, manufactured by the Pittsburgh Chemical Company) as reported by Reich et al. [9].

Briefly, the basic equation of IAST is the analogue of Raoult’s law for vapor-liquid equilibrium, i.e.

\[ p_i = P_i^0 x_i; \quad i = 1, 2, \ldots, n \]  

where $x_i$ is the mole fraction in the adsorbed phase

\[ x_i = \frac{q_i}{q_1 + q_2 + \ldots + q_n} \]  

and $P_i^0$ is the pressure for sorption of every component $i$, which yields the same spreading pressure, $\pi$ for each of the pure components, as that for the mixture:

\[ \frac{\pi A}{RT} = \int_0^{q_i^0} \frac{q_i^0(f)}{f} df = \int_0^{q_2^0} \frac{q_2^0(f)}{f} df = \int_0^{q_3^0} \frac{q_3^0(f)}{f} df = \ldots \]  

where $q_i^0(f)$ is the pure component adsorption isotherm, and $f$ is the gas phase fugacity. The units of $\frac{A}{RT}$ are mol kg$^{-1}$ and is referred to as the adsorption potential [10]. The adsorption potential can be determined by analytic integration of the unary isotherm data fits for each component. The total mixture loading is $q_i$ is calculated from

![Fig. 1. OCM process flow scheme with C$_2$H$_4$-selective adsorbent in the PSA adsorber beds; this flow scheme is adapted from Radaelli et al. [5].](image-url)
\[ q_t = q_1 + q_2 + \ldots + q_n = \frac{1}{q_1(\beta_1^2)} + \frac{1}{q_2(\beta_2^2)} + \ldots + \frac{1}{q_n(\beta_n^2)} \]  

(4)

The entire set of Eqs. (1)–(4) need to be solved numerically to obtain the molar loadings, \( q_i \), of the individual components in the flow reactor.

In Fig. 2, the IAST calculations of the adsorbed phase mole fraction of \( \text{C}_2\text{H}_4 \) for binary \( \text{C}_2\text{H}_4(1)/\text{CO}_2(2) \) mixtures, \( x_i \), is plotted as a function of the mole fraction of \( \text{C}_2\text{H}_4 \) in the bulk gas phase mixture. \( y_i \). The larger the departure from the parity line, \( x_i = y_i \), the more selective is adsorption from the mixture. The data for 5A, 4A, 13X, NaY, and CaX lie below the parity line, indicating that these materials preferentially adsorb \( \text{CO}_2 \). Zeolite 5A, the material with the largest deviation from the parity line, has the highest selectivity to \( \text{CO}_2 \), whereas the \( \text{CO}_2/\text{C}_2\text{H}_4 \) selectivity of CaX and NaY are close to unity. For selective adsorption of \( \text{C}_2\text{H}_4 \), the best performing material is Mn\(_2\)(m-dobdc), in agreement with the calculations in Bachman et al. [4] The IAST calculations for activated carbon (AC) also display selectivity towards \( \text{C}_2\text{H}_4 \).

In order to determine the reliability of IAST estimations for \( \text{C}_2\text{H}_4/\text{CO}_2 \) mixture adsorption, as shown in Fig. 2, transient breakthrough experiments were performed. The secondary objective of this article is to highlight some shortcomings of adopting a sorbent screening strategy relying only on IAST calculations of selectivities of mixture adsorption.

2. Transient breakthrough experiments

Transient breakthrough experiments were performed in a Flowerease flow reactor, described in earlier works [11,12], with multiple packed tubes (4 mm i.d., 300 mm height) that can be operated sequentially to test different sorbent materials for the same feed mixture under isothermal conditions; the experimental details are summarized in the Supplementary Material accompanying this publication. The sorbent beds are packed with six different commercial materials: 13X (Aldrich), CaX (Siliporite), NaY (CBV 100 CY, Zeolyst), 4A (=NaA = LTA-4A, Acros), 5A (=CaA = LTA-5A, Acros), and Activated carbon (GCN 3070 Cabot corp.), that were crushed and sieved to obtain 150–250 \( \mu \text{m} \) particles. At the start of each run, the materials are dried with flow of 25 N mL/min \( N_2 \) per tube at 473 K for 2 h. During the duration of the transient adsorption and desorption process, the packed bed is maintained under isothermal conditions at 313 K. The fixed-bed tube is first flushed, i.e. equilibrated, with pure \( N_2 \) at the specified total pressure, before injection of the feed mixture at time \( t = 0 \). The feed to each tube consists of \( \text{C}_2\text{H}_4/\text{CO}_2/N_2/\text{Ar} \) mixtures using different \( \text{C}_2\text{H}_4/\text{CO}_2 \) ratios; \( N_2 \) forms about 58% and serves as diluent in order to maintain nearly constant flow conditions and reduce axial dispersion. About 2% \( \text{Ar} \) in the feed serves as inert internal tracer to monitor the start of the component breakthroughs. All the experiments reported in this article are conducted at 1 bar absolute pressure and 313 K.

For each sorbent, four different \( \text{C}_2\text{H}_4/\text{CO}_2 \) ratios in the feed mixture are chosen: Run 1 (\( \text{C}_2\text{H}_4/\text{CO}_2 \approx 3 \)), Run 2 (\( \text{C}_2\text{H}_4/\text{CO}_2 \approx 1.5 \)), Run 3 (\( \text{C}_2\text{H}_4/\text{CO}_2 \approx 0.8 \)), and Run 4 (\( \text{C}_2\text{H}_4/\text{CO}_2 \approx 0.5 \)). Figs. S6–S11 provide a summary of the experimental breakthroughs for each of the six sorbents. As illustration, Figs. 3 and 4 provide comparisons of the breakthroughs for Runs 1 and 4, respectively, for each sorbent. For 13X, CaX, NaY, 5A, and AC, the breakthrough characteristics are reasonably sharp, indicating that diffusional limitations are of negligible importance. It is worth noting that the breakthroughs of \( \text{C}_2\text{H}_4 \) and \( \text{CO}_2 \) occur at practically the same time for CaX, and NaY. For 4A zeolite, the breakthroughs have distended characteristics, indicative of intra-crystalline diffusional limitations. The breakthroughs with 5A are remarkable because in Run 1, \( \text{C}_2\text{H}_4 \) breaks through before \( \text{CO}_2 \), whereas in Run 4, \( \text{CO}_2 \) breaks through earlier than \( \text{C}_2\text{H}_4 \).

3. Numerical analysis of transient breakthrough experiments

First, we seek comparisons of the breakthrough experiments with the IAST calculations in Fig. 2 by constructing a \( x_i \) vs \( y_i \) diagram using the methodology in earlier works [13,14]. Let \( m_{\text{ads}} \) represent the mass of adsorbent, expressed in kg, packed into the tube that is fed with the feed mixture at a constant flow rate of \( Q \) m\(^3\) s\(^{-1}\). The uptake of \( \text{C}_2\text{H}_4 \), expressed as moles per kg of adsorbent in the packed tube, can be determined from a material balance

\[ \dot{q}_i = \frac{c_i Q}{m_{\text{ads}}} \int_0^t (y_{i,\text{feed}} - y_{i,\text{exit}}) \, dt \]  

(5)

In Eq. (5), \( c_i \) represents the total molar concentration of the entering feed mixture at 1 bar, and 313 K. The upper limit of the integral, \( t_{\text{ss}} \), is the time required to reach steady-state. Analogously, the uptake of \( \text{CO}_2 \) is

\[ \dot{q}_i = \frac{c_i Q}{m_{\text{ads}}} \int_0^t (y_{i,\text{feed}} - y_{i,\text{exit}}) \, dt \]  

(6)

The integrals in Eqs. (5) and (6) can be numerically evaluated using a quadrature formula. In our analysis, we found that the use of the Simpson’s rule provided results of good accuracy. Combining Eqs. (5) and (6) we can determine the mole fraction of \( \text{C}_2\text{H}_4 \), \( x_i = \dot{q}_i/(\dot{q}_1 + \ldots + \dot{q}_n) \), essentially invoking the assumption that the mixture can be considered to be a pseudo-binary due to the relatively poor adsorptivity of both \( \text{Ar} \) and \( \text{N}_2 \) present in the feed mixture. Fig. 5a presents the results of this foregoing numerical analysis in which the adsorbed phase mole fraction of \( \text{C}_2\text{H}_4 \), \( x_i \), is plotted as a function of the mole fraction of \( \text{C}_2\text{H}_4 \) in the feed mixture, \( y_i \), treated as a pseudo-binary.

In agreement with the IAST estimations in Fig. 2, the sorbents 4A, and 13X are \( \text{CO}_2 \)-selective, and AC is \( \text{C}_2\text{H}_4 \)-selective. The data for CaX, and NaY lie close to the parity line in Fig. 5a; this indicates selectivities are close to unity for both these adsorbents. Indeed, examination of Figs. 3 and 4 show that the breakthroughs of \( \text{C}_2\text{H}_4 \) and \( \text{CO}_2 \) occur at practically the same time for CaX, and NaY.

In striking contrast to the expectations of the IAST estimates in Fig. 2, the data for 5A zeolite lie close to the parity line, indicating selectivities close to unity. Remarkably, 5A zeolite exhibits a tendency for selectivity reversal for \( y_i < 0.5 \). Analogous selectivity reversals for 5A zeolite have been reported in the experiments reported by Calleja et al. [15] and Basmajian and Hoieh [16]; see Figs. S19 and S20. The reasons for such selectivity reversal can be traced to the non-idealities in mixture adsorption, as detailed in earlier works [12,15,16]. Configurational Bias Monte Carlo (CBMC) simulations for mixtures of \( \text{CO}_2 \)-alkane mixtures in cation-exchanged zeolites reveal that the non-idealities are caused due to inhomogeneous distribution of guest molecules within the pore space, engendered by congregation of guest molecules around the extra-framework cations [17,18].

To account for non-ideality effects in mixture adsorption in 5A zeolite, the selectivity of \( \text{C}_2\text{H}_4 \) is plotted as a function of the mole fraction of \( \text{C}_2\text{H}_4 \) in the feed mixture, \( y \), as shown in Fig. 5b. The selectivity of \( \text{C}_2\text{H}_4 \) for each sorbent is plotted in Fig. 5c. The selectivity of \( \text{C}_2\text{H}_4 \) for each sorbent is plotted in Fig. 5c.
zeolite, we need to introduce activity coefficients $\gamma_i$ into Eq. (1)

$$P_i = P_i^0 \gamma_i$$

(7)

The implementation of the activity coefficients is termed as the Real Adsorbed Solution Theory (RAST). Following the approaches of Myers, Talu, and Sieperstein [8, 10, 19, 20] the excess Gibbs free energy for binary mixture adsorption is modeled as follows

$$\frac{G^{excess}}{RT} = x_1 \ln(\gamma_1) + x_2 \ln(\gamma_2)$$

(8)

Fig. 3. Experimental breakthroughs for Ar/C2H4/CO2/N2 mixtures in (a) 13 X, (b) CaX, (c) NaY, (d) 4A, (e) 5A, and (f) AC. The total pressure is 1 bar, and temperature $T = 313$ K. The feed mixture composition corresponds to Run 1 ($C_2H_4/CO_2 \approx 3$). The continuous solid black lines are breakthrough simulations using the IAST for determination of mixture adsorption equilibrium. The % N2 in the outlet gas can be determined by the taking the sum of the mole % = 100.

The Wilson model for activity coefficients are given for binary mixtures by
In Eq. (9), $\Lambda_1 = 1$; $\Lambda_2 = 1$, and $C$ is a constant with the units kg mol$^{-1}$. The introduction of \( \left(1 - \exp \left(\frac{-C}{RT}\right)\right) \) imparts the correct limiting behaviors $\gamma_i \to 1$; $\frac{\delta \gamma_i}{\delta \chi_i} \to 0$ for the activity coefficients in the Henry regime, $p_i \to 0$; $\frac{\delta \gamma_i}{\delta \chi_i} \to 0$. As pore saturation conditions are approached, this correction factor tends to unity \( \left(1 - \exp \left(\frac{-C}{RT}\right)\right) \to 1 \). The choice of $\Lambda_1 = \Lambda_2 = 1$ in Eq. (9), yields unity values for the activity coefficients reduces to the IAST.
4. Transient breakthrough simulations

Transient breakthroughs in fixed bed adsorbers are influenced by adsorption selectivities, uptake capacities, and intra-particle diffusional influences [21–24]. Therefore, we performed breakthrough simulations for direct comparison with the experimental breakthroughs. The use of more detailed process modelling of PSA operations, such as that described by Khalighi et al. [25], is beyond the scope of this work.

For an n-component gas mixture flowing through a fixed bed adsorber maintained under isothermal, isobaric, conditions, the molar concentrations in the gas phase at any position and instant of time are obtained by solving the following set of partial differential equations for each of the species i in the gas mixture [21–24]:
Combination of the discretized partial differential equations along with the algebraic IAST equations describing mixture adsorption equilibrium results in a set of differential-algebraic equations, which are solved using a sparse matrix solver based on the semi-implicit Runge-Kutta method; further numerical details are provided in the Supplementary material.

To match the experiments with 4A zeolite, intra-crystalline diffusional influences must be accounted for in the breakthrough simulations. The best match was obtained by taking the values of $D_i/r_c^2 = 0.1 \text{ s}^{-1}$ for Ar, N$_2$, and CO$_2$; For C$_2$H$_4$, the inter-cage hopping is

\begin{equation}
 t \geq 0; \quad p_i(0, t) = p_{i0}; \quad c_i(0, t) = c_{i0}
 \end{equation}
significantly hindered by cations, and the choice \( D_j/r_j^2 = 0.01 \text{ s}^{-1} \) yielded the best fits with experiments. For all other sorbents, intra-particle diffusion influences may be neglected. For Run 1, and Run 4, the continuous solid black lines in Figs. 3 and 4 represent the breakthrough simulations; more detailed comparisons for each of the four runs with different \( \text{C}_2\text{H}_4/\text{CO}_2 \) ratios are provided in Figs. S13–S18.

For 13X, CaX, and NaY zeolites, the breakthrough simulations show the correct qualitative features as the experimental data. However, the match is not quantitatively perfect; the simulations tend to predict a larger gap between the breakthrough times of \( \text{C}_2\text{H}_4 \) and \( \text{CO}_2 \). This indicates that the unary isomerths anticipate more \( \text{CO}_2 \)-selective separations than is achieved in practice.

For 5A zeolite the agreement between experimental data and breakthrough simulations, based on the IAST, is poor; the selectivity reversal observed in Run 4 in favor of \( \text{C}_2\text{H}_4 \) is not anticipated by the breakthrough simulations. The selectivity reversal with 5A zeolite is also confirmed in the breakthrough experiments of García et al. \[1\] for 20/80 \( \text{C}_2\text{H}_4/\text{CO}_2 \) and 40/4/49/7 \( \text{CH}_4/\text{C}_2\text{H}_4/\text{CO}_2/\text{C}_2\text{H}_4 \) feed mixtures. In earlier work \[12\] it has been established that the non-idealities in mixture adsorption equilibrium are the root cause of selectivity reversals.

Fig. 6 shows that the transient breakthrough simulations incorporating the RAST is able to quantitatively capture the selectivity reversal phenomena for Run 4 with 5A zeolite. In the RAST implementation, the thermodynamic non-idealities are characterized by the Wilson parameters \( \Lambda_{ij} = 32 \); \( \Lambda_{jj} = 0.03 \); \( C = 1 \text{ mol kg}^{-1} \), determined from fitting the \( x_i \) vs \( y_j \) data for 5A zeolite in Fig. Sb.

For AC, the transient breakthrough simulations show the same qualitative features as the experimental data but the quantitative match is poor because unary isotherm data used in the simulations were based on the literature data for microporous activated carbon (Type BPL, 6/16 mesh, manufactured by the Pittsburgh Chemical Company) and the experiments were performed with Cabot carbon.

5. Transient desorption: Experiments and simulations

For AC, the sorbent of choice, \( \text{C}_2\text{H}_4 \) is recovered in nearly purified form from extract phase of the PSA unit. To demonstrate the feasibility of this recovery, transient desorption experiments were conducted for each of the four runs 1, 2, 3, and 4. In the desorption experiments, the equilibrated bed is flushed with a constant flow of pure \( \text{N}_2 \), and the product compositions monitored by GC analysis. For the sake of completeness, desorption experiments were conducted for all six sorbents, not just for AC; the entire set of desorption experiments are presented in Figs. S19–S24. As illustration, the data for desorption for the equilibrated Run 4 are indicated by the symbols in Fig. 7. The continuous solid lines in Fig. 7 are the simulations of the desorption transience using the IAST for calculations of mixture adsorption equilibrium; the match with the experiments with AC are poor, as expected, because the unary isomerths are not for the Cabot AC used in the experiments.

For 13X and 4A zeolites, the data in Fig. 7a, d show that purified \( \text{CO}_2 \) can be recovered during the later stages of the transient desorption process. The data in Fig. 7b, c reinforce the conclusion, drawn earlier, that both CaX and NaY are non-selective to either constituent; neither constituent is available in pure form at the exit of the desorption cycle.

The desorption data for 5A shows that despite the selectivity reversal in favor of \( \text{C}_2\text{H}_4 \) is observed in the adsorption cycle (cf. Fig. 4e), neither of the constituent can be recovered in pure form during the desorption cycle; see Fig. 7e. Evidently, the selectivity reversal in favor of \( \text{C}_2\text{H}_4 \) is not strong enough to enable pure \( \text{C}_2\text{H}_4 \) recovery as raffinate.

The data in Fig. 7f provide confirmation of the ability of AC to produce nearly pure \( \text{C}_2\text{H}_4 \) for later stages of the desorption, \( r > 12 \text{ min} \).

6. Conclusions

Transient breakthrough experiments with \( \text{C}_2\text{H}_4/\text{CO}_2 \) feed mixtures in fixed beds packed with six different sorbents 13X, CaX, NaY, 5A, 4A, and AC were carried out to determine the most suitable adsorbent for selective adsorption of \( \text{C}_2\text{H}_4 \). The results indicate that AC is the most suitable adsorbent for this purpose. Though AC exhibits a lower \( \text{C}_2\text{H}_4/\text{CO}_2 \) selectivity than the tailor-made Mn\(_2\)(m-dobdc), its commercial availability obviates the need for materials development. Remarkably, the suitability of AC for selective adsorption of \( \text{C}_2\text{H}_4 \) from \( \text{CO}_2 \)-bearing mixtures has not been highlighted in the published literature \[1,4,5\].

For the other sorbents 4A, and 13X are \( \text{CO}_2 \)-selective, and suitable for \( \text{CO}_2 \) capture of refinery off-gases containing \( \text{C}_2 \) hydrocarbons. The sorbents CaX, NaY, and 5A zeolites are unable to produce purified products in either the raffinate (adsorption cycle) or extract (desorption cycle) phases. The results obtained also indicate that sorbent screening strategies relying on IAST calculations of mixture adsorption equilibrium, based on literature data on isomerths may be misleading. For 13X, NaY, CaX, and 5A zeolites, the actual separations are poorer than anticipated in the IAST calculations in Fig. 2.

CRediT authorship contribution statement

Ilona van Zandvoort: Conceptualization, Data curation, Investigation, Validation, Methodology, Project administration, Supervision, Writing – review & editing. Erik-Jan Ras: Conceptualization, Data curation, Investigation, Methodology, Project administration, Supervision, Writing – review & editing. Robbert de Graaf: Funding acquisition, Project administration, Supervision, Writing – review & editing. Rajamani Krishna: Methodology, Formal analysis, Software, Writing – original draft.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.seppur.2020.116706.

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